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## FACULTAD DE QUÍMICA
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# *EQUILIBRIO LÍQUIDO-VAPOR DE SISTEMAS BINARIOS Y TERNARIOS DE COMPUESTOS CONTENIDOS EN LAS GASOLINAS SIN PLOMO*

Memoria para optar al grado de Doctor en Ciencias Químicas

presentada por

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## CERTIFICAN QUE:

D^a^. SONIA LORAS GIMÉNEZ ha realizado bajo su dirección el trabajo que con el título ***"Equilibrio Líquido-Vapor de Sistemas Binarios y Ternarios de Compuestos Contenidos en las Gasolinas Sin Plomo"***, constituye su Tesis para optar al grado de Doctor en Ciencias Químicas.

La tesis doctoral se presenta como un compendio de publicaciones. A continuación se facilitan las referencias completas de los nueve artículos (seis publicados y tres enviados) que constituyen la presente memoria:

1. Azeotropic Behavior in the System Methanol + Methyl 1,1-Dimethylethyl Ether. Sonia Loras, Antonio Aucejo, Rosa Muñoz, Jaime Wisniak. *Journal of Chemical Engineering Data.* **1999**, 44, 203-208.

2. Isobaric Vapor-Liquid Equilibrium in the System 2-Methylpentane + Methyl 1,1-Dimethylethyl Ether, + Ethyl 1,1-Dimethylethyl Ether, and + Methyl 1,1-Dimethylpropyl Ether. Antonio Aucejo, Sonia Loras, Rosa Muñoz, Ricardo Reich, Hugo Segura. Journal of Chemical Engineering Data. **1998**, 43, 973-977.

3. Isobaric Vapor-Liquid Equilibrium for Binary Mixtures of 2-Methylpentane + Ethanol and + 2-Methyl-2-propanol. Antonio Aucejo, Sonia Loras, Rosa Muñoz, Luis Miguel Ordoñez. Fluid Phase Equilibria. **1999**, 156, 173-183.

4. Vapor-Liquid Equilibria in the Systems 3-Methylpentane + Methyl 1,1-dimethylethyl ether and 3-Methylpentane + Methyl 1,1-Dimethylpropyl Ether at 101.3 kPa. Sonia Loras, Antonio Aucejo, Rosa Muñoz. *Fluid Phase Equilibria.* **1999**, 156, 185-195.

5. Isobaric Vapor-Liquid Equilibrium in the System 3-Methylpentane + Ethyl 1,1-Dimethylethyl Ether, + Diisopropyl Ether, and + Tetrahydrofuran. Sonia Loras, Antonio Aucejo, Rosa Muñoz, Jaime Wisniak. *Journal of Chemical Engineering Data.* **1999**, 44, 583-587.

6. Isobaric Vapor-Liquid Equilibrium in the System 2,3-Dimethylpentane + Methyl 1,1-Dimethylethyl Ether, + Diisopropyl Ether, and + Methyl 1,1-Dimethylpropyl Ether. Juan B. Montón, Javier de la Torre, M. Cruz Burguet, Rosa Muñoz, Sonia Loras. *Journal of Chemical Engineering Data.* **1999**. Enviado para su publicación.

7. Isobaric Vapor-Liquid Equilibrium for Binary and Ternary Mixtures of Ethanol + 2-Methyl-2-Propanol and 2-Methylpentane + Ethanol + 2-Methyl-2-Propanol. Antonio Aucejo, Sonia Loras, Rosa Muñoz, Luis Miguel Ordoñez. *Fluid Phase Equilibria* **1999**. En prensa.

8. Phase Equilibria in the Systems 2-Methyl-2-Propanol + Methyl 1,1-Dimethylpropyl Ether and 2-Methylpentane + 2-Methyl-2-Propanol + Methyl 1,1-Dimethylpropyl Ether. Sonia Loras, Antonio Aucejo, Rosa Muñoz, Luis Miguel Ordoñez. *Journal of Chemical Engineering Data.* **1999**. Enviado para su publicación.

9. Isobaric Vapor-Liquid Equilibrium in the System Methyl 1,1-Dimethylethyl Ether + 2-Methyl-2-Propanol and Methyl 1,1-Dimethylethyl Ether + 2-Methylpentane + 2-Methyl-2-Propanol. *Journal of Chemical Engineering Data.* Sonia Loras, Antonio Aucejo, Rosa Muñoz. **1999**. Enviado para su publicación.

El factor de impacto (Journal Citation Reports 1997) de las revistas es **1.065** para *Fluid Phase Equilibria* y **0.885** para *Journal of Chemical Engineering Data.*

Y para que conste a los efectos oportunos firman el presente certificado en Valencia a 11 de Junio de 1999.

Dr. D. Antonio Aucejo Pérez

Dra. Dª. Rosa Muñoz Guillén

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*A la memoria de mi madre y mi abuelo*

*A mi padre y hermanos*

*A Rafa*

# ÍNDICE

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# 1.- INTRODUCCIÓN

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Los últimos veinticinco años han estado marcados por un creciente interés en los problemas de polución generados por la combustión ordinaria de gasolinas de automóviles, una de las principales fuentes de contaminación medioambiental en las grandes ciudades de los países más industrializados.

Los gases generados durante la combustión de hidrocarburos en automóviles son CO, $CO_2$, $NO_x$, $SO_x$ e hidrocarburos cuya combustión ha sido incompleta. Estos últimos actúan, junto con el $NO_x$ del aire, como reactantes en la formación de ozono (causante de problemas respiratorios) en las capas bajas de la atmósfera. Otro factor que contribuye a la polución atmosférica es la evaporación de compuestos volátiles de la gasolina en zonas de almacenamiento y suministro.

En la década de los 70, en Estados Unidos, la *Clean Air Act* (CAA) estableció un programa de medidas con el fin de controlar y reducir la emisión de productos contaminantes a la atmósfera. La solución adoptada por la industria automovilística fue la instalación generalizada del "catalizador de tres vías" en los tubos de escape (Turner, 1987). Estos convertidores catalíticos contenían, sobre un soporte cerámico, un componente metálico (platino o paladio) que facilitaba la combustión completa de los hidrocarburos procedentes del motor, antes de su salida al exterior. Sin embargo, la incorporación de estos convertidores requería la eliminación de los metales pesados (plomo y manganeso) presentes en el combustible y utilizados como aditivos antidetonantes, ya que provocaban la desactivación del catalizador por envenenamiento irreversible de su componente metálico. La eliminación del plomo en las gasolinas destinadas a vehículos con catalizador, inició una búsqueda de nuevos aditivos con características antidetonantes que permitieran disponer de gasolinas con un octanaje adecuado.

En 1991, la EPA (*Environmental Protection Agency*) propuso una serie de medidas destinadas a modificar la composición de los combustibles de automoción. Basándose en un Modelo Simple, la gasolina reformulada (RFG) debía contemplar los siguientes aspectos:

- Reducción de la presión de vapor Reid (RVP) por debajo de $55.847 \cdot 10^3$ Pa.
- Limitación del contenido máximo de aromáticos y de benceno al 25% y 1% en volumen, respectivamente.
- Eliminación de cualquier metal pesado, incluidos plomo y manganeso, utilizados como aditivos antidetonantes.
- Aumento del contenido de oxígeno en la gasolina, por encima del 2.5% en peso.

Para 1997, la EPA propuso la aplicación de un Modelo Complejo, con especificaciones más restrictivas, y que incluía la reducción del contenido de azufre y olefinas en el combustible. Con estas medidas se pretende reducir en un 15% las emisiones de compuestos orgánicos volátiles (VOC) y de productos tóxicos (benceno, aldehídos y butadienos), tomando como referencia los niveles correspondientes al año 1990.

En el año 2000, la EPA pretende conseguir una importante reducción del 29%, 22% y 6.8% en las emisiones de VOC, compuestos tóxicos y $NO_x$, respectivamente.

En Europa, la legislación no está definida de la misma forma que en Estados Unidos. Junto a una introducción progresiva de la gasolina sin plomo en el mercado, el Parlamento Europeo ha establecido un límite máximo para el contenido de benceno en un 5% en volumen. También ha especificado un máximo nivel de compuestos oxigenados en la gasolina, entre un 2.5 y un 3.7% en peso, dependiendo del país. Sin embargo, es muy probable que, a corto o a medio plazo, las refinerías tengan que aplicar los límites impuestos por la EPA en 1991.

La aplicación de la nueva legislación dirigida a regular la composición de los combustibles está teniendo un gran impacto en la industria del refino de petróleo, ya que se necesitan importantes cambios en los esquemas de refino para satisfacer las especificaciones de la RFG. Debido a que no existen soluciones generales, cada refinería habrá de establecer su propia estrategia con el fin de adaptar su producción a la nueva normativa.

## 1.1. GASOLINAS OXIGENADAS

Es bien conocido que los hidrocarburos constituyentes de una gasolina energéticamente adecuada, fundamentalmente alcanos saturados lineales y cíclicos y, en menor proporción, alquenos, alquinos y aromáticos, provocan detonaciones incontrolables que colapsan mecánicamente las piezas móviles de un motor de combustión interna. Adicionalmente, el uso de mezclas de hidrocarburos sin algún tipo de aditivo que mejore el octanaje, produce efluentes gaseosos con altos contenidos de monóxido de carbono, e hidrocarburos parcialmente quemados (Schuetzle y col. 1994; Westbrook y Pitz, 1991; Westbrook, 1992).

La adición de agentes antidetonantes a la gasolina es una investigación que se ha desarrollado paralelamente a la industria automovilística y, en la actualidad, a la formulación de gasolinas adecuadas para una combustión limpia e inocua para el ambiente. Los primeros aditivos utilizados comercialmente en combustibles fueron los compuestos alquilo-plomados, que intervienen desactivando las reacciones de ruptura de las cadenas carbonadas de hidrocarburos autodetonantes. Sin embargo, la toxicidad de estos compuestos alquilo-plomados, y la de los aditivos halogenados requeridos para eliminarlos en los gases de escape de la combustión, hace prohibitivo su uso. Desde entonces, numerosos compuestos organometálicos han sido estudiados como potenciales aditivos antidetonantes alternativos. Esta investigación no se ha llevado a cabo con éxito, debido a un compromiso entre el costo del combustible, la toxicidad de los aditivos, la durabilidad de los motores de combustión interna, y el efecto indeseable de hidrocarburos parcialmente quemados en los gases de escape de la combustión (Berwick, 1987).

En este contexto las líneas de investigación han marcado su interés en las propiedades antidetonantes de los compuestos oxigenados que, en sustitución de los compuestos alquilo-plomados, son actualmente añadidos a la gasolina en países con legislación ambiental. Los compuestos oxigenados son moléculas en las que los átomos de carbono enlazan átomos de oxígeno y, comúnmente, contienen de uno a seis átomos de carbono. Ejemplos típicos son los alcoholes (metanol, etanol, *terc*-butil alcohol) y los éteres ramificados (MTBE: metil *terc*-butil éter, ETBE: etil *terc*-butil éter, TAME: *terc*-amil metil éter, TAEE: *terc*-amil etil éter, DIPE: diisopropil éter) que, por razones de costo y disponibilidad en el mercado, son aditivos atractivos para la formulación de gasolinas comerciales de automóviles. El oxígeno de este tipo de compuestos no provee energía durante el proceso de combustión, pero sí una estructura molecular que otorga un efecto antidetonante razonable, que no condiciona la introducción de cambios tecnológicos considerables en el diseño de los motores de combustión interna. En el proceso de la combustión de gasolinas correctamente formuladas, los compuestos oxigenados aportan los siguientes efectos beneficiosos (Piel y Thomas, 1990):

- Sustituyen a los compuestos aromáticos de alto octanaje en la formulación gasolinas, que son responsables de las emisiones de monóxido de carbono e hidrocarburos parcialmente quemados.

- Inhiben las reacciones ineficientes de combustión de baja temperatura, estabilizando la oxidación de los hidrocarburos a mayores temperaturas y disminuyendo la tendencia de formación de nieblas (*smog*) en los gases de escape.

### 1.1.1. MTBE: principal aditivo oxigenado.

Desde 1992, y como resultado del mandato de la CAA, el MTBE es el compuesto oxigenado que aparece con mayor frecuencia en calidad de aditivo de gasolinas reformuladas norteamericanas, con la finalidad de reducir las emisiones de monóxido de carbono durante los meses de invierno.

El MTBE se obtiene al reaccionar catalíticamente en fase líquida, metanol con isobutileno sobre resinas de intercambio iónico fuertemente ácidas. La reacción es rápida y selectiva, pero está limitada por las condiciones del equilibrio. Por tanto, la conversión se favorece utilizando metanol en exceso: se consiguen altas conversiones con un exceso aproximadamente del 20% sobre la cantidad estequiométrica. El producto de reacción está formado por el MTBE junto con el metanol en exceso, dicha mezcla es difícil de separar mediante destilación debido a que el MTBE con el metanol forma un azeótropo. En todo proceso de fabricación del MTBE las etapas de separación de la mezcla de reacción en sus componentes son de gran importancia (Ver Figura 1). Se han estudiado numerosas técnicas de purificación del MTBE: Chase, 1984; Bitar y col., 1984; Farnand y col., 1989; Park y col., 1995; Chen y col., 1989.

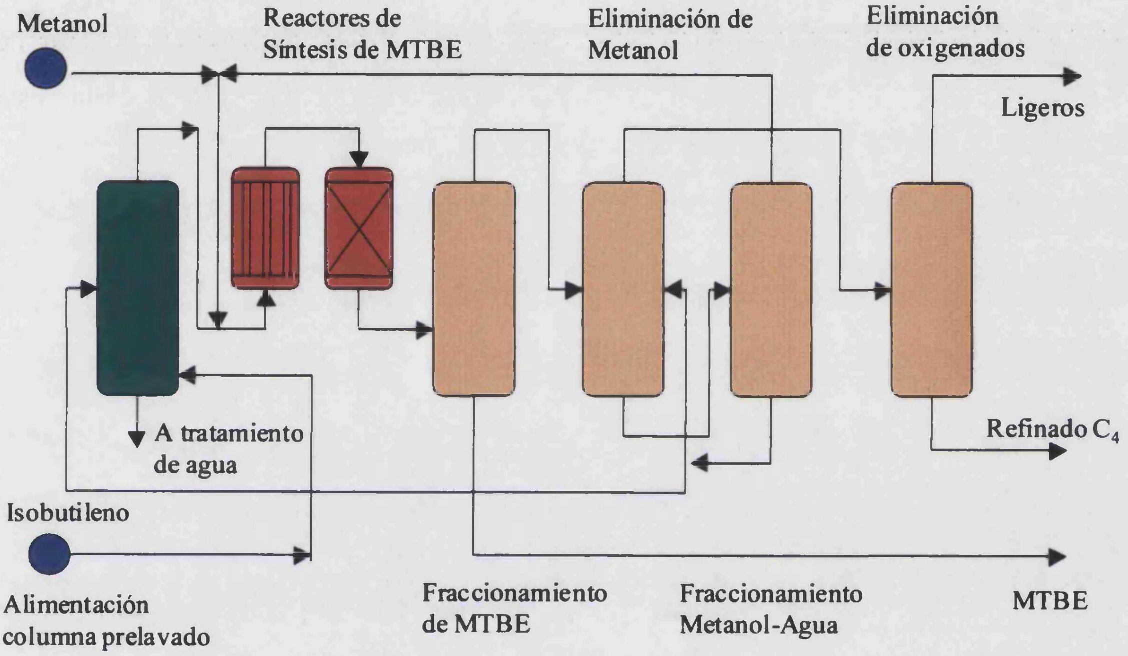

**Figura 1.** Diagrama de flujo para el proceso de fabricación de MTBE

El impacto que los aditivos tipo éteres para la preparación de gasolinas ha generado en los últimos años, ha conducido a un aumento de la fabricación de estos productos. Esto, unido al creciente interés que está tomando la purificación del MTBE por su valor como disolvente y reactivo, ha potenciado el estudio termodinámico de las mezclas que contienen estos éteres.

Por otra parte, existen estudios bien documentados (Zogorski y col., 1999; Foster, 1997) que indican que el MTBE produce problemas de contaminación de fuentes de agua, así como también riesgos de salud derivados de la exposición al compuesto. Por lo cual, se prevé que su uso quede restringido e incluso sea reemplazado por otros tipos de compuestos oxigenados de mayor peso molecular, que reúnan las características de ser menos solubles en agua, menos volátiles y de mayor estabilidad química, puesto que los éteres de bajo peso molecular se oxidan fácilmente en presencia de aire. Siguiendo en la línea de los éteres, se consideran como buenas alternativas al MTBE, el *terc*-amil metil éter (TAME), el etil *terc*-butil éter (ETBE), el diisopropil éter (DIPE) o el tetrahidrofurano (THF). Otra posibilidad es considerar la familia de los alcoholes. Es habitual encontrar metanol o etanol como compuestos oxigenados en la gasolina. Estos alcoholes presentan problemas de inmiscibilidad y pequeñas cantidades de agua pueden ocasionar la formación de dos fases líquidas. La adición de alcoholes superiores (isobutil alcohol, IBA, o *terc*-butil alcohol, TBA) evita este inconveniente.

# 2. OBJETIVOS

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Este trabajo se presenta como una aportación al conocimiento termodinámico de mezclas de gasolinas con aditivos oxigenados. De esta forma, se ha determinado experimentalmente el equilibrio líquido-vapor (ELV) de un conjunto de éteres y alcoholes con hidrocarburos constituyentes de la gasolina. Los éteres considerados han sido MTBE, TAME, ETBE, DIPE y THF. Los alcoholes elegidos han sido el etanol y el TBA. Dentro de la familia de hidrocarburos de la gasolina se han escogido alcanos ramificados, dos isómeros del hexano ($C_6H_{14}$): el 2-Metilpentano y el 3-Metilpentano, y uno del heptano ($C_7H_{16}$): el 2,3-Dimetilpentano.

Parte del trabajo elaborado para esta memoria se ha hecho en colaboración con los grupos de investigación en equilibrio de fases de la Universidad de Concepción (Chile) y de la Universidad de Ben-Gurion en Beer-Sheva (Israel). Aprovechando estancias pre-doctorales en sendas universidades se llevó a cabo la determinación experimental del ELV de algunos de los sistemas que constituyen el presente estudio.

La experimentación se ha realizado en condiciones isobáricas, a 101.3 kPa, que es la manera habitual del almacenaje y uso de las gasolinas. En este trabajo se ha determinado el ELV de dos tipos de **sistemas binarios**:

- Compuesto oxigenado (éter o alcohol) + hidrocarburo:

MTBE + 2-Metilpentano
TAME + 2-Metilpentano
ETBE + 2-Metilpentano
Etanol + 2-Metilpentano
TBA + 2-Metilpentano

MTBE + 3-Metilpentano
TAME + 3-Metilpentano

ETBE + 3-Metilpentano
DIPE + 3-Metilpentano
THF + 3-Metilpentano

MTBE + 2,3-Dimetilpentano
TAME + 2,3-Dimetilpentano
DIPE + 2,3-Dimetilpentano

- Mezcla de compuestos oxigenados:

Etanol + TBA
MTBE + TBA
TAME + TBA

El ELV de sistemas binarios formados por dos compuestos oxigenados se determinó con el fin de completar la información necesaria para la estimación de sistemas más complejos. De esta manera, como comprobación de que los valores obtenidos para sistemas binarios pueden utilizarse para estimar sistemas multicomponentes se ha obtenido el ELV de **sistemas ternarios** a las mismas condiciones que sus binarios constituyentes (101.3 kPa):

2-Metilpentano + Etanol + TBA
MTBE + 2-Metilpentano + TBA
2-Metilpentano + TAME + TBA

Los datos de ELV de los diferentes sistemas binarios han sido correlacionados utilizando modelos de energía de exceso de composición local (Wilson, NRTL y UNIQUAC). Basándose en esta modelización termodinámica de los sistemas binarios se han estimado los sistemas ternarios. La comparación de dicha estimación con los datos experimentales de ELV obtenidos, ha permitido verificar la hipótesis de predicción de sistemas multicomponentes en base a contribuciones binarias.

Por otra parte, también se ha abordado uno de los problemas que surgen en el proceso industrial de síntesis del MTBE. Como se ha comentado anteriormente, este éter se obtiene al reaccionar el isobutileno y el metanol. El producto de reacción está formado por el MTBE junto con el metanol en exceso, dicha mezcla es difícil de separar por destilación debido a que el MTBE con el metanol forma un azeótropo. Con el fin de estudiar la variación de la composición azeotrópica con la presión de trabajo se ha determinado experimentalmente el ELV del sistema **MTBE + Metanol** a tres presiones diferentes: 94 kPa, 78.4 kPa y 50 kPa.

La importancia de los datos experimentales de equilibrio líquido-vapor es pues notoria, no sólo desde el punto de vista del diseño, sino también por la determinación de parámetros para la aplicación de modelos de correlación totalmente contrastados y su incorporación a los bancos de datos, por su aportación al estudio comparativo de métodos de predicción fuertemente consolidados (UNIFAC, ASOG, etc.) y por su influencia en el desarrollo de los nuevos métodos de predicción.

## 2.1. PLAN DE TRABAJO

- Determinación de la pureza de los productos empleados

Los productos son adquiridos a determinadas firmas comerciales con purezas superiores al 99% en masa. Si el producto a utilizar (ya sea el compuesto oxigenado o el hidrocarburo) no está disponible en dicho grado de pureza se pasará a su purificación. De esta forma, el compuesto es sometido a un proceso de rectificación discontinua en una columna de relleno.

El grado de pureza del producto comercial y/o purificado se determina por cromatografía de gases. Asimismo, se determina su índice de refracción, su densidad y su temperatura de ebullición para comparar los valores obtenidos con los encontrados en la bibliografía.

- Determinación de las presiones de vapor de los compuestos puros

Fijado el sistema para el que se quieren obtener los datos ELV, se comienza determinando las presiones de vapor de los compuestos puros, contrastando los resultados obtenidos con los existentes en la bibliografía (si los hubiere).

- Calibrado de las condiciones cromatográficas

El análisis de las muestras de ambas fases se realiza por cromatografía de gases. Previamente se procede a determinar las condiciones del cromatógrafo más adecuadas para la separación: tipo de columna, caudal del gas portador (helio) y programación de temperaturas. La respuesta del detector cromatográfico se calibrará utilizando varias muestras patrón de cada uno de los sistemas, preparadas gravimétricamente.

- Determinación experimental del equilibrio líquido-vapor

El equipo experimental (modelo Labodest de Fischer) permite trabajar a presión reducida (hasta 2,5 mmHg) y a temperaturas de hasta 250 °C, estando dotado de los elementos de control y medida de temperatura, presión y potencia de calefacción.

Para la determinación de los datos ELV de sistemas binarios y ternarios se preparan diferentes mezclas de los componentes retirando del dispositivo experimental determinadas cantidades de mezcla y añadiendo iguales cantidades de uno de los compuestos puros (el que interese) hasta recorrer todo el intervalo de composiciones, en incrementos pequeños, lo que permite obtener de 20 a 25 puntos en sistemas binarios y de 40 a 50 puntos en sistemas ternarios. En cada punto, el sistema se lleva a ebullición y se mantiene así hasta tener la seguridad de que se ha alcanzado el estado estacionario (mínimo 45 minutos). Transcurrido este tiempo se toman muestras de vapor y líquido en equilibrio, que pasan a ser analizadas.

# 3. TERMODINÁMICA DEL EQUILIBRIO LÍQUIDO-VAPOR

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## 3.1. CARACTERIZACIÓN DEL EQUILIBRIO LÍQUIDO-VAPOR

Uno de los objetivos de la Termodinámica es el desarrollo de expresiones que establezcan las condiciones de equilibrio de un sistema.

De manera rigurosa el equilibrio se puede establecer en función de propiedades termodinámicas extensivas como la energía interna, entalpía, energía de Helmholtz y energía de Gibbs. La condición necesaria y suficiente para que un sistema cerrado multicomponente y heterogéneo se encuentre en equilibrio es que, a presión y temperatura constantes, la energía de Gibbs total sea mínima. Según ésto, cualquier variación infinitesimal de composición que tenga lugar en el equilibrio a presión y temperatura constantes no origina cambios estables en la energía de Gibbs total del sistema:

$$(dG)_{P,T} = 0 \qquad [1]$$

Normalmente resulta más práctico expresar el equilibrio utilizando magnitudes intensivas como la presión, la temperatura y potenciales químicos. Así, teniendo en cuenta que para un sistema de $N$ componentes, la energía interna es también función del número de moles de los distintos componentes presentes y que la energía de Gibbs está relacionada con la energía interna, partiendo de la ecuación [1] podemos obtener un criterio general para el equilibrio entre fases a presión y temperatura constantes, que se puede formular del modo siguiente:

$$\mu_i^1 = \mu_i^2 = \ldots = \mu_i^m \qquad i = 1, 2, \ldots, N \qquad [2]$$

Es decir, para un sistema de $m$ fases que se encuentran a la misma $T$ y $P$, la condición de equilibrio se satisface cuando el potencial químico de cada especie es el mismo en todas las fases.

La ecuación [2] no se suele aplicar de forma directa. Habitualmente el potencial químico se expresa en términos de alguna función termodinámica relacionada con magnitudes medibles experimentalmente, como puede ser la fugacidad.

La fugacidad del componente *i* en una fase $\alpha$, $\hat{f}_i^{\alpha}$, está directamente relacionada con su potencial químico por medio de la ecuación:

$$\mu_i^{\alpha} = RT^{\alpha} \ln \hat{f}_i^{\alpha} + C \qquad [3]$$

siendo:

$R$ = contante universal de los gases
$T$ = temperatura absoluta (K)
$C$ = parámetro dependiente de la temperatura y de la naturaleza del componente.

A partir de las ecuaciones [2] y [3] y admitiendo equilibrio térmico se deduce una nueva formulación del criterio de equilibrio en función de las fugacidades.

$$\hat{f}_i^1 = \hat{f}_i^2 = \ldots = \hat{f}_i^m \qquad i = 1, 2, \ldots, N \qquad [4]$$

Este último criterio para el equilibrio de fases requiere que, para que un sistema de *m* fases a la misma *T* y *P* se encuentre en equilibrio, la fugacidad de cada componente debe ser la misma en todas las fases.

Para un sistema formado por una fase líquida y otra vapor, y partiendo de la ecuación [4], el estado de equilibrio se puede expresar:

$$\hat{f}_i^L = \hat{f}_i^V \qquad [5]$$

Para sistemas no ideales existen fundamentalmente dos métodos para caracterizar esta igualdad de las fugacidades en equilibrio: el método *phi-phi* ($\phi$ - $\phi$), que describe ambas fases mediante ecuaciones de estado, y el método *gamma-phi* ($\gamma$- $\phi$) que utiliza un modelo para la descripción no ideal de la fase líquida y una ecuación de estado para la fase vapor. Este último método es el que se ha empleado en la caracterización del ELV de los sistemas presentados en esta memoria.

De acuerdo con el método *gamma-phi*, para sistemas no ideales la igualdad de las fugacidades puede escribirse en la forma:

$$y_i \, \hat{\phi}_i \, P = \gamma_i \, x_i \, f_i^o \qquad [6]$$

siendo:

$\gamma_i$ = coeficiente de actividad del componente *i* en la fase líquida.

$f_i^o$ = fugacidad del componente *i* en el estado de referencia elegido para la fase líquida.

$\hat{\phi}_i$ = coeficiente de fugacidad del componente *i* en la fase vapor.

Dado que el criterio de equilibrio en el que se basa el método *gamma-phi* es el que se ha utilizado en el tratamiento termodinámico de los datos de equilibrio presentados en este trabajo, sería conveniente describir algunos aspectos relacionados con los términos que constituyen la ecuación [6].

### 3.1.1. Fase vapor: coeficiente de fugacidad

La desviación con respecto a la idealidad de la fase vapor viene caracterizada por el coeficiente de fugacidad, $\hat{\phi}_i$, que se define como la relación entre su fugacidad y su presión parcial. Para un componente *i* en fase vapor, se expresa como:

$$\hat{\phi}_i = \frac{\hat{f}_i^V}{P_i} = \frac{\hat{f}_i^V}{y_i\, P} \qquad [7]$$

El coeficiente de fugacidad de un componente en una fase (líquida o vapor) puede determinarse a partir de las propiedades volumétricas de la fase (Prausnitz y col., 1986) mediante la ecuación:

$$\ln \hat{\phi}_i = \frac{1}{RT} \int_0^P \left( \bar{V}_i - \frac{RT}{P} \right) dP \qquad [8]$$

siendo $\bar{V}_i$ el volumen molar parcial del componente *i*, definido por

$$\bar{V}_i = \left[ \frac{\partial V}{\partial n_i} \right]_{T,P,n_j (j \neq i)} \qquad [9]$$

La ecuación [8] permite calcular el coeficiente de fugacidad si se dispone de una ecuación de estado a partir de la cual se pueda hallar el volumen. La ecuación de estado más utilizada en el cálculo de coeficientes de fugacidad es la ecuación del Virial (en los casos en los que sea aplicable), que para presiones bajas y moderadas (≤ 5 atm.) y prescindiendo de los términos posteriores al segundo, se puede escribir de la forma:

$$Z = 1 + \frac{BP}{RT} = \frac{P\bar{V}}{RT} \qquad [10]$$

donde:

$Z$ = factor de compresibilidad.

$\bar{V}$ = volumen molar parcial.

$B$ = segundo coeficiente del Virial.

$R$ = constante universal de los gases.

$T$ = temperatura absoluta.

Para una mezcla de $N$ componentes, el segundo coeficiente del Virial, $B$, se puede obtener mediante:

$$B=\sum_{i=1}^{N}\sum_{j=1}^{N} y_i y_j B_{ij} \qquad [11]$$

en donde $B_{ij} = B_{ji}$ representa las interacciones entre las moléculas $i$ y $j$.

Combinando las ecuaciones [8], [10] y [11] resulta finalmente:

$$\ln \hat{\phi}_i = \frac{P}{RT}\left(2\sum_{j=1}^{N} y_i B_{ij} - B\right) \qquad [12]$$

En general no suelen encontrarse en la bibliografía valores experimentales del segundo coeficiente del Virial por lo que normalmente se recurre a algún método de predicción entre los que debemos destacar el de O'Connell y Prausnitz (1967), Tsonopoulos (1974, 1975), Hayden y O'Connell (1975) y Abusleme y Vera (1989). De todos ellos, el más extendido y aplicado con buenos resultados a mezclas con sustancias polares o con tendencia a la asociación es el de Hayden y O'Connell, el cual emplea parámetros que dependen sólo de los componentes de la mezcla.

### 3.1.2. Fase líquida: coeficiente de actividad

En la ecuación [6] se ha introducido el *coeficiente de actividad de una especie i en disolución* definido como:

$$\gamma_i = \frac{\hat{f}_i}{x_i f_i^o} \qquad [13]$$

Es decir, la fugacidad de un componente en una fase líquida está relacionada con la fracción molar de ese componente en dicha fase por medio del coeficiente de actividad y de la fugacidad de referencia.

Para un componente *i* en una fase líquida, la fugacidad de referencia es la fugacidad de ese componente a la temperatura de la solución, aún cuando su presión y composición sean elegidas de modo arbitrario.

Normalmente se adopta como estado de referencia el correspondiente al líquido *i* puro a la temperatura de equilibrio y presión del sistema. Cuando puede tomarse este estado de referencia para todos los componentes de la mezcla se dice que los coeficientes de actividad están normalizados simétricamente, ya que, considerando que a presiones moderadas los coeficientes de actividad son independientes de la presión, se verifica que:

$$\gamma_i = 1 \qquad \text{cuando} \quad x_i = 1$$

En el equilibrio la fugacidad de una especie pura es la misma en todas las fases:

$$f_i^V = f_i^L = f_i^o \qquad [14]$$

donde $f_i^o$ indica el valor tanto para el líquido como para el vapor saturados.

En una primera aproximación la fugacidad del líquido puro se puede considerar igual a la presión de saturación de dicho componente $P_i^o$, a la misma temperatura. Sin embargo, para realizar un cálculo más preciso se deben introducir dos correcciones a esta aproximación: por un lado el coeficiente de fugacidad del componente en condiciones de saturación $\phi_i^o$, que corrige la desviación con respecto a la idealidad del vapor saturado. La segunda corrección, también llamada "corrección de Poynting", es un factor exponencial que tiene en cuenta que el líquido se encuentra a una presión diferente de la de saturación. De acuerdo con ésto, el cálculo de la fugacidad de un componente puro en las condiciones del sistema se puede realizar utilizando la ecuación:

$$f_i^o = P_i^o \phi_i^o \exp \int_{P_i^o}^{P} \frac{V_i^L}{RT} dP \qquad [15]$$

donde:

$P_i^o$ = presión de saturación del componente puro *i* a la temperatura *T*.

$\phi_i^o$ = coeficiente de fugacidad del componente *i* en las condiciones de saturación.

$V_i^L$ = volumen molar del líquido puro *i* a la temperatura *T*.

*R* = constante universal de los gases.

*T* = temperatura de equilibrio.

*P* = presión del sistema.

En general, el volumen de un líquido es función de la presión y de la temperatura, pero si éstas están alejadas de las condiciones críticas, el líquido se considera incompresible y entonces el factor de Poynting toma una forma más sencilla, con lo que la ecuación [15] se puede escribir ahora:

$$f_i^o = P_i^o \phi_i^o \exp \frac{V_i^L \left(P - P_i^o\right)}{RT} \qquad [16]$$

Todos los términos de la ecuación [16] se conocen o son fáciles de obtener. El coeficiente de fugacidad $\phi_i^o$ se calcula con la ecuación [12] como se indicó en el apartado anterior, pero ahora referido a las condiciones de saturación. La presión de saturación, $P_i^o$, se puede calcular empleando cualquiera de las ecuaciones recopiladas por Reid y col. (1987), aunque la más utilizada es la de Antoine:

$$\ln P_i^o = A - \frac{B}{T + C} \qquad [17]$$

siendo:

$A$, $B$, $C$ = constantes específicas para cada componente.

$T$ = temperatura, K

$P_i^o$ = presión de saturación, kPa.

El término exponencial de la ecuación [16] se puede hallar una vez conocido el volumen molar del líquido puro, $V_i^L$, a la temperatura del sistema. También existen numerosos procedimientos de estimación de $V_i^L$, entre ellos el basado en la ecuación de Rackett (Smith y Van Ness, 1987). Este método es el que se ha utilizado en esta memoria en el caso de no disponer del valor experimental correspondiente.

En resumen, el coeficiente de actividad de un componente $i$ en una fase líquida de $N$ componentes, puede determinarse a partir de datos experimentales de ELV. Considerando las ecuaciones [6], [12] y [16] se obtiene la siguiente ecuación (Van Ness y Abbot, 1982):

$$\ln\gamma_i = \ln\frac{y_i P}{x_i P_i^o} + \frac{(B_{ii} - V_i^L)(P - P_i^o)}{RT} + \frac{P}{2\,RT}\sum_{j=1}^{N}\sum_{k=1}^{N} y_i y_k \left(2\delta_{ji} - \delta_{jk}\right) \qquad [18]$$

donde

$$\delta_{ij} = 2B_{ij} - B_{jj} - B_{ii} \qquad [19]$$

Como regla acumulada de la experiencia se observa que, para la gran mayoría de los sistemas el primer término de la ecuación [18] contribuye al menos en un 95% al valor de $\gamma_i$. Ésto significa que una buena aproximación de dicha ecuación es:

$$\ln\gamma_i \approx \ln\frac{y_i P}{x_i P_i^o} \qquad [20]$$

$$y_i P = \gamma_i x_i P_i^o \qquad [21]$$

Se deduce inmediatamente que, si la solución líquida se comporta de manera ideal, $\gamma_i = 1$, se llega a la sencilla relación:

$$y_i\, P = x_i\, P_i^o \qquad [22]$$

Esta ecuación se conoce con el nombre de *ley de Raoult*, y consecuentemente muchos autores denominan a la ecuación [21] *ley de Raoult modificada*.

La principal razón para que existan desviaciones a la *ley de Raoult* en sistemas a presiones muy por debajo de la presión crítica, es que las disoluciones líquidas no suelen comportarse como disoluciones ideales ($\gamma_i \neq 1$). Así, el comportamiento de las fases a presiones bajas o moderadas se puede clasificar adecuadamente de acuerdo con el signo y magnitud de las desviaciones a la ley de Raoult:

a) $\gamma_i < 1$, desviación negativa de la ley de Raoult:

$$y_i\, P < x_i\, P_i^o$$

b) $\gamma_i > 1$, desviación positiva de la ley de Raoult:

$$y_i\, P > x_i\, P_i^o$$

En el primer caso, la curva *P-x* o curva del punto de burbuja en un diagrama *P-x-y* cae por debajo de la relación lineal *P-x* prevista por la ley de Raoult. Cuando las desviaciones se hacen suficientemente grandes respecto a la diferencia entre las presiones de vapor de los compuestos puros, la curva *P-x* presenta un mínimo. Al mismo tiempo, la curva *P-y* o curva del punto de rocío tiene un mínimo en el mismo punto ($x = y$). Un líquido de esta composición que esté hirviendo producirá un vapor que tendrá exactamente la misma composición, y el líquido no cambiará de composición conforme se vaya evaporando. No es posible la separación por destilación de una disolución de este tipo. Para describir este estado se utiliza el término **azeótropo**.

De igual modo, las desviaciones positivas pueden ser suficientemente grandes como para dar un máximo en la curva *P-x*, coincidiendo también con un máximo de la curva *P-y*. Este punto también representa la existencia de un azeótropo.

La disposición que adoptan las moléculas en una solución depende de sus tamaños y de las fuerzas de interacción. Por un lado, según la teoría de Flory (1941) las diferencias apreciables de tamaño dan lugar a desviaciones negativas de la ley de Raoult. Sin embargo, dependiendo de la naturaleza de las fuerzas de interacción predominantes entre las moléculas de la mezcla, se pueden encontrar desviaciones positivas o negativas respecto a la idealidad. A escala molecular, desviaciones negativas de la ley de Raoult reflejan que las fuerzas de atracción intermolecular entre pares de moléculas distintas son más fuertes que las existentes entre moléculas iguales. Por el contrario, se obtienen desviaciones positivas de la ley de Raoult cuando en la disolución las fuerzas intermoleculares entre moléculas iguales son mayores que las existentes entre moléculas distintas. En este último caso, las fuerzas entre las moléculas de un mismo componente pueden ser tan fuertes que lleguen a impedir la completa miscibilidad, y el sistema forma dos fases líquidas en un determinado intervalo de composición.

## 3.2. CORRELACIÓN DE DATOS DE ELV

El comportamiento que presenta una solución real difiere del mostrado por una solución ideal en las mismas condiciones de presión, temperatura y composición. Esta diferencia de comportamiento puede expresarse mediante las propiedades de exceso, que se definen como la diferencia entre una función termodinámica de una mezcla real y la misma función calculada para una mezcla ideal. En el caso particular de la energía de Gibbs, se tendrá:

$$g^E = g - g^{id} = h^E - T\,s^E \qquad [23]$$

donde $g^E$, $h^E$ y $s^E$ representan la energía de Gibbs, la entalpía y la entropía molares de exceso, respectivamente. La entalpía de exceso tiene en cuenta las interacciones entre las moléculas, y la entropía de exceso la disposición espacial de las mismas.

En una mezcla líquida todos los coeficientes de actividad están directamente relacionados con la energía de Gibbs molar de exceso mediante la siguiente expresión:

$$\frac{g^E}{RT} = \sum_i \left(x_i \ln\gamma_i\right) \qquad [24]$$

Expresando $g^E$ como función de la composición y de la temperatura, el coeficiente de actividad individual puede calcularse por medio de:

$$\ln\gamma_i = \left[\frac{\partial\left(\dfrac{n_T\, g^E}{RT}\right)}{\partial n_i}\right]_{T,P,n_{j(j\neq i)}} \qquad [25]$$

siendo $n_i$ el número de moles del componente *i*, $n_T$ el número de moles totales, *R* la constante universal de los gases y *T* la temperatura absoluta del sistema.

De esta forma, buscando expresiones que describan la energía de Gibbs molar de exceso como función de la composición y de la temperatura para una mezcla líquida determinada, se podrá obtener los valores de los coeficientes de actividad y por tanto mediante la ecuación [18] ó [21], los datos de ELV de dicha mezcla.

Partiendo de datos experimentales de equilibrio de un sistema determinado a unas condiciones dadas, se calculan los coeficientes de actividad con la ecuación [18]. Una vez calculados se pueden correlacionar con modelos o ecuaciones. De esta forma podremos utilizar dicho modelo para obtener datos de ELV de ese sistema en condiciones diferentes a las de la determinación experimental.

Tomando como base estos conceptos, surgieron un gran número de expresiones para correlacionar datos de ELV, haciendo uso de parámetros determinados por métodos de optimización que hacen mínima la desviación entre los datos experimentales y los calculados.

Inicialmente se desarrollaron modelos que solamente consideraban las interacciones entre las moléculas (término entálpico de la ecuación [23]) y suponían una distribución aleatoria de las mismas ($s^E = 0$). Dichos modelos expresan la energía de Gibbs como función exclusivamente de la composición y de unos parámetros de ajuste. Entre las ecuaciones polinómicas obtenidas a partir de estos modelos cabe citar las de Margules (1895), Van Laar (1910), Redlich-Kister (1948), etc. Sin embargo, para mezclas formadas por compuestos polares o que presentan enlaces tipo hidrógeno, se originan orientaciones preferenciales entre las moléculas y no se puede suponer una distribución aleatoria de las mismas.

En 1964 Wilson propone una ecuación que combina el modelo desarrollado por Flory (1941, 1942) y Huggins (1941) con el concepto de composición local. Según éste una mezcla no puede considerarse homogénea, desde el punto de vista macroscópico, si la composición difiere de unos puntos a otros. Así surgieron también las ecuaciones NRTL (Renon y Prausnitz, 1968), LEMF (Marina y Tassios, 1973), UNIQUAC (Abrams y Prausnitz, 1975) y sus sucesivas modificaciones tratando de buscar una mejor aplicación a sistemas concretos o una mejor descripción de las interacciones intermoleculares.

### 3.2.1. Ecuación de Wilson

Con la aparición de la ecuación de Wilson (1964) se produce un avance muy importante, puesto que se convierte en la primera de una serie de ecuaciones semiempíricas basadas en el concepto de composición local. Dicho concepto consiste en suponer que la concentración de moléculas de tipo *i* en torno a una molécula tipo *j* no es igual a la concentración de moléculas de tipo *j* alrededor de una molécula de tipo *i*, con lo que la composición de la mezcla no será homogénea.

El modelo de Wilson no sólo tiene en cuenta la energía de interacción intermolecular, sino también las diferencias de tamaño y la distribución espacial de las moléculas presentes en la mezcla. La deducción de este modelo comienza con la definición del concepto de composición local y de la fracción de volumen local.

En una mezcla, la distribución de las moléculas en torno a una molécula central de tipo *i* viene dada por la relación de probabilidades:

$$\frac{x_{ji}}{x_{ki}} = \frac{x_j\ \mathrm{e}^{-\lambda_{\mathrm{ji}}/RT}}{x_k\ \mathrm{e}^{-\lambda_{\mathrm{ki}}/RT}} \qquad [26]$$

donde $x_{ji}$ es la fracción molar local del componente *j* alrededor del componente *i* y los parámetros $\lambda_{ji}$ son proporcionales a la energía de interacción entre las moléculas *j* e *i*, siendo $\lambda_{ji} = \lambda_{ij}$. De acuerdo con ésto se define la fracción de volumen molar local del componente *i* en la proximidad de una molécula central del mismo tipo como:

$$\xi_i = \frac{x_i\ \overline{V}_i\ \mathrm{e}^{-\lambda_{\mathrm{ij}}/RT}}{\sum_j x_j\ \overline{V}_j\ \mathrm{e}^{-\lambda_{\mathrm{ji}}/RT}} \qquad [27]$$

siendo $\overline{V}_j$ el volumen molar del componente *j*.

Partiendo de esta definición Wilson expresó la energía de Gibbs molar de exceso:

$$\frac{g^E}{RT} = \sum_{i=1}^{N} x_i \ln \frac{\xi_i}{x_i} \qquad [28]$$

en la que para simplificar se introduce el término:

$$\Lambda_{ij} = \frac{\overline{V}_j}{\overline{V}_i} \exp\left( -\frac{\lambda_{ij} - \lambda_{ii}}{RT} \right) = \frac{\overline{V}_j}{\overline{V}_i} \exp\left( \frac{\Delta\lambda_{ij}}{RT} \right) \qquad [29]$$

resultando:

$$\frac{g^E}{RT} = -\sum_{i=1}^{N} x_i \ln\left( \sum_{j=1}^{N} x_j \Lambda_{ij} \right) \qquad [30]$$

y a partir de aquí, la expresión para el coeficiente de actividad sería:

$$\ln \gamma_i = 1 - \ln\left( \sum_{j=1}^{N} x_j \Lambda_{ij} \right) - \sum_{k=1}^{N} \frac{x_k \Lambda_{ki}}{\sum_{j=1}^{N} x_j \Lambda_{kj}} \qquad [31]$$

La ecuación de Wilson presenta la ventaja de que los parámetros ajustables $\Delta\lambda_{ij}$ pueden tratarse como independientes de la temperatura, lo cual permite el cálculo de los coeficientes de actividad tanto en condiciones isotérmicas como isobáricas. Además, su aplicación ha resultado ser válida para un gran número de mezclas, incluso en el caso de sistemas no ideales.

Su limitación más importante es la incapacidad de representar sistemas parcialmente miscibles ya que no predice la separación de fases. Para tratar de resolver este problema, Wilson incorporó a su ecuación un parámetro *C*, carente de significado físico, creando nuevos inconvenientes puesto que aumentaba la interdependencia entre los parámetros haciendo más difícil la regresión, incluso para sistemas binarios. Por esta razón, el uso de este parámetro añadido ha tenido poca aceptación y se utiliza de forma generalizada la ecuación de Wilson original.

### 3.2.2. Ecuación NRTL (Non-Random Two Liquids model)

En 1968, Renon y Prausnitz establecieron un modelo que utilizaba el concepto de composición local, similar al de Wilson, y la teoría de dos líquidos de Scott (1956). Este modelo considera que la composición interna del líquido no es aleatoria sino que las moléculas están semi-agregadas. En este modelo, denominado NRTL, la composición local se define como:

$$\frac{x_{ji}}{x_{ii}} = \frac{x_j \, \mathrm{e}^{-\alpha_{ji} g_{ji} / RT}}{x_i \, \mathrm{e}^{-\alpha_{ji} g_{ii} / RT}} \qquad [32]$$

donde $g_{ji}$ tiene un significado similar al de $\lambda_{ji}$ utilizado por Wilson y la única diferencia con la ecuación [26] es la introducción de un nuevo parámetro ajustable $\alpha_{ji}$, que se denomina *parámetro de desorden* y que es característico de la mezcla. Su valor está comprendido entre 0 (mezclas totalmente aleatorias: desorden total) y 1 (orden total). Para mezclas no aleatorias este parámetro es similar al inverso del número de coordinación $z$, introducido en la teoría de red de Guggenheim (1952). De hecho, los valores típicos de $\alpha_{ji}$ están comprendidos entre 0.1 y 0.5, sin embargo este parámetro es una constante empírica y no puede atribuírsele un significado físico, puesto que la teoría de red no se emplea en el desarrollo de la ecuación NRTL. Lo que sí tiene en cuenta este modelo es la teoría de Scott a la hora de considerar la expresión de la energía de Gibbs molar de exceso. Para una mezcla de $N$ componentes esta ecuación toma la forma:

$$\frac{g^E}{RT} = \sum_{i=1}^{N} x_i \frac{\sum_{j=1}^{N} \tau_{ji} G_{ji} x_j}{\sum_{k=1}^{N} G_{ki} x_k} \qquad [33]$$

donde:

$$\tau_{ji} = \frac{g_{ji} - g_{ii}}{RT} = \frac{\Delta g_{ji}}{RT} \qquad [34]$$

$$G_{ji} = \exp\left(-\alpha_{ji}\, \tau_{ji}\right) \qquad [35]$$

siendo $\alpha_{ji} = \alpha_{ij}$ con lo que la expresión para el coeficiente de actividad resultaría:

$$\ln \gamma_i = \frac{\sum_{j=1}^{N} \tau_{ji} G_{ji} x_j}{\sum_{j=1}^{N} G_{ki} x_k} + \sum_{j=1}^{N} \frac{x_j G_{ij}}{\sum_{k=1}^{N} G_{kj} x_k} \left( \tau_{ij} - \frac{\sum_{l=1}^{N} x_l \tau_{lj} G_{lj}}{\sum_{k=1}^{N} G_{kj} x_k} \right) \qquad [36]$$

Los parámetros ajustables $\Delta g_{ji}$ tienen el mismo significado que en el modelo de Wilson, pero a diferencia de éste, el modelo NRTL introduce el nuevo parámetro $\alpha_{ij}$, lo que complica la correlación e incrementa el cálculo. La ventaja que presenta es que para mezclas parcialmente miscibles proporciona una buena representación de los datos experimentales.

### 3.2.3. Ecuación UNIQUAC (UNIversal QUAsi-Chemical theory)

En 1975, Abrams y Prausnitz, haciendo uso de la mecánica estadística, proponen un modelo para la energía de Gibbs de exceso. Su modelo, denominado UNIQUAC, generaliza un análisis previo de Guggenheim (1952) y lo amplía a mezclas de moléculas que difieren apreciablemente tanto en la forma como en el tamaño.

Esta ecuación consta de dos partes, una combinatorial (*C*) que tiene en cuenta las contribuciones entrópicas, y otra residual (*R*) que describe las contribuciones entálpicas. Según esto la ecuación UNIQUAC toma la forma:

$$g^{E} = g^{E(C)} + g^{E(R)} \qquad [37]$$

La parte combinatorial describe las interacciones entre moléculas del mismo tipo, pero de diferente tamaño y forma y depende sólo de las propiedades de los componentes puros, mientras que la parte residual se refiere a las interacciones entre moléculas de diferente naturaleza química y depende de las propiedades de la mezcla.

Para una mezcla multicomponente los términos anteriores se definen como:

$$g^{E(C)} = \sum_{i=1}^{N} x_i \ln \frac{\Phi_i}{x_i} + \frac{z}{2} \sum_{i=1}^{N} q_i x_i \ln \frac{\theta_i}{\Phi_i} \qquad [38]$$

$$g^{E(R)} = -\sum_{i=1}^{N} q_i x_i \ln \left( \sum_{j=1}^{N} \theta_j \tau_{ji} \right) \qquad [39]$$

en donde $z = 10$ y las expresiones para el parámetro de energía, $\tau_{ji}$, la fracción de volumen, $\Phi_i$, y la fracción de área, $\theta_i$, vienen dadas por:

$$\tau_{ji} = \exp\left( -\frac{u_{ji} - u_{ii}}{RT} \right) = \exp\left( \frac{\Delta u_{ij}}{RT} \right) \qquad [40]$$

$$\theta_i = \frac{q_i x_i}{\sum_{j=1}^{N} q_j x_j} \qquad [41]$$

$$\Phi_i = \frac{r_i x_i}{\sum_{j=1}^{N} r_j x_j} \qquad [42]$$

donde $\Delta u_{ij}$ son los parámetros energéticos ajustables, y $q_i$ y $r_i$ son respectivamente los parámetros estructurales de área y volumen moleculares de Van der Waals con relación a los de un segmento patrón:

$$r_i = \frac{V_{wi}}{1.517 \cdot 10^{-2}} \qquad [43]$$

$$q_i = \frac{A_{wi}}{2.5 \cdot 10^{8}} \qquad [44]$$

siendo $V_{wi}$ ($m^3$/kmol) y $A_{wi}$ ($m^2$/kmol) respectivamente el volumen y área molecular calculados por Bondi (1968). Valores de estos parámetros para una gran cantidad de moléculas fueron recopilados por Daubert y Danner (1989).

A partir de las ecuaciones [37], [38] y [39] se pueden deducir las expresiones para los coeficientes de actividad:

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \qquad [45]$$

$$\ln \gamma_i^C = \ln \frac{\Phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\Phi_i} + l_i - \frac{\Phi_i}{x_i} \sum_{j=1}^{N} x_j l_j \qquad [46]$$

$$\ln \gamma_i^R = -q_i \ln \sum_{j=1}^{N} \theta_j \tau_{ji} + q_i - q_i \sum_{j=1}^{N} \frac{\theta_j \tau_{ij}}{\sum_{k=1}^{N} \theta_k \tau_{kj}} \qquad [47]$$

siendo:

$$l_i = \frac{z}{2}(r_i - q_i) - (r_i - 1) \qquad [48]$$

La ecuación UNIQUAC es más complicada y ligeramente menos precisa que los modelos de Wilson y NRTL, pero presenta la ventaja de su flexibilidad ya que puede aplicarse a mezclas de componentes con tamaños moleculares muy diferentes.

Los modelos de correlación señalados en los apartados anteriores presentan, en cuanto a su aplicación y fundamento, algunas características que sería conveniente reseñar. Los modelos de Wilson, NRTL y UNIQUAC asumen que los parámetros de interacción son independientes de la temperatura. Esto puede causar serias limitaciones en la representación de sistemas con elevadas entalpías de mezcla, especialmente si los parámetros han sido correlacionados a partir de datos de ELV obtenidos en pequeños intervalos de temperatura. Para subsanar este inconveniente se han propuesto modelos de coeficientes de actividad con formas en las que se tiene en cuenta esta dependencia de la temperatura.

Con el fin de mejorar la representación de la entalpía de exceso y de la energía de Gibbs de exceso, Skjold-Jørgensen y col. (1980) han desarrollado formas para expresar la dependencia con la temperatura tanto de los parámetros del modelo UNIQUAC, como del índice de coordinación. De manera análoga, Ferino y col. (1983), han propuesto parámetros de interacción dependientes de la temperatura para el modelo NRTL. Sin embargo, la ventaja que ofrecen estas expresiones sólo es importante para la descripción simultánea del equilibrio líquido-vapor y las entalpías de exceso.

Las ecuaciones de Wilson, NRTL y UNIQUAC pueden emplearse para representar la energía de Gibbs de exceso de sistemas multicomponentes a partir de parámetros de correlación de los sistemas binarios correspondientes. Además, estos dos últimos modelos también se utilizan para describir el equilibrio líquido-líquido (Anderson y Prausnitz, 1978), pero los parámetros obtenidos con estas correlaciones no pueden emplearse para reproducir datos de ELV y viceversa. Skjold-Jørgensen y col. (1982) introdujeron modificaciones al modelo UNIQUAC para tratar de resolver este problema, muy importante sobre todo en el caso de mezclas altamente no ideales con fuertes interacciones específicas tales como asociación y solvatación.

### 3.2.4. Ecuaciones Wisniak-Tamir

Wisniak y Tamir (1976) desarrollaron un modelo con el propósito de relacionar de forma directa la temperatura de ebullición de una mezcla con su composición, sin necesidad de conocer los coeficientes de actividad.

A bajas presiones, la temperatura de ebullición de una mezcla a presión contante puede calcularse resolviendo la siguiente ecuación:

$$1 = \sum_{i=1}^{N} \left(P_i^o x_i / P\right) \gamma_i \qquad [49]$$

No obstante, para resolver esta ecuación se necesita conocer los coeficientes de actividad en función de la composición y de la temperatura.

Considerando un comportamiento ideal de la fase vapor y utilizando un modelo polinómico para la energía de Gibbs molar en la ecuación [24], Wisniak y Tamir obtuvieron la siguiente expresión para el cálculo de las temperaturas de ebullición de un sistema binario:

$$T=\sum_{i=1}^{2}x_iT_i^o+w+x_1x_2\sum_{k=0}^{m}C_k(x_1-x_2)^k \qquad [50]$$

donde $T_i^o$ es la temperatura de ebullición del componente $i$ puro y $m$ es el número de términos considerados en la serie de expansión de $(x_1 - x_2)$. El término $w$ viene dado por la siguiente expresión:

$$w=\sum_{i=1}^{N}x_i\ln\frac{y_i}{x_i} \qquad [51]$$

Se observa que el valor de $w$ es siempre negativo y su máximo valor es cero para el punto azeotrópico y para dilución infinita. Si se analiza la expresión [51] se deduce que la contribución de $w$ para el cálculo de $T$ solamente será significativa cuando $y_i$ sea muy diferente a $x_i$, es decir para volatilidades relativas elevadas. En general, su contribución puede incoporarse a las constantes $C_k$ de correlación, de esta forma se puede calcular la composición de la fase líquida para una temperatura de ebullición dada, y viceversa, sin necesidad de conocer la composición del vapor.

Para un sistema ternario:

$$T=\sum_{i=1}^{3}x_iT_i^o+\sum_{i,j=1}^{3}\left[x_ix_j\sum_{k=0}^{m}C_k\left(x_i-x_j\right)^k\right]+$$
$$+x_1x_2x_3\left[A+B\left(x_1-x_2\right)+C\left(x_1-x_3\right)+D\left(x_2-x_3\right)+\ldots\right] \qquad [52]$$

donde $C_k$ son las constantes correspondientes a los sistemas binarios, y $A$, $B$, $C$ y $D$ son constantes del ternario. Para una mezcla con mayor número de componentes, por ejemplo para un sistema cuaternario en el cálculo de $T$ existirá una contribución de los binarios, otra de los ternarios y por último otra cuaternaria. Es decir, el número de los parámetros va aumentando considerablemente conforme se incrementa el número de componentes del sistema. Además, toda la información necesaria (datos binarios, ternarios, etc.) para una mezcla multicomponente difícilmente está disponible de forma completa cuando el número de componentes es superior a tres. Por esta razón, Tamir (1981) desarrolló una expresión que permite una correlación directa de los datos para sistemas con $N$ componentes:

$$T = \sum_{i=1}^{N} x_i T_i^o + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} x_i x_j \left[ A_{ij} + B_{ij}(x_i - x_j) + C_{ij}(x_i - x_j)^2 + \ldots \right] \qquad [53]$$

donde $A_{ij}$, $B_{ij}$ y $C_{ij}$ no son constantes binarias sino parámetros multicomponentes determinados directamente de los datos.

La principal ventaja de este tipo de ecuaciones es su sencillez y son especialmente útiles para aquellos sistemas donde existen fuertes asociaciones tanto en la fase líquida como en el vapor, y también cuando los efectos de las entalpías de mezcla son importantes, ya que en dichos casos es cuando precisamente la información necesaria para la correlación de los coeficientes de actividad suele ser muy escasa.

## 3.3. SOLUCIONES REGULARES

La teoría de Scatchard-Hildebrand (Prausnitz y col., 1986) define una solución regular como aquella en la que los componentes se mezclan sin exceso de entropía, siempre que no haya cambios de volumen al mezclarse. La consecuencia de que la entropía de exceso se anule es que la energía de Gibbs molar de exceso y la entalpía molar de exceso se igualen (ver ecuación [23]), indicando que sólo hay fuerzas físicas de tipo dispersivo en disolución.

Las fuerzas de dispersión (también conocidas como fuerzas de van der Waals) aparecen en moléculas simétricas, en las que el centro de cargas es equivalente al centro de masas. Este tipo de fuerzas moleculares no depende de la orientación sino sólo de la distancia entre los centros de masas de dos moléculas. Este hecho permite definir un parámetro que caracterice las interacciones entre moléculas diferentes a partir de los parámetros correspondientes a las interacciones entre moléculas iguales:

$$c_{12} = \sqrt{c_{11}c_{22}} \qquad [54]$$

donde $c_{ij}$ representa una constante característica del campo de dispersión denominada energía cohesiva, entendida como la energía necesaria para juntar dos moléculas infinitamente separadas y se calcula como la razón entre la energía interna de vaporización y el volumen del líquido. Esta aproximación es correcta cuando las moléculas son perfectamente esféricas.

Existe otro tipo de fuerzas moleculares que imponen determinadas posiciones preferenciales a las moléculas, es decir son fuerzas orientacionales. Las fuerzas electrostáticas generadas por dos dipolos es un ejemplo de dichas fuerzas. Así, físicamente, las moléculas polares no satisfacen el supuesto de regularidad, pues sus interacciones no pueden ser promediadas por la regla geométrica [54].

La ecuación fundamental para el cálculo de $g^E$ en soluciones reales es la siguiente relación entre dicha propiedad y la energía interna de exceso $u^E$:

$$u^E = g^E + Ts^E - Pv^E \qquad [55]$$

Si suponemos que $s^E = 0$ y $v^E = 0$, se obtiene que:

$$u^E = g^E = h^E \qquad [56]$$

El hecho de considerar que la entropía de exceso es nula tiene su consecuencia en el cálculo de los coeficientes de actividad. Para una solución regular el logaritmo de cada uno de los coeficientes de actividad a composición constante, debe ser inversamente proporcional a la temperatura absoluta (Prausnitz y col., 1986):

$$RT \ln \gamma_1 = A' \Phi_2^2 \qquad [57]$$

$$RT \ln \gamma_2 = B' \Phi_1^2 \qquad [58]$$

siendo $\Phi_i$ la fracción volumétrica del componente $i$ definida por:

$$\Phi_i = \frac{x_i V_i^L}{x_i V_i^L + x_j V_j^L} \qquad [59]$$

donde $V_i^L$ es el volumen molar del líquido $i$ puro, y las constantes de las ecuaciones [57] y [58] cumplen la siguiente relación $A'/B' = V_1^L/V_2^L$. Se observa, como dichas expresiones siempre predicen $\gamma_i \geq 1$, es decir una solución regular solamente puede exhibir desviaciones positivas respecto a la ley de Raoult.

Combinando las ecuaciones [57], [58], [59] y [24], se obtiene la siguiente expresión para la energía de Gibbs molar de exceso:

$$\frac{g^E}{RT} = \frac{1}{RT} \frac{A'B' x_1 x_2}{x_1 A' + x_2 B'} \qquad [60]$$

Esta ecuación es conocida como ecuación de Van Laar y representa sistemas regulares con una diferencia apreciable de tamaño molecular entre sus componentes.

En el caso de que los componentes de la mezcla tengan el mismo tamaño ($A'=B'$) se llega a la sencilla relación:

$$\frac{g^{\mathrm{E}}}{RT}=\frac{A'}{RT}x_1x_2 \tag{61}$$

Esta función describe un comportamiento simétrico para la energía de Gibbs molar de exceso respecto a la composición: $g^E$ presenta un valor máximo para $x_1 = 0.5$; para esta misma composición los valores de los coeficientes de actividad de ambos componentes se igualan. A la ecuación [61] se le conoce también con el nombre de ecuación de Porter o ecuación de Margules de segundo orden.

La teoría regular tiene importantes limitaciones para describir sistemas reales, y principalmente sistemas altamente no ideales. En soluciones reales ni la entropía de exceso ni el volumen de exceso pueden ser cero. Lo que sí puede suceder es que la diferencia ($Ts^E - Pv^E$) tienda a anularse y por tanto, es posible observar comportamiento regular en soluciones reales. Por esta razón, algunos sistemas polares e incluso con asociación, pueden describirse bajo el supuesto de regularidad. En tales sistemas la entropía de exceso es importante, sin embargo el término entrópico puede llegar a compensarse con el correspondiente al del volumen de exceso.

## 3.4. CONSISTENCIA TERMODINÁMICA DE LOS DATOS DE ELV

Los tests de consistencia son herramientas de la Termodinámica que permiten, en principio, verificar la calidad y fiabilidad de datos experimentales de ELV. Cabe citar la revisión realizada por Wisniak y col. (1997a) de los principales tests de consistencia termodinámica que se pueden encontrar en la bibliografía. En dicho estudio se define la función de un test de consistencia de la siguiente manera:

*"si los datos satisfacen el criterio de un test de consistencia bien formulado, entonces se consideran apropiados para el diseño y la modelización, y es posible reproducirlos y adaptarlos adecuadamente mediante cualquier relación termodinámica."*

En la determinación experimental del ELV se obtiene un conjunto de datos que son el resultado de la medida de cuatro variables, *x-y-T-P*, sin embargo sólo son necesarias dos de ellas para caracterizar completamente el sistema. Las otras dos son variables dependientes que pueden calcularse por medio de las relaciones termodinámicas. La información suplementaria nos permite comparar los valores calculados con los obtenidos experimentalmente y con ello comprobar la consistencia termodinámica de los datos.

Con este propósito se han desarrollado diferentes métodos de evaluación, independientes del factor humano, que consideran la consistencia de los datos experimentales basándose en conocidas ecuaciones termodinámicas.

Entre las muchas relaciones termodinámicas que deben satisfacerse, una de gran valor para probar la consistencia de unos datos es la ecuación de Gibbs-Duhem. Para un sistema de $N$ componentes esta ecuación puede escribirse en la forma:

$$\frac{h^E}{RT^2}\,\mathrm{d}T - \frac{v^E}{RT}\,\mathrm{d}P + \sum_{i=1}^{N} x_i\,\mathrm{d}\ln\gamma_i = 0 \qquad [62]$$

donde $h^E$ y $v^E$ son la entalpía y el volumen molar de exceso de la mezcla respectivamente. Esta ecuación proporciona una relación fundamental entre los coeficientes de actividad de los componentes de una disolución. Si los valores experimentales son buenos deben satisfacer la ecuación de Gibbs-Duhem dentro de unos límites de tolerancia (criterio de consistencia). Lo contrario no siempre es cierto: puede suceder que unos datos sean incorrectos pero casualmente cumplan el criterio de consistencia. Es decir, el hecho de cumplir el criterio de consistencia impuesto por un determinado test es una condición necesaria, pero no suficiente, para afirmar la bondad de unos datos experimentales.

En el caso de datos isotermos d$T$ = 0, y si además la presión del sistema es baja o moderada, se puede comprobar que el término $v^E/RT$ es relativamente pequeño y puede despreciarse, con lo que la ecuación [62] queda reducida a:

$$\sum_{i=1}^{N} x_i \,\mathrm{d}\ln\gamma_i = 0 \qquad [63]$$

Para datos isobáricos d$P$ = 0, y la ecuación que se debe utilizar es:

$$\frac{h^E}{RT^2}\,\mathrm{d}T + \sum_{i=1}^{N} x_i \,\mathrm{d}\ln\gamma_i = 0 \qquad [64]$$

El término $(h^E/RT^2)\mathrm{d}T$ representa la variación de $g^E$ con la temperatura. Sin embargo, como habitualmente los valores de $h^E$ necesarios para evaluar dicho término son escasos, normalmente se aplica la ecuación [63] también para sistemas a presión constante.

Los tests de consistencia pueden llevarse a cabo de dos formas diferentes. Un método consiste en realizar un test global basándose en una forma integrada de las ecuaciones anteriores, mientras que en el otro método los puntos se examinan de forma individual.

Para verificar la consistencia termodinámica de los datos de equilibrio presentados en este trabajo se ha optado por los métodos punto a punto debido a su mayor rigurosidad y a su frecuente utilización por numerosos autores. Para los sistemas binarios se ha utilizado el test propuesto por Van Ness y col. (1973) modificado por Fredenslund y col. (1977), y para los sistemas ternarios se han aplicado dos tratamientos distintos: el test de McDermott-Ellis (1965) modificado por Wisniak y Tamir (1977) y el método L-W desarrollado por Wisniak (1993).

### 3.4.1. Test puntual de Fredenslund para sistemas binarios

El test de consistencia termodinámica propuesto por Fredenslund y col. (1977) está basado en el método $\gamma$- $\phi$ y fue desarrollado para sistemas binarios. Utiliza polinomios de Legendre para representar la energía de Gibbs molar de exceso:

$$g = \frac{g^E}{RT} = x_1(1-x_1)\sum_k a_k L_k(x_1) \qquad k = 0,1,\cdots,n \qquad [65]$$

$$L_k(x_1) = \{(2k-1)(2x_1-1)L_{k-1}(x_1) - (k-1)L_{k-2}(x_1)\}/k \qquad [66]$$

$$L_0(x_1) = 1 \qquad L_1(x_1) = 2x_1 - 1 \qquad [67]$$

donde $n$ es el orden del polinomio utilizado y $a_k$ son los coeficientes del mismo. Éstos se ajustan para obtener una representación óptima de los datos experimentales. Así mismo, el orden del polinomio también es otra variable a optimizar.

Para obtener los valores $a_k$ hay que definir una función objetivo a minimizar, normalmente se propone:

$$F.O = \sum \left(P^{calc} - P^{expt}\right)^2 \qquad [68]$$

en la que $P^{calc}$ se obtiene mediante la ecuación:

$$P^{calc} = x_1 P_1^o \gamma_1^{calc} + x_2 P_2^o \gamma_2^{calc} \qquad [69]$$

siendo:

$$\gamma_1^{calc} = \exp(g + x_2 g') \qquad \gamma_2^{calc} = \exp(g - x_1 g') \qquad [70]$$

donde:

$$g' = \frac{\mathrm{d}g}{\mathrm{d}x_1} \qquad [71]$$

De esta forma, con los valores de los coeficientes de actividad calculados se obtendrá la composición de la fase vapor con la ecuación [18] ó [21], según se considere o no el comportamiento no ideal de la fase vapor. Por tanto, se puede comparar la diferencia entre el valor calculado y el experimental para cada una de las composiciones de la fase vapor:

$$\Delta y_i = \left| y_i^{expt} - y_i^{calc} \right| \qquad [72]$$

De acuerdo con el criterio adoptado por Fredenslund, un dato se estima consistente cuando $\Delta y_i$ es menor de 0.01. El criterio de consistencia también incluye un análisis de los valores residuales de $\Delta y_i$ y de $\Delta P_i$. Dichos valores deben distribuirse de forma aleatoria para considerar un conjunto de datos de ELV termodinámicamente consistente.

### 3.4.2. Test de McDermott-Ellis

McDermott y Ellis desarrollaron este método de consistencia basándose en el hecho de que la precisión de datos de ELV en sistemas multicomponentes está limitada principalmente por la precisión que permite el método de análisis utilizado para determinar las composiciones.

Este test analiza la consistencia termodinámica entre un par de puntos experimentales. Para ello, los puntos se han de disponer en orden creciente en *T*. De esta forma, dos puntos experimentales *a* y *b* se consideran termodinámicamente consistentes si cumplen la siguiente condición:

$$D_i < D_{max} \qquad [73]$$

La desviación local $D_i$ viene dada por:

$$D_i = \sum_{i=1}^{N} (x_{ia} + x_{ib})(\ln \gamma_{ib} - \ln \gamma_{ia}) \qquad [74]$$

La desviación $D_i$ está directamente relacionada con el error en los coeficientes de actividad de los puntos considerados. McDermott y Ellis recomendaron el uso de un valor fijo de 0.01 para la desviación máxima $D_{max}$. Sin embargo, Wisniak y Tamir (1977) consideraron que la máxima desviación, $D_{max}$, debida a errores experimentales no tiene un valor constante, y puede ser estimada teniendo en cuenta la contribución de las diferentes fuentes de error en [74]:

$$D = D(\, x_{ia}, x_{ib}, \gamma_{ia}, \gamma_{ib} \,) \qquad [75]$$

De esta forma, para analizar la diferencial total d*D* se ha de tener también en cuenta el efecto de la temperatura y la presión. Dicho efecto es introducido considerando la ley de Raoult modificada [21] para el cálculo de $\gamma_i$:

$$\mathrm{d} \ln \gamma_i = \mathrm{d} \ln P - \mathrm{d} \ln P_i^o + \mathrm{d} \ln y_i - \mathrm{d} \ln x_i \qquad [76]$$

La dependencia de $P_i^o$ se obtiene a partir de la ecuación de Antoine [17]. El error en la determinación experimental en la fase líquida es el mismo que para la fase vapor. Con todo ello, la expresión final para la máxima desviación resulta:

$$
\begin{aligned}
D_{max} &= \sum_{i=1}^{N} (x_{ia} + x_{ib}) \left( \frac{1}{x_{ia}} + \frac{1}{y_{ia}} + \frac{1}{x_{ib}} + \frac{1}{y_{ib}} \right) \Delta x + \\
&+ \sum_{i=1}^{N} (x_{ia} + x_{ib}) \frac{\Delta P}{P} + 2 \sum_{i=1}^{N} \ln \gamma_{ib} - \ln \gamma_{ia} \, \Delta x + \\
&+ \sum_{i=1}^{N} (x_{ia} + x_{ib}) B_j \left\{ (T_a + C_j)^{-2} + (T_b + C_j)^{-2} \right\} \Delta T
\end{aligned}
\qquad [77]
$$

donde $\Delta x$, $\Delta P$ y $\Delta T$ representan la precisión en la determinación experimental de la composición, de la presión y de la temperatura, respectivamente. El primer término de la ecuación [77] es, en general, el de mayor magnitud.

### 3.4.3. Test de Wisniak

En 1993 Wisniak desarrolló un nuevo test de consistencia termodinámico tanto para sistemas binarios como para sistemas con más componentes. El esquema general fue expuesto por Malesinski (1965) y está basado en la relación existente entre la energía de Gibbs molar de exceso de una mezcla y su punto de ebullición.

Recordando la expresión de $g^E$ para una mezcla multicomponente:

$$g^E = RT \sum_i x_i \ln \gamma_i \qquad [24]$$

Si suponemos que la fase vapor se comporta idealmente podremos utilizar la ecuación [21] para el cálculo de los coeficientes de actividad, y si además suponemos que la entalpía de vaporización de cada componente es constante en el intervalo de los puntos de ebullición de los compuestos puros y que el volumen molar del líquido es despreciable frente al del vapor, se puede aplicar la ecuación de Clausius-Clapeyron para estimar el cociente $P/P_i^o$:

$$\ln \frac{P}{P_i^o} = \frac{\Delta h_i^o (T_i^o - T)}{R T_i^o T} = \frac{\Delta s_i^o (T_i^o - T)}{RT} \qquad [78]$$

donde $T_i^o$, $\Delta h_i^o$ y $\Delta s_i^o$ son el punto de ebullición, la entalpía de vaporización y la entropía de vaporización del componente puro $i$ a la presión de trabajo $P$, y $P_i^o$ es la presión de vapor a la temperatura $T$.

Sustituyendo las ecuaciones [21] y [78] en la ecuación [24], resulta:

$$g^E = \sum_i x_i \Delta s_i^o (T_i^o - T) + RT \sum_i x_i \ln \frac{y_i}{x_i} \qquad [79]$$

y definiendo:

$$\Delta s = \sum_i x_i \Delta s_i^o \qquad [80]$$

$$w = \sum_i x_i \ln \frac{y_i}{x_i} \qquad [51]$$

se obtiene la siguiente expresión que describe el punto de ebullición de una mezcla:

$$T = \sum_i T_i^o x_i \frac{\Delta s_i^o}{\Delta s} - \frac{g^E}{\Delta s} + RT \frac{w}{\Delta s} \qquad [81]$$

anteriormente ya se comentó que $w$ siempre es negativo y que su máximo valor es cero en el punto azeotrópico.

La ecuación [79] se puede transformar en un test puntual de consistencia termodinámica organizando dicha ecuación de la siguiente manera:

$$L_i = \sum_i T_i^o x_i \frac{\Delta s_i^o}{\Delta s} - T = \frac{g^E}{\Delta s} - RT\frac{w}{\Delta s} = W_i \qquad [82]$$

La primera parte de la igualdad, $L_i$, será siempre positivo excepto en el caso en que esté presente un azeótropo. El signo de $g^E$ (calculado con la ecuación [24]) será positivo o negativo dependiendo de si el sistema presenta desviaciones positivas o negativas respecto a la idealidad. El signo de la segunda parte de la igualdad, $W_i$, deberá ser coincidente con el de $L_i$.

Si se aplica el test de forma puntual un dato es considerado consistente de acuerdo con el criterio adoptado por Wisniak, cuando los valores de $L_i/W_i$ se encuentren entre 0.96 y 1.04.

También se puede aplicar el test en forma global. Multiplicando ambos miembros de [82] por d$x_1$ e integrando en el intervalo completo de concentraciones, se obtiene:

$$L = \int_0^1 L_i \,\mathrm{d}x_1 = \int_0^1 W_i \,\mathrm{d}x_1 = W \qquad [83]$$

Ahora bien, para los datos reales este requisito no se cumple de manera exacta, ya que las aproximaciones efectuadas teniendo en cuenta la fase vapor como ideal y la desviación debida, en gran parte, al considerar la ecuación de Clausius-Clapeyron, dan lugar a que los valores de $L$ y $W$ no sean idénticos. De esta forma. se define la desviación $D$ como:

$$D = 100\frac{|L - W|}{L + W} \qquad [84]$$

donde valores de $D<3$ indican una buena consistencia termodinámica. En el caso en que las entalpías de vaporización no se conozcan y deban ser estimadas, se considera que se cumple la consistencia para valores de $D<5$.

Como se ha comentado anteriormente, los tests puntuales son mucho más rigurosos que los aplicados globalmente, por lo que el test de Wisniak se ha utilizado en su forma puntual [82]. Además, los tests punto a punto permiten detectar valores experimentales inconsistentes y así desecharlos del conjunto de datos.

# 4. PARTE EXPERIMENTAL

# 4. PARTE EXPERIMENTAL

El trabajo realizado se ha plasmado en nueve artículos publicados en dos revistas periódicas de importancia significativa dentro del área de Ingeniería Química: *Journal of Chemical Engineering Data* (JCED) y *Fluid Phase Equilibria* (FPE).

- *"Azeotropic Behavior in the System Methanol + Methyl 1,1-Dimethylethyl Ether"*. JCED

- *"Isobaric Vapor-Liquid Equilibrium in the System 2-Methylpentane + Methyl 1,1-Dimethylethyl Ether, + Ethyl 1,1-Dimethylethyl Ether, and + Methyl 1,1-Dimethylpropyl Ether"*. JCED

- *"Isobaric Vapor-Liquid Equilibrium for Binary Mixtures of 2-Methylpentane + Ethanol and + 2-Methyl-2-propanol"*. FPE

- *"Vapor-Liquid Equilibria in the Systems 3-Methylpentane + Methyl 1,1-dimethylethyl ether and 3-Methylpentane + Methyl 1,1-Dimethylpropyl Ether at 101.3 kPa"*. FPE

- *"Isobaric Vapor-Liquid Equilibrium in the System 3-Methylpentane + Ethyl 1,1-Dimethylethyl Ether, + Diisopropyl Ether, and + Tetrahydrofuran"*. JCED

- *"Isobaric Vapor-Liquid Equilibrium in the System 2,3-Dimethylpentane + Methyl 1,1-Dimethylethyl Ether, + Diisopropyl Ether, and + Methyl 1,1-Dimethylpropyl Ether"*. JCED

- *"Isobaric Vapor-Liquid Equilibrium for Binary and Ternary Mixtures of Ethanol + 2-Methyl-2-Propanol and 2-Methylpentane + Ethanol + 2-Methyl-2-Propanol"*. FPE

- "*Phase Equilibria in the Systems 2-Methyl-2-Propanol + Methyl 1,1-Dimethylpropyl Ether and 2-Methylpentane + 2-Methyl-2-Propanol + Methyl 1,1-Dimethylpropyl Ether*". JCED

- "*Isobaric Vapor-Liquid Equilibrium in the System Methyl 1,1-Dimethylethyl Ether + 2-Methyl-2-Propanol and Methyl 1,1-Dimethylethyl Ether + 2-Methylpentane + 2-Methyl-2-Propanol*". JCED

Los artículos incluyen, además de los datos experimentales obtenidos y del tratamiento termodinámico correspondiente, una sección experimental que contiene información sobre los reactivos empleados, el dispositivo experimental y el análisis utilizado para la determinación de las composiciones. Como se comentó anteriormente, el trabajo experimental se ha llevado a cabo en tres laboratorios diferentes, de ahí que en dicha sección experimental se aprecien diferencias en cuanto a los equipos utilizados (destilador de equilibrio, cromatógrafo y columna de rectificación para la purificación de los reactivos). No obstante, es importante destacar que la compatibilidad de los resultados obtenidos es absoluta, ya que el procedimiento experimental es en esencia el mismo. Además, se ha utilizado en todos los sistemas un destilador de equilibrio Fischer modelo Labodest para la determinación del ELV.

Los nueve artículos se exponen a continuación en el formato requerido por ambas revistas, tanto en lo referido a la división en apartados como a la presentación de tablas, figuras, referencias bibliográficas, etc. La numeración de los distintos elementos se ha conservado en la forma original de los artículos, considerando cada uno de ellos de manera independiente.

# 4.1. AZEOTROPIC BEHAVIOR IN THE SYSTEM METHANOL + METHYL 1,1-DIMETHYLETHYL ETHER

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## ABSTRACT

Vapor-liquid equilibrium for the binary system methanol + methyl 1,1-dimethylethyl ether has been measured at 50, 78.4 and 94 kPa. The system presents a minimum boiling point azeotrope that is enriched in the ether when the pressure decreases. The activity coefficients and boiling points of the solutions were correlated with its composition by the Wohl, Wilson, UNIQUAC, NRTL, and Wisniak – Tamir equations.

## Introduction

Environmental legislation around the world has forced the use of oxygenates for gasoline blending to phase out the lead additives and to reduce the reactive evaporative and exhaust emissions. The US Clean Air Act Amendments of 1990 set forth the basic guidelines for future transportation fuel composition and require the manufacture of oxygenated and reformulated gasolines. Methyl 1,1-dimethylethyl ether (MTBE) is the primary oxygenated compound being used to reformulate gasolines to improve their octane rating and pollution-reducing capability.

MTBE is produced by the reaction of methanol with isobutylene in the liquid phase over a strongly acidic ion-exchange resin catalyst. Excess concentration of methanol up to about 20% of the stoichiometric amount are generally used to achieve high conversions. (Chase, 1984). The use of excess methanol, however, causes a purification problem because methanol forms a minimum-boiling azeotrope with MTBE at an approximate composition of 14 wt% methanol at 760 mmHg. The conventional separation process (Bitar et al., 1984).is both capital and energy intensive. Pervaporation has been considered as an alternative separation technique (Farnand et al., 1989; Park et al., 1995). The possibility of a hybrid distillation-pervaporation process, in which pervaporation is used only in a limited area of separation such as for breaking the azeotrope, can be demonstrated by the Total Recovery Improvement for MTBE (TRIM) process which has been developed by Air Products & Chemicals using cellulose acetate membranes (Chen et al., 1989).

Another potential technique for separation of MTBE from methanol is distillation at pressures other than atmospheric, in order to enrich the azeotrope in one of the components. Hence, it is of interest to consider the distillation behavior of the reactor effluent (MTBE with excess methanol) under different pressures in order to obtain a richer azeotropic mixture in one of the components. Vapor-liquid equilibrium (VLE) for the binary system methanol + MTBE has been measured by Churkin et al. (1979), Aim and Ciprian (1980), Zong et al. (1987) and Arce et al. (1996) at 101.33 kPa, by Acosta et al. (1980) at 78.4 kPa, and by Wang et al. (1989) at 0.5 MPa and 1 MPa. Isothermal VLE data for the system has been determined by Yu et al. (1984) at 313 K, by Mullins et al. (1989) at 303, 313 and 323 K, by Park and Lee (1995) at 313 K, by Farkova et al. (1995) at 315 K and 325 K, by Fischer et al. (1996) at 363 K, and by Coto et al. (1996) at six temperatures between 298 and 338 K. Toghiani et al. (1996) have reported isobaric data at 53.33 and 101.33 kPa, and isothermal data at 313 and 333 K. Gmehling et al. (1995) determined experimental azeotropic data for MTBE-methanol system at different conditions.

VLE data and infinite dilution activity coefficients have been measured by Lee et al. (1994, 1995) at 318.15 and 338.15 K using head-space gas chromatography. Activity coefficients of the system at 298.15 K and 1 atm. were measured by Gao et al. (1986) using head-space gas chromatography. The activity coefficients at infinite dilution of the binary system have measured by Pividal et al. (1992) at 288.15 K and by Delcros et al. (1995) at 323.15 K. The literature also contains VLE measurements for MTBE + methanol mixtures subject to the salt effect (Velasco et al., 1990), the results show that addition of salt has a favorable effect on the separation of the mixture components.

The present work was undertaken to measure VLE data for the title system at 94 kPa, 78.4 kPa and 50 kPa, for which isobaric data are not available or are incomplete, as well as to study the mobility of the azeotropic composition with the pressure and temperature.

## Experimental Section

***Materials.*** MTBE (99.8 mass %, HPLC grade) and methanol (99.9+ mass %, HPLC grade) were purchased from Aldrich and used without further purification, after gas chromatography failed to show any significant impurities. The properties and purity (as determined by GLC) of the pure components appear in Table 1. Appropriate precautions were taken when handling MTBE in order to avoid peroxide formation.

**Table 1. Purities (mass %), Densities d, Refractive Index $n_D$, and Normal Boiling Points $T_b$ of Pure Components**

| component (purity/mass %) | d(298.15 K)/ g.cm$^{-3}$ | | $n_D$ (298.15 K) | | Tb (101.3 kPa)/K | |
|---|---|---|---|---|---|---|
| | exptl.[a] | lit. | exptl.[a] | lit. | exptl.[a] | lit. |
| methanol(99.9+) | 0.78732 | 0.78730[b] | 1.3270 | 1.3267[b] | 337.84 | 337.65[b] |
| MTBE(99.8) | 0.73520 | 0.73528[c] | 1.3664 | 1.3663[d] | 327.83 | 327.83[e] |

[a] Measured. [b] TRC Tables, a-5030. [c] Daubert and Danner (1989) [d] TRC Tables, a-6040. [e] Reich et al. (1998).

***Apparatus and Procedure.*** An all glass vapor-liquid-equilibrium apparatus model 602, manufactured by Fischer Labor und Verfahrenstechnik (Germany), was used in the equilibrium determinations. General details of the experimental equipment and procedure appear in another publication (Wisniak et al., 1997). The equilibrium temperature was measured with an accuracy of 0.02 K using a Lauda thermometer, model R42/2, provided with a 4-mm diameter Pt-100 temperature sensor. The total pressure of the system was controlled by a vacuum pump capable of working at pressures down to 0.25 kPa. The pressure was measured by a Vac Probs pressure transducer with an accuracy of 0.07 kPa; a 5-L Erlenmeyer flask connected between the separating chamber and the Vac Probs dampens the pressure variations to no more than 0.01 kPa. The overall accuracy of the pressure is ±0.1 kPa. On the average the system reached equilibrium conditions after 60 min. operation. Samples, taken by syringing 1.0 μL after the system had achieved equilibrium, were analyzed by gas chromatography on a Gow-Mac series 550P apparatus provided with a thermal conductivity detector and a Spectra Physics Model SP 4290 electronic integrator. The column was 3 m long and 0.2 cm in diameter, packed with SE-30. Column, injector and detector temperatures were (348.15, 493.15, 543.15) K. Very good separation was achieved under these conditions, and calibration analyses were carried out to convert the peak ratio to the mass composition of the sample. The pertinent polynomial fit had a correlation coefficient $R^2$ better than 0.99. Concentration measurements were accurate to better than ±0.001 mole fraction.

## Results

The temperature *T* and liquid-phase $x_i$ and vapor-phase $y_i$ mole fraction at 50, 78.4, and 94 kPa are reported in Tables 2, 3 and 4, and in Figure 1 for the system methanol (1) + MTBE (2) at 78.4 kPa. In this Figure appear the experimental data obtained together with the data of Acosta et al. (1980), we can observe the scarce experimental information in their work. The activity coefficients $\gamma_i$ that were calculated from the following equation (Van Ness and Abbott, 1982):

$$\ln \gamma_i = \ln \frac{y_i P}{x_i P_i^0} + \frac{(B_{ii} - V_i^L)(P - P_i^0)}{RT} + y_j^2 \frac{\delta_{ij} P}{RT} \tag{1}$$

where *T* and *P* are the boiling point and the total pressure, $V_i^L$ is the molar liquid volume of component i, $B_{ii}$ and $B_{jj}$ are the second virial coefficients of the pure gases, $B_{ij}$ the cross second virial coefficient and

$$\delta_{ij} = 2 B_{ij} - B_{jj} - B_{ii} \tag{2}$$

The standard state for calculation of activity coefficients is the pure component at the pressure and temperature of the solution. Eq. 1 is valid at low and moderate pressures when the virial equation of state truncated after the second coefficient is adequate to describe the vapor phase of the pure components and their mixtures, and liquid volumes of the pure components are incompressible over the pressure range under consideration. The molar virial coefficients $B_{ii}$ and $B_{ij}$ were estimated by the method of Hayden and O'Connell (1975) using the molecular parameters suggested by Prausnitz et al. (1980). Critical properties of all components were taken from DIPPR (Daubert and Danner, 1989). The last two terms in eq 1., particularly the second one that expresses the correction due to the non ideal behavior of the vapor phase, contributed less than 3% to the activity coefficients.

**Table 2. Experimental Vapor-Liquid Equilibrium Data for Methanol (1) + MTBE (2) at 50 KPa**

| $T$ / K | $x_1$ | $y_1$ | $\gamma_1$ | $\gamma_2$ | $-B_{11}$ / $\mathrm{cm^3 \cdot mol^{-1}}$ | $-B_{22}$ / $\mathrm{cm^3 \cdot mol^{-1}}$ | $-B_{12}$ / $\mathrm{cm^3 \cdot mol^{-1}}$ |
|---|---|---|---|---|---|---|---|
| 307.47 | 0.0386 | 0.0670 | 3.2844 | 0.9934 | 2258 | 1290 | 862 |
| 307.04 | 0.0696 | 0.1047 | 2.8935 | 1.0016 | 2281 | 1295 | 865 |
| 306.71 | 0.1073 | 0.1474 | 2.6792 | 1.0069 | 2299 | 1298 | 867 |
| 306.53 | 0.1293 | 0.1660 | 2.5235 | 1.0170 | 2308 | 1301 | 868 |
| 306.34 | 0.1788 | 0.2070 | 2.2902 | 1.0334 | 2318 | 1303 | 870 |
| 306.33 | 0.2160 | 0.2296 | 2.1004 | 1.0525 | 2319 | 1303 | 870 |
| 306.30 | 0.2501 | 0.2498 | 1.9743 | 1.0731 | 2321 | 1303 | 870 |
| 306.33 | 0.2980 | 0.2734 | 1.8088 | 1.1095 | 2319 | 1303 | 870 |
| 306.35 | 0.3330 | 0.2903 | 1.7157 | 1.1400 | 2318 | 1303 | 869 |
| 306.42 | 0.3604 | 0.3035 | 1.6511 | 1.1638 | 2314 | 1302 | 869 |
| 306.67 | 0.4276 | 0.3272 | 1.4801 | 1.2451 | 2301 | 1299 | 867 |
| 306.97 | 0.4846 | 0.3553 | 1.3965 | 1.3107 | 2285 | 1296 | 865 |
| 307.49 | 0.5589 | 0.3835 | 1.2730 | 1.4370 | 2257 | 1290 | 862 |
| 307.79 | 0.5941 | 0.3993 | 1.2284 | 1.5051 | 2242 | 1286 | 859 |
| 307.97 | 0.6154 | 0.4151 | 1.2217 | 1.5366 | 2232 | 1284 | 858 |
| 308.85 | 0.6857 | 0.4533 | 1.1469 | 1.7020 | 2188 | 1274 | 852 |
| 309.62 | 0.7380 | 0.4853 | 1.0990 | 1.8698 | 2150 | 1266 | 847 |
| 310.61 | 0.7715 | 0.5163 | 1.0671 | 1.9432 | 2102 | 1255 | 840 |
| 311.37 | 0.8108 | 0.5662 | 1.0733 | 2.0507 | 2066 | 1247 | 835 |
| 313.35 | 0.8742 | 0.6356 | 1.0191 | 2.4154 | 1977 | 1226 | 823 |
| 314.19 | 0.9024 | 0.6847 | 1.0228 | 2.6178 | 1941 | 1217 | 817 |
| 315.85 | 0.9349 | 0.7572 | 1.0125 | 2.8551 | 1872 | 1200 | 807 |
| 316.84 | 0.9484 | 0.7964 | 1.0043 | 2.9176 | 1833 | 1190 | 801 |
| 317.77 | 0.9649 | 0.8453 | 1.0051 | 3.1609 | 1797 | 1181 | 795 |

**Table 3. Experimental Vapor-Liquid Equilibrium Data for Methanol (1) + MTBE (2) at 78.4 KPa**

| $T$ / K | $x_1$ | $y_1$ | $\gamma_1$ | $\gamma_2$ | $-B_{11}$ / $cm^3 \cdot mol^{-1}$ | $-B_{22}$ / $cm^3 \cdot mol^{-1}$ | $-B_{12}$ / $cm^3 \cdot mol^{-1}$ |
|---|---|---|---|---|---|---|---|
| 319.67 | 0.0289 | 0.0607 | 3.5258 | 0.9887 | 1726 | 1163 | 783 |
| 318.97 | 0.0620 | 0.1129 | 3.1447 | 0.9904 | 1751 | 1169 | 788 |
| 318.33 | 0.1082 | 0.1673 | 2.7357 | 1.0003 | 1775 | 1176 | 792 |
| 317.93 | 0.1582 | 0.2083 | 2.3660 | 1.0221 | 1790 | 1179 | 794 |
| 317.74 | 0.1940 | 0.2377 | 2.2157 | 1.0352 | 1798 | 1181 | 795 |
| 317.61 | 0.2401 | 0.2627 | 1.9874 | 1.0673 | 1803 | 1183 | 796 |
| 317.59 | 0.2695 | 0.2801 | 1.8867 | 1.0854 | 1804 | 1183 | 796 |
| 317.62 | 0.3089 | 0.3017 | 1.7694 | 1.1120 | 1802 | 1183 | 796 |
| 317.63 | 0.3568 | 0.3249 | 1.6465 | 1.1555 | 1802 | 1182 | 796 |
| 317.71 | 0.4045 | 0.3483 | 1.5495 | 1.2022 | 1799 | 1182 | 795 |
| 317.87 | 0.4540 | 0.3677 | 1.4455 | 1.2660 | 1793 | 1180 | 794 |
| 318.02 | 0.5019 | 0.3864 | 1.3640 | 1.3403 | 1787 | 1179 | 793 |
| 318.24 | 0.5453 | 0.4055 | 1.3038 | 1.4124 | 1779 | 1176 | 792 |
| 318.53 | 0.5865 | 0.4255 | 1.2547 | 1.4870 | 1768 | 1174 | 790 |
| 319.26 | 0.6650 | 0.4583 | 1.1530 | 1.6896 | 1741 | 1167 | 786 |
| 320.22 | 0.7205 | 0.5011 | 1.1146 | 1.8072 | 1706 | 1157 | 780 |
| 320.95 | 0.7695 | 0.5362 | 1.0808 | 1.9906 | 1680 | 1150 | 776 |
| 321.86 | 0.8104 | 0.5732 | 1.0542 | 2.1626 | 1649 | 1142 | 771 |
| 323.21 | 0.8642 | 0.6367 | 1.0355 | 2.4627 | 1604 | 1130 | 763 |
| 325.49 | 0.9263 | 0.7475 | 1.0293 | 2.9373 | 1532 | 1109 | 750 |
| 328.10 | 0.9687 | 0.8695 | 1.0277 | 3.2979 | 1454 | 1086 | 736 |
| 329.64 | 0.9853 | 0.9381 | 1.0241 | 3.1910 | 1411 | 1073 | 728 |

**Table 4. Experimental Vapor-Liquid Equilibrium Data for Methanol (1) + MTBE (2) at 94 KPa**

| $T$ / K | $x_1$ | $y_1$ | $\gamma_1$ | $\gamma_2$ | $-B_{11}$ / $\mathrm{cm^3 \cdot mol^{-1}}$ | $-B_{22}$ / $\mathrm{cm^3 \cdot mol^{-1}}$ | $-B_{12}$ / $\mathrm{cm^3 \cdot mol^{-1}}$ |
|---|---|---|---|---|---|---|---|
| 324.83 | 0.0223 | 0.0584 | 4.2099 | 0.9874 | 1552 | 1115 | 754 |
| 324.27 | 0.0461 | 0.1020 | 3.6384 | 0.9832 | 1570 | 1120 | 757 |
| 323.32 | 0.0950 | 0.1638 | 2.9365 | 0.9963 | 1600 | 1129 | 762 |
| 322.99 | 0.1358 | 0.2033 | 2.5795 | 1.0055 | 1611 | 1132 | 764 |
| 322.67 | 0.1915 | 0.2468 | 2.2446 | 1.0278 | 1622 | 1134 | 766 |
| 322.49 | 0.2523 | 0.2840 | 1.9706 | 1.0638 | 1628 | 1136 | 767 |
| 322.48 | 0.2695 | 0.2937 | 1.9072 | 1.0747 | 1628 | 1136 | 767 |
| 322.45 | 0.2847 | 0.3005 | 1.8488 | 1.0883 | 1629 | 1136 | 767 |
| 322.48 | 0.3037 | 0.3121 | 1.7970 | 1.0986 | 1628 | 1136 | 767 |
| 322.54 | 0.3351 | 0.3252 | 1.6911 | 1.1268 | 1626 | 1136 | 767 |
| 322.58 | 0.4141 | 0.3614 | 1.5152 | 1.2098 | 1625 | 1135 | 767 |
| 322.74 | 0.5058 | 0.3999 | 1.3607 | 1.3422 | 1619 | 1134 | 766 |
| 322.83 | 0.5185 | 0.4036 | 1.3344 | 1.3652 | 1616 | 1133 | 765 |
| 323.01 | 0.5720 | 0.4281 | 1.2717 | 1.4652 | 1611 | 1131 | 764 |
| 323.63 | 0.6169 | 0.4495 | 1.2051 | 1.5448 | 1590 | 1126 | 761 |
| 323.88 | 0.6926 | 0.4849 | 1.1440 | 1.7892 | 1582 | 1123 | 759 |
| 325.28 | 0.7547 | 0.5195 | 1.0599 | 2.0001 | 1538 | 1111 | 751 |
| 325.66 | 0.7854 | 0.5354 | 1.0328 | 2.1841 | 1526 | 1107 | 749 |
| 327.18 | 0.8501 | 0.6002 | 1.0031 | 2.5674 | 1481 | 1094 | 741 |
| 329.23 | 0.9076 | 0.6870 | 0.9877 | 3.0674 | 1423 | 1077 | 730 |
| 329.60 | 0.9176 | 0.7072 | 0.9905 | 3.1819 | 1412 | 1073 | 728 |
| 332.09 | 0.9634 | 0.8371 | 1.0100 | 3.7105 | 1346 | 1053 | 715 |

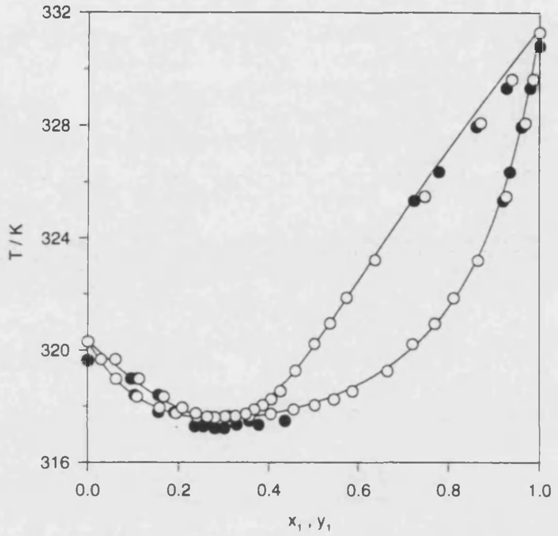

**Figure 1**. Boiling temperature diagram for the system methanol (1) + MTBE (2) at 78.4 kPa. Experimental data (○); Experimental data of Acosta et al. (●). Smoothed with the Wilson model (—).

The vapor pressures of the pure compounds $P_i^0$ were expressed by the Antoine equation:

$$\log\left(P_i^0 / \mathrm{mmHg}\right) = A_i - \frac{B_i}{(T/{}^\circ\mathrm{C}) + C_i} \tag{3}$$

The constants $A_i$, $B_i$, and $C_i$ were taken from literature: TRC Tables (1974) for methanol and Reich et al. (1998) for MTBE, the values are reported in Table 5.

**Table 5. Antoine Coefficients, Equation 3**

| compound | $A_i$ | $B_i$ | $C_i$ |
|---|---|---|---|
| methanol[a] | 7.8975 | 1474.08 | 229.13 |
| MTBE[b] | 6.7359 | 1032.99 | 213.27 |

[a]TRC Tables, a-5030. [b]Reich et al. (1998)

The calculated activity coefficients reported in Tables 2, 3 and 4 are estimated accurate to within ±3%. The results reported in these Tables indicate that the measured system exhibits positive deviations from ideal behavior and presents a minimum boiling azeotrope at the three pressures. The experimental azeotropic points are summarized in Table 6 along with a comparison with literature values. Azeotropic compositions were obtained, in all cases, by determining the $x_1$ values that make zero the best polynomial fit of the function $(x_1\text{-}y_1) = f(x_1)$. Azeotropic temperatures or pressures have been obtained from the best polynomial fit for $T=f(x_1)$ or for $P=f(x_1)$, using the $x_1$ values previously determined.

The vapor-liquid equilibria data reported in Tables 2, 3 and 4 were found to be thermodynamically consistent by the point-to-point method of Van Ness et al. (1973) as modified by Fredenslund et al. (1977). Consistency criteria ($\Delta y \leq 10^{-2}$) was met using a zeroth-order Legendre polynomial, which is equivalent to the symmetric regular solution model given by

$$\frac{G^{\mathrm{E}}}{RT} = Ax_1x_2 \tag{4}$$

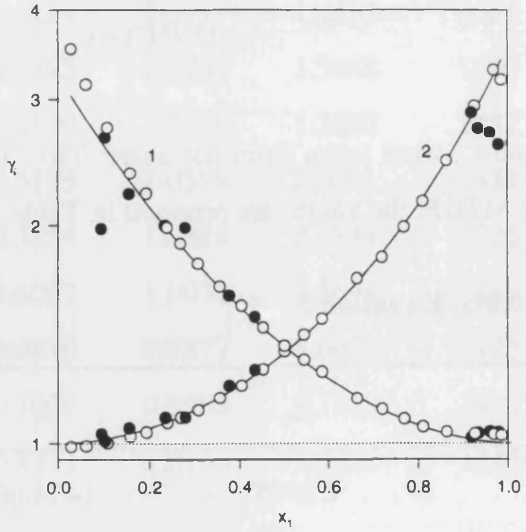

**Figure 2**. Activity coefficient plot for the system methanol (1) + MTBE (2) at 78.4 kPa. Experimental data (○); Experimental data of Acosta et al. (●). Smoothed with the Wilson model (—).

**Table 6. Azeotropic points for MTBE (1) + methanol (2)**

| $x_1$ | $T$/K | $P$/kPa | Ref. |
|---|---|---|---|
| 0.7994 | 296.15 | 32.84 | Gmehling et al., 1995 |
| 0.804 | 298.15 | 35.27 | Velasco et al., 1990 |
| 0.795 | 298.15 | 36.00 | Coto et al., 1996 |
| 0.7865 | 300.15 | 39.36 | Gmehling et al., 1995 |
| 0.770 | 303.15 | 43.75 | Mullins et al., 1989 |
| 0.776 | 303.15 | 44.53 | Coto et al., 1996 |
| 0.755 | 306.49 | 50.00 | This work |
| 0.769 | 307.64 | 53.33 | Toghiani et al., 1996 |
| 0.759 | 308.15 | 54.48 | Coto et al., 1996 |
| 0.750 | 313.15 | 64.36 | Park and Lee, 1995 |
| 0.738 | 313.15 | 65.69 | Mullins et al., 1989 |
| 0.757 | 313.15 | 66.27 | Toghiani et al., 1996 |
| 0.7341 | 313.15 | 66.57 | Gmehling et al., 1995 |
| 0.726 | 315.00 | 71.11 | Farkova et al., 1995 |
| 0.749 | 317.49 | 74.37 | Gao et al., 1986 |
| 0.788 | 317.55 | 74.37 | Yu et al., 1984 |
| 0.692 | 317.20 | 78.40 | Acosta et al., 1980 |
| 0.711 | 317.58 | 78.40 | This work |
| 0.727 | 318.15 | 79.63 | Lee et al., 1994 |
| 0.717 | 318.15 | 80.26 | Coto et al., 1996 |
| 0.686 | 322.48 | 94.00 | This work |
| 0.732 | 323.15 | 95.52 | Mullins et al., 1989 |
| 0.678 | 324.91 | 100.00 | Zong et al., 1987 |
| 0.6994 | 296.15 | 100.50 | Gmehling et al., 1995 |
| 0.700 | 324.75 | 101.32 | Churkin et al., 1979 |
| 0.688 | 324.39 | 101.32 | Aim and Ciprian, 1980 |
| 0.688 | 324.33 | 101.32 | Gao et al., 1986 |
| 0.694 | 324.32 | 101.32 | Arce et al., 1996 |
| 0.703 | 324.39 | 101.33 | Toghiani et al., 1996 |
| 0.695 | 325.00 | 103.15 | Farkova et al., 1995 |
| 0.681 | 328.15 | 115.85 | Coto et al., 1996 |
| 0.662 | 333.15 | 138.09 | Toghiani et al., 1996 |
| 0.637 | 338.15 | 162.23 | Coto et al., 1996 |
| 0.639 | 338.15 | 164.40 | Lee et al., 1994 |
| 0.458 | 363.54 | 354.60 | Fischer et al., 1996 |
| 0.496 | 374.93 | 500.00 | Wang et al., 1989 |
| 0.412 | 403.42 | 1000.00 | Wang et al., 1989 |

The variation of activity coefficients with composition appears in Figure 2 for the system at 78.4 kPa, together with the values from Acosta et al. (1980). This Figure shows a symmetric behavior of the activity coefficients with an intersection about the composition $x_1 = 0.5$. Thus the activity coefficients are reasonably represented by eq. 4.

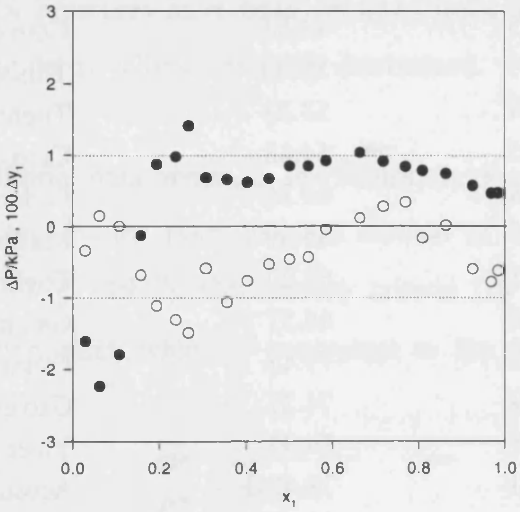

**Figure 3**. Consistency residuals plot for the system methanol (1) + MTBE (2) at 78.4 kPa. ΔP/kPa (●); 100·Δy₁ (○).

The pertinent consistency statistics together with the parameter $A$ in eq. 4 are shown in Table 7. Residuals of the Fredenslund test are represented in Figure 3 for the system at 78.4 kPa.

**Table 7. Consistency Test for the System Methanol (1) + MTBE (2) at 50, 78.4 and 94 KPa**

| Pressure / kPa | $A^a$ | $100 \times \text{MAD}y_1{}^b$ | $\text{MAD}P^c$ / kPa |
|---|---|---|---|
| 50.0 | 1.172 | 0.59 | 0.25 |
| 78.4 | 1.229 | 0.54 | 0.91 |
| 94.0 | 1.229 | 0.96 | 1.12 |

[a] Zero$^{th}$ order Legendre Polynomial (or Porter model) parameter in Eq 5. [b] Average absolute deviation in vapor phase composition. [c] Average absolute deviation in pressure

The activity coefficients were correlated with the Wohl, Wilson, NRTL, and UNIQUAC equations (Walas, 1985). The parameters of these equations were obtained by minimizing the following objective function (*OF*):

$$\mathrm{OF} = \sum_{i=1}^{N} 100 \times \left( \left| \frac{P_i^{\mathrm{exptl}} - P_i^{\mathrm{calc}}}{P_i^{\mathrm{exptl}}} \right| + \left| y_i^{\mathrm{exptl}} - y_i^{\mathrm{calc}} \right| \right) \tag{5}$$

and are reported in Table 8, together with the pertinent statistics of VLE interpolation. Inspection of the results given in Table 8 shows that all the models fitted well the methanol + MTBE system, the best fit corresponding to the Wilson model.

**Table 8. Parameters and Deviations between Experimental and Calculated Values for Different $G^E$ Models**

| Model | $P$ | $A_{ij}$ | $A_{ji}$ | $q_i / q_j$ | $\alpha_{ij}$ | Bubble-point pressures | | Dew-point pressures | |
|---|---|---|---|---|---|---|---|---|---|
| | kPa | | | | | $\Delta P^a / \%$ | $100 \times \Delta y^b$ | $\Delta P^a / \%$ | $100 \times \Delta y^b$ |
| Wohl | 50.0 | 1.1579 | 1.1821 | 0.9229 | | 0.56 | 0.55 | 0.62 | 0.74 |
| | 78.4 | 1.1528 | 1.2443 | 0.9229 | | 0.53 | 0.41 | 0.52 | 0.46 |
| | 94.0 | 1.1657 | 1.3250 | 0.9229 | | 0.96 | 0.79 | 1.19 | 0.81 |
| Wilson[d] | 50.0 | 4758.19[c] | -1117.82[c] | | | 0.39 | 0.46 | 0.47 | 0.64 |
| | 78.4 | 4772.06[c] | -925.77[c] | | | 0.51 | 0.36 | 0.58 | 0.42 |
| | 94.0 | 4843.70[c] | -687.62[c] | | | 1.03 | 0.71 | 1.43 | 0.69 |
| NRTL | 50.0 | 1935.94[c] | 1288.10[c] | | 0.2 | 0.54 | 0.49 | 0.52 | 0.60 |
| | 78.4 | 2410.05[c] | 1036.14[c] | | 0.2 | 0.54 | 0.43 | 0.53 | 0.50 |
| | 94.0 | 2839.93[c] | 852.48[c] | | 0.2 | 1.13 | 0.83 | 1.36 | 0.90 |
| UNIQUAC[e] | 50.0 | -523.50[c] | 3262.68[c] | | | 0.55 | 0.50 | 0.57 | 0.65 |
| | 78.4 | -471.30[c] | 3297.00[c] | | | 0.52 | 0.41 | 0.52 | 0.48 |
| | 94.0 | -409.22[c] | 3316.82[c] | | | 1.05 | 0.80 | 1.31 | 0.83 |

[a] Average percentual deviation in bubble pressure $\Delta P = 100/\mathrm{N}\sum_i^N \left|P_i^{\mathrm{exptl}} - P_i^{\mathrm{calc}}\right| / P_i^{\mathrm{exptl}}$ (N : number of data points). [b] Average absolute deviation in vapor phase composition. [c] Parameters in J·mol$^{-1}$. [d] Liquid volumes have been estimated from the Rackett equation (Rackett, 1970). [e] Volume and surface parameters calculated from Prausnitz et al. (1980).

We can follow a simple procedure to determine the variation of the azeotropic point with pressure and composition. If at low pressures the vapor phase is assumed to behave ideally then the activity coefficients can be calculated from the following simplified relation:

$$\gamma_i = \frac{y_i P}{x_i P_i^0} \tag{6}$$

For a binary system at the azeotropic point we have

$$\frac{\gamma_1}{\gamma_2} = \frac{P_2^0}{P_1^0} \tag{7}$$

The first term of eq 7 can be obtained from any activity coefficients model and the second one from the Antoine equation for each of the components. So, knowing the azeotropic temperature or pressure and the parameters of a model (for instance Wilson) it is possible to obtain the azeotropic composition. In Figure 4 are represented the curves $P_2^o/P_1^o = f(T)$ using the Antoine constants given in Table 5, and $\gamma_1/\gamma_2$, using the parameters of the Wilson model at 94 kPa given in Table 8. In Figure 5 appear azeotropic temperatures and pressures as a function of azeotropic compositions. In these Figures component 1 is MTBE and component 2 is methanol. All the values in Table 6 are represented in both figures and show the dispersion of the information available in the literature. Some workers measured the liquid phase composition and equilibrium temperature and calculated the vapor phase composition (Churkin et al., 1979; Wang et al., 1989; Fischer et al., 1996 and Coto et al., 1996). Gao et al. (1986) calculated VLE data at 74.37 and 101.33 kPa from measured values of the activity coefficients at 298.15 K and 1 atm. Velasco et al. (1990) measured the liquid and vapor phase compositions and calculated the values of the pressure. In all the cases, the azeotropic points were determined in the way described before, using the variables reported as calculated values in the pertinent papers. In general, good agreement is observed between the calculated curve and the experimental points.

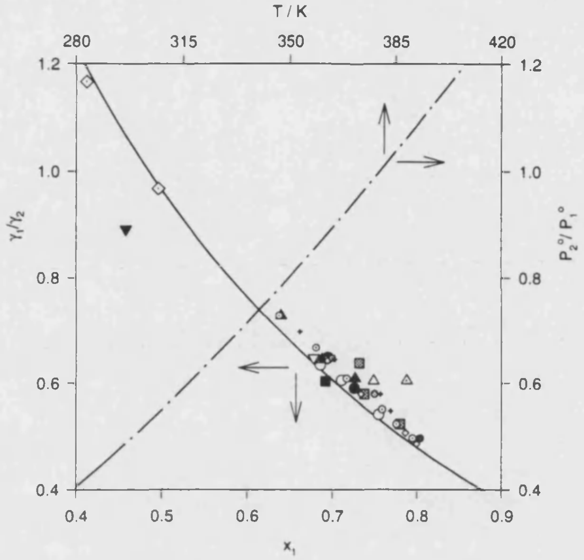

**Figure 4**. Activity coefficients and vapor pressures ratios vs. composition and temperature. This work (open circle); Farkova et al. (filled circle); Gao et al. (open triangle, pointed up); Lee et al. (filled triangle, pointed up); Wang et al. (dotted diamond); Zong et al. (open triangle, pointed down); Arce et al. (open square); Aim and Ciprian (filled diamond); Acosta et al. (filled square); Churkin et al. (dotted square); Mullins et al. (shaded square); Yu et al. (dotted triangle); Gmehling et al. (open diamond); Fischer et al. (filled triangle, pointed down); Coto et al.(dotted open circle); Velasco et al. (dotted closed circle); Toghiani et al. (plus); Park and Lee (shaded circle); Wilson model (solid line); Antoine equations (dotted-dashed line).

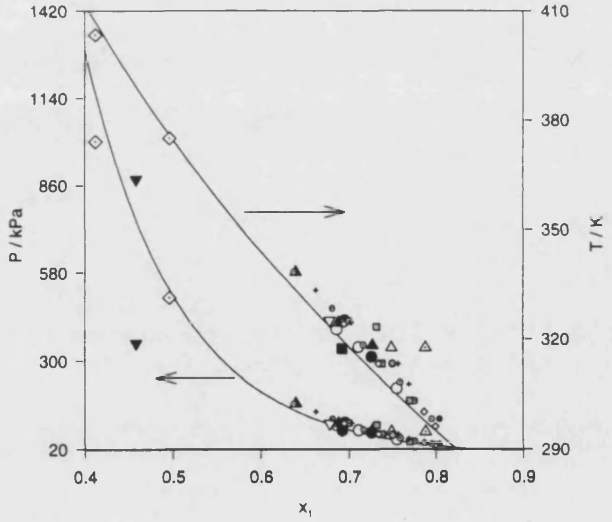

**Figure 5**. Azeotropic pressures and temperatures vs. azeotropic compositions. This work (open circle); Farkova et al. (filled circle); Gao et al. (open triangle, pointed up); Lee et al. (filled triangle, pointed up); Wang et al. (dotted diamond); Zong et al. (open triangle, pointed down); Arce et al. (open square); Aim and Ciprian (filled diamond); Acosta et al. (filled square); Churkin et al. (dotted square); Mullins et al. (shaded square); Yu et al. (dotted triangle); Gmehling et al. (open diamond); Fischer et al. (filled triangle, pointed down); Coto et al.(dotted open circle); Velasco et al. (dotted closed circle); Toghiani et al. (plus); Park and Lee (shaded circle); smoothed data using equation 7 (line).

An alternative procedure to determine the azeotropic conditions is to use the fact that the solution behaves regularly. In this case we have

$$\ln \gamma_1 = A x_2^2 \tag{8}$$

$$\ln \gamma_2 = A x_1^2 \tag{9}$$

and, assuming ideal behavior for the vapor phase:

$$P = x_1 P_1^0 \gamma_1 + x_2 P_2^0 \gamma_2 \tag{10}$$

For the azeotropic point we have

$$\frac{dP}{dx_1} = [1 - 2x_1 x_2 A]\left[P_1^0 \exp\left(A x_2^2\right) - P_2^0 \exp\left(A x_1^2\right)\right] = 0 \tag{11}$$

From eq. 11 it is possible to obtain azeotropic compositions for different azeotropic temperatures. The values of the azeotropic compositions obtained by this procedure are reported in Table 9, together with the experimental values and again very good agreement is observed.

**Table 9. Azeotropic Compositions Obtained Using Equation 12 for the System MTBE (1) + Methanol (2) at 50, 78.4 and 94 KPa**

| Pressure kPa | Temperature K | Azeotropic compositions ($x_1$) exptl. | $A$= 1.229 [a] | $A$= 1.172 [a] | $A$= 1.210 [b] |
|---|---|---|---|---|---|
| 50.0 | 306.49 | 0.755 | 0.749 | 0.761 | 0.753 |
| 78.4 | 317.58 | 0.711 | 0.705 | 0.715 | 0.708 |
| 94.0 | 322.48 | 0.686 | 0.686 | 0.695 | 0.689 |

[a] values of parameter $A$ (regular model) in Table 7; [b] average value of parameter $A$ in Table 7.

From Figure 5 we see that a decrease in the operating pressure causes an increase in the concentration of MTBE. According to Malesinski (1965):

$$\frac{dx_2}{dP} = \frac{\Delta\bar{V}_2\Delta\bar{H}_1 - \Delta\bar{V}_1\Delta\bar{H}_2}{x_1\Delta\bar{H}_1 + x_2\Delta\bar{H}_2}\left(\frac{\partial^2 G^{\mathrm{E}}}{\partial x_2^2}\right)^{-1}_{T,P} \tag{12}$$

where $\Delta\bar{V}_{\mathrm{i}}$ is the partial molar vaporization volume (i.e., $\bar{V}_{\mathrm{i}}^{\mathrm{V}} - \bar{V}_{\mathrm{i}}^{\mathrm{L}}$), and $\Delta\bar{H}_{\mathrm{i}}$ is the partial molar vaporization enthalpy (i.e., $\bar{H}_{\mathrm{i}}^{\mathrm{V}} - \bar{H}_{\mathrm{i}}^{\mathrm{L}}$), both positive quantities. For a minimum boling temperature azeotrope, if pressure rises, azeotrope becomes enriched in the component that has the largest vaporization enthalpy, which in this case is the methanol.

The boiling point of the solution was correlated with its composition by the equation proposed by Wisniak and Tamir (1976):

$$T/\mathrm{K} = x_1T_1^0 + x_2T_2^0 + x_1x_2\sum_{k=1}^{m} C_k(x_1 - x_2)^k \tag{13}$$

In this equation $T_{\mathrm{i}}^0$ / K is the boiling point of the pure component i and m are the number of terms in the series expansion of ($x_1$ - $x_2$). The various constants of eq. 13 are reported in Table 10, which also contains information indicating the degree of goodness of the correlation.

**Table 10. Coefficients in Correlation of Boiling Points, Equation 13, average deviation and Root Mean Square Deviations in Temperature (rmsd)**

| P / kPa | $C_0$ | $C_1$ | $C_2$ | $C_3$ | max dev [a] / K | avg dev [b] / K | rmsd [c] / K |
|---|---|---|---|---|---|---|---|
| 50.0 | -28.24 | -9.60 | -27.17 | -17.77 | 0.43 | 0.20 | 0.051 |
| 78.4 | -27.95 | -3.14 | -38.90 | -33.60 | 1.01 | 0.43 | 0.113 |
| 94.0 | -28.90 | -9.37 | -41.59 | -18.98 | 0.90 | 0.40 | 0.101 |

[a] maximum deviation. [b] average deviation. [c] root mean square deviation

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# 4.2. ISOBARIC VAPOR-LIQUID EQUILIBRIUM IN THE SYSTEMS 2-METHYLPENTANE + METHYL 1,1-DIMETHYLETHYL ETHER, + ETHYL 1,1-DIMETHYLETHYL ETHER, AND + METHYL 1,1-DIMETHYLPROPYL ETHER

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## ABSTRACT

Vapor-liquid equilibrium data for the binary systems 2-methylpentane + methyl 1,1-dimethylethyl ether (MTBE), + ethyl 1,1-dimethylethyl ether (ETBE), and + methyl 1,1-dimethylpropyl ether (TAME) are reported at 101.3 kPa, including pure component vapor pressures. The measured systems, which deviate slightly from ideal behavior, can be described as symmetric regular solutions and only the system 2-methylpentane + MTBE presents an azeotrope. Boiling points are correlated with the Wisniak -Tamir equation.

## Introduction

Amendments of the U.S. Clean Air Act in 1990 has mandated that new gasoline formulations be sold in highly polluted areas of the country, with oxygenated gasolines being supplied particularly during the winter. Methyl 1,1-dimethylethyl ether (MTBE) is the primary oxygenated compound being used to reformulate gasolines to improve their octane rating and pollution-reducing capability. However potential and documented contamination of water resources by MTBE has become a major public issue over the past few years, and restrictions in its use as additive are expected. MTBE readily dissolves in water, can move rapidly through soils and aquifers, is resistant to microbial decomposition and is difficult to remove in water treatment. The US Environmental Protection Agency has classified it as a possible human carcinogen. Finally, it is reported to have an unpleasant taste and odor in water. These factors have caused widespread concern that drinking water supplies and human health may be at risk, a situation which promotes further research with other ethers as potential additives. Methyl 1,1-dimethylpropyl ether (TAME) is an additive that is effective at reducing automotive CO emissions. In addition, ethanol-based ethers provide refiners with greater flexibility and economic advantages in making reformulated gasoline. Ethyl 1,1-dimethylethyl ether (ETBE) shows good characteristics as a gasoline additive including: low volatility, low water solubility, high octane value, excellent distillation curve response, large reductions in carbon monoxide (CO) and hydrocarbon (HC) emissions and superior drive-ability.

Phase equilibrium data of oxygenated mixtures are important for predicting the vapor phase composition that would be in equilibrium with hydrocarbon mixtures, and the systems reported here constitute examples of such mixtures. The present work was undertaken to measure vapor-liquid equilibrium (VLE) data of the entitled systems at 101.3 kPa, for which no data have been previously published.

## Experimental Section

***Chemicals.*** 2-Methylpentane (99+ mass %), MTBE (99.8 mass %, *HPLC grade*) and TAME (97 mass %) were purchased from *Aldrich Ltd.*, and ETBE (96+ mass %) was purchased from *Tokyo Chemical Industry Co. Ltd.* (Japan). 2-Methylpentane and MTBE were used without further purification after chromatography failed to show any significant impurities. ETBE and TAME were purified to 99.9+ mass %, in a 1 m height × 30 mm diameter Normschliffgerätebau adiabatic column (packed with 3 x 3 mm SS spirals) working at a 1:100 reflux ratio. The properties and purity (as determined by GLC) of the pure components, as used for VLE measurements, appear in Table 1. Appropriate precautions were taken when handling ethers in order to avoid peroxide formation.

**Table 1. Purities (mass %), Refractive Index $n_D$, and Normal Boiling Points $T_b$ of Pure Components.**

| component (purity/mass %) | $n_D$ (298.15 K) | | $T_b$ (101.3 kPa)/K | |
|---|---|---|---|---|
| | exptl. | lit. | exptl. | lit. |
| 2-methylpentane (99+) | 1.3689 | 1.3687[a] | 333.4 | 333.37[c] |
| methyl 1,1-dimethylethyl ether (99.80) | 1.3664 | 1.3663[b] | 328.2 | 328.11[c] |
| ethyl 1,1-dimethylethyl ether (99.95) | 1.3730 | 1.3729[a] | 345.8 | 345.86[d] |
| methyl 1,1-dimethylpropyl ether (99.97) | 1.3858 | 1.3859[a] | 359.3 | 359.33[c] |

[a] DIPPR (Daubert and Danner, 1989). [b] TRC Tables, a-6040. [c] Martínez-Ageitos (1996). [d] Krähenbühl and Gmehling (1994).

***Apparatus and procedure.*** The equilibrium vessel was an all-glass, dynamic-recirculating still described by Walas (1985), equipped with a Cottrell circulation pump. The still (Labodest model), manufactured by Fischer Labor und Verfahrenstechnik (Germany), is capable of handling pressures from 0.25 to 400 kPa, and temperature up to 523 K. The

Cottrell pump ensures that both liquid and vapor phases are in intimate contact during boiling and also in contact with the temperature sensing element. The equilibrium temperature was measured with a digital Fischer thermometer with an accuracy of ±0.1 K. The apparatus is equipped with two digital sensors of pressure: one for the low pressure zone with an accuracy of ±0.01 kPa, and another one for the high pressures with an accuracy of ±0.1 kPa. The temperature probe was calibrated against the ice and steam points of distilled water. The manometers were calibrated using the vapor pressure of ultrapure water. The still was operated under constant pressure until equilibrium was reached. Equilibrium conditions were assumed when constant temperature and pressure were obtained for 60 min or longer. Then, samples of liquid and condensate were taken for analysis. The sample extractions were carried out with special syringes that allowed one to withdraw small volume samples (1.0 μl) in a system under partial vacuum or under overpressure conditions.

***Analysis.*** Mole fractions of the liquid and condensed vapor phase samples were determined using a Hewlett-Packard 5890 S-II gas chromatograph (GC), after calibration with gravimetrically prepared standard solutions. A flame ionization detector was used together with a 60 m, 0.2 mm i.d., fused silica capillary column, SUPELCOWAX 10. The GC response peaks were integrated with a Hewlett-Packard 3396 integrator. Column, injector and detector temperatures were 333, 373, 413 K for all the systems. Very good separation was achieved under these conditions, and calibration analyses were carried out to convert the peak ratio to the mass composition of the sample. At least three analyses were made of each vapor composition; the standard deviation in the mole fraction was usually less than 0.001.

## Results and Discussion

The temperature $T$, the liquid-phase $x_i$ and vapor-phase $y_i$ mole fractions at 101.3 kPa are reported in Figures 1, 2 and 3 and in Tables 2, 3 and 4. Figures 4, 5 and 6 show the activity coefficients $\gamma_i$ that, for the system 2-methylpentane (1) + MTBE (2), were calculated from the following equation (Van Ness and Abbott, 1982):

**Table 2. Experimental Vapor-Liquid Equilibrium Data for 2-Methylpentane (1) + MTBE (2) at 101.3 KPa**

| $T/K$ | $x_1$ | $y_1$ | $\gamma_1$ | $\gamma_2$ | $-B_{11}$ / $cm^3\ mol^{-1}$ | $-B_{22}$ / $cm^3\ mol^{-1}$ | $-B_{12}$ / $cm^3\ mol^{-1}$ |
|---|---|---|---|---|---|---|---|
| 328.2 | 0.000 | 0.000 |  | 1.000 | 1359 | 1187 | 1252 |
| 328.2 | 0.019 | 0.020 | 1.237 | 0.998 | 1359 | 1187 | 1252 |
| 328.2 | 0.020 | 0.021 | 1.234 | 0.998 | 1359 | 1187 | 1252 |
| 328.2 | 0.052 | 0.053 | 1.198 | 0.998 | 1359 | 1187 | 1252 |
| 328.2 | 0.104 | 0.103 | 1.164 | 1.000 | 1359 | 1187 | 1252 |
| 328.2 | 0.156 | 0.151 | 1.137 | 1.005 | 1359 | 1187 | 1252 |
| 328.3 | 0.206 | 0.197 | 1.120 | 1.007 | 1358 | 1186 | 1251 |
| 328.4 | 0.260 | 0.246 | 1.105 | 1.012 | 1356 | 1185 | 1250 |
| 328.5 | 0.311 | 0.292 | 1.092 | 1.017 | 1355 | 1184 | 1249 |
| 328.6 | 0.367 | 0.342 | 1.081 | 1.026 | 1354 | 1183 | 1248 |
| 328.8 | 0.424 | 0.390 | 1.060 | 1.038 | 1352 | 1182 | 1246 |
| 329.0 | 0.475 | 0.439 | 1.055 | 1.038 | 1349 | 1179 | 1243 |
| 329.1 | 0.496 | 0.456 | 1.049 | 1.048 | 1349 | 1179 | 1243 |
| 329.5 | 0.568 | 0.520 | 1.032 | 1.066 | 1344 | 1175 | 1239 |
| 329.8 | 0.624 | 0.574 | 1.027 | 1.077 | 1341 | 1172 | 1236 |
| 330.2 | 0.682 | 0.630 | 1.019 | 1.092 | 1337 | 1168 | 1232 |
| 330.6 | 0.745 | 0.694 | 1.014 | 1.113 | 1332 | 1165 | 1228 |
| 331.2 | 0.812 | 0.766 | 1.008 | 1.133 | 1326 | 1159 | 1222 |
| 331.7 | 0.861 | 0.821 | 1.003 | 1.154 | 1320 | 1155 | 1218 |
| 332.0 | 0.891 | 0.857 | 1.000 | 1.162 | 1316 | 1151 | 1214 |
| 332.2 | 0.911 | 0.882 | 1.003 | 1.170 | 1315 | 1150 | 1213 |
| 332.5 | 0.932 | 0.909 | 1.001 | 1.170 | 1312 | 1147 | 1210 |
| 333.0 | 0.973 | 0.963 | 1.001 | 1.181 | 1307 | 1143 | 1205 |
| 333.3 | 0.993 | 0.990 | 0.999 | 1.220 | 1303 | 1140 | 1202 |
| 333.4 | 1.000 | 1.000 | 1.000 |  | 1302 | 1139 | 1202 |

**Table 3. Experimental Vapor-Liquid Equilibrium Data for 2-Methylpentane (1) + ETBE (3) at 101.3 KPa (Vapor Phase Considered Ideal)**

| $T/K$ | $x_1$ | $y_1$ | $\gamma_1$ | $\gamma_3$ |
|---|---|---|---|---|
| 345.8 | 0.000 | 0.000 | | 1.000 |
| 344.3 | 0.067 | 0.103 | 1.098 | 1.009 |
| 343.6 | 0.108 | 0.162 | 1.094 | 1.009 |
| 342.6 | 0.167 | 0.240 | 1.080 | 1.011 |
| 341.9 | 0.219 | 0.305 | 1.069 | 1.009 |
| 341.2 | 0.264 | 0.356 | 1.057 | 1.015 |
| 340.7 | 0.304 | 0.403 | 1.055 | 1.011 |
| 339.8 | 0.367 | 0.468 | 1.043 | 1.020 |
| 339.3 | 0.408 | 0.510 | 1.038 | 1.021 |
| 338.8 | 0.450 | 0.552 | 1.034 | 1.022 |
| 338.2 | 0.499 | 0.598 | 1.029 | 1.026 |
| 337.7 | 0.546 | 0.640 | 1.023 | 1.031 |
| 337.2 | 0.593 | 0.681 | 1.018 | 1.036 |
| 336.7 | 0.635 | 0.718 | 1.018 | 1.039 |
| 336.1 | 0.698 | 0.767 | 1.008 | 1.059 |
| 335.5 | 0.751 | 0.810 | 1.008 | 1.068 |
| 335.1 | 0.795 | 0.845 | 1.006 | 1.073 |
| 334.7 | 0.846 | 0.884 | 1.002 | 1.083 |
| 334.2 | 0.906 | 0.930 | 1.000 | 1.089 |
| 333.8 | 0.947 | 0.960 | 1.000 | 1.119 |
| 333.6 | 0.972 | 0.979 | 1.000 | 1.120 |
| 333.4 | 1.000 | 1.000 | 1.000 | |

**Table 4. Experimental Vapor-Liquid Equilibrium Data for 2-Methylpentane (1) + TAME (4) at 101.3 KPa (Vapor Phase Considered Ideal)**

| $T/K$ | $x_1$ | $y_1$ | $\gamma_1$ | $\gamma_3$ |
|---|---|---|---|---|
| 359.3 | 0.000 | 0.000 | | 1.000 |
| 357.6 | 0.038 | 0.088 | 1.132 | 0.996 |
| 354.2 | 0.123 | 0.253 | 1.105 | 0.995 |
| 352.4 | 0.171 | 0.331 | 1.093 | 0.998 |
| 351.3 | 0.206 | 0.382 | 1.081 | 0.997 |
| 349.6 | 0.257 | 0.452 | 1.076 | 0.998 |
| 348.2 | 0.300 | 0.503 | 1.068 | 1.005 |
| 347.3 | 0.331 | 0.544 | 1.074 | 0.994 |
| 345.8 | 0.384 | 0.597 | 1.062 | 1.002 |
| 343.4 | 0.484 | 0.690 | 1.046 | 0.997 |
| 342.2 | 0.536 | 0.727 | 1.031 | 1.017 |
| 341.0 | 0.589 | 0.762 | 1.020 | 1.043 |
| 340.0 | 0.636 | 0.798 | 1.020 | 1.034 |
| 338.9 | 0.692 | 0.834 | 1.013 | 1.044 |
| 337.8 | 0.743 | 0.866 | 1.014 | 1.049 |
| 336.9 | 0.803 | 0.898 | 1.000 | 1.075 |
| 335.9 | 0.852 | 0.926 | 1.003 | 1.076 |
| 335.1 | 0.901 | 0.952 | 1.000 | 1.073 |
| 334.2 | 0.951 | 0.976 | 0.999 | 1.119 |
| 333.4 | 1.000 | 1.000 | 1.000 | |

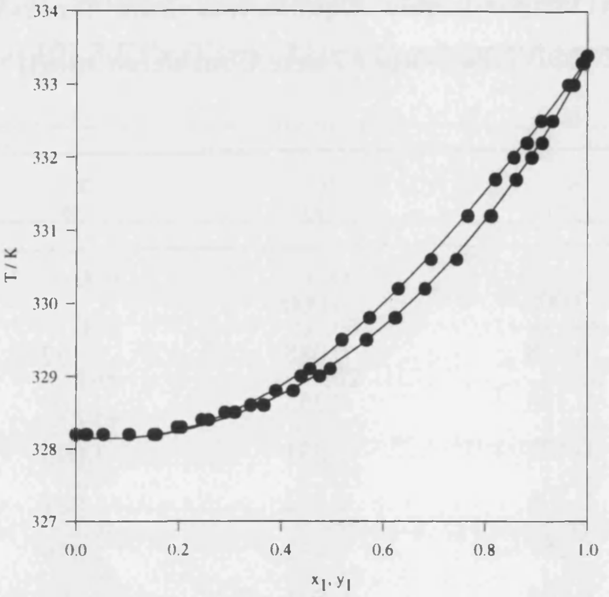

**Figure 1**. Experimental data for the system 2-methylpentane (1) + MTBE (2) at 101.3 kPa. Experimental data (●). Smoothed data using the regular model with the parameters given in Table 7, eq 5 ( — ).

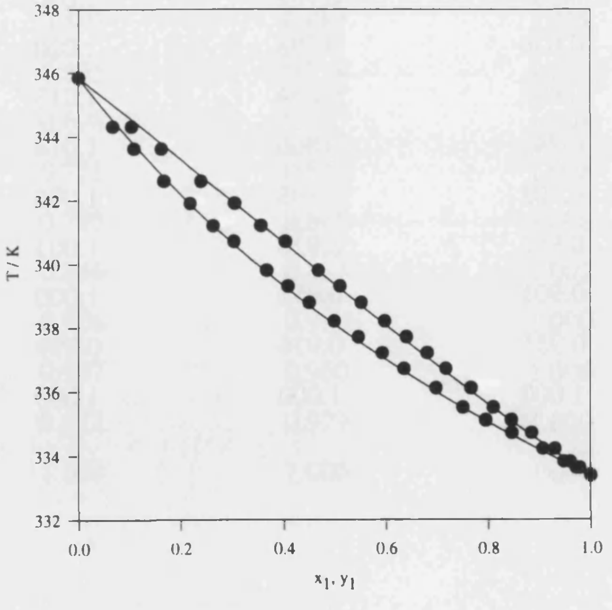

**Figure 2**. Experimental data for the system 2-methylpentane (1) + ETBE (3) at 101.3 kPa. Experimental data (●). Smoothed data using the regular model with the parameters given in Table 7, eq 5 ( — ).

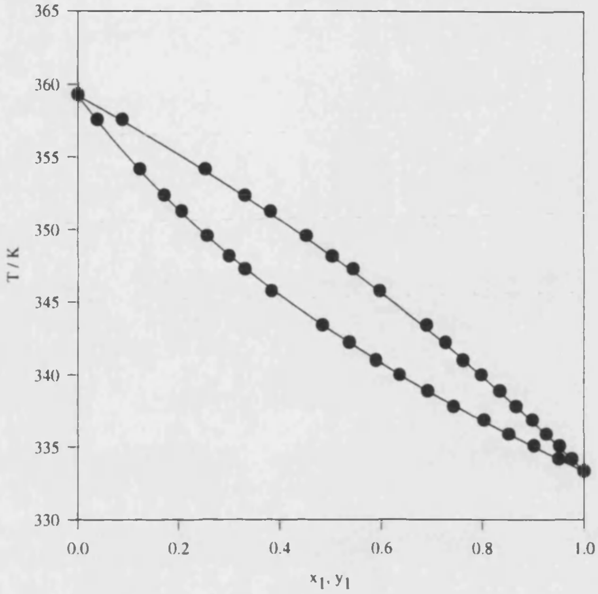

**Figure 3**. Experimental data for the system 2-methylpentane (1) + TAME (4) at 101.3 kPa. Experimental data (●). Smoothed data using the regular model with the parameters given in Table 7, eq 5 ( — ).

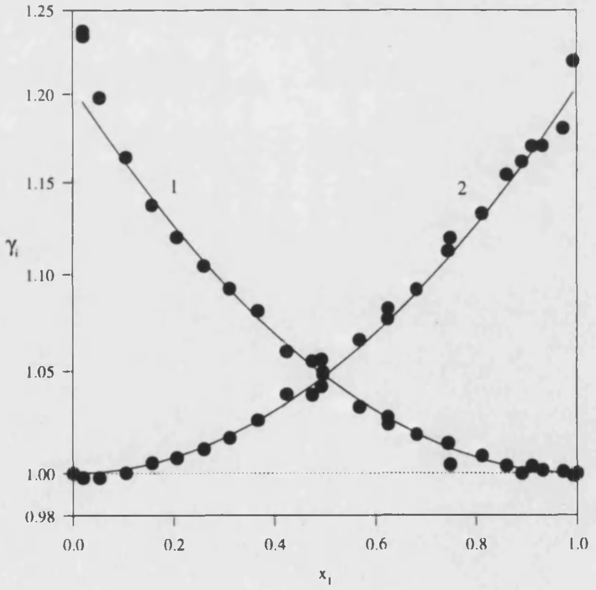

**Figure 4**. Activity coefficient plot of the system 2-methylpentane (1) + MTBE (2) at 101.3 kPa, calculated from experimental data. Experimental data (●). Smoothed data using the regular model with the parameters given in Table 7, eq 5 ( — ).

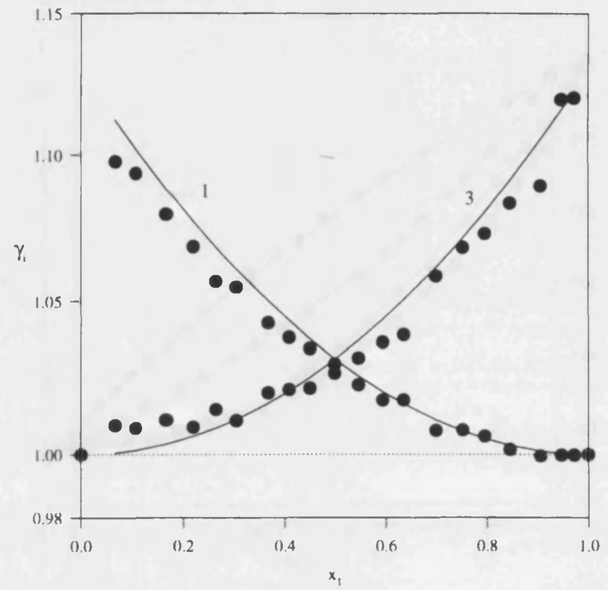

**Figure 5**. Activity coefficient plot of the system 2-methylpetane (1) + ETBE (3) at 101.3 kPa, calculated from experimental data. Experimental data (●). Smoothed data using the regular model with the parameters given in Table 7, eq 5 ( — ).

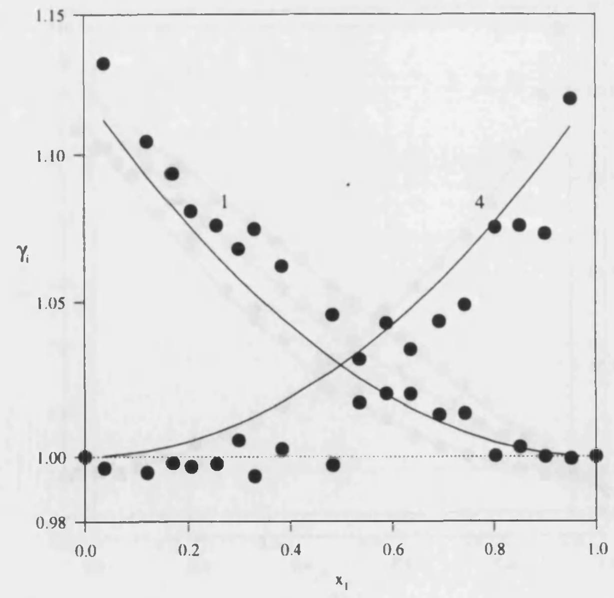

**Figure 6**. Activity coefficient plot of the system 2-methylpetane (1) + TAME (4) at 101.3 kPa, calculated from experimental data. Experimental data (●). Smoothed data using the regular model with the parameters given in Table 7, eq 5 ( — ).

$$\ln \gamma_i = \ln \frac{y_i P}{x_i P_i^0} + \frac{(B_{ii} - V_i^L)(P - P_i^0)}{RT} + y_j^2 \frac{\delta_{ij} P}{RT} \tag{1}$$

where $T$ and $P$ are the boiling point and the total pressure, $V_i^L$ is the molar liquid volume of component i, $B_{ii}$ and $B_{jj}$ are the second virial coefficients of the pure gases, $P_i^0$ is the vapor pressure, $B_{ij}$ the cross second virial coefficient and

$$\delta_{ij} = 2\,B_{ij} - B_{jj} - B_{ii} \tag{2}$$

The standard state for calculation of activity coefficients is the pure component at the pressure and temperature of the solution. Equation 1 is valid at low and moderate pressures when the virial equation of state truncated after the second coefficient is adequate to describe the vapor phase of the pure components and their mixtures, and liquid volumes of the pure components are incompressible over the pressure range under consideration.

For the systems 2-methylpentane (1) + ETBE (3) and 2-methylpentane (1) + TAME (4), activity coefficients were calculated according to the ideal relation (Van Ness and Abbott, 1982):

$$\gamma_i = \frac{y_i P}{x_i P_i^0} \tag{3}$$

because, on the one hand, the low pressure makes this assumption reasonable and, on the other hand, as discussed by Reich et al. (1998a), the scarce physical information available for mixtures of ETBE and TAME with alkanes does not allow a reliable estimation of the second virial coefficient.

The pure component vapor pressure $P_i^0$ for ETBE was taken from Reich et al. (1998a). For 2-methylpentane, MTBE and TAME, pure component vapor pressures were determined experimentally as a function of the temperature, using the same equipment as that for obtaining the VLE data. The pertinent results appear in Table 5.

**Table 5. Experimental Vapor Pressures Determined For Pure Species**

| 2-methylpentane | | MTBE | | TAME | |
|---|---|---|---|---|---|
| *T*/K | *P*/kPa | *T*/K | *P*/kPa | *T*/K | *P*/kPa |
| 310.0 | 45.10 | 315.4 | 65.04 | 313.8 | 20.16 |
| 312.9 | 50.23 | 317.3 | 69.55 | 319.2 | 25.11 |
| 315.4 | 55.05 | 319.4 | 74.96 | 323.8 | 30.08 |
| 317.9 | 60.14 | 321.3 | 80.06 | 327.9 | 35.14 |
| 320.1 | 65.07 | 322.9 | 84.71 | 331.5 | 40.13 |
| 322.2 | 70.02 | 324.7 | 90.01 | 334.7 | 45.11 |
| 324.3 | 75.21 | 326.3 | 95.07 | 337.7 | 50.14 |
| 326.2 | 80.08 | 328.0 | 100.61 | 340.5 | 55.17 |
| 328.0 | 85.05 | 328.2 | 101.33 | 343.0 | 60.15 |
| 329.7 | 89.99 | 329.3 | 105.10 | 345.4 | 65.10 |
| 331.4 | 95.03 | 330.7 | 110.01 | 347.6 | 70.12 |
| 333.0 | 100.23 | 332.1 | 115.15 | 349.7 | 74.96 |
| 333.4 | 101.33 | 333.4 | 120.03 | 351.7 | 80.02 |
| 333.7 | 102.30 | 335.9 | 129.90 | 353.6 | 85.02 |
| 334.5 | 104.85 | 338.3 | 140.00 | 355.4 | 89.93 |
| 336.0 | 110.00 | 340.5 | 149.70 | 357.2 | 95.07 |
| 337.4 | 115.02 | 342.6 | 159.70 | 359.3 | 101.33 |
| 338.7 | 119.83 | 344.7 | 169.80 | 360.4 | 104.88 |
| 340.0 | 124.73 | 346.6 | 179.90 | 362.0 | 110.04 |
| 342.6 | 134.90 | 348.5 | 189.80 | | |
| 343.8 | 139.90 | 350.2 | 199.70 | | |
| 346.1 | 149.80 | 351.9 | 209.70 | | |
| 347.2 | 154.70 | 353.5 | 219.70 | | |
| 348.3 | 159.70 | 355.1 | 229.30 | | |
| 349.3 | 164.40 | 356.7 | 239.70 | | |
| 350.4 | 169.60 | 358.2 | 249.90 | | |
| 353.4 | 184.80 | 359.6 | 260.00 | | |
| 355.2 | 194.40 | 361.0 | 269.60 | | |
| 356.2 | 199.80 | 362.4 | 279.80 | | |
| 358.0 | 210.10 | 363.6 | 289.50 | | |
| 358.9 | 215.20 | 365.0 | 300.00 | | |
| 359.7 | 220.10 | | | | |

The measured vapor pressures were correlated using the Antoine equation:

$$\log(P_i^0/\mathrm{kPa}) = A_i - \frac{B_i}{(T/\mathrm{K}) - C_i} \tag{4}$$

whose parameters $A_i$, $B_i$, and $C_i$ are reported in Table 6. The vapor pressures were correlated with a mean absolute deviation [*MADP*] of 0.13% for 2-methylpentane, 0.07% for MTBE and 0.05% for TAME. In addition, the parameters presented in Table 6 give a fair prediction of the experimental vapor pressures reported by Boublík et al. (1984) for 2-methylpentane [*MADP* = 0.12%], by Reich et al. (1998b) for MTBE [*MADP* = 0.37%] and by Krähenbühl and Gmehling (1994) for TAME [*MADP* = 0.30%], as shown in Figure 7.

**Table 6. Antoine Coefficients, Eq 4**

| compound | $A_i$ | $B_i$ | $C_i$ |
|---|---|---|---|
| 2-methylpentane [a] | 6.10678 | 1212.34 | 37.75 |
| methyl 1,1-dimethylethyl ether [a] | 6.34991 | 1312.52 | 26.03 |
| ethyl 1,1-dimethylethyl ether [b] | 5.96651 | 1151.73 | 55.06 |
| methyl 1,1-dimethylpropyl ether [a] | 6.23218 | 1351.21 | 39.52 |

[a] Antoine's parameters were calculated from the experimental data in Table 5. [b] Reich et al. (1998a).

When required, the molar virial coefficients $B_{ii}$ and $B_{ij}$ were estimated by the method of Hayden and O'Connell (1975) assuming the association parameter $\eta$ to be zero. Critical properties of all components were taken from DIPPR (Daubert and Danner, 1989).

The last two terms in eq 1, particularly the second one that expresses the correction due to the non-ideal behavior of the vapor phase, contributed less than 2% for the system 2-methylpentane (1) + MTBE (2) at 101.3 kPa; in general, their influence was important only at very dilute concentrations. The calculated activity coefficients reported in Tables 2, 3 and 4 are estimated to be accurate to within ± 2 %. The results reported in these Tables indicate that the measured systems exhibit moderate positive deviations from ideal behavior. An azeotrope composition is present in the system 2-methylpentane (1) + MTBE (2) at $x_1 \approx 0.08$ and $T = 328.2$ K.

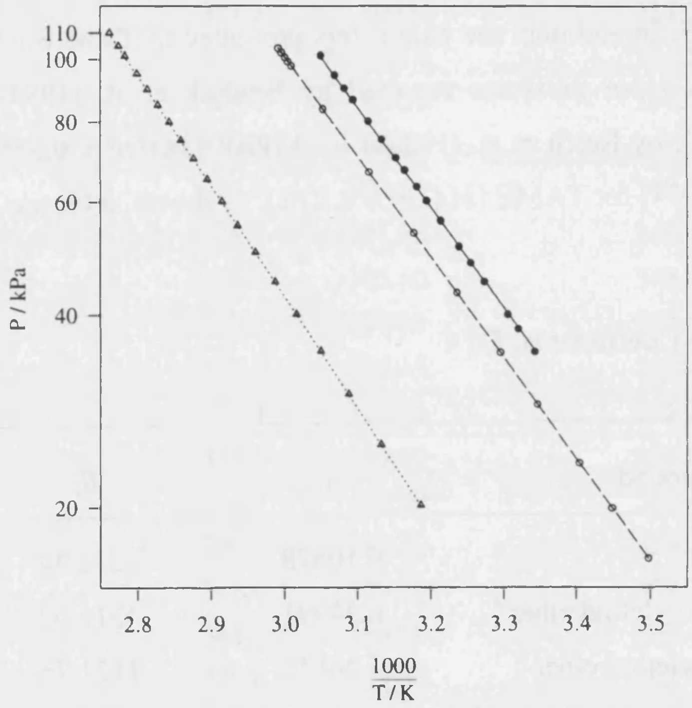

**Figure 7.** Comparison of correlated vapor pressures with other references. Experimental data reported by Boublík et al. (1984) for 2-methylpentane (○). Experimental data of Reich et al. (1998b) for MTBE (●). Experimental data of Krähenbuhl and Gmehling (1994) for TAME (▵). Predicted by eq 4 and parameters in Table 6 for MTBE ( — ), for 2-methylpentane (– – –) and for TAME (…).

The vapor-liquid equilibria data reported in Tables 2, 3 and 4 were found to be thermodynamically consistent by the point-to-point method of Van Ness et al. (1973), as modified by Fredenslund et al. (1977). Consistency was achieved using a one parameter (zeroth order) Legendre polynomial, the regular model, which reduces the functionality of the excess Gibbs energy $G^E$ to the following symmetric relation

$$G^E = Ax_1x_2 \tag{5}$$

The parameter $A$ in eq 5, together with the pertinent statistics required by the Fredenslund et al. test, are shown in Table 7 for the different systems considered in this work. From Table 7 it is concluded that eq 5 gives an excellent fit to the data.

**Table 7. Consistency Test for the Various Experimental Systems Considered in VLE Measurements**

| System | $A^a$ | $100 \times \text{MAD}y_1{}^b$ | $\text{MAD}P^c$ / kPa |
|---|---|---|---|
| 1 + 2 | 0.186 | 0.1 | 0.13 |
| 1 + 3 | 0.122 | 0.1 | 0.25 |
| 1 + 4 | 0.115 | 0.3 | 0.16 |

[a] Zero$^{th}$ order Legendre Polynomial (or Porter model) parameter in eq 5. [b] Average absolute deviation in vapor phase composition. [c] Average absolute deviation in pressure.

The variation of activity coefficients with composition appears in Figures 4, 5 and 6. Inspection of these Figures shows a symmetric trend of experimental activity coefficients that, in high dilution ranges, are approximately equivalent for both components in each binary system. In addition, from the Figures, it is clear that activity coefficients exhibit intersection about the composition $x_1 = 0.5$, and are reasonably represented by eq 5. Thus, according to the present experimental data, and the pertinent consistency test, it is concluded that the systems can be satisfactorily explained by regular solution behavior.

The boiling point temperatures of each system at 101.3 kPa were well correlated with mole fractions by the equation proposed by Wisniak and Tamir (1976) :

$$T/\mathrm{K} = x_1 T_1^0/\mathrm{K} + x_2 T_2^0/\mathrm{K} + x_1 x_2 \sum_{k=0}^{m} C_k (x_1 - x_2)^k \tag{6}$$

In this equation $T_i^0/\mathrm{K}$ is the boiling point of the pure component i, and m is the number of terms used in the series expansion of $(x_1 - x_2)$, usually two. The various constants of eq 6 are reported in Table 8, with information indicating the goodness of fit of the correlation.

**Table 8. Coefficients in Correlation of Boiling Points, Eq 6. Average deviation, Standard Deviation and Maximum Deviation in Temperature**

| system | $C_0$ | $C_1$ | $C_2$ | avg dev. / K[a] | $\sigma$/ K[b] | max dev. / K[c] |
|---|---|---|---|---|---|---|
| 1+2 | -6.611 | -1.411 | -0.724 | 0.03 | 0.03 | 0.11 |
| 1+3 | -5.517 | 2.080 | -2.065 | 0.03 | 0.03 | 0.11 |
| 1+4 | -13.500 | 5.080 | -0.823 | 0.04 | 0.04 | 0.11 |

[a] Average deviation. [b] Standard deviation. [c] Maximum deviation.

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# 4.3. ISOBARIC VAPOR-LIQUID EQUILIBRIUM FOR BINARY MIXTURES OF 2-METHYLPENTANE + ETHANOL AND + 2-METHYL-2-PROPANOL

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## ABSTRACT

Vapor-liquid equilibrium data for the binary systems 2-methylpentane + ethanol and 2-methylpentane + 2-methyl-2-propanol (TBA) are reported at 101.3 kPa, including pure component vapor pressures. The systems deviate remarkably from ideal behaviour presenting one positive azeotrope. The activity coefficients and boiling points of the solutions were correlated with its composition by Wilson, UNIQUAC, NRTL, and Wisniak-Tamir equations.

*Keywords:* VLE data; Activity coefficient; Vapor pressure; Experimental

## 1. Introduction.

Alkanols and ethers are usually added to gasoline as oxygenates to replace lead anti-knock agents, to inhibit the reactivity of combustion emissions and to reduce pollution. The commonly used oxygenating additives are methyl 1,1-dimethylethyl ether (MTBE) and light alkanols like methanol and ethanol. 2-Methyl-2-propanol (TBA) is added in the oxygenated gasolines with ethanol to avoid the formation of two liquid phases in presence of small quantities of water. Phase equilibrium data of oxygenated mixtures are important to predicting the vapor phase composition that would be in equilibrium with gasoline mixtures, for which *iso*-paraffins may constitute up to 30% weight. The systems reported here constitute a particular case of such mixtures.

The present work was undertaken to measure vapor-liquid equilibrium (VLE) data of the entitled systems at 101.3 kPa, for which no data have been previously published. It is part of a project to determine VLE of oxygenates with main hydrocarbons in gasoline.

## 2. Experimental

### *2.1. Chemicals*

2-Methylpentane [99+ mass %, GC grade], 2-Methyl-2-propanol [99.5 mass %, high-performance liquid chromatography (HPLC) grade] were purchased from Aldrich Chemie Co., and Ethanol (99.5 vol. %) was purchased from Prolabo. The reagents were used without further purification after chromatography failed to show any significant impurities. The densities of the pure liquids were measured at 298.15 K using an Anton Paar DMA 55 densimeter. The refractive indexes of the pure liquids were measured at 298.15 K in an Abbe refractometer, Atago 3T. Temperature was controlled to ±0.01 K with a thermostated bath. The accuracies in density and refractive index measurements are ±0.01 kg $m^{-3}$ and ±0.0002, respectively. The experimental values of these properties and the boiling points are given in Table 1 together with those given in Ref. [1-5].

**Table 1. Density, $d$, refractive index, $n_D$, and normal boiling point, $T_b$, of the chemicals**

| Component | $d$(298.15K) (Kg m$^{-3}$) | | $n_D$ (298.15K) | | $T_b$ (101.3 kPa) (K) | |
|---|---|---|---|---|---|---|
| | exptl. | lit. | exptl. | lit. | exptl. | lit. |
| 2-methylpentane | 648.39 | 648.86[b] | 1.3689 | 1.3687[e] | 333.4 | 333.41[e] |
| Ethanol | 785.04 | 785.07[c] | 1.3592 | 1.3663[c] | 351.6 | 351.45[f] |
| 2-methyl-2-propanol | 775.40[a] | 775.43[a,d] | 1.3851 | 1.3859[e] | 355.6 | 355.52[f] |

[a] Measured to 303.15 K. [b] Ref. [1]. [c] Ref [2]. [d] Ref. [3]. [e] Ref [4]. [f] Ref. [5]

### *2.2. Apparatus and procedure*

An all glass Fischer LABODEST vapor-liquid-equilibrium apparatus model 602/D, manufactured by Fischer Labor und Verfahrenstechnik (Germany), was used in the equilibrium determinations. The equilibrium vessel was an dynamic-recirculating still described by Walas [6], equipped with a Cottrell circulation pump. The still is capable of handling pressures from 0.25 to 400 kPa, and temperature up to 523 K. The Cottrell pump ensures that both liquid and vapor phases are in intimate contact during boiling and also in contact with the temperature sensing element.

The equilibrium temperature was measured with a digital Fischer thermometer with an accuracy of ±0.1 K. The apparatus is equipped with two digital sensors of pressure: one for the low pressure zone with an accuracy of ±0.01 kPa, and another one for the high pressures with an accuracy of ±0.1 kPa. The temperature probe was calibrated against the ice and steam points of distilled water. The manometers were calibrated using the vapor pressure of ultrapure water. The still was operated under constant pressure until equilibrium was reached. Equilibrium conditions were assumed when constant temperature and pressure were obtained for 60 min or longer. Then, samples of liquid and condensate were taken for analysis. The sample extractions were carried out with special syringes that allowed one to withdraw small volume samples (1.0 μl) in a system under partial vacuum or under overpressure conditions.

### *2.3. Analysis*

Compositions of the liquid and condensed vapor phase samples were determined using a Hewlett-Packard 5890 S-II gas chromatograph (GC), after calibration with gravimetrically prepared standard solutions. A flame ionization detector was used together with a 60 m, 0.2 mm i.d., fused silica capillary column, SUPELCOWAX 10. The GC response peaks were integrated with a Hewlett-Packard 3396 integrator. Column, injector and detector temperatures were 343, 423, 473 K for all the systems. Very good separation of peaks was achieved under these conditions, and calibration analyses were carried out to convert the peak area ratios to the mass composition of the sample. At least three analyses were made of each vapor composition; the standard deviation in the mole fraction was usually less than 0.001.

## 3. Results and Discussion

The temperature $T$, the liquid-phase $x_i$ and vapor-phase $y_i$ mole fractions at 101.3 kPa are reported in Figs. 1 and 2 and in Tables 2 and 3. Figures 3 and 4 show the activity coefficients $\gamma_i$ that were calculated from the following equation [7]:

$$\ln\gamma_i = \ln\frac{y_i P}{x_i P_i^0} + \frac{\left(B_{ii} - V_i^L\right)\left(P - P_i^0\right)}{RT} + y_j^2\frac{\delta_{ij} P}{RT} \qquad (1)$$

where $T$ and $P$ are the boiling point and the total pressure, $V_i^L$ is the molar liquid volume of component $i$, $B_{ii}$ and $B_{jj}$ are the second virial coefficients of the pure gases, $P_i^0$ is the vapor pressure, $B_{ij}$ the cross second virial coefficient and

$$\delta_{ij} = 2\,B_{ij} - B_{jj} - B_{ii} \qquad (2)$$

The standard state for calculation of activity coefficients is the pure component at the pressure and temperature of the solution. Eq. (1) is valid at low and moderate pressures when the virial equation of state truncated after the second coefficient is adequate to describe the vapor phase of the pure components and their mixtures, and liquid volumes of the pure components are incompressible over the pressure range under consideration.

**Table 2. Experimental vapor-liquid equilibrium data for 2-methylpentane (1) + ethanol (2) at 101.3 kPa**

| $T$ (K) | $x_1$ | $y_1$ | $\gamma_1$ | $\gamma_2$ | $-B_{11}$ ($\mathrm{cm^3\ mol^{-1}}$) | $-B_{22}$ ($\mathrm{cm^3\ mol^{-1}}$) | $-B_{12}$ ($\mathrm{cm^3\ mol^{-1}}$) |
|---|---|---|---|---|---|---|---|
| 333.4 | 1.000 | 1.000 | 1.000 | | | | |
| 329.9 | 0.984 | 0.875 | 0.991 | 19.350 | 1340 | 1278 | 670 |
| 327.5 | 0.955 | 0.794 | 1.001 | 12.735 | 1367 | 1325 | 682 |
| 326.6 | 0.900 | 0.766 | 1.056 | 6.798 | 1377 | 1344 | 686 |
| 326.4 | 0.852 | 0.758 | 1.110 | 4.813 | 1380 | 1348 | 687 |
| 326.2 | 0.798 | 0.748 | 1.179 | 3.690 | 1382 | 1352 | 688 |
| 326.2 | 0.750 | 0.742 | 1.245 | 3.051 | 1382 | 1352 | 688 |
| 326.2 | 0.696 | 0.738 | 1.332 | 2.559 | 1382 | 1352 | 688 |
| 326.3 | 0.647 | 0.734 | 1.422 | 2.219 | 1381 | 1350 | 687 |
| 326.4 | 0.544 | 0.731 | 1.679 | 1.732 | 1380 | 1348 | 687 |
| 326.7 | 0.438 | 0.720 | 2.032 | 1.444 | 1376 | 1342 | 685 |
| 326.9 | 0.387 | 0.718 | 2.280 | 1.318 | 1374 | 1337 | 685 |
| 328.3 | 0.277 | 0.696 | 2.953 | 1.130 | 1358 | 1309 | 678 |
| 329.3 | 0.214 | 0.677 | 3.609 | 1.054 | 1347 | 1290 | 673 |
| 330.5 | 0.176 | 0.651 | 4.071 | 1.026 | 1334 | 1267 | 667 |
| 331.8 | 0.142 | 0.617 | 4.611 | 1.019 | 1320 | 1243 | 661 |
| 333.3 | 0.110 | 0.581 | 5.320 | 1.006 | 1304 | 1216 | 654 |
| 334.7 | 0.093 | 0.546 | 5.670 | 1.005 | 1289 | 1191 | 648 |
| 336.8 | 0.073 | 0.490 | 6.120 | 1.007 | 1268 | 1156 | 638 |
| 338.3 | 0.061 | 0.454 | 6.491 | 0.998 | 1253 | 1132 | 632 |
| 341.3 | 0.042 | 0.369 | 7.011 | 0.995 | 1224 | 1086 | 619 |
| 343.1 | 0.032 | 0.314 | 7.414 | 0.994 | 1207 | 1060 | 612 |
| 345.3 | 0.023 | 0.243 | 7.786 | 0.992 | 1187 | 1029 | 603 |
| 347.6 | 0.013 | 0.159 | 8.453 | 0.995 | 1167 | 998 | 593 |
| 349.1 | 0.008 | 0.101 | 8.582 | 0.998 | 1154 | 979 | 588 |
| 351.6 | 0.000 | 0.000 | | 1.000 | | | |

**Table 3. Experimental vapor-liquid equilibrium data for 2-methylpentane (1) + TBA (2) at 101.3 kPa**

| $T$ (K) | $x_1$ | $y_1$ | $\gamma_1$ | $\gamma_2$ | $-B_{11}$ (cm$^3$ mol$^{-1}$) | $-B_{22}$ (cm$^3$ mol$^{-1}$) | $-B_{12}$ (cm$^3$ mol$^{-1}$) |
|---|---|---|---|---|---|---|---|
| 333.4 | 1.000 | 1.000 | 1.000 | | | | |
| 332.6 | 0.984 | 0.955 | 0.995 | 7.527 | 1311 | 1423 | 984 |
| 331.6 | 0.954 | 0.910 | 1.009 | 5.507 | 1322 | 1438 | 992 |
| 331.2 | 0.906 | 0.875 | 1.034 | 3.813 | 1326 | 1444 | 995 |
| 331.1 | 0.857 | 0.852 | 1.069 | 2.966 | 1327 | 1445 | 995 |
| 331.2 | 0.806 | 0.834 | 1.108 | 2.449 | 1326 | 1444 | 995 |
| 331.3 | 0.755 | 0.821 | 1.160 | 2.086 | 1325 | 1442 | 994 |
| 331.5 | 0.703 | 0.804 | 1.213 | 1.866 | 1323 | 1439 | 992 |
| 331.9 | 0.649 | 0.790 | 1.277 | 1.654 | 1319 | 1433 | 989 |
| 332.2 | 0.597 | 0.776 | 1.350 | 1.515 | 1316 | 1429 | 987 |
| 332.8 | 0.544 | 0.759 | 1.425 | 1.397 | 1309 | 1421 | 983 |
| 333.3 | 0.494 | 0.747 | 1.518 | 1.296 | 1304 | 1413 | 979 |
| 334.0 | 0.445 | 0.725 | 1.605 | 1.238 | 1297 | 1404 | 974 |
| 334.8 | 0.404 | 0.709 | 1.687 | 1.178 | 1288 | 1393 | 968 |
| 335.9 | 0.344 | 0.683 | 1.846 | 1.106 | 1277 | 1378 | 960 |
| 337.0 | 0.298 | 0.646 | 1.956 | 1.097 | 1266 | 1363 | 952 |
| 338.9 | 0.242 | 0.583 | 2.057 | 1.098 | 1247 | 1338 | 939 |
| 341.1 | 0.188 | 0.516 | 2.198 | 1.080 | 1226 | 1310 | 924 |
| 343.4 | 0.139 | 0.450 | 2.429 | 1.047 | 1205 | 1282 | 909 |
| 346.3 | 0.094 | 0.341 | 2.530 | 1.054 | 1178 | 1248 | 890 |
| 349.3 | 0.059 | 0.238 | 2.610 | 1.037 | 1152 | 1214 | 872 |
| 352.4 | 0.027 | 0.127 | 2.738 | 1.017 | 1126 | 1181 | 853 |
| 355.6 | 0.000 | 0.000 | | 1.000 | | | |

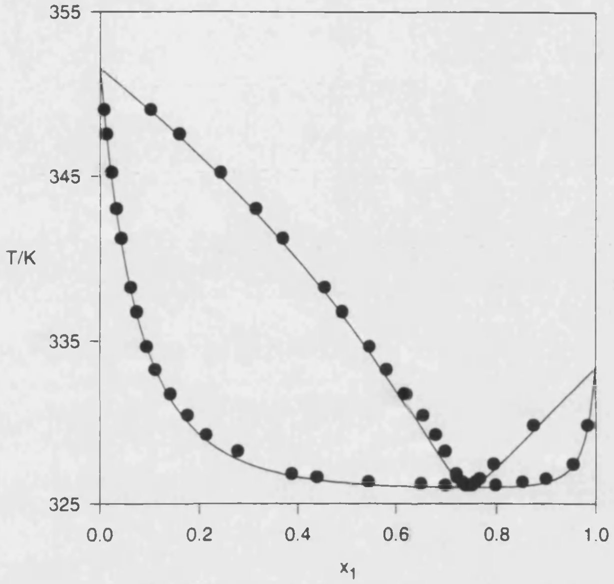

**Figure 1.** Boiling temperature diagram for the system 2-methylpentane (1) + ethanol (2) at 101.3 kPa. Experimental data (●); Wilson model (—).

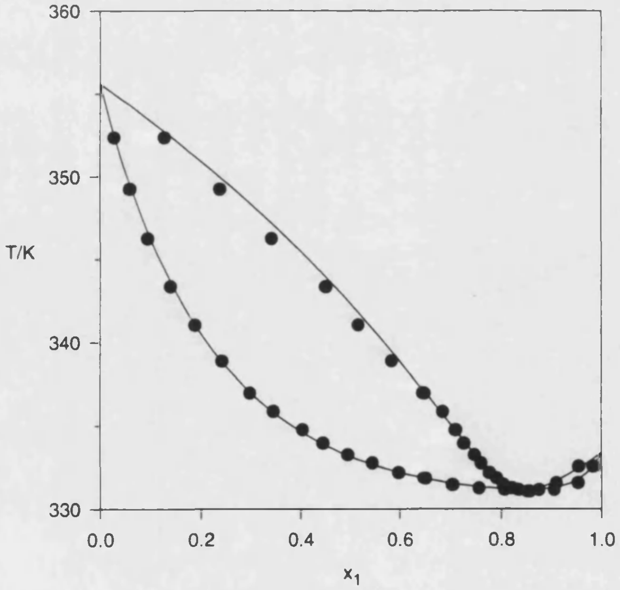

**Figure 2.** Boiling temperature diagram for the system 2-methylpentane (1) + TBA (2) at 101.3 kPa. Experimental data (●); Wilson model (—).

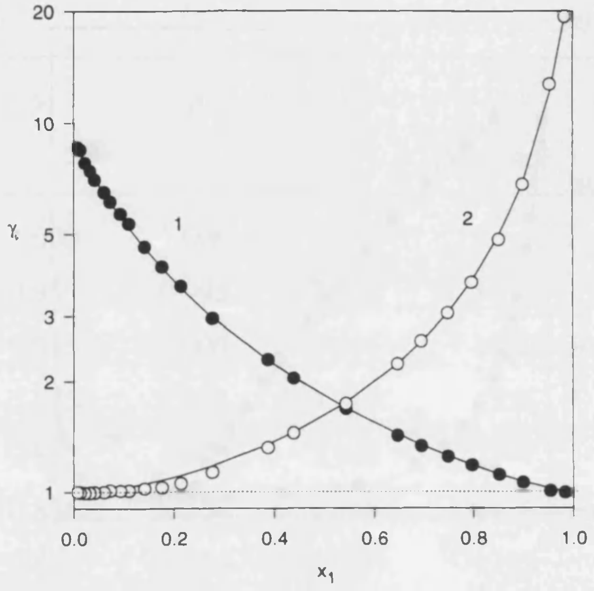

**Figure 3.** Activity coefficient plot for the system 2-methylpentane (1) + ethanol (2) at 101.3 kPa. $\gamma_1$ (●); $\gamma_2$ (○); Wilson model (—).

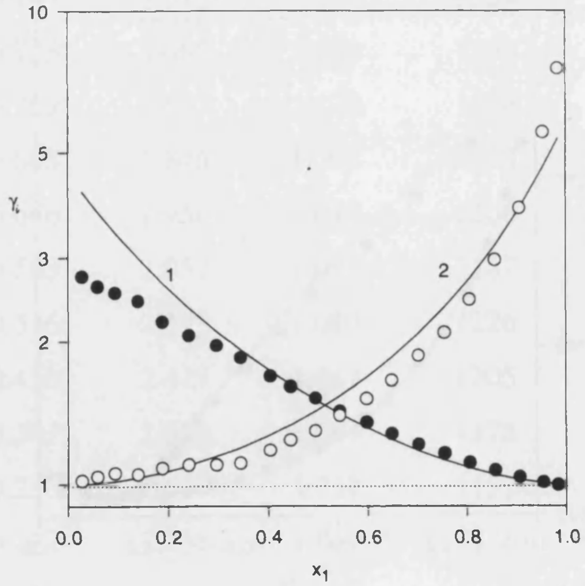

**Figure 4.** Activity coefficient plot for the system 2-methylpentane (1) + TBA (2) at 101.3 kPa. $\gamma_1$ (●); $\gamma_2$ (○); Wilson model (—).

The molar virial coefficients $B_{ii}$ and $B_{ij}$ were estimated by the method of Hayden and O'Connell [8] using the molecular parameters suggested by Prausnitz et al. [9]. Critical properties of all components were taken from DIPPR [4] and are shown in Table 4.

**Table 4. Critical properties of the components from Ref. [4]**

| Component | $P_c$ (bar) | $T_c$ (K) | $Z_c$ |
|---|---|---|---|
| 2-methylpentane | 30.10 | 497.50 | 0.267 |
| Ethanol | 63.38 | 516.25 | 0.248 |
| TBA | 39.70 | 506.20 | 0.260 |

The last two terms in Eq. (1), particularly the second one that expresses the correction due to the non ideal behaviour of the vapor phase, contributed less than 5.5% for the system 2-methylpentane + ethanol and less than 5% for the system 2-methylpentane + TBA; in general, their influence was important only at very dilute concentrations. The calculated activity coefficients reported in Tables 2 and 3 are estimated to be accurate to within ± 3 %. The results reported in these Tables indicate that the measured systems exhibit remarkable positive deviations from ideal behavior and present a minimum boiling azeotrope.

The pure component vapor pressures $P_i^\circ$ for 2-methylpentane were taken from Ref. [10]. For ethanol and TBA, pure component vapor pressures was determined experimentally as a function of the temperature, using the same equipment as that for obtaining the VLE data. The pertinent results appear in Table 5. The measured vapor pressures were correlated using the Antoine equation:

$$\ln(P_i^\circ / \mathrm{kPa}) = A_i - \frac{B_i}{(T/\mathrm{K}) - C_i} \qquad (3)$$

whose parameters $A_i$, $B_i$, and $C_i$ are reported in Table 6. The vapor pressures were correlated with an mean absolute deviation [MADP] of 0.05% for ethanol and 0.05% for TBA. In addition, the parameters presented in Table 6 give a fair prediction of the experimental vapor pressures reported by Ambrose and Sprake [5] for ethanol [MADP = 0.38%], and for TBA [MADP = 0.39%], as shown in Figure 5.

**Table 5. Experimental vapor pressures determined for pure components**

| Ethanol | | TBA | |
|---|---|---|---|
| $T$ (K) | $P$ (kPa) | $T$ (K) | $P$ (kPa) |
| 323.65 | 30.17 | 320.75 | 20.63 |
| 326.95 | 35.27 | 325.05 | 25.76 |
| 329.85 | 40.29 | 328.35 | 30.37 |
| 332.35 | 45.16 | 331.45 | 35.33 |
| 334.65 | 50.06 | 334.15 | 40.21 |
| 336.85 | 55.11 | 336.65 | 45.17 |
| 338.85 | 60.02 | 338.85 | 49.98 |
| 340.75 | 65.08 | 341.05 | 55.12 |
| 342.45 | 70.01 | 342.95 | 59.92 |
| 344.15 | 75.09 | 344.85 | 65.12 |
| 345.75 | 80.23 | 346.45 | 69.66 |
| 347.15 | 84.94 | 348.15 | 74.84 |
| 348.55 | 89.82 | 349.75 | 79.98 |
| 349.95 | 95.06 | 351.25 | 85.09 |
| 351.25 | 100.11 | 352.65 | 90.08 |
| 351.55 | 101.33 | 353.95 | 94.97 |
| 352.45 | 104.95 | 355.15 | 99.63 |
| 353.65 | 109.93 | 355.65 | 101.33 |
| 354.85 | 115.07 | 356.55 | 105.13 |
| 355.95 | 120.21 | 357.65 | 109.82 |
| 356.95 | 124.96 | 358.85 | 115.07 |
| 357.95 | 129.63 | | |

**Table 6. Antoine Coefficients (Eq. (3))**

| Compound | $A_i$ | $B_i$ | $C_i$ |
|---|---|---|---|
| 2-Methylpentane [a] | 14.0614 | 2791.52 | 37.75 |
| Ethanol[b] | 16.4298 | 3545.95 | 51.36 |
| TBA[b] | 14.8533 | 2649.89 | 96.69 |

[a] Ref. [10]. [b] Antoine's parameters were calculated from the experimental data in Table 5.

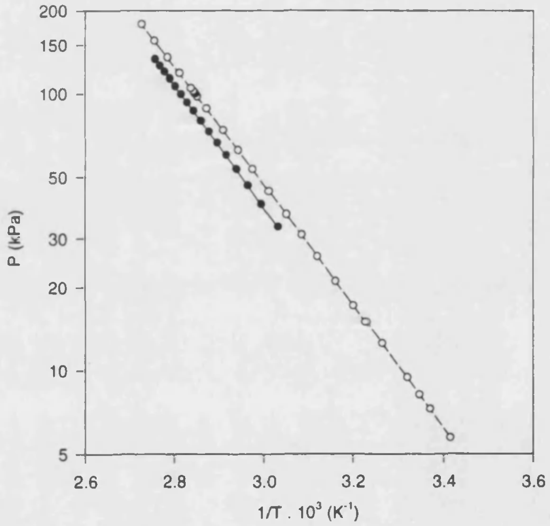

**Figure 5.** Comparison of correlated vapor pressures with other references. Experimental data reported by Ambrose and Sprake [5] for ethanol (●) and for TBA (○). Predicted by Eq. (3) and parameters in Table 6 for ethanol (- - -) and for TBA ( — ) .

The VLE data reported in Tables 2 and 3 were found to be thermodynamically consistent by the point-to-point method of Van Ness et al. [11], as modified by Fredenslund et al. [12]. The pertinent statistics required by the Fredenslund et al. test, together with the number of parameters of the Legendre polynomial used for consistency, are shown in Table 7 for the different systems considered in this work.

**Table 7. Consistency test for the various experimental systems considered in VLE measurements**

| System | $n$ | $100 \times \mathrm{MAD}y_1$[a] | MADP[b] (kPa) |
|---|---|---|---|
| 2-Methylpentane (1) + ethanol (2) | 5 | 0.72 | 0.42 |
| 2-Methylpentane (1) + TBA (2) | 4 | 0.86 | 0.21 |

[a] Mean absolute deviation in vapor phase composition. [b] Mean absolute deviation in pressure.

The parameters of the Wilson, NRTL and UNIQUAC equations were obtained by minimizing the following objective function (OF):

$$\mathrm{OF} = \sum_{i=1}^{N} 100 \times \left( \frac{\left| P_i^{\mathrm{exptl}} - P_i^{\mathrm{calc}} \right|}{P_i^{\mathrm{exptl}}} + \left| y_i^{\mathrm{exptl}} - y_i^{\mathrm{calc}} \right| \right) \qquad (4)$$

and are reported in Table 8, together with the pertinent statistics of VLE interpolation. Inspection of the results given in Table 8 shows that the best fit corresponding to the Wilson model for both systems.

The boiling point temperatures of each system at 101.3 kPa were well correlated with composition by the equation proposed by Wisniak and Tamir [13]:

$$T/K = x_1 T_1^0/\mathrm{K} + x_2 T_2^0/\mathrm{K} + x_1 x_2 \sum_{k=0}^{m} C_k (x_1 - x_2)^k \qquad (5)$$

In this equation $T_i^0/\mathrm{K}$ is the boiling point of the pure component i, and $m$ is the number of terms used in the series expansion of $(x_1 - x_2)$. The various constants of Eq. (5) are reported in Table 9, with information indicating goodness of fit of the correlation.

**Table 8. Parameters and deviations between experimental and calculated values for different $G^E$ models**

| Model | $A_{ij}$ | $A_{ji}$ | $\alpha_{ij}$ | Bubble-point pressures | | Dew-point pressures | |
|---|---|---|---|---|---|---|---|
| | ($J \cdot mol^{-1}$) | ($J \cdot mol^{-1}$) | | $\Delta P$ [a]/ % | $100 \times \Delta y$ [b] | $\Delta P$ [a]/ % | $100 \times \Delta x$ [b] |
| *2-Methylpentane (1) + ethanol (2)* | | | | | | | |
| Wilson[c] | 1187.08 | 9489.34 | | 0.69 | 0.44 | 1.33 | 1.25 |
| NRTL | 6356.65 | 3990.00 | 0.47 | 0.70 | 0.68 | 1.30 | 2.19 |
| UNIQUAC[d] | 4271.12 | -475.03 | | 2.12 | 1.66 | 1.69 | 3.85 |
| *2-Methylpentane(1) + TBA (2)* | | | | | | | |
| Wilson[c] | -14.98 | 5658.90 | | 0.45 | 0.69 | 1.10 | 0.87 |
| NRTL | 4362.09 | 983.72 | 0.47 | 0.74 | 0.68 | 1.22 | 1.02 |
| UNIQUAC[d] | 2844.32 | -1030.28 | | 0.97 | 0.71 | 1.47 | 1.17 |

[a] Average percentual deviation in bubble pressure $\Delta P = 100 / N \sum_{i}^{N} \left| P_i^{exptal} - P_i^{calc} \right| / P_i^{exptal}$ (N : number of data points). [b] Average absolute deviation in vapor phase composition. [c] Liquid volumes have been estimated from the Rackett equation [14]. [d] Volume and surface parameters from Ref. [15].

**Table 9. Coefficients in correlation of boiling points (Eq. (5)), average deviation and root mean square deviations in temperature (rmsd)**

| System | $C_0$ | $C_1$ | $C_2$ | Max dev[a] (K) | Avg dev[b] (K) | rmsd[c] (K) |
|---|---|---|---|---|---|---|
| 2-Methylpentane (1) + ethanol (2) | -36.27 | 36.80 | -198.06 | 6.71 | 2.07 | 0.569 |
| 2-Methylpentane (1) + TBA (2) | -42.23 | 17.62 | -43.70 | 0.92 | 0.38 | 0.103 |

[a] Maximum deviation. [b] Average deviation. [c] Root mean square deviation.

## 4. List of Symbols

| | | |
|---|---|---|
| $A_i$ | Antoine's equation parameter, Eq. (4) | |
| $B_i$ | Antoine's equation parameter, Eq. (4) | |
| $B_{ii}$ | pure component second virial coefficient | $cm^3 \cdot mol^{-1}$ |
| $B_{ij}$ | cross second virial coefficient | $cm^3 \cdot mol^{-1}$ |
| $C_i$ | Antoine's equation parameter, Eq. (3); parameters in Eq. (5) | |
| $G^E$ | excess Gibbs energy | $J\ mol^{-1}$ |
| $P$ | absolute pressure | kPa |
| $P^0$ | pure component vapor pressure | kPa |
| $R$ | universal gas constant | $J \cdot mol^{-1} \cdot K^{-1}$ |
| $T$ | absolute temperature | K |
| $V$ | molar volume | $cm^3 \cdot mol^{-1}$ |
| $x$, $y$ | compositions of the liquid and vapor phases | |

*Greek*

| | | |
|---|---|---|
| $\delta_{ij}$ | parameter defined in Eq. (2) | $cm^3 \cdot mol^{-1}$ |
| $\gamma$ | activity coefficient | |

*Superscripts*

| | |
|---|---|
| $^E$ | excess property |
| $^L$ | pertaining to the liquid phase |

*Subscripts*

| | |
|---|---|
| $i,j$ | component $i$, $j$ respectively |

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## 4.4. VAPOR-LIQUID EQUILIBRIA IN THE SYSTEMS 3-METHYLPENTANE + METHYL 1,1-DIMETHYLETHYL ETHER AND 3-METHYLPENTANE + METHYL 1,1-DIMETHYLPROPYL ETHER AT 101.3 kPa

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### ABSTRACT

Pure-component vapor pressure of 3-methylpentane and vapor-liquid equilibrium (VLE) for the binary systems of 3-methylpentane with methyl 1,1-dimethylethyl ether (MTBE) and with methyl 1,1-dimethylpropyl ether (TAME) at 101.3 kPa have been measured. Both systems exhibit small positive deviations from ideality. They can be described as regular solutions and do not present azeotrope. The activity coefficients and boiling points of the solutions were correlated with its composition by Wilson, UNIQUAC, NRTL, and Wisniak-Tamir equations.

*Keywords:* VLE data; activity coefficient; Vapor pressure; Experimental

## 1. Introduction

Environmental legislation around the world has forced the use of oxygenates for gasoline blending to phase out the lead additives and to reduce the reactive evaporative and exhaust emissions. The US Clean Air Act Amendments of 1990 set forth the basic guidelines for future transportation fuel composition and require the manufacture of oxygenated and reformulated gasolines. Methyl 1,1-dimethylethyl ether (MTBE) is the primary oxygenated compound being used to reformulate gasolines to improve their octane rating and pollution-reducing capability. However potential and documented contamination of water resources by MTBE has become a major public issue over the past few years, and restrictions in its use as additive are expected. MTBE readily dissolves in water, can move rapidly through soils and aquifers, is resistant to microbial decomposition and is difficult to remove in water treatment.

The US Environmental Protection Agency has classified it as a possible human carcinogen. Finally, it is reported to have an unpleasant taste and odor in water. These factors have caused widespread concern that drinking water supplies and human health may be at risk, a situation which promotes further research with other ethers as potential additives. Methyl 1,1-dimethylpropyl ether (TAME) is an additive that is effective at reducing automotive CO emissions.

Phase equilibrium data of oxygenated mixtures are important for predicting the vapor phase composition that would be in equilibrium with hydrocarbon mixtures, and the systems reported here constitute examples of such mixtures. The present work was undertaken to measure vapor-liquid equilibrium (VLE) data of the entitled systems at 101.3 kPa, for which no data have been previously published.

## 2. Experimental

### *2.1. Chemicals*

3-Methylpentane (99+ mass %), MTBE (99.8 mass %, HPLC grade) and TAME (97 mass %) were purchased from Aldrich Chemie. 3-Methylpentane and MTBE were used without further purification after chromatography failed to show any significant impurities. TAME was purified to 99.9+ mass % by batch distillation in a Fischer SPALTROHR-column HMS-500, controlled by a Fischer System D301-C. The densities of the pure liquids were measured at 298.15 K using an Anton Paar DMA 55 densimeter. The refractive indexes of the pure liquids were measured at 298.15 K in an Abbe refractometer, Atago 3T. Temperature was controlled to ±0.01 K with a thermostated bath. The accuracies in density and refractive index measurements are ±0.01 kg $m^{-3}$ and ±0.0002, respectively. The experimental values of these properties and the boiling points are given in Table 1 together with those given in Ref. [1-5].

**Table 1. Density, *d*, refractive index, $n_D$, and normal boiling point, $T_b$, of the chemicals**

| Component | $d$(298.15K) (Kg $m^{-3}$) | | $n_D$ (298.15K) | | $T_b$ (101.3 kPa) (K) | |
|---|---|---|---|---|---|---|
| | exptl. | lit. | exptl. | lit. | exptl. | lit. |
| 3-Methylpentane | 659.51 | 660.04[a] | 1.3738 | 1.3739[b] | 336.3 | 336.43[d] |
| MTBE | 735.20 | 735.28[b] | 1.3664 | 1.3663[b] | 328.2 | 328.11[e] |
| TAME | 765.94 | 765.77[c] | 1.3858 | 1.3859[b] | 359.3 | 359.33[e] |

[a] Ref. [1]. [b] Ref [2]. [c] Ref. [3]. [d] Ref [4]. [e] Ref. [5]

### *2.2. Apparatus and procedure*

The equilibrium vessel was an all-glass, dynamic-recirculating still described by Walas [6], equipped with a Cottrell circulation pump. The still (Labodest model), manufactured by Fischer Labor und Verfahrenstechnik (Germany), is capable of handling pressures from 0.25

to 400 kPa, and temperature up to 523 K. The Cottrell pump ensures that both liquid and vapor phases are in intimate contact during boiling and also in contact with the temperature sensing element. The equilibrium temperature was measured with a digital Fischer thermometer with an accuracy of ±0.1 K. The apparatus is equipped with two digital sensors of pressure: one for the low pressure zone with an accuracy of ±0.01 kPa, and another one for the high pressures with an accuracy of ±0.1 kPa. The temperature probe was calibrated against the ice and steam points of distilled water. The manometers were calibrated using the vapor pressure of ultrapure water. The still was operated under constant pressure until equilibrium was reached. Equilibrium conditions were assumed when constant temperature and pressure were obtained for 60 min or longer. Then, samples of liquid and condensate were taken for analysis. The sample extractions were carried out with special syringes that allowed one to withdraw small volume samples (1.0 μl) in a system under partial vacuum or under overpressure conditions.

### *2.3. Analysis*

Compositions of the liquid and condensed vapor phase samples were determined using a Hewlett-Packard 5890 S-II gas chromatograph (GC), after calibration with gravimetrically prepared standard solutions. A flame ionization detector was used together with a 60 m, 0.2 mm i.d., fused silica capillary column, SUPELCOWAX 10. The GC response peaks were integrated with a Hewlett-Packard 3396 integrator. Column, injector and detector temperatures were 343, 423, 473 K for all the systems. Very good separation of peaks was achieved under these conditions, and calibration analyses were carried out to convert the peak area ratios to the mass composition of the sample. At least three analyses were made of each vapor composition; the standard deviation in the mole fraction was usually less than 0.001.

## 3. Results and discussion

The temperature $T$, the liquid-phase $x_i$ and vapor-phase $y_i$ mole fractions at 101.3 kPa are reported in Figs. 1 and 2 and in Tables 2 and 3.

**Table 2. Experimental vapor-liquid equilibrium data for MTBE (1) + 3-methylpentane (2) at 101.3 kPa**

| $T$ (K) | $x_1$ | $y_1$ | $\gamma_1$ | $\gamma_2$ | $-B_{11}$ ($cm^3$ $mol^{-1}$) | $-B_{22}$ ($cm^3$ $mol^{-1}$) | $-B_{12}$ ($cm^3$ $mol^{-1}$) |
|---|---|---|---|---|---|---|---|
| 336.3 | 0.000 | 0.000 |  | 1.000 |  |  |  |
| 335.9 | 0.026 | 0.038 | 1.176 | 1.000 | 1077 | 1281 | 1152 |
| 335.3 | 0.061 | 0.090 | 1.192 | 1.000 | 1082 | 1287 | 1157 |
| 334.3 | 0.126 | 0.177 | 1.167 | 1.002 | 1090 | 1297 | 1166 |
| 333.7 | 0.181 | 0.243 | 1.132 | 1.002 | 1095 | 1303 | 1172 |
| 332.9 | 0.235 | 0.305 | 1.126 | 1.008 | 1102 | 1312 | 1179 |
| 332.4 | 0.289 | 0.362 | 1.100 | 1.013 | 1106 | 1317 | 1184 |
| 331.9 | 0.329 | 0.402 | 1.091 | 1.021 | 1110 | 1322 | 1188 |
| 331.5 | 0.370 | 0.443 | 1.082 | 1.026 | 1113 | 1326 | 1192 |
| 331.0 | 0.432 | 0.502 | 1.063 | 1.036 | 1117 | 1332 | 1197 |
| 330.6 | 0.488 | 0.554 | 1.053 | 1.042 | 1121 | 1336 | 1200 |
| 330.5 | 0.508 | 0.572 | 1.050 | 1.041 | 1122 | 1337 | 1201 |
| 330.1 | 0.565 | 0.622 | 1.039 | 1.052 | 1125 | 1342 | 1205 |
| 329.8 | 0.620 | 0.670 | 1.029 | 1.063 | 1128 | 1345 | 1208 |
| 329.4 | 0.674 | 0.715 | 1.022 | 1.085 | 1131 | 1349 | 1212 |
| 329.2 | 0.722 | 0.755 | 1.014 | 1.100 | 1133 | 1351 | 1213 |
| 329.0 | 0.765 | 0.792 | 1.011 | 1.110 | 1135 | 1354 | 1215 |
| 328.8 | 0.811 | 0.831 | 1.006 | 1.132 | 1136 | 1356 | 1217 |
| 328.7 | 0.858 | 0.872 | 1.001 | 1.144 | 1137 | 1357 | 1218 |
| 328.5 | 0.905 | 0.913 | 1.000 | 1.168 | 1139 | 1359 | 1220 |
| 328.4 | 0.950 | 0.954 | 0.998 | 1.192 | 1140 | 1360 | 1221 |
| 328.3 | 0.978 | 0.980 | 0.999 | 1.198 | 1141 | 1361 | 1222 |
| 328.2 | 1.000 | 1.000 | 1.000 |  |  |  |  |

**Table 3. Experimental vapor-liquid equilibrium data for 3-methylpentane (1) + TAME (2) at 101.3 kPa. (Vapor phase considered ideal)**

| $T$ (K) | $x_1$ | $y_1$ | $\gamma_1$ | $\gamma_2$ |
|---|---|---|---|---|
| 359.3 | 0.000 | 0.000 | | 1.000 |
| 358.7 | 0.019 | 0.040 | 1.099 | 0.996 |
| 357.8 | 0.046 | 0.094 | 1.086 | 0.993 |
| 356.4 | 0.087 | 0.171 | 1.085 | 0.992 |
| 354.9 | 0.130 | 0.241 | 1.062 | 0.999 |
| 353.5 | 0.171 | 0.309 | 1.076 | 0.998 |
| 351.8 | 0.230 | 0.391 | 1.065 | 0.999 |
| 350.6 | 0.273 | 0.445 | 1.058 | 1.002 |
| 349.3 | 0.319 | 0.497 | 1.051 | 1.010 |
| 348.0 | 0.373 | 0.557 | 1.046 | 1.008 |
| 346.8 | 0.424 | 0.607 | 1.038 | 1.013 |
| 345.7 | 0.470 | 0.648 | 1.033 | 1.024 |
| 344.7 | 0.521 | 0.695 | 1.031 | 1.013 |
| 343.6 | 0.571 | 0.731 | 1.022 | 1.035 |
| 342.9 | 0.608 | 0.760 | 1.019 | 1.036 |
| 341.9 | 0.656 | 0.793 | 1.017 | 1.051 |
| 341.1 | 0.708 | 0.828 | 1.008 | 1.057 |
| 340.3 | 0.750 | 0.857 | 1.009 | 1.059 |
| 339.5 | 0.800 | 0.887 | 1.004 | 1.077 |
| 338.7 | 0.848 | 0.915 | 1.001 | 1.095 |
| 337.9 | 0.894 | 0.941 | 1.002 | 1.114 |
| 337.2 | 0.945 | 0.970 | 0.999 | 1.126 |
| 336.8 | 0.967 | 0.982 | 1.001 | 1.133 |
| 336.3 | 1.000 | 1.000 | 1.000 | |

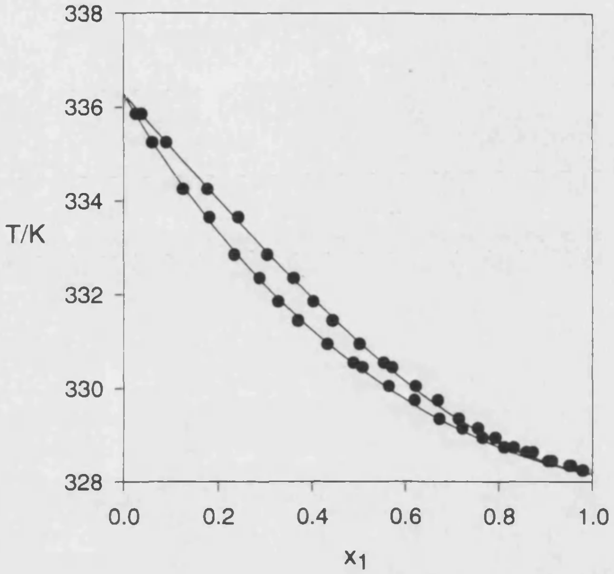

**Figure 1.** Boiling temperature diagram for the system MTBE (1) + 3-methylpentane (2) at 101.3 kPa. Experimental data (●); Wilson model (—).

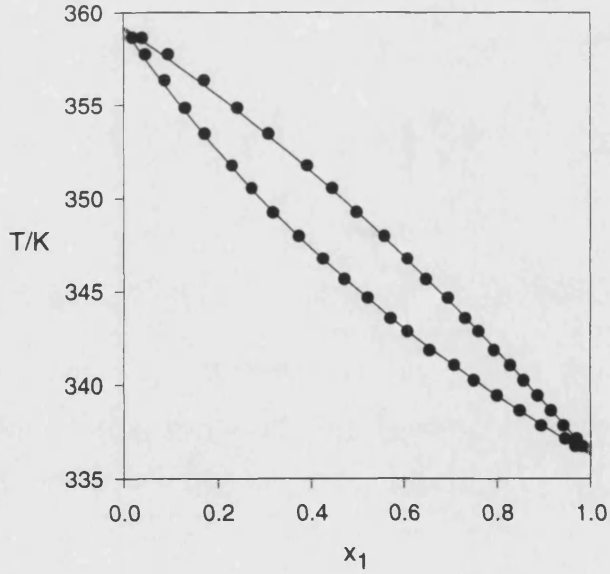

**Figure 2.** Boiling temperature diagram for the system 3-methylpentane (1) + TAME (2) at 101.3 kPa. Experimental data (●); Wilson model (—).

Figures 3 and 4 show the activity coefficients $\gamma_i$ that, for the system MTBE (1) + 3-methylpentane (2), were calculated from the following equation [7]:

$$\ln \gamma_i = \ln \frac{y_i P}{x_i P_i^0} + \frac{\left(B_{ii} - V_i^L\right)\left(P - P_i^0\right)}{RT} + y_j^2 \frac{\delta_{ij} P}{RT} \tag{1}$$

where $T$ and $P$ are the boiling point and the total pressure, $V_i^L$ is the molar liquid volume of component i, $B_{ii}$ and $B_{jj}$ are the second virial coefficients of the pure gases, $P_i^0$ is the vapor pressure, $B_{ij}$ the cross second virial coefficient and:

$$\delta_{ij} = 2\,B_{ij} - B_{jj} - B_{ii} \tag{2}$$

The standard state for calculation of activity coefficients is the pure component at the pressure and temperature of the solution. Eq. (1) is valid at low and moderate pressures when the virial equation of state truncated after the second coefficient is adequate to describe the vapor phase of the pure components and their mixtures, and liquid volumes of the pure components are incompressible over the pressure range under consideration.

For the system 3-methylpentane (1) + TAME (2), activity coefficients were calculated according to the ideal relation [7]:

$$\gamma_i = \frac{y_i P}{x_i P_i^0} \tag{3}$$

because, on the one hand, the low pressure makes this assumption reasonable and, on the other hand, as discussed by Reich et al. [8], the scarce physical information available for mixtures of ETBE and TAME with alkanes does not allow a reliable estimation of the second virial coefficient.

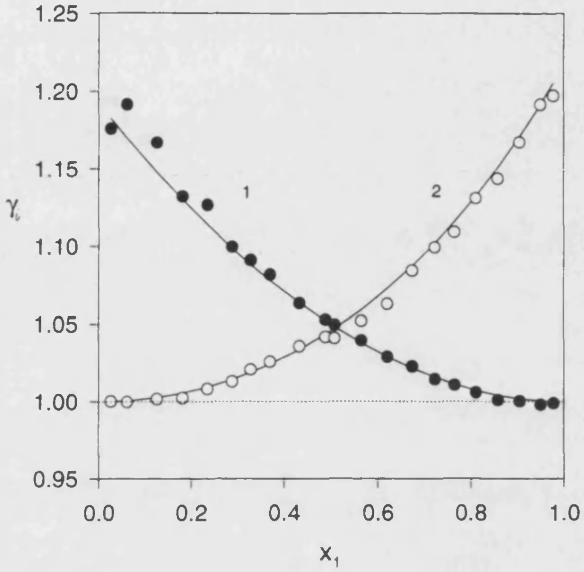

**Figure 3.** Activity coefficient plot for the system MTBE (1) + 3-methylpentane (2) at 101.3 kPa. $\gamma_1$ (●); $\gamma_2$ (○); Wilson model (—).

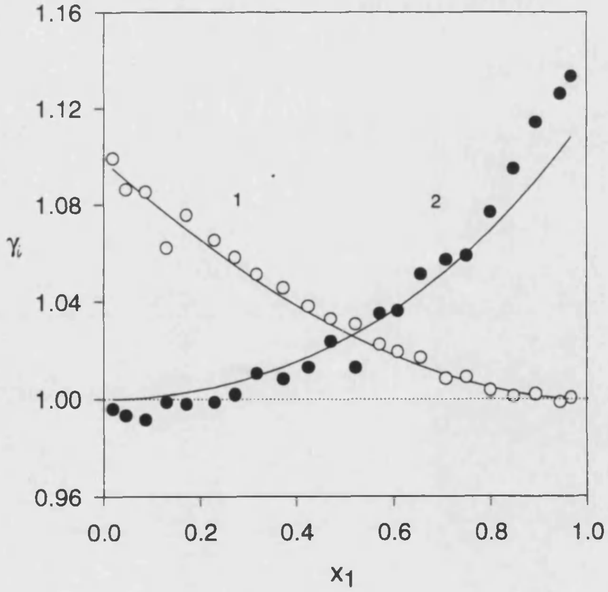

**Figure 4.** Activity coefficient plot for the system 3-methylpentane (1) + TAME (2) at 101.3 kPa. $\gamma_1$ (○); $\gamma_2$ (●); Wilson model (—).

The pure component vapor pressures $P_i^0$ for MTBE and TAME were taken from Ref. [9]. For 3-methylpentane, pure component vapor pressures was determined experimentally as a function of the temperature, using the same equipment as that for obtaining the VLE data. The pertinent results appear in Table 4.

**Table 4. Experimental vapor pressures determined for 3-methylpentane**

| $T$ (K) | $P$ (kPa) | $T$ (K) | $P$ (kPa) |
|---|---|---|---|
| 315.6 | 50.07 | 340.3 | 114.87 |
| 318.3 | 55.06 | 341.7 | 119.84 |
| 320.7 | 60.03 | 341.8 | 120.00 |
| 322.9 | 64.95 | 344.4 | 130.00 |
| 325.1 | 70.08 | 346.9 | 140.00 |
| 327.1 | 74.94 | 349.2 | 149.90 |
| 329.0 | 79.87 | 351.4 | 159.90 |
| 330.9 | 84.99 | 353.5 | 169.60 |
| 332.7 | 90.08 | 355.5 | 179.70 |
| 334.3 | 94.95 | 357.5 | 189.70 |
| 336.3 | 101.33 | 359.4 | 199.90 |
| 337.5 | 104.96 | 361.0 | 209.20 |
| 338.9 | 109.88 | | |

The measured vapor pressures were correlated using the Antoine equation:

$$\log(P_i^0/\mathrm{kPa}) = A_i - \frac{B_i}{(T/\mathrm{K}) - C_i} \qquad (4)$$

whose parameters $A_i$, $B_i$, and $C_i$ are reported in Table 5. The vapor pressures were correlated with a mean absolute deviation [MADP] of 0.08 %. In addition, the parameters presented in

Table 5 give a fair prediction of the experimental vapor pressures reported by Willingham et al. [4] [MADP 0.54%], as shown in Fig. 5.

**Table 5. Antoine Coefficients, Eq. (4)**

| Compound | $A_i$ | $B_i$ | $C_i$ |
|---|---|---|---|
| 3-Methylpentane [a] | 6.24116 | 1302.78 | 28.69 |
| Methyl 1,1-dimethylethyl ether [b] | 6.34991 | 1312.52 | 26.03 |
| Methyl 1,1-dimethylpropyl ether [b] | 6.23218 | 1351.21 | 39.52 |

[a] Antoine's parameters were calculated from the experimental data in Table 5. [b] Ref. [9]

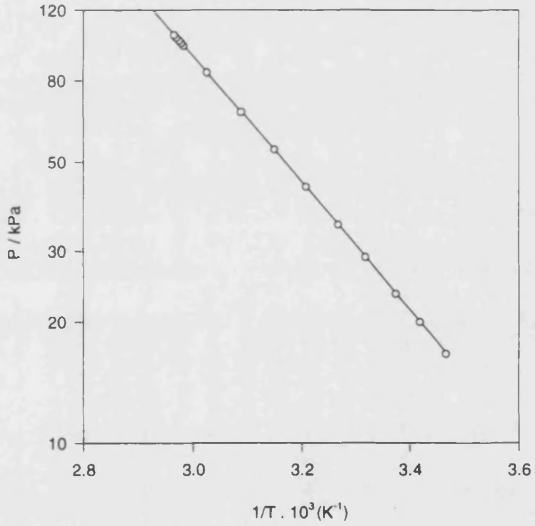

**Figure 5.** Comparison of correlated vapor pressures of 3-methylpentane with other reference. Experimental data reported by Willingham et al. [4] (○). Predicted by Eq. (4) and parameters in Table 5 ( — ) .

When required, the molar virial coefficients $B_{ii}$ and $B_{ij}$ were estimated by the method of Hayden and O'Connell [10] assuming the association parameter $\eta$ to be zero. Critical properties of all components were taken from Ref. [2] and are shown in Table 6. The last two terms in Eq. (1), particularly the second one that expresses the correction due to the non-ideal behavior of the vapor phase, contributed less than 1.5% for the system MTBE (1) + 3-methylpentane (2) at 101.3 kPa; in general, their influence was important only at very dilute concentrations. The calculated activity coefficients reported in Tables 2 and 3 are estimated to be accurate to within ± 2 %. The results reported in these tables indicate that the measured systems exhibit moderate positive deviations from ideal behavior and do not present azeotrope.

**Table 6. Critical properties of the components from Ref. [2]**

| Component | $P_c$ (bar) | $T_c$ (K) | $Z_c$ |
|---|---|---|---|
| 3-methylpentane | 31.24 | 504.43 | 0.273 |
| MTBE | 34.30 | 497.10 | 0.273 |
| TAME | 30.40 | 534.00 | 0.262 |

The vapor-liquid equilibria data reported in Tables 2 and 3 were found to be thermodynamically consistent by the point-to-point method of Van Ness et al. [11], as modified by Fredenslund et al. [12]. Consistency was achieved using a one parameter (zeroth order) Legendre polynomial, the regular model, which reduces the functionality of the excess Gibbs energy $G^E$ to the following symmetric relation:

$$G^E = Ax_1x_2 \tag{5}$$

The parameter $A$ in Eq. (5), together with the pertinent statistics required by the Fredenslund et al. test, are shown in Table 7 for the different systems considered in this work. From Table 6 it is concluded that Eq. (5) gives an excellent fit to the data.

**Table 7. Consistency test for the various experimental systems considered in VLE measurements.**

| System | $A^a$ | $100 \times \mathrm{MAD}y_1{}^b$ | MADP [c] (kPa) |
|---|---|---|---|
| MTBE (1) + 3-methylpentane (2) | 0.183 | 0.12 | 0.13 |
| 3-methylpentane (1) + TAME (2) | 0.095 | 0.15 | 0.29 |

[a] Zeroth order Legendre Polynomial (or Porter model) parameter in Eq. (5). [b] Mean absolute deviation in vapor phase composition. [c] Mean absolute deviation in pressure.

The parameters of the Wilson, NRTL and UNIQUAC equations were obtained by minimizing the following objective function (OF):

$$\mathrm{OF} = \sum_{i=1}^{N} 100 \times \left( \left| \frac{P_i^{\mathrm{exptl}} - P_i^{\mathrm{calc}}}{P_i^{\mathrm{exptl}}} \right| + \left| y_i^{\mathrm{exptl}} - y_i^{\mathrm{calc}} \right| \right) \tag{6}$$

and are reported in Table 8, together with the pertinent statistics of VLE interpolation. Inspection of the results given in Table 8 shows that all the models fitted well both systems, the best fit corresponding to the Wilson model (Eq. (7) from Ref. [13]) for the 3-methylpentane (1) + TAME (2) system and in the case of the MTBE (1) + 3-methylpentane (2) system, all of models give a similar fit to the data.

$$\ln \gamma_i = -\ln\left(x_i + \Lambda_{ij} x_j\right) + x_j \left( \frac{\Lambda_{ij}}{x_i + \Lambda_{ij} x_j} - \frac{\Lambda_{ji}}{\Lambda_{ji} x_i + x_j} \right)$$

$$\Lambda_{ij} = \frac{V_j}{V_i} \exp\left( -\frac{A_{ij}}{RT} \right) \tag{7}$$

**Table 8. Parameters and deviations between experimental and calculated values for different $G^E$ models**

| Model | $A_{ij}$ (J/mol) | $A_{ji}$ (J/mol) | $\alpha_{ij}$ | Bubble-point pressures $\Delta P$ [a]/ % | Bubble-point pressures $100 \times \Delta y$ [b] | Dew-point pressures $\Delta P$ [a]/ % | Dew-point pressures $100 \times \Delta x$ [b] |
|---|---|---|---|---|---|---|---|
| *MTBE (1) + 3-methylpentane (2)* | | | | | | | |
| Wilson[c] | 309.33 | 225.19 | | 0.17 | 0.08 | 0.17 | 0.08 |
| NRTL | 675.98 | -139.21 | 0.3 | 0.17 | 0.09 | 0.17 | 0.08 |
| UNIQUAC[d] | 141.87 | -11.48 | | 0.17 | 0.08 | 0.17 | 0.08 |
| *3-Methylpentane(1) + TAME (2)* | | | | | | | |
| Wilson[c] | -213.68 | 528.20 | | 0.21 | 0.12 | 0.26 | 0.13 |
| NRTL | -29.74 | 331.11 | 0.3 | 0.24 | 0.13 | 0.29 | 0.15 |
| UNIQUAC[d] | -121.45 | 194.90 | | 0.22 | 0.13 | 0.28 | 0.14 |

[a] Average percentual deviation in bubble pressure $\Delta P = 100/N\sum_{i}^{N}\left|P_i^{exptal} - P_i^{calc}\right| / P_i^{exptal}$ (N : number of data points). [b] Average absolute deviation in vapor phase composition. [c] Liquid volumes have been estimated from the Rackett equation [15]. [d] Volume and surface parameters from Ref. [13].

The boiling point temperatures of each system at 101.3 kPa were well correlated with composition by the equation proposed by Wisniak and Tamir [14] :

$$T/K = x_1 T_1^0/\mathrm{K} + x_2 T_2^0/\mathrm{K} + x_1 x_2 \sum_{k=0}^{m} C_k (x_1 - x_2)^k \tag{8}$$

In this equation $T_i^0/\mathrm{K}$ is the boiling point of the pure component i, and $m$ is the number of terms used in the series expansion of ( $x_1$ - $x_2$ ). The various constants of Eq. (8) are reported in Table 9, with information indicating goodness of fit of the correlation.

**Table 9. Coefficients in correlation of boiling points, Eq. (8), average deviation and root mean square deviations in temperature, rmsd**

| System | $C_0$ | $C_1$ | $C_2$ | max dev[a] (K) | avg dev[b] (K) | rmsd[c] (K) |
|---|---|---|---|---|---|---|
| MTBE (1) + 3-methylpentane (2) | -7.16 | 2.08 | -0.65 | 0.11 | 0.03 | 0.009 |
| 3-Methylpentane (1) + TAME (2) | -11.21 | 2.26 | 0.91 | 0.16 | 0.06 | 0.016 |

[a] Maximum deviation. [b] Average deviation. [c] Root mean square deviation.

## 4. List of Symbols

| | | |
|---|---|---|
| $A_i$ | Antoine's equation parameter, Eq. (4) | |
| $A_{ij}$ | adjustable parameter in Wilson equation (Eq. (7)) | $J\cdot mol^{-1}$ |
| $B_i$ | Antoine's equation parameter, Eq. (4) | |
| $B_{ii}$ | pure component second virial coefficient | $cm^3\cdot mol^{-1}$ |
| $B_{ij}$ | cross second virial coefficient | $cm^3\cdot mol^{-1}$ |
| $C_i$ | Antoine's equation parameter, Eq. (4); parameters in Eq. (8) | |
| $G^E$ | excess Gibbs energy | $J\cdot mol^{-1}$ |
| $P$ | absolute pressure | kPa |
| $P^o$ | pure component vapor pressure | kPa |
| $R$ | universal gas constant | $J\cdot mol^{-1}\cdot K^{-1}$ |
| $T$ | absolute temperature | K |
| $V$ | volume | $cm^3\cdot mol^{-1}$ |
| $x$, $y$ | compositions of the liquid and vapor phases | |

*Greek*

| | | |
|---|---|---|
| $\delta_{ij}$ | parameter defined in Eq. (2) | $cm^3 \cdot mol^{-1}$ |
| $\gamma$ | activity coefficient | |
| $\Lambda_{ij}$ | parameter in Wilson equation (Eq. (7)) | |

*Superscripts*

| | |
|---|---|
| $^E$ | excess property |
| $^L$ | pertaining to the liquid phase |

*Subscripts*

| | |
|---|---|
| $i,j$ | component *i, j* respectively |

## Acknowledgements

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# 4.5. ISOBARIC VAPOR-LIQUID EQUILIBRIUM IN THE SYSTEMS 3-METHYLPENTANE + ETHYL 1,1-DIMETHYLETHYL ETHER, + DIISOPROPYL ETHER, AND + TETRAHYDROFURAN

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## ABSTRACT

New consistent vapor-liquid equilibrium data for the binary systems 3-methylpentane + ethyl 1,1-dimethylethyl ether, + diisopropyl ether, and + tetrahydrofuran are reported at 101.3 kPa. The measured systems, which deviate from ideal behavior, can be described as symmetric solutions and only the system 3-methylpentane + tetrahydrofuran presents an azeotrope. The activity coefficients and boiling points of the solutions were correlated with its composition by Wilson, UNIQUAC, NRTL, and Wisniak-Tamir equations.

## Introduction

Environmental legislation around the world has forced the use of oxygenates for gasoline blending to phase out the lead additives and to reduce the reactive evaporative and exhaust emissions. Amendments of the U.S. Clean Air Act in 1990 have mandated that new gasoline formulations be sold in highly polluted areas of the country, with oxygenated gasolines being supplied particularly during the winter. Methyl 1,1-dimethylethyl ether (MTBE) is the primary oxygenated compound being used to reformulate gasolines to improve their octane rating and pollution-reducing capability.

However potential and documented contamination of water resources by MTBE has become a major public issue over the past few years and restrictions in its use as additive are expected. MTBE readily dissolves in water, can move rapidly through soils and aquifers, is resistant to microbial decomposition and is difficult to remove in water treatment. The US Environmental Protection Agency has classified it as a possible human carcinogen. Finally, it is reported to have an unpleasant taste and odor in water. These factors have caused widespread concern that drinking water supplies and human health may be at risk, a situation which promotes further research with other branched or cyclic ethers as potential additives. Ethyl-1,1-dimethylethyl ether (ETBE), diisopropyl ether (DIPE) and tetrahydrofuran (THF) show good characteristics as a gasoline additive including: low volatility, low water solubility, high octane value and large reductions in carbon monoxide and hydrocarbon emissions.

Phase equilibrium data of oxygenated mixtures are important for predicting the vapor phase composition that would be in equilibrium with hydrocarbon mixtures, and the systems reported here constitute examples of such mixtures. The present work was undertaken to measure vapor-liquid equilibrium (VLE) data of the entitled systems at 101.3 kPa, for which no data (isobaric or isothermal) have been published in the literature.

## Experimental Section

***Chemicals.*** 3-Methylpentane (99+ mass %), DIPE (99.8+ mass %, HPLC grade) and THF (99.9 mass %) were purchased from Aldrich Ltd., and ETBE (96+ mass %) was purchased from Tokyo Chemical Industry Co. Ltd. 3-Methylpentane, DIPE and THF were used without further purification after chromatography failed to show any significant impurities. ETBE was purified to 99.9+ mass %, in a 1 m height × 30 mm diameter Normschliffgerätebau adiabatic column (packed with 3 x 3 mm SS spirals) working at a 1:100 reflux ratio. The properties and purity (as determined by GLC) of the pure components, as used for VLE measurements, appear in Table 1. Appropriate precautions were taken when handling ethers in order to avoid peroxide formation.

**Table 1. Densities *d*, Refractive Index $n_D$, and Normal Boiling Points $T_b$ of Pure Components**

| component | $d$(298.15K)/(Kg m$^{-3}$) | | $n_D$ (298.15K) | | $T_b$ (101.3 kPa) /K | |
|---|---|---|---|---|---|---|
| | exptl. | lit. | exptl. | lit. | exptl. | lit. |
| 3-methylpentane | 659.51 | 660.04[a] | 1.3738 | 1.3739[b] | 336.3 | 336.43[C] |
| ETBE | 735.62 | 735.09[b] | 1.3730 | 1.3729[b] | 345.8 | 345.86[d] |
| DIPE | 718.14 | 718.36[e] | 1.3656 | 1.3655[f] | 341.4 | 341.42[g] |
| THF | 881.91 | 882.30[h] | 1.4046 | 1.4050[f] | 339.1 | 339.08[i] |

[a] Awwad and Pethrick (1983) [b] DIPPR (Daubert and Danner, 1989). [c] Willingham et al. (1945). [d] Krähenbühl and Gmehling (1994). [e] Nakanishi and Shirai (1970). [f] Kobe et al. (1956). [g] Reid et al. (1977). [h] Ramkumar and Kudchadker (1989). [i] Wu and Sandler (1988).

***Apparatus and procedure.*** The equilibrium vessel was an all-glass, dynamic-recirculating still equipped with a Cottrell circulation pump. General details of the experimental equipment and procedure appear in another publication (Wisniak et al., 1997). The still (Labodest model), manufactured by Fischer Labor und Verfahrenstechnik (Germany), is capable of handling pressures from (0.25 to 400) kPa, and temperature up to 523 K. The Cottrell pump ensures that both liquid and vapor phases are in intimate contact during boiling and also in contact with the temperature sensing element. The equilibrium temperature was measured with a digital Fischer thermometer with an accuracy of ±0.1 K. The apparatus is equipped with two digital sensors of pressure: one for the low pressure zone with an accuracy of ±0.01 kPa, and another one for the high pressures with an accuracy of ±0.1 kPa. The temperature probe was calibrated against the ice and steam points of distilled water. The manometers were calibrated using the vapor pressure of ultrapure water.

The still was operated under constant pressure until equilibrium was reached. Equilibrium conditions were assumed when constant temperature and pressure were obtained for 60 min or longer. Then, samples of liquid and condensate were taken for analysis. The sample extractions were carried out with special syringes that allowed one to withdraw small volume samples (1.0 μL) in a system under partial vacuum or under overpressure conditions.

***Analysis.*** Mole fractions of the liquid and condensed vapor phase samples were determined using a Hewlett-Packard 5890 S-II gas chromatograph (GC), after calibration with gravimetrically prepared standard solutions. A flame ionization detector was used together with a 60 m, 0.2 mm i.d., fused silica capillary column, SUPELCOWAX 10. The GC response peaks were integrated with a Hewlett-Packard 3396 integrator. Column, injector and detector temperatures were (333, 373, 413) K for all the systems. Very good separation was achieved under these conditions, and calibration analyses were carried out to convert the peak ratio to the mass composition of the sample. At least three analyses were made of each vapor composition; the standard deviation in the mole fraction was usually less than 0.001.

## Results and Discussion

The temperature $T$, the liquid-phase $x_i$ and vapor-phase $y_i$ mole fractions at 101.3 kPa are reported in Figures 1, 2 and 3 and in Tables 2, 3 and 4. Figures 4, 5 and 6 show the activity coefficients $\gamma_i$ that, for the systems 3-methylpentane (1) + DIPE (3) and 3-methylpentane (1) + THF (4), were calculated from the following equation (Van Ness and Abbott, 1982):

**Table 2. Experimental Vapor-Liquid Equilibrium Data for 3-Methylpentane (1) + ETBE (2) at 101.3 KPa (Vapor Phase Considered Ideal)**

| $T/K$ | $x_1$ | $y_1$ | $\gamma_1$ | $\gamma_2$ |
|---|---|---|---|---|
| 336.3 | 1.000 | 1.000 | 1.000 | |
| 336.6 | 0.969 | 0.975 | 0.997 | 1.103 |
| 336.8 | 0.940 | 0.952 | 0.997 | 1.083 |
| 337.0 | 0.895 | 0.915 | 0.999 | 1.083 |
| 337.2 | 0.859 | 0.886 | 1.002 | 1.065 |
| 337.7 | 0.802 | 0.839 | 1.001 | 1.055 |
| 338.1 | 0.742 | 0.790 | 1.006 | 1.043 |
| 338.6 | 0.681 | 0.741 | 1.012 | 1.027 |
| 339.0 | 0.631 | 0.699 | 1.017 | 1.019 |
| 339.3 | 0.590 | 0.662 | 1.021 | 1.015 |
| 339.8 | 0.534 | 0.611 | 1.025 | 1.015 |
| 340.1 | 0.491 | 0.571 | 1.033 | 1.013 |
| 340.5 | 0.446 | 0.529 | 1.040 | 1.009 |
| 340.9 | 0.389 | 0.475 | 1.054 | 1.006 |
| 341.3 | 0.353 | 0.437 | 1.061 | 1.006 |
| 341.9 | 0.304 | 0.386 | 1.065 | 1.002 |
| 342.3 | 0.260 | 0.338 | 1.076 | 1.001 |
| 342.8 | 0.218 | 0.291 | 1.089 | 1.000 |
| 343.4 | 0.170 | 0.230 | 1.090 | 1.002 |
| 344.1 | 0.123 | 0.172 | 1.099 | 0.998 |
| 344.8 | 0.068 | 0.099 | 1.118 | 1.001 |
| 345.2 | 0.031 | 0.047 | 1.151 | 1.003 |
| 345.8 | 0.000 | 0.000 | | 1.000 |

**Table 3. Experimental Vapor-Liquid Equilibrium Data For 3-Methylpentane (1) + DIPE (3) at 101.3 KPa**

| $T/K$ | $x_1$ | $y_1$ | $\gamma_1$ | $\gamma_3$ | $-B_{11}$/ cm$^3$ mol$^{-1}$ | $-B_{33}$/ cm$^3$ mol$^{-1}$ | $-B_{13}$/ cm$^3$ mol$^{-1}$ |
|---|---|---|---|---|---|---|---|
| 336.3 | 1.000 | 1.000 | 1.000 | | | | |
| 336.5 | 0.971 | 0.972 | 0.995 | 1.102 | 1274 | 1328 | 1288 |
| 336.6 | 0.946 | 0.950 | 0.995 | 1.076 | 1273 | 1327 | 1286 |
| 336.6 | 0.904 | 0.911 | 0.999 | 1.071 | 1273 | 1327 | 1286 |
| 336.7 | 0.860 | 0.873 | 1.002 | 1.056 | 1272 | 1326 | 1285 |
| 336.8 | 0.814 | 0.832 | 1.006 | 1.048 | 1271 | 1325 | 1284 |
| 336.9 | 0.774 | 0.796 | 1.010 | 1.040 | 1270 | 1324 | 1283 |
| 337.0 | 0.712 | 0.743 | 1.021 | 1.027 | 1269 | 1322 | 1282 |
| 337.2 | 0.669 | 0.705 | 1.025 | 1.020 | 1267 | 1320 | 1280 |
| 337.5 | 0.610 | 0.648 | 1.024 | 1.022 | 1264 | 1317 | 1277 |
| 337.6 | 0.557 | 0.601 | 1.038 | 1.016 | 1263 | 1316 | 1276 |
| 337.9 | 0.526 | 0.568 | 1.030 | 1.018 | 1260 | 1313 | 1273 |
| 338.1 | 0.478 | 0.523 | 1.037 | 1.014 | 1258 | 1311 | 1271 |
| 338.3 | 0.427 | 0.476 | 1.051 | 1.008 | 1256 | 1309 | 1269 |
| 338.5 | 0.396 | 0.448 | 1.059 | 1.002 | 1254 | 1307 | 1267 |
| 338.7 | 0.344 | 0.397 | 1.074 | 1.001 | 1252 | 1305 | 1265 |
| 339.1 | 0.295 | 0.346 | 1.079 | 0.998 | 1248 | 1300 | 1261 |
| 339.3 | 0.252 | 0.301 | 1.091 | 0.999 | 1246 | 1298 | 1259 |
| 339.7 | 0.201 | 0.246 | 1.103 | 0.997 | 1242 | 1294 | 1255 |
| 340.0 | 0.159 | 0.198 | 1.114 | 0.997 | 1240 | 1291 | 1252 |
| 340.2 | 0.122 | 0.154 | 1.127 | 1.000 | 1238 | 1289 | 1250 |
| 340.6 | 0.069 | 0.089 | 1.136 | 1.004 | 1234 | 1285 | 1246 |
| 341.0 | 0.033 | 0.043 | 1.129 | 1.003 | 1230 | 1281 | 1243 |
| 341.4 | 0.000 | 0.000 | | 1.000 | | | |

**Table 4. Experimental Vapor-Liquid Equilibrium Data For 3-Methylpentane (1) + THF (4) at 101.3 KPa**

| $T/K$ | $x_1$ | $y_1$ | $\gamma_1$ | $\gamma_4$ | $-B_{11}/$ $cm^3\ mol^{-1}$ | $-B_{44}/$ $cm^3\ mol^{-1}$ | $-B_{14}/$ $cm^3\ mol^{-1}$ |
|---|---|---|---|---|---|---|---|
| 336.3 | 1.000 | 1.000 | 1.000 | | | | |
| 336.0 | 0.981 | 0.972 | 1.002 | 1.598 | 1280 | 919 | 1020 |
| 335.5 | 0.950 | 0.931 | 1.004 | 1.580 | 1285 | 922 | 1024 |
| 334.9 | 0.901 | 0.870 | 1.009 | 1.512 | 1291 | 927 | 1029 |
| 334.4 | 0.851 | 0.814 | 1.015 | 1.459 | 1296 | 930 | 1033 |
| 334.0 | 0.802 | 0.764 | 1.023 | 1.410 | 1300 | 933 | 1036 |
| 333.8 | 0.752 | 0.717 | 1.031 | 1.359 | 1302 | 934 | 1038 |
| 333.5 | 0.701 | 0.672 | 1.047 | 1.317 | 1305 | 937 | 1040 |
| 333.4 | 0.650 | 0.630 | 1.063 | 1.272 | 1306 | 937 | 1041 |
| 333.4 | 0.597 | 0.591 | 1.084 | 1.223 | 1306 | 937 | 1041 |
| 333.4 | 0.548 | 0.554 | 1.108 | 1.189 | 1306 | 937 | 1041 |
| 333.5 | 0.491 | 0.512 | 1.139 | 1.152 | 1305 | 937 | 1040 |
| 333.6 | 0.443 | 0.474 | 1.165 | 1.130 | 1304 | 936 | 1039 |
| 333.8 | 0.395 | 0.440 | 1.207 | 1.100 | 1302 | 934 | 1038 |
| 334.0 | 0.348 | 0.405 | 1.252 | 1.078 | 1300 | 933 | 1036 |
| 334.4 | 0.298 | 0.364 | 1.299 | 1.056 | 1296 | 930 | 1033 |
| 334.8 | 0.246 | 0.319 | 1.363 | 1.039 | 1292 | 927 | 1030 |
| 335.4 | 0.195 | 0.271 | 1.436 | 1.021 | 1286 | 923 | 1025 |
| 336.0 | 0.148 | 0.222 | 1.517 | 1.011 | 1280 | 919 | 1020 |
| 336.8 | 0.099 | 0.161 | 1.613 | 1.003 | 1271 | 914 | 1014 |
| 337.8 | 0.053 | 0.094 | 1.702 | 0.998 | 1261 | 907 | 1007 |
| 338.4 | 0.026 | 0.048 | 1.782 | 1.000 | 1256 | 903 | 1002 |
| 339.1 | 0.000 | 0.000 | | 1.000 | | | |

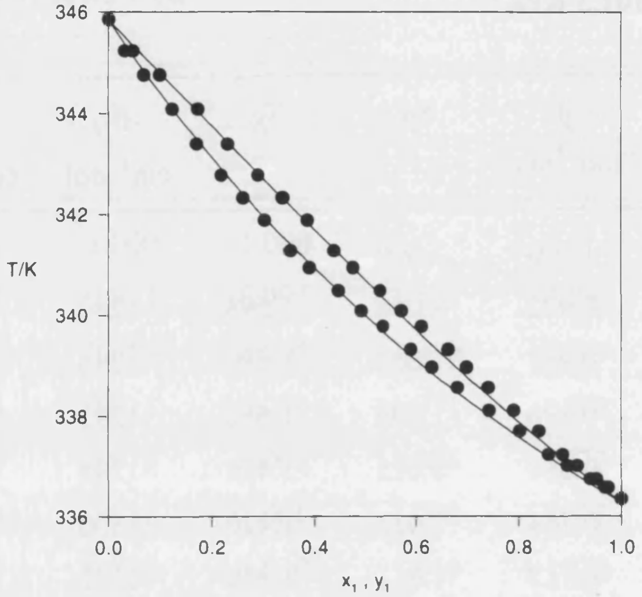

**Figure 1.** Experimental data for the system 3-methylpentane (1) + ETBE (2) at 101.3 kPa. Experimental data (●). Smoothed data using the regular model with the parameters given in Table 6, eq 5 ( — ).

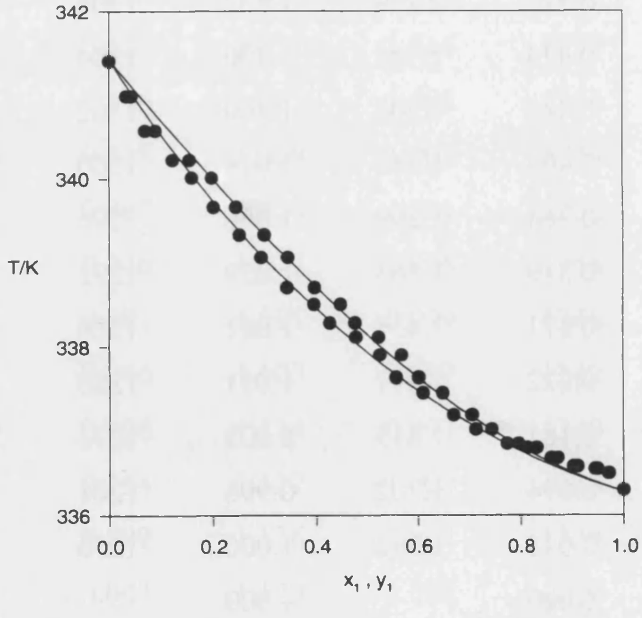

**Figure 2.** Experimental data for the system 3-methylpentane (1) + DIPE (3) at 101.3 kPa. Experimental data (●). Smoothed data using the regular model with the parameters given in Table 6, eq 5 ( — ).

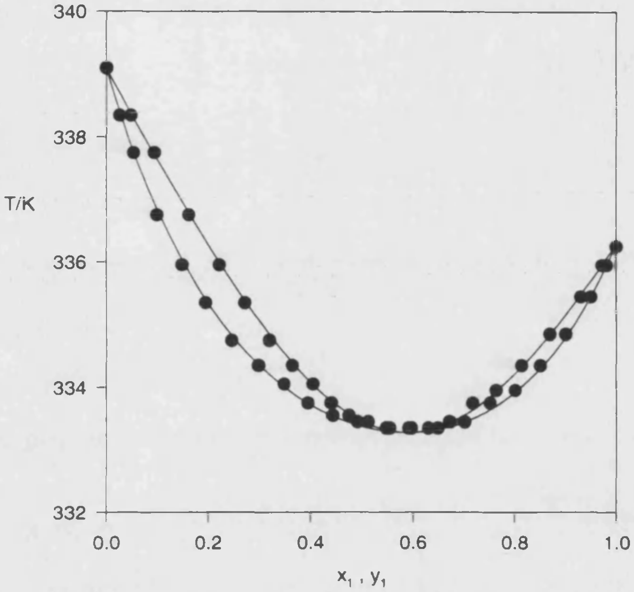

**Figure 3.** Experimental data for the system 3-methylpentane (1) + THF (4) at 101.3 kPa. Experimental data (●). Smoothed data using the regular model with the parameters given in Table 6, eq 5 ( — ).

$$\ln \gamma_i = \ln \frac{y_i P}{x_i P_i^0} + \frac{\left(B_{ii} - V_i^L\right)\left(P - P_i^0\right)}{RT} + y_j^2 \frac{\delta_{ij} P}{RT} \tag{1}$$

where $T$ and $P$ are the boiling point and the total pressure, $V_i^L$ is the molar liquid volume of component i, $B_{ii}$ and $B_{jj}$ are the second virial coefficients of the pure gases, $P_i^0$ is the vapor pressure, $B_{ij}$ the cross second virial coefficient and

$$\delta_{ij} = 2\,B_{ij} - B_{jj} - B_{ii} \tag{2}$$

The standard state for calculation of activity coefficients is the pure component at the pressure and temperature of the solution. Equation 1 is valid at low and moderate pressures when the virial equation of state truncated after the second coefficient is adequate to describe the vapor phase of the pure components and their mixtures, and liquid volumes of the pure components are incompressible over the pressure range under consideration.

For the system 3-methylpentane (1) + ETBE (2), activity coefficients were calculated according to the ideal relation (Van Ness and Abbott, 1982):

$$\gamma_i = \frac{y_i P}{x_i P_i^0} \tag{3}$$

because, on the one hand, the low pressure makes this assumption reasonable and, on the other hand, as discussed by Reich et al. (1999), the scarce physical information available for mixtures of ETBE with alkanes does not allow a reliable estimation of the second virial coefficient.

The vapor pressures of the pure compounds $P_i^0$ were expressed by the Antoine equation:

$$\log(P_i^0 / \text{kPa}) = A_i - \frac{B_i}{(T/\text{K}) - C_i} \tag{4}$$

The constants $A_i$, $B_i$, and $C_i$ were taken from literature: Loras et al. (1998) for 3-methylpentane, Reich et al. (1998) for ETBE, Reid et al. (1977) for DIPE and Wu and Sandler (1988) for THF, the values are reported in Table 5.

**Table 5. Antoine Coefficients, Equation 4**

| compound | $A_i$ | $B_i$ | $C_i$ |
|---|---|---|---|
| 3-methylpentane [a] | 6.24116 | 1302.78 | 28.69 |
| ethyl 1,1-dimethylethyl ether [b] | 5.96651 | 1151.73 | 55.06 |
| diisopropyl ether [c] | 6.22201 | 1257.61 | 43.15 |
| tetrahydrofuran [d] | 6.44102 | 1384.21 | 27.00 |

[a] Loras et al. (1998). [b] Reich et al. (1998). [c] Reid et al. (1977). [d] Wu and Sandler (1988).

When required, the molar virial coefficients $B_{ii}$ and $B_{ij}$ were estimated by the method of Hayden and O'Connell (1975) assuming the association parameter $\eta$ to be zero. Critical properties of all components were taken from DIPPR (Daubert and Danner, 1989). The last two terms in eq 1, particularly the second one that expresses the correction due to the non-ideal behavior of the vapor phase, contributed less than 1% for the systems 3-methylpentane (1) + DIPE (3) and 3-methylpentane (1) + THF (4), at 101.3 kPa; in general, their influence was important only at very dilute concentrations. The calculated activity coefficients reported in Tables 2, 3 and 4 are estimated to be accurate to within ± 2 %. The results reported in these Tables indicate that the measured systems exhibit positive deviations from ideal behavior. An azeotrope composition is present in the system 3-methylpentane (1) + THF (4) at $x_1 \approx 0.59$ and $T = 333.3$ K.

The vapor-liquid equilibria data reported in Tables 2, 3 and 4 were found to be thermodynamically consistent by the point-to-point method of Van Ness et al. (1973), as modified by Fredenslund et al. (1977). Consistency was achieved using a one parameter (zeroth-order) Legendre polynomial, the Porter or two-suffix Margules model, which reduces the functionality of the excess Gibbs energy $G^E$ to the following symmetric relation

$$G^E = Ax_1x_2 \tag{5}$$

The parameter $A$ in eq 5, together with the pertinent statistics required by the Fredenslund et al. test, are shown in Table 6 for the different systems considered in this work. From Table 6 it is concluded that eq 5 gives an excellent fit to the data.

The variation of activity coefficients with composition appears in Figures 4, 5 and 6. These Figures shows a symmetric trend of experimental activity coefficients that, in high dilution ranges, are approximately equivalent for both components in each binary system. In addition, from the Figures, it is clear that activity coefficients exhibit intersection about the composition $x_1 = 0.5$, and are reasonably represented by eq 5. Thus, according to the present experimental data, and the pertinent consistency test, it is concluded that the systems can be satisfactorily explained by symmetrical solution behavior.

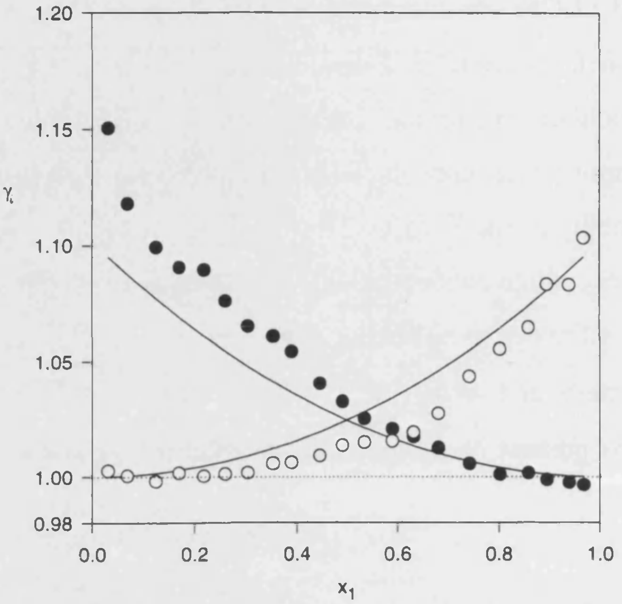

**Figure 4.** Activity coefficient plot of the system 3-methylpentane (1) + ETBE (2) at 101.3 kPa, calculated from experimental data. $\gamma_1$ (●); $\gamma_2$ (○). Smoothed data using the regular model with the parameters given in Table 6, eq 5 ( — ).

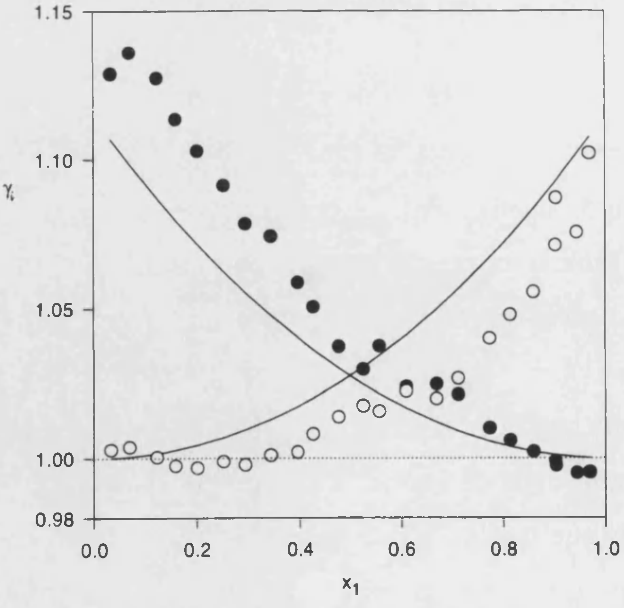

**Figure 5.** Activity coefficient plot of the system 3-methylpentane (1) + DIPE (3) at 101.3 kPa, calculated from experimental data. $\gamma_1$ (●); $\gamma_3$ (○). Smoothed data using the regular model with the parameters given in Table 6, eq 5 ( — ).

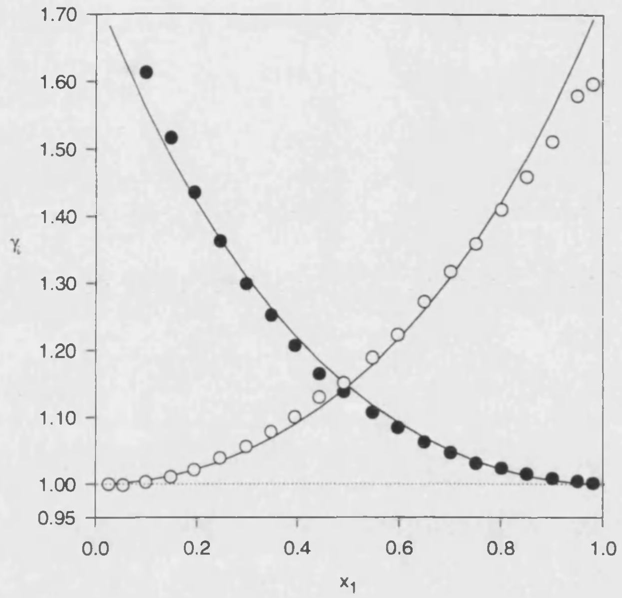

**Figure 6.** Activity coefficient plot of the system 3-methylpentane (1) + THF (4) at 101.3 kPa, calculated from experimental data. $\gamma_1$ (●); $\gamma_4$ (○). Smoothed data using the regular model with the parameters given in Table 6, eq 5 ( — ).

**Table 6. Consistency Test for the Various Experimental Systems Considered in VLE Measurements**

| system | $A^{a}$ | $100 \times \mathrm{AAD}y_1{}^{b}$ | AADP$^{c}$ / kPa | $\gamma_1^{\infty\, d}$ |
|---|---|---|---|---|
| 1 + 2 | 0.097 | 0.35 | 0.29 | 1.102 |
| 1 + 3 | 0.108 | 0.49 | 0.27 | 1.114 |
| 1 + 4 | 0.548 | 0.34 | 0.15 | 1.730 |

[a] Zero-order Legendre Polynomial (or Porter model) parameter in eq 5. [b] Average absolute deviation in vapor phase composition. [c] Average absolute deviation in pressure. [d] Limiting activity coefficient of 3-methylpentane, predicted by eq 5.

The activity coefficients were correlated with the Wilson, NRTL, and UNIQUAC equations (Walas, 1985). The parameters of these equations were obtained by minimizing the following objective function (OF):

$$\mathrm{OF} = \sum_{i=1}^{N} 100 \times \left( \left| \frac{P_i^{\mathrm{exptl}} - P_i^{\mathrm{calc}}}{P_i^{\mathrm{exptl}}} \right| + \left| y_i^{\mathrm{exptl}} - y_i^{\mathrm{calc}} \right| \right) \tag{6}$$

and are reported in Table 7, together with the pertinent statistics of VLE interpolation. Inspection of the results given in Table 7 shows that all the models fitted well the systems, the best fit corresponding to the UNIQUAC model for the 3-methylpentane (1) + ETBE (2) system, and in the case of the 3-methylpentane (1) + DIPE (3) and 3-methylpentane (1) + THF (4) systems all of models give a similar fit to the data.

The boiling point temperatures of each system at 101.3 kPa were well correlated with mole fractions by the equation proposed by Wisniak and Tamir (1976):

$$T/\mathrm{K} = x_1 T_1^0/\mathrm{K} + x_2 T_2^0/\mathrm{K} + x_1 x_2 \sum_{k=0}^{m} C_k (x_1 - x_2)^k \tag{7}$$

In this equation $T_i^0/\mathrm{K}$ is the boiling point of the pure component i, and $m$ is the number of terms used in the series expansion of $(x_1 - x_2)$, usually two. The various constants of eq 7 are reported in Table 8, with information indicating the goodness of fit of the correlation.

**Table 7. Parameters and Deviations between Experimental and Calculated Values for Different $G^E$ Models**

| model | $A_{ij}$ | $A_{ji}$ | $\alpha_{ij}$ | bubble-point pressures | | dew-point pressures | |
|---|---|---|---|---|---|---|---|
| | (J/mol) | (J/mol) | | $\Delta P$ [a] | $100 \times \Delta y$ [b] | $\Delta P$ [a] | $100 \times \Delta x$ [b] |
| | | | 3-methylpentane (1) + ETBE (2) | | | | |
| [c]Wilson | -337.50 | 701.81 | | 0.38 | 0.30 | 0.39 | 0.30 |
| NRTL | 1933.52 | -1340.45 | 0.3 | 0.48 | 0.25 | 0.47 | 0.24 |
| [d]UNIQUAC | -1299.15 | 410.93 | | 0.37 | 0.14 | 0.36 | 0.13 |
| | | | 3-methylpentane (1) + DIPE (3) | | | | |
| [c]Wilson | -126.76 | 472.68 | | 0.31 | 0.47 | 0.31 | 0.47 |
| NRTL | -138.44 | 460.00 | 0.3 | 0.26 | 0.50 | 0.26 | 0.51 |
| [e]UNIQUAC | -214.89 | 305.57 | | 0.26 | 0.49 | 0.27 | 0.50 |
| | | | 3-methylpentane (1) + THF (4) | | | | |
| [c]Wilson | -189.70 | 1882.85 | | 0.17 | 0.09 | 0.19 | 0.09 |
| NRTL | -227.56 | 1870.29 | 0.2 | 0.13 | 0.10 | 0.16 | 0.10 |
| [e]UNIQUAC | 796.32 | -230.81 | | 0.15 | 0.10 | 0.17 | 0.09 |

[a] Average percentual deviation in bubble pressure $\Delta P = 100/\mathrm{N}\sum_{i}^{N}\left|P_i^{exptal} - P_i^{calc}\right| / P_i^{exptal}$ (N : number of data points). [b] Average absolute deviation in vapor phase composition. [c] Liquid volumes have been estimated from the Rackett equation (Rackett, 1970). [d] Volume and surface parameters calculated from UNIFAC (Gmehling et al., 1993). [e] Volume and surface parameters from DECHEMA (Gmehling and Onken, 1990).

**Table 8. Coefficients in Correlation of Boiling Points, Equation 7, Average Deviation, Root Mean Square Deviation and Maximum Deviation in Temperature**

| system | $C_0$ | $C_1$ | $C_2$ | avg dev[a] / K | rmsd[b] / K | max dev[c] / K |
|---|---|---|---|---|---|---|
| 1+2 | -4.11 | 3.58 | -0.29 | 0.09 | 0.023 | 0.20 |
| 1+3 | -3.74 | 3.01 | 1.05 | 0.13 | 0.029 | 0.27 |
| 1+4 | -16.98 | 2.79 | -6.29 | 0.04 | 0.012 | 0.11 |

[a] Average deviation. [b] Root mean square deviation. [c] Maximum deviation.

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# 4.6. ISOBARIC VAPOR-LIQUID EQUILIBRIUM IN THE SYSTEMS 2,3-DIMETHYLPENTANE + METHYL 1,1-DIMETHYLETHYL ETHER, + DIISOPROPYL ETHER AND + METHYL 1,1-DIMETHYLPROPYL ETHER

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## ABSTRACT

New consistent vapor-liquid equilibrium data for the binary systems 2,3-dimethylpentane + methyl 1,1-dimethylethyl ether, + diisopropyl ether, and + methyl 1,1-dimethylpropyl ether are reported at 101.3 kPa. The measured systems deviate slightly from ideal behavior and only the system methyl 1,1-dimethylproyl ether + 2,3-dimethylpentane presents an azeotrope. The activity coefficients of the solutions were correlated with its composition by Wilson, UNIQUAC and NRTL models. Wisniak-Tamir equations were used to correlate the boiling points of the solutions with its composition.

## Introduction

Environmental legislation around the world has forced the use of oxygenates for gasoline blending to phase out the lead additives and to reduce the reactive evaporative and exhaust emissions. Methyl 1,1-dimethylethyl ether (MTBE) is the primary oxygenated compound being used to reformulate gasolines to improve their octane rating and pollution-reducing capability. However potential and documented contamination of water resources by MTBE has become a major public issue over the past few years and restrictions in its use as additive are expected. MTBE readily dissolves in water, can move rapidly through soils and aquifers, is resistant to microbial decomposition and is difficult to remove in water treatment. Finally, it is reported to have an unpleasant taste and odor in water. These factors have caused widespread concern that drinking water supplies and human health may be at risk, a situation which promotes further research with other branched ethers as potential additives. Diisopropyl ether (DIPE) and methyl-1,1-dimethylproyl ether (TAME) show good characteristics as a gasoline additive including: low volatility, low water solubility, high octane value and large reductions in carbon monoxide and hydrocarbon emissions.

Phase equilibrium data of hydrocarbon and oxygenated compound mixtures are important to predict the vapor phase composition that would be in equilibrium with reformulated gasolines, and the systems reported here constitute examples of such mixtures. The present work was undertaken to measure vapor-liquid equilibrium (VLE) data of the 2,3-dimethylpentane + methyl 1,1-dimethylethyl ether, + diisopropyl ether, and + methyl 1,1-dimethylpropyl ether binary systems at 101.3 kPa, for which no data have been previously reported.

## Experimental Section

***Chemicals.*** 2,3-Dimethylpentane (99+ mass %), MTBE (99.8+ mass %, *HPLC grade*), DIPE (99 mass %) and TAME (97 mass %) were purchased from *Aldrich Ltd.* 2,3-Dimethylpentane, MTBE and DIPE were used without further purification after chromatography failed to show any significant impurities. TAME was purified to 99.9+ mass %, by batch distillation in a

Fisher SPALTROHR - column HMS-500, controlled by a Fisher System D301-C. The densities and refractive indexes of pure liquids were measured at 298.15 K using an Anton Paar DMA 55 densimeter and an Abbe refractometer Atago 3T, respectively. Temperature was controlled to ±0.01 K with a thermostated bath. The accuracies in density and refractive index measurements are ±0.01 Kg.m$^{-3}$ and ±0.0002, respectively. The experimental values of these properties and the boiling points are given in Table 1 together with those given in the literature. Appropriate precautions were taken when handling ethers in order to avoid peroxide formation.

**Table 1. Densities *d*, Refractive Index $n_D$, and Normal Boiling Points $T_b$ of Pure Components**

| component | $d$(298.15K) /Kg m$^{-3}$ | | $n_D$ (298.15K) | | $T_b$ (101.3 kPa) /K | |
|---|---|---|---|---|---|---|
| | expt | lit. | expt | lit. | expt | lit. |
| MTBE | 735.29 | 735.28[a] | 1.3664 | 1.3663[b] | 328.2 | 328.11[c] |
| DIPE | 718.13 | 718.36[d] | 1.3658 | 1.3655[e] | 341.6 | 341.42[f] |
| TAME | 765.98 | 765.77[g] | 1.3862 | 1.3859[a] | 359.2 | 359.33[c] |
| 2,3-dimethylpentane | 690.80 | 690.89[b] | 1.3894 | 1.3895[a] | 363.0 | 362.93[a] |

[a]DIPPR (Daubert and Danner, 1989). [b]TRC tables, a-6040. [c]Martinez-Ageitos. (1996). [d]Nakanishi and Shirai (1970). [e]Kobe et al. (1956). [f]Reid et al. (1977). [g] Linek (1987).

***Apparatus and procedure.*** The equilibrium vessel was an all-glass, dynamic-recirculating still equipped with a Cottrell circulation pump. General details of the experimental equipment and procedure appear in Walas (1985). The still (Labodest model), manufactured by Fischer Labor und Verfahrenstechnik (Germany), is capable of handling pressures from (0.25 to 400) kPa, and temperature up to 523 K. The Cottrell pump ensures that both liquid and vapor phases are in intimate contact during boiling and also in contact with the temperature sensing element. The equilibrium temperature was measured with a digital Fischer thermometer with an accuracy of ±0.1 K. For the pressure measurement a digital manometer with an accuracy of ±0.01 kPa, was used. The temperature probe was calibrated against the ice and steam points of distilled water. The manometer was calibrated using the vapor pressure of ultrapure water.

The still was operated under constant pressure until equilibrium was reached. Equilibrium conditions were assumed when constant temperature and pressure were obtained for 60 min or longer. Then, samples of liquid and condensate were taken for analysis. The sample extractions were carried out with special syringes that allowed one to withdraw small volume samples (1.0 μL).

***Analysis.*** Composition of the liquid and condensed phase samples were determined using a CE Instruments GC 8000 Top gas chromatograph (GC), after calibration with gravimetrically prepared standard solutions. A flame ionization detector was used together with a 30 m., 0.454 mm i.d., capillary column, DB-MTBE (J & W Scientific). The GC response peaks were treated with Chrom-Card for Windows, version 1.2. Column, injector and detector temperatures were 393, 498, 523 K for all systems. Very good separation of peaks was achieved under these conditions, and calibration analyses were carried out to convert the peak area ratios to the mass composition of the sample. At least three analyses were made of each liquid and vapor composition. The standard deviation in the mole fraction was usually less than 0.001.

## Results and Discussion

The pure component vapor pressures $P_i^0$ for MTBE and TAME were taken from Aucejo et al. (1998). For DIPE and 2,3-dimethylpentane, pure component vapor pressures were determined experimentally as a function of the temperature, using the same equipment as that for obtaining the VLE data. The pertinent results appear in Table 2. The measured vapor pressures were correlated using the Antoine equation:

$$\log(P_i^0 / \mathrm{kPa}) = A_i - \frac{B_i}{(T/\mathrm{K}) - C_i} \qquad (1)$$

whose parameters $A_i$, $B_i$, and $C_i$ are reported in Table 3.

**Table 2. Experimental Vapor Pressures Determined for DIPE and 2,3-Dimethylpentane**

| 2,3-dimethylpentane | | DIPE | |
|---|---|---|---|
| $T/\mathrm{K}$ | $P/\mathrm{kPa}$ | $T/\mathrm{K}$ | $P/\mathrm{kPa}$ |
| 309.3 | 15.40 | 306.5 | 28.49 |
| 313.2 | 18.05 | 310.1 | 32.96 |
| 316.3 | 20.45 | 312.7 | 36.45 |
| 320.1 | 23.83 | 315.6 | 40.78 |
| 322.8 | 26.36 | 318.2 | 45.01 |
| 326.2 | 30.08 | 321.1 | 50.16 |
| 329.4 | 33.78 | 323.1 | 53.93 |
| 332.5 | 37.75 | 325.2 | 58.19 |
| 335.3 | 41.66 | 327.4 | 62.92 |
| 337.8 | 45.45 | 329.0 | 66.50 |
| 339.4 | 47.96 | 330.9 | 71.04 |
| 342.4 | 53.13 | 332.6 | 75.29 |
| 344.5 | 56.98 | 334.9 | 81.32 |
| 347.8 | 63.45 | 336.6 | 85.99 |
| 350.1 | 68.33 | 338.3 | 90.90 |
| 350.4 | 68.73 | 340.0 | 96.06 |
| 352.8 | 74.23 | 341.6 | 101.08 |
| 354.7 | 78.73 | 342.7 | 104.61 |
| 356.5 | 83.29 | 344.1 | 109.44 |
| 358.1 | 87.51 | 345.4 | 114.02 |
| 359.9 | 92.36 | 345.3 | 113.61 |
| 361.8 | 97.55 | 346.5 | 117.97 |
| 363.3 | 101.63 | 347.6 | 121.85 |
| 363.1 | 101.48 | 349.3 | 128.35 |
| 364.2 | 104.62 | | |
| 365.4 | 108.39 | | |
| 366.7 | 112.50 | | |
| 368.1 | 117.09 | | |
| 369.4 | 121.48 | | |
| 371.3 | 127.95 | | |

**Table 3. Antoine Coefficients, Equation 1**

| compound | $A_i$ | $B_i$ | $C_i$ |
|---|---|---|---|
| methyl 1,1-dimethylethyl ether (MTBE)[a] | 6.34991 | 1312.52 | 26.03 |
| diisopropyl ether (DIPE)[b] | 6.05151 | 1185.74 | 48.54 |
| methyl 1,1-dimethylproyl ether (TAME)[a] | 6.23218 | 1351.21 | 39.52 |
| 2,3-dimethylpentane [b] | 6.10469 | 1323.67 | 40.11 |

[a] Aucejo et al. (1998). [b] Antoine's parameters were calculated from the experimental data in Table 2.

The vapor pressures were correlated with a mean absolute deviation (MADP) of 0.05% for DIPE, and 0.10% for 2,3-dimethylpentane. In Figure 1, it can be observed that the parameters presented in table 3 give a fair prediction of the experimental vapor pressures reported by Ambrose et al. (1976) for DIPE (MADP=0.31%), and by Forziati et al. (1949) for 2,3-dimethylpentane (MADP=1.49%).

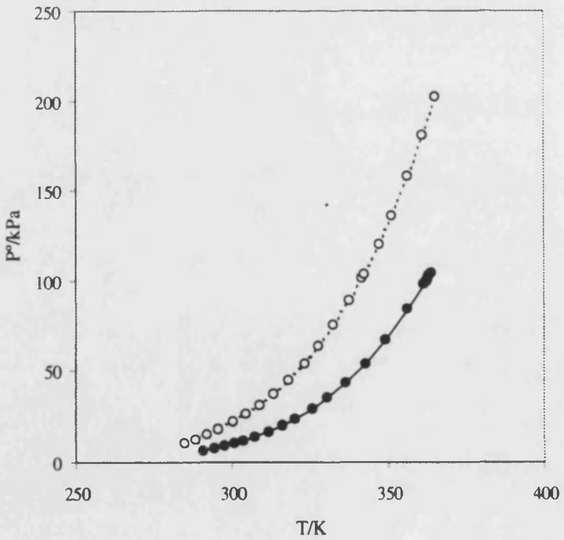

**Figure 1.** Comparison of correlated vapor pressures with other references. Experimental data reported by Ambrose et al. (1976) for DIPE (○). Experimental data of Forziati et al. (1949) for 2,3-dimethylpentane (●). Predicted by eq 1 and parameters in Table 3 for DIPE (– – –) and for 2,3-dimethylpentane (—).

The temperature $T$, the liquid-phase $x_i$ and vapor-phase $y_i$ mole fractions at 101.3 kPa are reported in Figures 2, 3 and 4 and in Tables 4, 5 and 6.

**Table 4. Experimental Vapor-Liquid Equilibrium Data for MTBE (1) + 2,3-Dimethylpentane (4) at 101.3 KPa**

| $T/K$ | $x_1$ | $y_1$ | $\gamma_1$ | $\gamma_4$ | $-B_{11}/$ $\text{cm}^3\ \text{mol}^{-1}$ | $-B_{44}/$ $\text{cm}^3\ \text{mol}^{-1}$ | $-B_{14}/$ $\text{cm}^3\ \text{mol}^{-1}$ |
|---|---|---|---|---|---|---|---|
| 363.0 | 0.000 | 0.000 | | 1.000 | | | |
| 361.6 | 0.022 | 0.063 | 1.121 | 0.998 | 900 | 1465 | 1119 |
| 359.5 | 0.056 | 0.152 | 1.122 | 0.993 | 913 | 1488 | 1135 |
| 356.8 | 0.102 | 0.252 | 1.102 | 0.994 | 930 | 1519 | 1157 |
| 354.3 | 0.142 | 0.337 | 1.122 | 0.993 | 945 | 1549 | 1178 |
| 352.0 | 0.182 | 0.414 | 1.142 | 0.986 | 960 | 1577 | 1198 |
| 349.9 | 0.229 | 0.482 | 1.119 | 0.985 | 974 | 1603 | 1217 |
| 347.4 | 0.286 | 0.555 | 1.104 | 0.987 | 992 | 1636 | 1240 |
| 345.4 | 0.332 | 0.608 | 1.101 | 0.988 | 1006 | 1662 | 1258 |
| 343.6 | 0.381 | 0.657 | 1.089 | 0.990 | 1019 | 1687 | 1276 |
| 341.7 | 0.438 | 0.711 | 1.084 | 0.974 | 1032 | 1713 | 1294 |
| 340.1 | 0.488 | 0.744 | 1.064 | 0.999 | 1044 | 1736 | 1310 |
| 338.4 | 0.544 | 0.784 | 1.056 | 1.002 | 1057 | 1761 | 1328 |
| 337.7 | 0.566 | 0.799 | 1.057 | 1.000 | 1063 | 1772 | 1335 |
| 335.6 | 0.653 | 0.849 | 1.037 | 1.006 | 1079 | 1803 | 1357 |
| 334.5 | 0.701 | 0.871 | 1.023 | 1.042 | 1088 | 1820 | 1369 |
| 333.2 | 0.759 | 0.898 | 1.014 | 1.064 | 1099 | 1841 | 1383 |
| 332.0 | 0.816 | 0.925 | 1.008 | 1.069 | 1109 | 1860 | 1397 |
| 330.8 | 0.872 | 0.947 | 1.002 | 1.130 | 1119 | 1880 | 1410 |
| 329.6 | 0.930 | 0.971 | 0.999 | 1.185 | 1129 | 1900 | 1424 |
| 328.9 | 0.965 | 0.984 | 0.997 | 1.378 | 1135 | 1912 | 1432 |
| 328.2 | 1.000 | 1.000 | 1.000 | | | | |

**Table 5. Experimental Vapor-Liquid Equilibrium Data for DIPE (2) + 2,3-dimethylpentane (4) at 101.3 KPa**

| $T/K$ | $x_2$ | $y_2$ | $\gamma_2$ | $\gamma_4$ | $-B_{22}$/ $cm^3\ mol^{-1}$ | $-B_{44}$/ $cm^3\ mol^{-1}$ | $-B_{24}$/ $cm^3\ mol^{-1}$ |
|---|---|---|---|---|---|---|---|
| 363.0 | 0.000 | 0.000 |  | 1.000 |  |  |  |
| 362.5 | 0.013 | 0.029 | 1.232 | 1.000 | 1149 | 1455 | 1279 |
| 361.5 | 0.041 | 0.085 | 1.186 | 0.997 | 1157 | 1466 | 1289 |
| 360.1 | 0.086 | 0.161 | 1.123 | 0.997 | 1169 | 1481 | 1302 |
| 358.8 | 0.122 | 0.227 | 1.144 | 0.994 | 1180 | 1496 | 1315 |
| 357.7 | 0.164 | 0.285 | 1.104 | 0.995 | 1190 | 1509 | 1326 |
| 356.5 | 0.205 | 0.345 | 1.105 | 0.993 | 1201 | 1523 | 1338 |
| 355.4 | 0.248 | 0.399 | 1.085 | 0.995 | 1210 | 1536 | 1349 |
| 354.2 | 0.292 | 0.453 | 1.082 | 0.996 | 1221 | 1550 | 1361 |
| 353.1 | 0.339 | 0.504 | 1.071 | 0.998 | 1231 | 1563 | 1373 |
| 352.1 | 0.381 | 0.549 | 1.065 | 1.000 | 1241 | 1576 | 1383 |
| 351.1 | 0.427 | 0.591 | 1.053 | 1.008 | 1250 | 1588 | 1394 |
| 350.2 | 0.473 | 0.633 | 1.044 | 1.011 | 1259 | 1599 | 1404 |
| 349.4 | 0.512 | 0.667 | 1.039 | 1.016 | 1266 | 1610 | 1412 |
| 348.2 | 0.575 | 0.720 | 1.034 | 1.017 | 1278 | 1625 | 1426 |
| 347.1 | 0.630 | 0.760 | 1.029 | 1.033 | 1289 | 1639 | 1438 |
| 346.2 | 0.684 | 0.806 | 1.031 | 1.008 | 1298 | 1651 | 1448 |
| 345.2 | 0.739 | 0.844 | 1.028 | 1.013 | 1308 | 1665 | 1460 |
| 344.4 | 0.794 | 0.880 | 1.021 | 1.015 | 1316 | 1676 | 1469 |
| 343.6 | 0.849 | 0.914 | 1.015 | 1.021 | 1324 | 1687 | 1478 |
| 342.7 | 0.913 | 0.951 | 1.009 | 1.036 | 1334 | 1699 | 1489 |
| 342.0 | 0.959 | 0.977 | 1.009 | 1.038 | 1341 | 1709 | 1497 |
| 341.8 | 0.978 | 0.988 | 1.006 | 1.039 | 1343 | 1712 | 1500 |
| 341.4 | 1.000 | 1.000 | 1.000 |  |  |  |  |

**Table 6. Experimental Vapor-Liquid Equilibrium Data for TAME (3) + 2,3-dimethylpentane (4) at 101.3 KPa (Vapor Phase Considered Ideal)**

| $T/K$ | $x_3$ | $y_3$ | $\gamma_3$ | $\gamma_4$ |
|---|---|---|---|---|
| 363.0 | 0.000 | 0.000 | | 1.000 |
| 362.9 | 0.017 | 0.021 | 1.106 | 1.000 |
| 362.6 | 0.043 | 0.053 | 1.113 | 1.002 |
| 362.2 | 0.090 | 0.109 | 1.107 | 1.003 |
| 361.9 | 0.137 | 0.162 | 1.090 | 1.004 |
| 361.6 | 0.188 | 0.217 | 1.074 | 1.006 |
| 361.2 | 0.241 | 0.275 | 1.075 | 1.008 |
| 360.9 | 0.293 | 0.328 | 1.064 | 1.012 |
| 360.6 | 0.345 | 0.380 | 1.056 | 1.017 |
| 360.4 | 0.395 | 0.428 | 1.045 | 1.022 |
| 360.2 | 0.447 | 0.479 | 1.040 | 1.024 |
| 360.0 | 0.500 | 0.527 | 1.029 | 1.034 |
| 359.7 | 0.552 | 0.577 | 1.030 | 1.042 |
| 359.6 | 0.602 | 0.624 | 1.024 | 1.045 |
| 359.5 | 0.656 | 0.673 | 1.017 | 1.055 |
| 359.4 | 0.713 | 0.725 | 1.011 | 1.067 |
| 359.3 | 0.770 | 0.777 | 1.006 | 1.083 |
| 359.2 | 0.823 | 0.827 | 1.005 | 1.095 |
| 359.2 | 0.878 | 0.879 | 1.002 | 1.111 |
| 359.2 | 0.929 | 0.929 | 1.000 | 1.120 |
| 359.2 | 0.948 | 0.948 | 1.000 | 1.120 |
| 359.2 | 0.966 | 0.965 | 0.999 | 1.153 |
| 359.2 | 1.000 | 1.000 | 1.000 | |

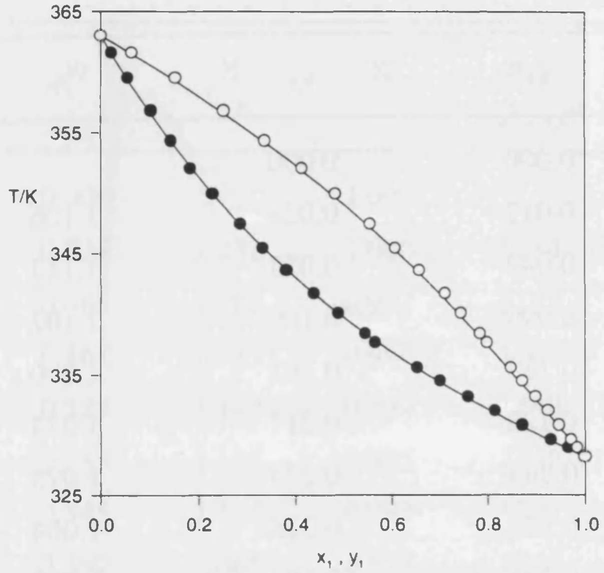

**Figure 2.** Experimental data for the system MTBE (1) + 2,3-dimethylpentane (4) at 101.3 kPa. Experimental data: $x_1$(●); $y_1$(o). Smoothed data using the Legendre polynomial used in consistency test ( — ).

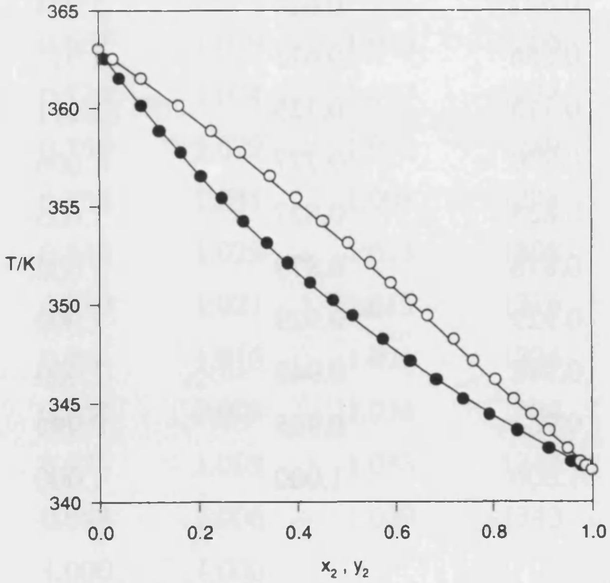

**Figure 3.** Experimental data for the system DIPE (2) + 2,3-dimethylpentane (4) at 101.3 kPa. Experimental data: $x_1$(●); $y_1$(o). Smoothed data using the Legendre polynomial used in consistency test (—).

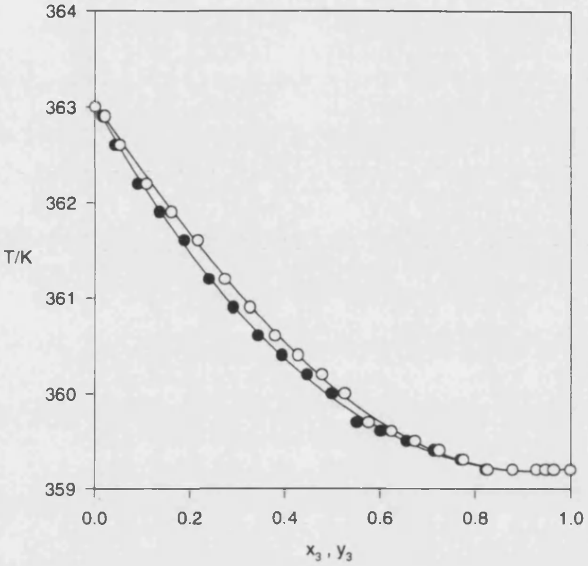

**Figure 4.** Experimental data for the system TAME (3) + 2,3-dimethylpentane (4) at 101.3 kPa. Experimental data: $x_1$(●); $y_1$(o). Smoothed data using the Legendre polynomial used in consistency test ( — ).

The activity coefficients $\gamma_i$ for the systems MTBE (1) + 2,3-dimethylpentane (4) and DIPE (2) + 2,3-dimethylpentane (4), were calculated from the following equation (Van Ness and Abbott, 1982):

$$\ln \gamma_i = \ln \frac{y_i P}{x_i P_i^0} + \frac{(B_{ii} - V_i^L)(P - P_i^0)}{RT} + y_j^2 \frac{\delta_{ij} P}{RT} \tag{2}$$

where $T$ and $P$ are the boiling point and the total pressure, $V_i^L$ is the molar liquid volume of component i, $B_{ii}$ and $B_{jj}$ are the second virial coefficients of the pure gases, $P_i^0$ is the vapor pressure, $B_{ij}$ the cross second virial coefficient and

$$\delta_{ij} = 2 B_{ij} - B_{jj} - B_{ii} \tag{3}$$

The standard state for calculation of activity coefficients is the pure component at the pressure and temperature of the solution. Equation 2 is valid at low and moderate pressures when the virial equation of state truncated after the second coefficient is adequate to describe the vapor phase of the pure components and their mixtures, and liquid volumes of the pure components are incompressible over the pressure range under consideration.

For the system TAME (3) + 2,3-dimethylpentane (4), activity coefficients were calculated according to the ideal relation (Van Ness and Abbott, 1982):

$$\gamma_i = \frac{y_i P}{x_i P_i^0} \tag{4}$$

because, on the one hand, the low pressure makes this assumption reasonable and, on the other hand, as discussed by Reich et al. (1999), the scarce physical information available for mixtures of TAME with alkanes does not allow a reliable estimation of the second virial coefficient.

When required, the molar virial coefficients $B_{ii}$ and $B_{ij}$ were estimated by the method of Hayden and O'Connell (1975) assuming the association parameter $\eta$ to be zero. Critical properties of all components were taken from DIPPR (Daubert and Danner, 1989). The last two terms in equation 2, particularly the second one that expresses the correction due to the non ideal behavior of the vapor phase, contributed less than 4.5% for the systems MTBE (1) + 2,3-dimethylpentane (4) and DIPE (2) + 2,3-dimethylpentane (4), at 101.3 kPa; in general, their influence was important only at very dilute concentrations. The calculated activity coefficients reported in tables 4, 5 and 6 indicate that the measured systems exhibit positive deviations from ideal behavior. An azeotrope composition is present in the system TAME (3) + 2,3-dimethylpentane (4) at $x_l \approx 0.93$ and $T = 359.1$ K.

The vapor-liquid equilibria data reported in this work were found to be thermodynamically consistent by the point-to-point method of Van Ness et al. (1973), as modified by Fredenslund et al. (1977). Consistency was achieved using a Legendre polynomial with two parameters for the three systems; the pertinent statistics required by the Fredenslund test, are shown in Table 7 for the different systems considered in this work. The variation of activity coefficients with composition is similar for the three studied systems. Figure 5 is shown as example of this behavior for the system TAME (3) + 2,3-Dimethylpentane (4).

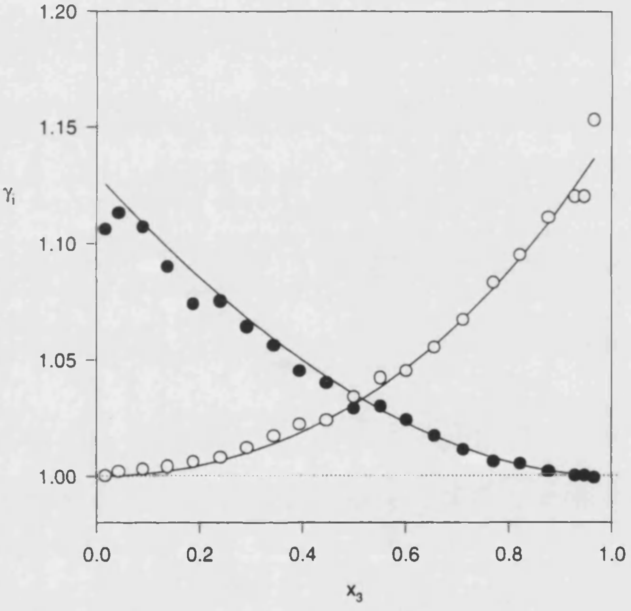

**Figure 5.** Activity coefficient plot of the system TAME (3) + 2,3-dimethylpentane (4) at 101.3 kPa, calculated from experimental data. $\gamma_1$ (●); $\gamma_4$ (○). Smoothed data using the Legendre polynomial used in consistency test (—).

**Table 7. Consistency Test for the Various Experimental Systems Considered in VLE Measurements**

| System | $n^a$ | $100 \times \mathrm{AAD}y_i{}^b$ | $\mathrm{AADP}^c$ / kPa |
|---|---|---|---|
| MTBE (1) + 2,3-dimethylpentane (4) | 2 | 0.53 | 0.33 |
| DIPE (2) + 2,3-dimethylpentane (4) | 2 | 0.49 | 0.23 |
| TAME (3) + 2,3-dimethylpentane (4) | 2 | 0.08 | 0.08 |

[a] Number of parameters used in the consistency test. [b] Average absolute deviation in vapor phase composition. [c] Average absolute deviation in pressure.

The activity coefficients were correlated with the Wilson, NRTL, and UNIQUAC equations (Walas, 1985). The parameters of these equations were obtained by minimizing the following objective function (OF):

$$\mathrm{OF} = \sum_{i=1}^{N} 100 \times \left( \left| \frac{P_i^{\mathrm{exptl}} - P_i^{\mathrm{calc}}}{P_i^{\mathrm{exptl}}} \right| + \left| y_i^{\mathrm{exptl}} - y_i^{\mathrm{calc}} \right| \right) \tag{5}$$

and are reported in Table 8, together with the pertinent statistics of VLE correlation. Inspection of the results given in Table 8 shows that all the models fitted well the systems.

The boiling point temperatures of each system at 101.3 kPa were well correlated with mole fractions by the equation proposed by Wisniak and Tamir (1976):

$$T/\mathrm{K} = x_i T_i^0/\mathrm{K} + x_j T_j^0/\mathrm{K} + x_i x_j \sum_{k=0}^{m} C_k (x_i - x_j)^k \tag{6}$$

In this equation $T_i^0/\mathrm{K}$ is the boiling point of the pure component i, and $m$ is the number of terms used in the series expansion of $(x_i - x_j)$, usually two. The various constants of eq 6 are reported in Table 9, with information indicating the goodness of fit of the correlation.

**Table 8. Parameters and Deviations between Experimental and Calculated Values for Different $G^E$ Models**

| model | $A_{ij}$ /J mol$^{-1}$ | $A_{ji}$ /J mol$^{-1}$ | $\alpha_{ij}$ | Bubble-point pressures $\Delta P$ [a] | Bubble-point pressures $100 \times \Delta y$ [b] |
|---|---|---|---|---|---|
| | MTBE (1) + 2,3-dimethylpentane (4) | | | | |
| [c]Wilson | -992.62 | 2001.60 | | 0.44 | 0.48 |
| NRTL | 1293.69 | -717.96 | 0.3 | 0.38 | 0.61 |
| [d]UNIQUAC | 664.88 | -487.67 | | 0.38 | 0.56 |
| | DIPE (2) + 2,3-dimethylpentane (4) | | | | |
| [c]Wilson | -823.78 | 1336.27 | | 0.22 | 0.49 |
| NRTL | 161.58 | 185.73 | 0.3 | 0.25 | 0.56 |
| [d]UNIQUAC | 92.33 | -670.09 | | 0.28 | 0.33 |
| | TAME (3) + 2,3-dimethylpentane (4) | | | | |
| [c]Wilson | 31.77 | 369.78 | | 0.08 | 0.07 |
| NRTL | 318.15 | 76.19 | 0.3 | 0.08 | 0.07 |
| [d]UNIQUAC | 62.28 | 21.82 | | 0.08 | 0.07 |

[a] Average percentual deviation in bubble pressure $\Delta P = 100/\mathrm{N}\sum_{i}^{N}\left|P_i^{\exp} - P_i^{calc}\right| / P_i^{\exp}$ (N:number of data points). [b] Average absolute deviation in vapor phase composition. [c] Liquid volumes have been estimated from the Rackett equation (Rackett, 1970). [d] Volume and surface parameters from DECHEMA (Gmehling and Onken, 1990).

**Table 9. Coefficients in Correlation of Boiling Points, Equation 6, Average Deviation, Root Mean Square Deviation and Maximum Deviation in Temperature**

| system | $C_0$ | $C_1$ | $C_2$ | av dev[a]. / K | rmsd[b] / K | max dev[c]. / K |
|---|---|---|---|---|---|---|
| 1+4 | -24.04 | 8.75 | 0.42 | 0.09 | 0.025 | 0.33 |
| 2+4 | -10.34 | 3.60 | -4.01 | 0.07 | 0.019 | 0.18 |
| 3+4 | -4.64 | 0.62 | -1.64 | 0.03 | 0.008 | 0.07 |

[a] Average deviation, [b] Root mean square deviation. [c] Maximum deviation.

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# 4.7. ISOBARIC VAPOR-LIQUID EQUILIBRIUM FOR BINARY AND TERNARY MIXTURES OF ETHANOL + 2-METHYL-2-PROPANOL AND 2-METHYLPENTANE + ETHANOL + 2-METHYL-2-PROPANOL

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## Abstract

Consistent vapor-liquid equilibrium data for the binary and ternary systems ethanol + 2-methyl-2-propanol (TBA) and 2-methylpentane + ethanol + 2-methyl-2-propanol are reported at 101.3 kPa. In the binary system the results indicate a negative deviation from ideality and no azeotrope is present. The ternary system shows negative and positive deviations from ideality, does not present azeotrope and is well predicted from binary data. The activity coefficients and boiling points of the solutions were correlated with its composition by Wilson, UNIQUAC and NRTL equations.

*Keywords:* VLE data; Activity coefficients; Experimental

# 1. Introduction.

Ethers and alkanols used as gasoline additive are excellent anti-knock quality and environmental protection substances. The commonly used oxygenating additives are methyl 1,1-dimethylethyl ether (MTBE) and light alkanols like methanol and ethanol. 2-Methyl-2-propanol (TBA) is added in the oxygenated gasolines with ethanol to avoid the formation of two liquid phases in presence of small quantities of water. Phase equilibrium data of oxygenated mixtures are important to predicting the vapor phase composition that would be in equilibrium with gasoline mixtures, for which iso-paraffins may constitute up to 30% weight. The systems reported here constitute a particular case of such mixtures.

Isothermal vapor-liquid data for the system ethanol + TBA have been reported at 313.15 by Oracz [1]. Limiting activity coefficient $\gamma_i^\infty$ for ethanol with TBA at 298.15 K has been measured by Park et al. [2] using a headspace analyzer. Isobaric vapor-liquid data for the system ethanol + TBA at 101.3 kPa have been reported previously by Suska et al. [3].

The present work was undertaken to measure vapor-liquid equilibrium (VLE) data of the ternary system 2-methylpentane (1) + ethanol (2) + TBA (3) and constituent binary system ethanol (2) + TBA (3); for the ternary system, data are not available. VLE data for the binary systems 2-methylpentane (1) + ethanol (2) and 2-methylpentane (1) + 2-methyl-2-propanol (3) have already been reported at 101.3 kPa in Ref. [4]; both systems deviate remarkably form ideality and present a minimum boiling temperature azeotrope.

# 2. Experimental

## 2.1. Chemicals

2-Methylpentane (99+ mass %, GC grade), 2-Methyl-2-propanol (99.5 mass %, HPLC grade) were purchased from Aldrich Chemie Co., and Ethanol (99.5 vol. %) was purchased from Prolabo. The reagents were used without further purification after chromatography failed to show any significant impurities. The densities of the pure liquids were measured at 298.15 K using an Anton Paar DMA 55 densimeter. The refractive indexes of the pure liquids were measured at 298.15 K in an Abbe refractometer, Atago 3T. Temperature was controlled to ±0.01 K with a thermostated bath. The accuracies in density and refractive index measurements are ±0.01 kg m$^{-3}$ and ±0.0002, respectively. The experimental values of these properties and the boiling points are given in Table 1 together with those given in Ref. [5-9].

**Table 1. Density, $d$, refractive index, $n_D$, and normal boiling point, $T_b$, of the chemicals.**

| Component | $d$(298.15K) (Kg m$^{-3}$) | | $n_D$ (298.15K) | | $T_b$ (101.3 kPa) (K) | |
|---|---|---|---|---|---|---|
| | expt. | lit. | expt. | lit. | expt. | lit. |
| 2-Methylpentane | 648.39 | 648.86[b] | 1.3689 | 1.3687[e] | 333.4 | 333.41[e] |
| Ethanol | 785.04 | 785.07[c] | 1.3592 | 1.3663[c] | 351.6 | 351.45[f] |
| 2-Methyl-2-propanol | 775.40[a] | 775.43[a,d] | 1.3851 | 1.3859[e] | 355.6 | 355.52[f] |

[a] Measured to 303.15 K. [b] Ref. [5]. [c] Ref [6]. [d] Ref. [7]. [e] Ref [8]. [f] Ref. [9]

### *2.2. Apparatus and procedure*

An all glass Fischer LABODEST vapor-liquid-equilibrium apparatus model 602/D, manufactured by Fischer Labor und Verfahrenstechnik (Germany), was used in the equilibrium determinations. The equilibrium vessel was a dynamic-recirculating still described by Walas [10], equipped with a Cottrell circulation pump. The still is capable of handling pressures from 0.25 to 400 kPa, and temperature up to 523 K. The Cottrell pump ensures that both liquid and vapor phases are in intimate contact during boiling and also in contact with the temperature sensing element.

The equilibrium temperature was measured with a digital Fischer thermometer with an accuracy of ±0.1 K. The apparatus is equipped with two digital sensors of pressure: one for the low pressure zone with an accuracy of ±0.01 kPa, and another one for the high pressures with an accuracy of ±0.1 kPa. The temperature probe was calibrated against the ice and steam points of distilled water. The manometers were calibrated using the vapor pressure of ultrapure water. The still was operated under constant pressure until equilibrium was reached. Equilibrium conditions were assumed when constant temperature and pressure were obtained for 60 min or longer. Then, samples of liquid and condensate were taken for analysis. The sample extractions were carried out with special syringes that allowed one to withdraw small volume samples (1.0μl) in a system under partial vacuum or under overpressure conditions.

### *2.3. Analysis*

Compositions of the liquid and condensed vapor phase samples were determined using a Hewlett-Packard 5890 S-II gas chromatograph (GC), after calibration with gravimetrically prepared standard solutions. A flame ionization detector was used together with a 60 m, 0.2 mm i.d., fused silica capillary column, SUPELCOWAX 10. The GC response peaks were integrated with a Hewlett-Packard 3396 integrator. Column, injector and detector temperatures were 343, 423, 473 K for all the systems.

Very good separation was achieved under these conditions, and calibration analyses were carried out to convert the peak ratio to the mass composition of the sample. At least three analyses were made of each vapor composition; the standard deviation in the mole fraction was usually less than 0.001.

## 3. Results and Discussion

Vapor pressures $P_i^o$ were calculated with the Antoine equation whose parameters $A_i$, $B_i$, and $C_i$ are reported in Table 2.

$$\ln (P_i^\circ / \mathrm{kPa}) = A_i - \frac{B_i}{(T/\mathrm{K}) - C_i} \tag{1}$$

**Table 2. Antoine coefficients, Eq. (1)**

| Compound | $A_i$ | $B_i$ | $C_i$ |
|---|---|---|---|
| 2-Methylpentane[a] | 14.0614 | 2791.52 | 37.75 |
| Ethanol[b] | 16.4298 | 3545.95 | 51.36 |
| TBA[b] | 14.8533 | 2649.89 | 96.69 |

[a]Ref. [11]. [b]Ref. [4].

The Antoine constants for 2-methylpentane were taken from Ref. [11]. For ethanol and TBA, the values given in Ref. [4] were used.

### 3.1. Binary System.

The temperature $T$, the liquid-phase $x_i$ and vapor-phase $y_i$ mole fractions at 101.3 kPa are reported in Table 3. Figure 1 shows a graphical comparison between boiling-point temperatures measured for the system ethanol (2) + TBA (3) in this work and those determined by Suska et al. [3]. Good agreement among these different sets of data is deduced from the figure. Figure 2 shows the activity coefficients $\gamma_i$ that were calculated from the following equation [12]:

$$\ln \gamma_i = \ln \frac{y_i P}{x_i P_i^0} + \frac{\left(B_{ii} - V_i^L\right)\left(P - P_i^0\right)}{RT} + \frac{P}{2RT} \sum \sum y_i y_k \left(2\delta_{ji} - \delta_{jk}\right) \tag{2}$$

where $T$ and $P$ are the boiling point and the total pressure, $V_i^L$ is the molar liquid volume of component i, $B_{ii}$ and $B_{jj}$ are the second virial coefficients of the pure gases, $P_i^0$ is the vapor pressure, $B_{ij}$ the cross second virial coefficient and

$$\delta_{ij} = 2\,B_{ij} - B_{jj} - B_{ii} \tag{3}$$

**Table 3. Experimental vapor-liquid equilibrium data for ethanol (2) + TBA (3) at 101.3 kPa**

| $T$ (K) | $x_2$ | $y_2$ | $\gamma_2$ | $\gamma_3$ | $-B_{22}$ (cm$^3$ mol$^{-1}$) | $-B_{33}$ (cm$^3$ mol$^{-1}$) | $-B_{23}$ (cm$^3$ mol$^{-1}$) |
|---|---|---|---|---|---|---|---|
| 355.6 | 0.019 | 0.021 | 0.913 | 0.998 | 891 | 1146 | 1160 |
| 355.5 | 0.049 | 0.052 | 0.920 | 1.000 | 892 | 1147 | 1161 |
| 355.4 | 0.098 | 0.106 | 0.928 | 0.998 | 893 | 1148 | 1163 |
| 355.3 | 0.147 | 0.160 | 0.939 | 0.996 | 894 | 1149 | 1164 |
| 355.2 | 0.195 | 0.211 | 0.937 | 0.995 | 895 | 1150 | 1166 |
| 355.1 | 0.245 | 0.265 | 0.944 | 0.991 | 896 | 1151 | 1168 |
| 355.0 | 0.292 | 0.317 | 0.949 | 0.986 | 897 | 1152 | 1169 |
| 354.9 | 0.342 | 0.371 | 0.954 | 0.980 | 898 | 1153 | 1171 |
| 354.7 | 0.393 | 0.429 | 0.967 | 0.972 | 901 | 1155 | 1174 |
| 354.5 | 0.445 | 0.479 | 0.960 | 0.977 | 903 | 1157 | 1177 |
| 354.3 | 0.492 | 0.526 | 0.962 | 0.978 | 905 | 1159 | 1180 |
| 354.1 | 0.543 | 0.580 | 0.969 | 0.970 | 907 | 1161 | 1183 |
| 353.9 | 0.587 | 0.627 | 0.976 | 0.960 | 910 | 1163 | 1186 |
| 353.7 | 0.641 | 0.680 | 0.977 | 0.955 | 912 | 1165 | 1190 |
| 353.4 | 0.690 | 0.729 | 0.986 | 0.944 | 915 | 1168 | 1194 |
| 353.1 | 0.742 | 0.779 | 0.990 | 0.938 | 919 | 1171 | 1199 |
| 352.8 | 0.789 | 0.824 | 0.996 | 0.923 | 922 | 1174 | 1204 |
| 352.5 | 0.847 | 0.873 | 0.995 | 0.926 | 926 | 1178 | 1209 |
| 352.2 | 0.897 | 0.917 | 0.999 | 0.905 | 929 | 1181 | 1214 |
| 351.9 | 0.945 | 0.957 | 1.000 | 0.893 | 933 | 1184 | 1219 |
| 351.7 | 0.977 | 0.982 | 1.000 | 0.886 | 935 | 1186 | 1222 |

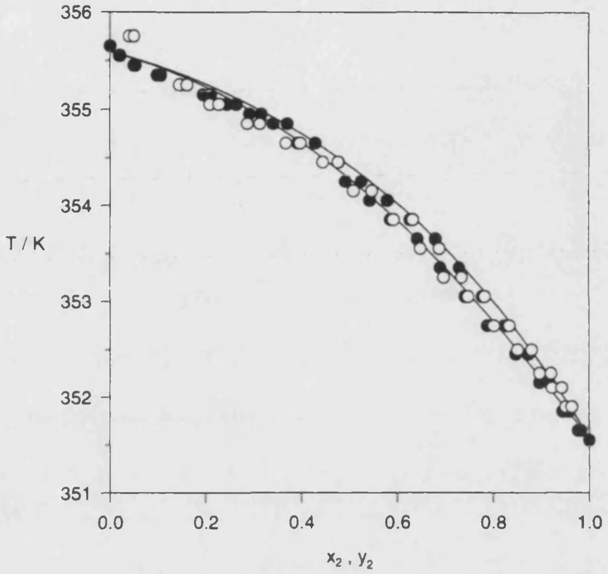

**Figure 1.** Boiling temperature diagram for the system ethanol (2) + 2-methyl-2-propanol (3) at 101.3 kPa. Experimental data (●); data of Suska et al. [3] (O); smoothed with the Legendre polynomial used in consistency test (—).

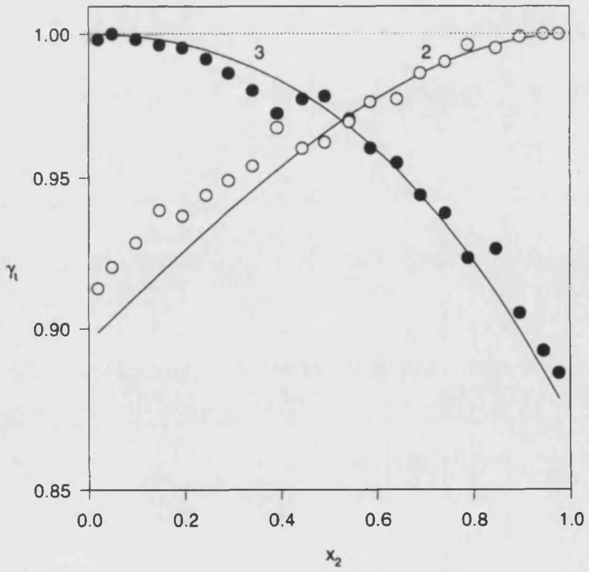

**Figure 2.** Activity coefficient plot for the system ethanol (2) + 2-methyl-2-propanol (3) at 101.3 kPa. $\gamma_2$ (O); $\gamma_3$ (●); smoothed with the Legendre polynomial used in consistency test (—).

The standard state for calculation of activity coefficients is the pure component at the pressure and temperature of the solution. Eq. (2) is valid at low and moderate pressures when the virial equation of state truncated after the second coefficient is adequate to describe the vapor phase of the pure components and their mixtures, and liquid volumes of the pure components are incompressible over the pressure range under consideration. The molar virial coefficients $B_{ii}$ and $B_{ij}$ were estimated by the method of Hayden and O'Connell [13] using the molecular parameters suggested by Prausnitz et al. [14]. Critical properties of all components were taken from DIPPR [8]. The last two terms in Eq. (2), particularly the second one that expresses the correction due to the non ideal behaviour of the vapor phase, contributed less than 2.5% for the system ethanol + TBA; in general, their influence was important only at very dilute concentrations.

The calculated activity coefficients reported in Table 3 are estimated to be accurate to within ± 3%. The results reported in that Table indicate that the measured system exhibit remarkable negative deviation from ideal behavior and no present azeotrope. This trend of activity coefficients is in agreement with the data reported by Oracz [1] and by Park et al. [2]; in the three works it is shown a clear negative deviation from ideality.

The VLE data reported in Table 3 were found to be thermodynamically consistent by the point-to-point method of Van Ness et al. [15], as modified by Fredenslund et al. [16]. The pertinent statistics required by the Fredenslund et al. test together with the number of parameters of the Legendre polynomial used for consistency are shown in Table 4.

**Table 4. Consistency test for the binary mixture ethanol (2) + TBA (3)**

| $n$ | $100 \times \mathrm{MAD}y_2$ [a] | MAD$P$ [b] (kPa) |
|---|---|---|
| 2 | 0.17 | 0.10 |

[a] Mean absolute deviation in vapor phase composition. [b] Mean absolute deviation in pressure.

The parameters of the Wilson, NRTL and UNIQUAC equations were obtained by minimizing the following objective function (*OF*):

$$OF = \sum_{i=1}^{N} 100 \times \left( \left| \frac{P_i^{expt} - P_i^{calc}}{P_i^{expt}} \right| + \left| y_i^{expt} - y_i^{calc} \right| \right) \tag{4}$$

and are reported in Table 5, together with the pertinent statistics of VLE interpolation.

**Table 5. Parameters and deviations between experimental and calculated values for different $G^E$ models for the binary system ethanol (2) + TBA (3)**

| Model | $A_{ij}$ (J mol$^{-1}$) | $A_{ji}$ (J mol$^{-1}$) | $\alpha_{ij}$ | Bubble-point pressures | | Dew-point pressures | |
|---|---|---|---|---|---|---|---|
| | | | | $\Delta P$ [a] (%) | $100 \times \Delta y$ [b] | $\Delta P$ [a] (%) | $100 \times \Delta x$ [b] |
| Wilson[c] | -343.43 | 784.63 | | 0.11 | 0.16 | 0.12 | 0.15 |
| NRTL | 714.30 | -989.00 | 0.3 | 0.13 | 0.15 | 0.13 | 0.14 |
| UNIQUAC[d] | -195.04 | 194.90 | | 0.13 | 0.16 | 0.14 | 0.15 |

[a] Average percentual deviation in pressure $\Delta P = 100/N \sum_{i}^{N} \left| P_i^{expt} - P_i^{calc} \right| / P_i^{expt}$ (N : number of data points). [b] Average absolute deviation in vapor and liquid phase composition; [c] Liquid volumes have been estimated from the Rackett equation [21]. [d] Volume and surface parameters from Ref. [20] (See Table 7).

Inspection of the results given in Table 5 shows that all models are adequate to predict the binary data but the best fit corresponding to the Wilson model.

### 3.2. Ternary System.

The VLE data for the ternary system are shown in Table 6 and Figure 3. The activity coefficients $\gamma_i$ were calculated from Eq. (2) and the molar virial coefficients were estimated than the binary system.

**Table 6. Experimental vapor-liquid equilibrium data for 2-methylpentane (1) + ethanol (2) + TBA (3) at 101.3 kPa**

| $T$ (K) | $x_1$ | $x_2$ | $y_1$ | $y_2$ | $\gamma_1$ | $\gamma_2$ | $\gamma_3$ | $-B_{11}$ | $-B_{22}$ | $-B_{33}$ | $-B_{12}$ | $-B_{13}$ | $-B_{23}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | $(cm^3\ mol^{-1})$ | | | | | |
| 329.0 | 0.896 | 0.050 | 0.824 | 0.121 | 1.056 | 6.315 | 3.247 | 1350 | 1296 | 1484 | 675 | 1008 | 1734 |
| 330.7 | 0.701 | 0.052 | 0.793 | 0.058 | 1.233 | 2.738 | 1.749 | 1332 | 1264 | 1458 | 667 | 995 | 1687 |
| 332.8 | 0.503 | 0.051 | 0.740 | 0.041 | 1.502 | 1.775 | 1.297 | 1309 | 1225 | 1428 | 657 | 980 | 1631 |
| 336.5 | 0.304 | 0.051 | 0.638 | 0.036 | 1.919 | 1.290 | 1.127 | 1271 | 1162 | 1376 | 640 | 953 | 1539 |
| 348.7 | 0.064 | 0.051 | 0.288 | 0.044 | 2.942 | 0.962 | 0.991 | 1157 | 984 | 1226 | 589 | 873 | 1286 |
| 344.6 | 0.101 | 0.101 | 0.409 | 0.076 | 2.937 | 0.992 | 1.005 | 1194 | 1039 | 1274 | 606 | 898 | 1364 |
| 339.4 | 0.204 | 0.103 | 0.555 | 0.070 | 2.284 | 1.114 | 1.057 | 1243 | 1115 | 1338 | 627 | 933 | 1472 |
| 335.8 | 0.307 | 0.103 | 0.652 | 0.067 | 1.987 | 1.257 | 1.090 | 1278 | 1173 | 1386 | 643 | 958 | 1556 |
| 333.5 | 0.406 | 0.102 | 0.703 | 0.069 | 1.731 | 1.449 | 1.182 | 1302 | 1213 | 1418 | 654 | 974 | 1613 |
| 331.9 | 0.513 | 0.101 | 0.733 | 0.077 | 1.500 | 1.731 | 1.359 | 1319 | 1241 | 1441 | 661 | 986 | 1654 |
| 330.7 | 0.604 | 0.102 | 0.762 | 0.087 | 1.376 | 2.065 | 1.495 | 1332 | 1264 | 1458 | 667 | 995 | 1687 |
| 329.6 | 0.705 | 0.102 | 0.782 | 0.110 | 1.251 | 2.740 | 1.722 | 1344 | 1285 | 1475 | 672 | 1004 | 1717 |
| 328.5 | 0.798 | 0.102 | 0.791 | 0.144 | 1.156 | 3.784 | 2.113 | 1356 | 1306 | 1491 | 677 | 1012 | 1748 |
| 327.8 | 0.695 | 0.206 | 0.760 | 0.195 | 1.306 | 2.615 | 1.501 | 1364 | 1320 | 1502 | 680 | 1017 | 1769 |
| 329.2 | 0.600 | 0.206 | 0.753 | 0.159 | 1.432 | 2.004 | 1.416 | 1348 | 1292 | 1481 | 674 | 1007 | 1728 |
| 330.6 | 0.494 | 0.209 | 0.733 | 0.141 | 1.622 | 1.642 | 1.237 | 1333 | 1266 | 1460 | 667 | 996 | 1689 |
| 332.2 | 0.393 | 0.208 | 0.706 | 0.128 | 1.870 | 1.387 | 1.127 | 1316 | 1236 | 1436 | 660 | 984 | 1646 |
| 334.6 | 0.294 | 0.208 | 0.657 | 0.124 | 2.167 | 1.206 | 1.066 | 1291 | 1194 | 1402 | 649 | 966 | 1585 |
| 340.6 | 0.151 | 0.205 | 0.537 | 0.131 | 2.893 | 0.994 | 0.953 | 1231 | 1097 | 1323 | 622 | 925 | 1446 |
| 348.5 | 0.054 | 0.203 | 0.263 | 0.173 | 3.200 | 0.963 | 1.003 | 1159 | 987 | 1228 | 590 | 874 | 1290 |

| $T$ (K) | $x_1$ | $x_2$ | $y_1$ | $y_2$ | $\gamma_1$ | $\gamma_2$ | $\gamma_3$ | $-B_{11}$ | $-B_{22}$ | $-B_{33}$ | $-B_{12}$ | $-B_{13}$ | $-B_{23}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | ($cm^3$ $mol^{-1}$) | | | |
| 343.6 | 0.091 | 0.308 | 0.424 | 0.220 | 3.489 | 0.984 | 0.958 | 1203 | 1053 | 1286 | 610 | 905 | 1383 |
| 337.2 | 0.189 | 0.308 | 0.572 | 0.187 | 2.718 | 1.093 | 1.028 | 1264 | 1150 | 1367 | 637 | 948 | 1522 |
| 333.3 | 0.294 | 0.308 | 0.655 | 0.175 | 2.246 | 1.218 | 1.093 | 1304 | 1216 | 1421 | 654 | 976 | 1618 |
| 331.0 | 0.392 | 0.306 | 0.703 | 0.177 | 1.940 | 1.376 | 1.132 | 1329 | 1258 | 1454 | 665 | 993 | 1678 |
| 329.1 | 0.494 | 0.303 | 0.736 | 0.189 | 1.708 | 1.617 | 1.158 | 1349 | 1294 | 1482 | 674 | 1007 | 1731 |
| 327.1 | 0.647 | 0.300 | 0.745 | 0.234 | 1.407 | 2.215 | 1.383 | 1372 | 1334 | 1513 | 684 | 1023 | 1789 |
| 327.8 | 0.496 | 0.403 | 0.736 | 0.233 | 1.771 | 1.591 | 1.033 | 1364 | 1320 | 1502 | 680 | 1017 | 1769 |
| 329.6 | 0.400 | 0.400 | 0.713 | 0.218 | 2.013 | 1.383 | 1.051 | 1344 | 1285 | 1475 | 672 | 1004 | 1717 |
| 332.0 | 0.288 | 0.408 | 0.669 | 0.217 | 2.434 | 1.206 | 1.025 | 1318 | 1240 | 1439 | 660 | 985 | 1652 |
| 335.8 | 0.180 | 0.411 | 0.595 | 0.232 | 3.097 | 1.080 | 0.967 | 1278 | 1173 | 1386 | 643 | 958 | 1556 |
| 346.4 | 0.053 | 0.401 | 0.335 | 0.314 | 4.420 | 0.961 | 0.924 | 1177 | 1015 | 1252 | 598 | 887 | 1329 |
| 340.9 | 0.090 | 0.506 | 0.478 | 0.323 | 4.311 | 0.982 | 0.895 | 1228 | 1092 | 1319 | 621 | 923 | 1440 |
| 334.3 | 0.180 | 0.509 | 0.613 | 0.269 | 3.329 | 1.083 | 0.927 | 1294 | 1199 | 1407 | 650 | 969 | 1592 |
| 330.6 | 0.267 | 0.519 | 0.678 | 0.252 | 2.781 | 1.173 | 0.949 | 1333 | 1266 | 1460 | 667 | 996 | 1689 |
| 327.5 | 0.419 | 0.518 | 0.718 | 0.263 | 2.069 | 1.416 | 1.002 | 1367 | 1326 | 1507 | 682 | 1020 | 1778 |
| 329.2 | 0.280 | 0.613 | 0.686 | 0.284 | 2.806 | 1.193 | 0.884 | 1348 | 1292 | 1481 | 674 | 1007 | 1728 |
| 332.6 | 0.189 | 0.609 | 0.634 | 0.298 | 3.453 | 1.081 | 0.885 | 1311 | 1229 | 1431 | 658 | 981 | 1636 |
| 344.4 | 0.051 | 0.604 | 0.344 | 0.455 | 4.936 | 1.001 | 0.911 | 1195 | 1042 | 1276 | 607 | 900 | 1367 |
| 338.2 | 0.088 | 0.708 | 0.496 | 0.419 | 4.948 | 1.020 | 0.849 | 1254 | 1134 | 1354 | 633 | 941 | 1499 |
| 329.4 | 0.232 | 0.710 | 0.678 | 0.307 | 3.320 | 1.104 | 0.798 | 1346 | 1288 | 1478 | 673 | 1005 | 1723 |
| 336.9 | 0.093 | 0.806 | 0.515 | 0.448 | 5.029 | 1.014 | 0.790 | 1267 | 1155 | 1371 | 638 | 950 | 1529 |
| 341.4 | 0.044 | 0.906 | 0.374 | 0.604 | 6.869 | 1.003 | 0.787 | 1223 | 1085 | 1313 | 619 | 919 | 1429 |

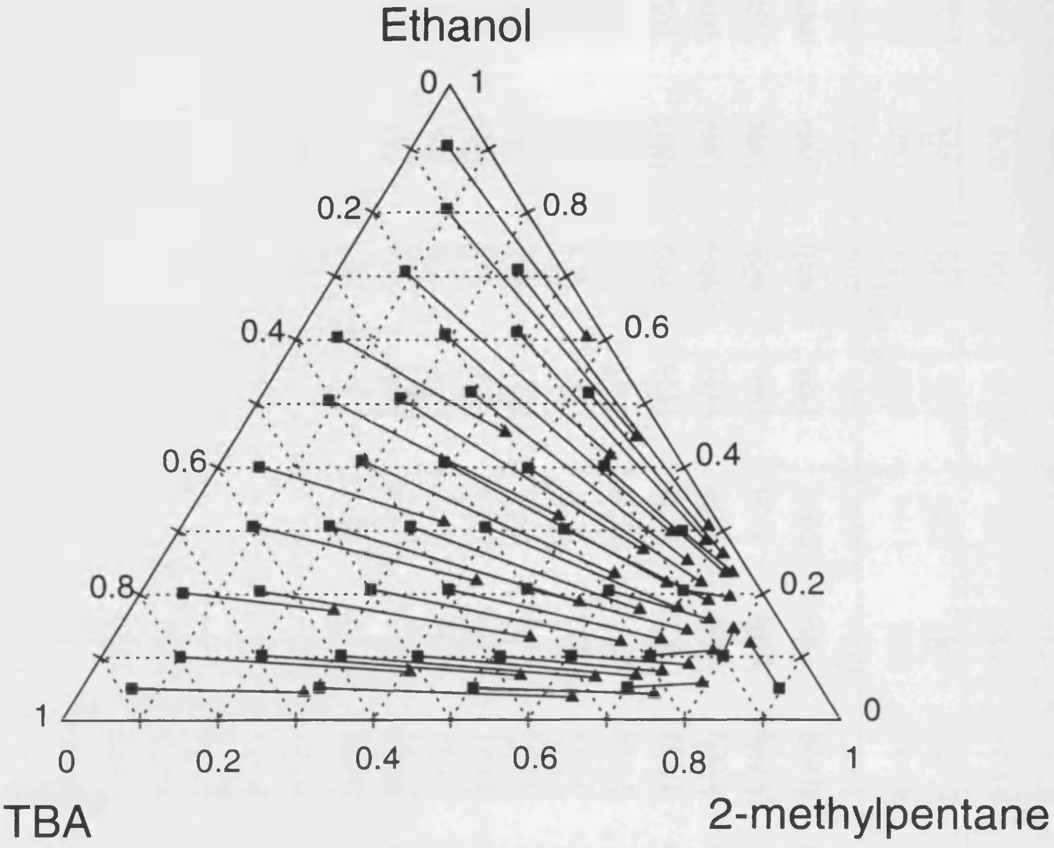

**Figure 3**. Diagram of VLE for the ternary system 2-methylpentane (1)+ ethanol (2) + 2-methyl-2-propanol (3) at 101.3 kPa: (■) liquid phase mole fractions; (▲) vapor phase mole fractions.

The ternary data were found to be thermodynamically consistent, as tested by the L-W method of Wisniak [17] and the McDermott-Ellis method [18] modified by Wisniak and Tamir [19]. The test requires that $D<D_{max}$ for every experimental point where the local deviation D is given by:

$$D=\sum_{i=1}^{N}(x_{ia}+x_{ib})(\ln\gamma_{ia}-\ln\gamma_{ib}) \quad (5)$$

and N is the number of components. The maximum deviation $D_{max}$ is given by:

$$\begin{aligned} D_{max} &= \sum_{i=1}^{N}(x_{ia}+x_{ib})\left(\frac{1}{x_{ia}}+\frac{1}{y_{ia}}+\frac{1}{x_{ib}}+\frac{1}{y_{ib}}\right)\Delta x \\ &+\sum_{i=1}^{N}(x_{ia}+x_{ib})\frac{\Delta P}{p}+2\sum_{i=1}^{N}\left|\ln\gamma_{b}-\ln\gamma_{ia})\right|\Delta x \\ &+\sum_{i=1}^{N}(x_{ia}+x_{ib})B_{j}\left\{(T_{a}+C_{j})^{-2}+(T_{b}+C_{j})^{-2}\right\}\Delta T \end{aligned} \quad (6)$$

The error in the measurements $\Delta x$, $\Delta P$ and $\Delta T$ were as previously indicated.

Vapor-liquid equilibrium was correlated by using Wilson, NRTL, and UNIQUAC models for the activity coefficients of the components with the binary interaction parameters. The values of the binary interaction parameters for the two binaries 2-methylpentane (1) + ethanol (2) and 2-methylpentane (1) + TBA (3) were used from the data of Ref. [4] and corresponding parameters of the system ethanol (2) + TBA (3) were calculated in this work. The values of volume and surfaces parameters of UNIQUAC model were taken from Ref. [20] and appear in Table 7.

**Table 7. Critical properties from Ref. [8], volume ($r_i$) and surface ($q_i$) parameters of UNIQUAC model from Ref. [20]**

| Component | $P_c$ (bar) | $T_c$ (K) | $Z_c$ | r | q |
|---|---|---|---|---|---|
| 2-Methylpentane | 30.10 | 497.50 | 0.267 | 4.4990 | 3.8520 |
| Ethanol | 63.38 | 516.25 | 0.248 | 2.1055 | 1.9720 |
| TBA | 39.70 | 506.20 | 0.260 | 3.4528 | 3.1280 |

Table 8 shows the pertinent statistics of VLE interpolation. The three models yield similar deviations, representing the data successfully while the best fit corresponding with the Wilson model. In Fig. 4 show the boiling isotherms for the ternary system calculated by this model.

**Table 8. Correlation of experimental ternary data with Wilson, NRTL, and UNIQUAC equations using binary interaction parameters**

| Model | $ij$ | $A_{ij}$ | $A_{ji}$ | $\alpha_{ij}$ | System | Buble-point pressures | | | Dew-point pressures | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | (J.mol$^{-1}$) | (J.mol$^{-1}$) | | | $\Delta P^e$ (%) | 100 x $\Delta y_1$[f] | 100 x $\Delta y_2$[f] | $\Delta P^e$ (%) | 100 x $\Delta x_1$[f] | 100 x $\Delta x_2$[f] |
| Wilson[a] | 1-2[c] | 1187.08 | 9489.34 | | 1+2+3 | 1.25 | 1.14 | 0.70 | 1.38 | 1.72 | 1.04 |
| | 1-3[c] | -14.98 | 5658.90 | | | | | | | | |
| | 2-3[d] | -343.43 | 784.63 | | | | | | | | |
| NRTL | 1-2[c] | 6356.65 | 3990.00 | 0.47 | 1+2+3 | 1.39 | 1.34 | 0.70 | 1.36 | 2.36 | 1.16 |
| | 1-3[c] | 4362.09 | 983.72 | 0.47 | | | | | | | |
| | 2-3[d] | 714.30 | -989.00 | 0.30 | | | | | | | |
| UNIQUAC[b] | 1-2[c] | 4271.12 | -475.03 | | 1+2+3 | 1.66 | 1.50 | 0.73 | 1.42 | 3.60 | 1.96 |
| | 1-3[c] | 2844.32 | -1030.28 | | | | | | | | |
| | 2-3[d] | -195.04 | 194.90 | | | | | | | | |

[a] Liquid volumes have been estimated from the Racket [21] equation. [b] Volume and surface parameters from Ref. [20] (See Table 7). [c] Ref. [4]. [d] Calculated in this work. [e] Average percentual deviation in bubble and dew pressure: $\Delta P = 100/N\ \Sigma | P_i^{expt} - P_i^{calc} | / P_i^{expt}$ (N: number of data points). [f] Average absolute deviation in composition $\Delta y = 1/N\ \Sigma | y_i^{expt} - y_i^{calc} |$ ; $\Delta x = 1/N\ \Sigma | x_i^{expt} - x_i^{calc} |$

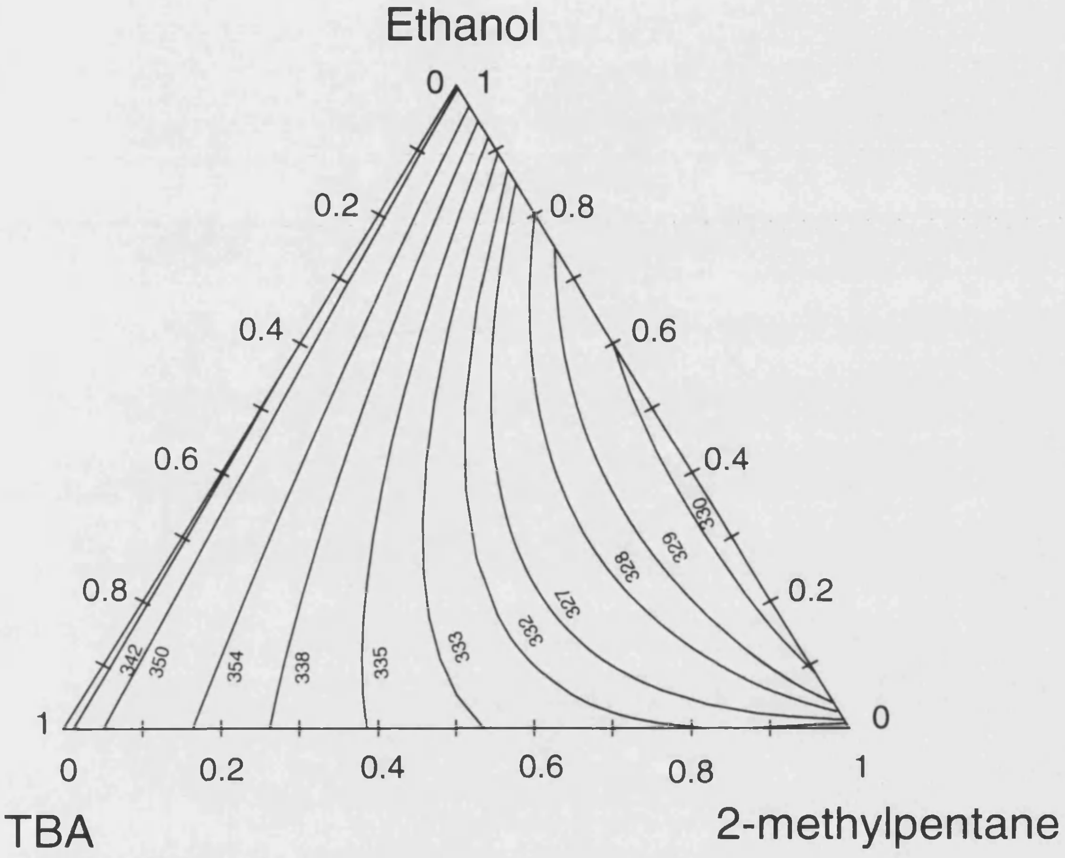

**Figure. 4**. Isothermals (K) for the ternary system 2-methylpentane (1) + ethanol (2) + 2-methyl-2-propanol (3) at 101.3 kPa, calculated with Wilson model.

## 4. List of symbols

| | | |
|---|---|---|
| $A_i$ | Antoine's equation parameter, Eq. (1) | |
| $B_i$ | Antoine's equation parameter, Eq. (1) | |
| $B_{ii}$ | pure component second virial coefficient | $cm^3\ mol^{-1}$ |
| $B_{ij}$ | cross second virial coefficient | $cm^3\ mol^{-1}$ |
| $C_i$ | Antoine's equation parameter, Eq. (1) | |
| $D$ | Parameter in Eq. (5) | |
| $D_{max}$ | Parameter in Eq. (6) | |
| $G^E$ | excess Gibbs energy | $J\ mol^{-1}$ |
| $P$ | absolute pressure | kPa |
| $P^o$ | pure component vapor pressure | kPa |
| $q_i$ | surface parameter of component *i* in UNIQUAC model | |
| $R$ | universal gas constant | $J\ mol^{-1}\ K^{-1}$ |
| $r_i$ | volume parameter of component *i* in UNIQUAC model | |
| $T$ | absolute temperature | K |
| $V$ | molar volume | $cm^3\ mol^{-1}$ |
| $x$, $y$ | compositions of the liquid and vapor phases | |
| $Z_c$ | critical compressibility | |

### Greek

| | | |
|---|---|---|
| $\delta_{ij}$ | parameter defined in Eq. (3) | $cm^3\ mol^{-1}$ |
| $\gamma$ | activity coefficient | |

### Superscripts

| | |
|---|---|
| $^E$ | excess property |
| $^L$ | pertaining to the liquid phase |

### Subscripts

| | |
|---|---|
| $i,j$ | component *i*, *j* respectively |

**Acknowledgements**

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# 4.8. ISOBARIC VAPOR-LIQUID EQUILIBRIUM IN THE SYSTEMS METHYL 1,1-DIMETHYLETHYL ETHER + 2-METHYL-2-PROPANOL AND METHYL 1,1-DIMETHYLETHYL ETHER + 2-METHYLPENTANE + 2-METHYL-2-PROPANOL

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## ABSTRACT

Consistent vapor-liquid equilibrium data for the binary and ternary systems methyl 1,1-dimethylethyl ether (MTBE) + 2-methyl-2-propanol (TBA) and methyl 1,1-dimethylethyl ether (MTBE) + 2-methylpentane + 2-methyl-2-propanol (TBA) are reported at 101.3 kPa. The results indicate that the systems deviate positively from ideality and that no azeotrope is present. The activity coefficients of the solutions were correlated with its composition by Wilson, NRTL and UNIQUAC models. It is shown that the models allow a very good prediction of the phase equilibrium of the ternary system using the pertinent parameters of the binary system. In addition, the Wisniak-Tamir relations were used for correlating bubble-point temperatures.

## Introduction

Alcohol + ether + alkane systems are of interest as model mixtures for gasoline where the alcohol and the ether component act as anti-knocking agents substituting the formerly used lead compounds to reduce pollution. The gasoline including about 7 to 15 % of Methyl 1,1-dimethylethyl ether (MTBE) has been used for a high performance premium gasoline. However, it was recommended that the use of gasoline additive is not only pure MTBE but also mixtures with alcohols for the high-octane gasoline.

In this research, for the knowledge of phase behavior of alkanes with MTBE and alcohols mixtures, isobaric vapor-liquid equilibrium (VLE) data of the ternary system MTBE (1) + 2-methylpentane (2) + TBA (3) and constituent binary system MTBE (1) + TBA (3) at 101.3 kPa have been measured. Isobaric VLE data at 101.3 kPa for the binary system have been reported previously by Churkin et al. (1979) and by Zong et al. (1987). Both references present contradictory information about the system MTBE + TBA: in the first one it is observed a no-azeotropic behavior, while the results of the Zong et al. indicate the presence of a minimum boiling point. For this reason it has been considered of interest to measure VLE data at same conditions of this binary system. For the ternary system no VLE data have been previously published. VLE data at 101.3 kPa of the other binary constituent systems MTBE (1) + 2-methylpentane (2) and 2-methylpentane (2) + TBA (3), have already been reported by Aucejo et al. (1998) and Aucejo et al. (1999a), respectively. Both systems present positive deviations from ideality and present a minimum boliling azeotrope: the first one behave essentially as regular solution and the second one deviate remarkably from ideal behavior.

## Experimental Section

***Chemicals.*** MTBE (99.8 mass %, HPLC grade), 2-Methylpentane (99+ mass %, GC grade) and TBA (99.5 mass %, HPLC grade) were purchased from Aldrich Chemie Co. The reagents were used without further purification after chromatography failed to show any significant impurities. The densities of the pure liquids were measured at 298.15 K using an Anton Paar

DMA 55 densimeter. The refractive indexes of the pure liquids were measured at 298.15 K in an Abbe refractometer, Atago 3T. Temperature was controlled to ±0.01 K with a thermostated bath. The accuracies in density and refractive index measurements are ±0.01 kg m$^{-3}$ and ±0.0002, respectively. The experimental values of these properties and the boiling points are given in Table 1 together with those given in literature.

**Table 1. Density, *d*, Refractive Index, $n_D$, and Normal Boiling Point, $T_b$, of the Chemicals**

| component | $d$(298.15K) /Kg m$^{-3}$ | | $n_D$ (298.15K) | | $T_b$ (101.3 kPa) /K | |
|---|---|---|---|---|---|---|
| | exptl. | lit. | exptl. | lit. | exptl. | lit. |
| methyl 1,1-dimethylethyl ether | 735.20 | 735.28[a] | 1.3664 | 1.3663[a] | 328.2 | 328.11[b] |
| 2-methylpentane | 648.39 | 648.86[c] | 1.3689 | 1.3687[a] | 333.4 | 333.41[a] |
| 2-methyl-2-propanol | 775.40[d] | 775.43[d,e] | 1.3851 | 1.3859[a] | 355.6 | 355.52[f] |

[a] DIPPR (Daubert and Danner, 1998). [b] Martínez-Ageitos (1996). [c] Awwad and Pethrick (1983). [d] Measured to 303.15 K. [e] Hales et al. (1983). [f] Ambrose and Sprake (1970).

***Apparatus and procedure.*** An all glass Fischer LABODEST vapor-liquid-equilibrium apparatus model 602/D, manufactured by Fischer Labor und Verfahrenstechnik (Germany), was used in the equilibrium determinations. The equilibrium vessel was a dynamic-recirculating still described by Walas (1985), equipped with a Cottrell circulation pump. The still is capable of handling pressures from 0.25 to 400 kPa, and temperature up to 523 K. The Cottrell pump ensures that both liquid and vapor phases are in intimate contact during boiling and also in contact with the temperature sensing element. The equilibrium temperature was measured with a digital Fischer thermometer with an accuracy of ±0.1 K. The apparatus is equipped with two digital sensors of pressure: one for the low pressure zone with an accuracy of ±0.01 kPa, and another one for the high pressures with an accuracy of ±0.1 kPa. The temperature probe was calibrated against the ice and steam points of distilled water. The manometers were calibrated using the vapor pressure of ultrapure water. The still was operated under constant pressure until equilibrium was reached. Equilibrium conditions were assumed when constant temperature and pressure were obtained for 60 min or longer. Then, samples of liquid and condensate were taken for analysis. The sample extractions were carried out with special syringes that allowed one to withdraw small volume samples (1.0μL) in a system under partial vacuum or under overpressure conditions.

***Analysis.*** Compositions of the liquid and condensed vapor phase samples were determined using a CE Instruments GC 8000 Top gas chromatograph (GC), after calibration with gravimetrically prepared standard solutions. A flame ionization detector was used together with a 30 m, 0.454 mm i.d., capillary column, DB-MTBE (J&W Scientific). The GC response peaks were treated with Chrom-Card for Windows, Version 1.20. Column, injector and detector temperatures were 323, 498, 523 K for the two systems. Very good separation was achieved under these conditions, and calibration analyses were carried out to convert the peak ratio to the mass composition of the sample. At least three analyses were made of each vapor composition; the standard deviation in the mole fraction was usually less than 0.001.

## Results and Discussion

Vapor pressures $P_i^o$ were calculated with the Antoine equation whose parameters $A_i$, $B_i$, and $C_i$ are reported in Table 2.

$$\ln(P_i^\circ / \mathrm{kPa}) = A_i - \frac{B_i}{(T/\mathrm{K}) - C_i} \qquad (1)$$

The Antoine constants for MTBE and 2-methylpentane were taken from Aucejo et al. (1998). For TBA, the values given in Aucejo et al. (1999a) were used.

**Table 2. Antoine coefficients, Equation 1**

| compound | $A_i$ | $B_i$ | $C_i$ |
|---|---|---|---|
| methyl 1,1-dimethylpropyl ether[a] | 14.6212 | 3022.19 | 26.03 |
| 2-methylpentane[a] | 14.0614 | 2791.52 | 37.75 |
| 2-methyl-2-propanol[b] | 14.8533 | 2649.89 | 96.69 |

[a] Aucejo et al. (1998). [b] Aucejo et al. (1999a).

***Binary System.*** The temperature $T$, the liquid-phase $x_i$ and vapor-phase $y_i$ mole fractions at 101.3 kPa are reported in Table 3. Figure 1 shows a graphical comparison between boiling-point temperatures measured for the system MTBE (1) + TBA (3) in this work and those determined by Churkin et al. (1979) and by Zong et al. (1987). From the figure is deduced good agreement among the data of Churkin et al. and the data of this work, although it should be pointed out that the data of Churkin et al. do not include experimental determination of vapor-phase compositions. Nevertheless, the data of Zong et al. present an azeotropic behavior of the system, which can not be observed in our data.

Figure 2 shows the activity coefficients $\gamma_i$ that were calculated from the following equation (Van Ness and Abbott, 1982):

$$\ln \gamma_i = \ln \frac{y_i P}{x_i P_i^0} + \frac{(B_{ii} - V_i^L)(P - P_i^0)}{RT} + \frac{P}{2RT} \sum \sum y_i y_k (2\delta_{ji} - \delta_{jk}) \tag{2}$$

where $T$ and $P$ are the boiling point and the total pressure, $V_i^L$ is the molar liquid volume of component i, $B_{ii}$ and $B_{jj}$ are the second virial coefficients of the pure gases, $P_i^0$ is the vapor pressure, $B_{ij}$ the cross second virial coefficient and

$$\delta_{ij} = 2\,B_{ij} - B_{jj} - B_{ii} \tag{3}$$

**Table 3. Experimental Vapor-Liquid Equilibrium Data for MTBE (1) + TBA (3) at 101.3 kPa**

| $T$/K | $x_1$ | $y_3$ | $\gamma_1$ | $\gamma_3$ | $-B_{11}$/ $\mathrm{cm^3\ mol^{-1}}$ | $-B_{33}$/ $\mathrm{cm^3\ mol^{-1}}$ | $-B_{13}$/ $\mathrm{cm^3\ mol^{-1}}$ |
|---|---|---|---|---|---|---|---|
| 328.20 | 1.000 | 1.000 | 1.000 | | | | |
| 328.45 | 0.980 | 0.989 | 1.000 | 1.713 | 1138 | 1490 | 1295 |
| 328.75 | 0.949 | 0.973 | 1.006 | 1.656 | 1136 | 1485 | 1292 |
| 329.55 | 0.898 | 0.949 | 1.012 | 1.514 | 1129 | 1473 | 1284 |
| 330.25 | 0.846 | 0.926 | 1.025 | 1.399 | 1123 | 1463 | 1278 |
| 331.15 | 0.793 | 0.902 | 1.036 | 1.322 | 1115 | 1450 | 1269 |
| 331.95 | 0.743 | 0.880 | 1.053 | 1.257 | 1109 | 1438 | 1262 |
| 332.75 | 0.688 | 0.856 | 1.079 | 1.203 | 1102 | 1426 | 1254 |
| 333.85 | 0.637 | 0.832 | 1.096 | 1.141 | 1093 | 1411 | 1244 |
| 334.75 | 0.587 | 0.809 | 1.125 | 1.095 | 1086 | 1398 | 1236 |
| 335.85 | 0.538 | 0.783 | 1.150 | 1.058 | 1077 | 1383 | 1226 |
| 336.95 | 0.488 | 0.754 | 1.182 | 1.031 | 1068 | 1368 | 1216 |
| 338.15 | 0.439 | 0.719 | 1.208 | 1.021 | 1059 | 1352 | 1206 |
| 339.15 | 0.405 | 0.692 | 1.224 | 1.009 | 1051 | 1339 | 1197 |
| 340.45 | 0.359 | 0.654 | 1.257 | 0.995 | 1041 | 1323 | 1186 |
| 341.95 | 0.311 | 0.606 | 1.288 | 0.988 | 1030 | 1304 | 1174 |
| 343.75 | 0.260 | 0.539 | 1.304 | 0.997 | 1017 | 1282 | 1159 |
| 345.85 | 0.206 | 0.476 | 1.371 | 0.969 | 1002 | 1257 | 1142 |
| 347.85 | 0.156 | 0.390 | 1.406 | 0.977 | 988 | 1234 | 1127 |
| 350.05 | 0.107 | 0.290 | 1.424 | 0.986 | 973 | 1210 | 1110 |
| 352.45 | 0.059 | 0.170 | 1.430 | 0.994 | 957 | 1184 | 1092 |
| 354.05 | 0.028 | 0.086 | 1.444 | 0.998 | 947 | 1167 | 1080 |
| 355.60 | 0.000 | 0.000 | | 1.000 | | | |

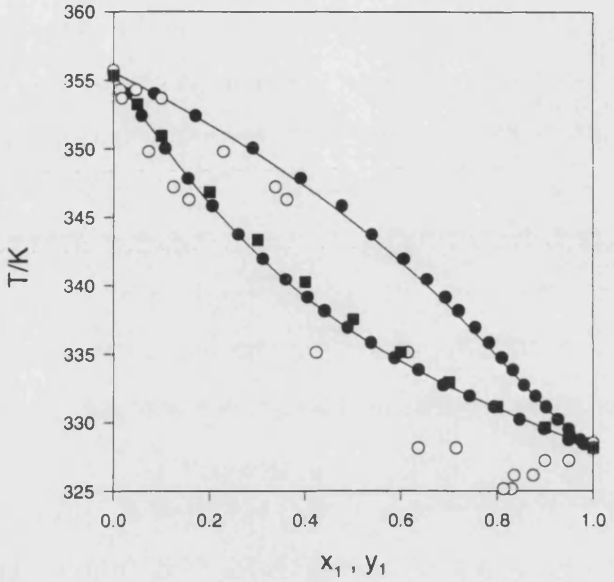

**Figure 1**. Boiling temperature diagram for the system MTBE (1) + TBA (3) at 101.3 kPa. Experimental data (●); data of Churkin et al. (1979) (■); data of Zong et al. (1987) (○); smoothed with the Legendre polynomial used in consistency test (—).

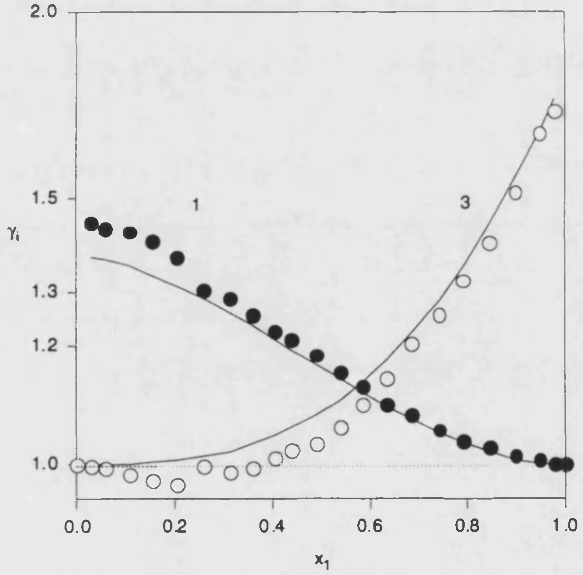

**Figure 2**. Activity coefficient plot for the system MTBE (1) + TBA (3) at 101.3 kPa. $\gamma_1$ (●); $\gamma_3$ (○); smoothed with the Legendre polynomial used in consistency test (—).

The standard state for calculation of activity coefficients is the pure component at the pressure and temperature of the solution. Equation 2 is valid at low and moderate pressures when the virial equation of state truncated after the second coefficient is adequate to describe the vapor phase of the pure components and their mixtures, and liquid volumes of the pure components are incompressible over the pressure range under consideration. The molar virial coefficients $B_{ii}$ and $B_{ij}$ were estimated by the method of Hayden and O'Connell (1975) using the molecular parameters suggested by Prausnitz et al. (1980). Critical properties of all components were taken from DIPPR (Daubert and Danner, 1989). The last two terms in eq 2, particularly the second one that expresses the correction due to the non ideal behaviour of the vapor phase, contributed less than 4.5% for the system MTBE + TBA; their influence was important only at very dilute concentrations. The calculated activity coefficients reported in Table 3 are estimated to be accurate to within ± 3%. The results reported in that Table indicate that the measured system exhibit positive deviation from ideal behavior and no azeotrope is present.

The VLE data reported in Table 3 were found to be thermodynamically consistent by the point-to-point method of Van Ness et al. (1973), as modified by Fredenslund et al. (1977). The pertinent statistics required by the Fredenslund et al. test together with the number of parameters of the Legendre polynomial used for consistency are shown in Table 4.

**Table 4. Consistency Test for the Binary Mixture MTBE (1) + TBA (3)**

| $n$ | $100 \times \mathrm{MAD}y_1$[a] | MAD$P$[b] /kPa |
|---|---|---|
| 2 | 0.69 | 0.23 |

[a] Mean absolute deviation in vapor phase composition. [b] Mean absolute deviation in pressure

The parameters of the Wilson, NRTL and UNIQUAC equations were obtained by minimizing the following objective function (OF):

$$\mathrm{OF} = \sum_{i=1}^{N} 100 \times \left( \left| \frac{P_i^{\mathrm{exptl}} - P_i^{\mathrm{calc}}}{P_i^{\mathrm{exptl}}} \right| + \left| y_i^{\mathrm{exptl}} - y_i^{\mathrm{calc}} \right| \right) \tag{4}$$

and are reported in Table 5, together with the pertinent statistics of VLE interpolation, for the data of the system MTBE (1) + 2-methylpentane (2) reported in Aucejo et al. (1998), and for the data of the system MTBE (1) + TBA (2) reported in this work. Inspection of the results given in Table 5 shows that all models are adequate to predict the binary data.

**Table 5. Parameters and Deviations between Experimental and Calculated Values for Different $G^E$ Models for the Binary Systems MTBE (1) + 2-Methylpentane (2) and MTBE (1) +TBA (3)**

| model | $A_{ij}$/ J mol$^{-1}$ | $A_{ji}$/ J mol$^{-1}$ | $\alpha_{ij}$ | Bubble-point pressures $\Delta P$ $^a$ /% | Bubble-point pressures $100 \times \Delta y^b$ | Dew-point pressures $\Delta P$ $^a$ /% | Dew-point pressures $100 \times \Delta x^b$ |
|---|---|---|---|---|---|---|---|
| | | | MTBE (1) + 2-methylpentane (2)$^e$ | | | | |
| $^c$Wilson | 523.28 | 22.45 | | 0.11 | 0.05 | 0.11 | 0.05 |
| NRTL | 272.05 | 265.27 | 0.2 | 0.11 | 0.05 | 0.11 | 0.05 |
| $^d$UNIQUAC | -119.81 | 261.33 | | 0.10 | 0.05 | 0.11 | 0.06 |
| | | | MTBE (1) + TBA (3) | | | | |
| $^c$Wilson | -687.80 | 2263.48 | | 0.56 | 0.84 | 1.34 | 1.17 |
| NRTL | 3080.07 | -1211.97 | 0.3 | 0.13 | 0.76 | 0.96 | 0.91 |
| $^d$UNIQUAC | 2267.27 | -1295.30 | | 0.32 | 0.61 | 0.95 | 0.64 |

[a] Average percentual deviation in pressure $\Delta P = 100 / \mathrm{N} \sum_i^{N} \left| P_i^{\mathrm{exptl}} - P_i^{\mathrm{calc}} \right| / P_i^{\mathrm{exptl}}$ (N : number of data points); [b] Average absolute deviation in vapor and liquid phase composition; [c] Liquid volumes have been estimated from the Rackett equation (Rackett, 1970); [d] Volume and surface parameters from DECHEMA (Gmehling and Oken, 1990). [E] Parameters calculated from data of Aucejo et al. (1998).

***Ternary System.*** The VLE data for the ternary system are shown in Table 6 and Figure 3.

**Table 6. Experimental Vapor-Liquid Equilibrium Data for MTBE (1) + 2-Methylpentane (2) + TBA (3) at 101.3 KPa**

| $T$ / K | $x_1$ | $x_2$ | $y_1$ | $y_2$ | $\gamma_1$ | $\gamma_2$ | $\gamma_3$ | $-B_{11}$ | $-B_{22}$ | $-B_{33}$ | $-B_{12}$ | $-B_{13}$ | $-B_{23}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | / $cm^3$ $mol^{-1}$ | | | |
| 328.65 | 0.719 | 0.233 | 0.735 | 0.234 | 1.006 | 1.164 | 2.067 | 1137 | 1354 | 1487 | 1217 | 1293 | 1011 |
| 328.95 | 0.890 | 0.047 | 0.915 | 0.052 | 1.003 | 1.276 | 1.616 | 1134 | 1351 | 1482 | 1215 | 1290 | 1009 |
| 329.15 | 0.500 | 0.432 | 0.524 | 0.424 | 1.016 | 1.119 | 2.379 | 1132 | 1348 | 1479 | 1213 | 1288 | 1008 |
| 329.35 | 0.598 | 0.292 | 0.622 | 0.310 | 1.002 | 1.204 | 1.889 | 1131 | 1346 | 1476 | 1211 | 1286 | 1006 |
| 329.65 | 0.397 | 0.493 | 0.420 | 0.499 | 1.008 | 1.136 | 2.252 | 1128 | 1343 | 1472 | 1208 | 1283 | 1004 |
| 329.75 | 0.310 | 0.643 | 0.340 | 0.607 | 1.044 | 1.056 | 3.376 | 1127 | 1342 | 1470 | 1207 | 1282 | 1003 |
| 329.85 | 0.780 | 0.091 | 0.827 | 0.107 | 1.005 | 1.321 | 1.520 | 1126 | 1341 | 1469 | 1206 | 1281 | 1002 |
| 330.15 | 0.197 | 0.708 | 0.215 | 0.689 | 1.025 | 1.076 | 2.998 | 1124 | 1337 | 1464 | 1203 | 1279 | 1000 |
| 330.25 | 0.301 | 0.514 | 0.323 | 0.557 | 1.002 | 1.195 | 1.925 | 1123 | 1336 | 1463 | 1202 | 1278 | 999 |
| 330.25 | 0.502 | 0.299 | 0.540 | 0.352 | 1.007 | 1.297 | 1.606 | 1123 | 1336 | 1463 | 1202 | 1278 | 999 |
| 330.55 | 0.096 | 0.809 | 0.107 | 0.784 | 1.038 | 1.057 | 3.357 | 1120 | 1333 | 1458 | 1199 | 1275 | 997 |
| 330.65 | 0.096 | 0.713 | 0.105 | 0.749 | 1.014 | 1.142 | 2.231 | 1120 | 1332 | 1457 | 1199 | 1274 | 996 |
| 330.65 | 0.195 | 0.593 | 0.211 | 0.648 | 1.001 | 1.188 | 1.936 | 1120 | 1332 | 1457 | 1199 | 1274 | 996 |
| 330.65 | 0.389 | 0.381 | 0.421 | 0.450 | 1.002 | 1.288 | 1.614 | 1120 | 1332 | 1457 | 1199 | 1274 | 996 |
| 330.75 | 0.589 | 0.190 | 0.648 | 0.242 | 1.014 | 1.385 | 1.431 | 1119 | 1331 | 1455 | 1198 | 1273 | 995 |
| 330.75 | 0.692 | 0.099 | 0.769 | 0.130 | 1.024 | 1.426 | 1.389 | 1119 | 1331 | 1455 | 1198 | 1273 | 995 |
| 331.15 | 0.047 | 0.904 | 0.056 | 0.859 | 1.091 | 1.017 | 4.967 | 1115 | 1327 | 1450 | 1194 | 1269 | 992 |
| 331.15 | 0.047 | 0.685 | 0.053 | 0.771 | 1.008 | 1.206 | 1.877 | 1115 | 1327 | 1450 | 1194 | 1269 | 992 |
| 331.15 | 0.302 | 0.397 | 0.341 | 0.507 | 1.027 | 1.368 | 1.435 | 1115 | 1327 | 1450 | 1194 | 1269 | 992 |
| 331.25 | 0.096 | 0.601 | 0.107 | 0.716 | 1.009 | 1.272 | 1.661 | 1114 | 1326 | 1448 | 1193 | 1268 | 992 |

| $T$ / K | $x_1$ | $x_2$ | $y_1$ | $y_2$ | $\gamma_1$ | $\gamma_2$ | $\gamma_3$ | $-B_{11}$ | $-B_{22}$ | $-B_{33}$ | $-B_{12}$ | $-B_{13}$ | $-B_{23}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | / cm$^3$ mol$^{-1}$ | | | | | |
| 331.25 | 0.195 | 0.498 | 0.218 | 0.612 | 1.014 | 1.313 | 1.567 | 1114 | 1326 | 1448 | 1193 | 1268 | 992 |
| 331.65 | 0.500 | 0.200 | 0.578 | 0.297 | 1.036 | 1.476 | 1.314 | 1111 | 1321 | 1442 | 1189 | 1264 | 989 |
| 331.95 | 0.394 | 0.286 | 0.454 | 0.393 | 1.023 | 1.437 | 1.304 | 1109 | 1318 | 1438 | 1186 | 1262 | 986 |
| 332.15 | 0.095 | 0.497 | 0.112 | 0.679 | 1.036 | 1.420 | 1.392 | 1107 | 1316 | 1435 | 1185 | 1260 | 985 |
| 332.35 | 0.195 | 0.392 | 0.234 | 0.567 | 1.047 | 1.497 | 1.297 | 1105 | 1314 | 1432 | 1183 | 1258 | 983 |
| 332.95 | 0.048 | 0.477 | 0.058 | 0.708 | 1.041 | 1.505 | 1.290 | 1100 | 1307 | 1423 | 1177 | 1252 | 979 |
| 333.05 | 0.304 | 0.288 | 0.371 | 0.438 | 1.047 | 1.544 | 1.207 | 1100 | 1306 | 1422 | 1176 | 1251 | 978 |
| 333.05 | 0.391 | 0.200 | 0.492 | 0.324 | 1.079 | 1.644 | 1.163 | 1100 | 1306 | 1422 | 1176 | 1251 | 978 |
| 333.45 | 0.095 | 0.397 | 0.120 | 0.639 | 1.065 | 1.608 | 1.213 | 1096 | 1302 | 1416 | 1173 | 1248 | 975 |
| 333.65 | 0.497 | 0.101 | 0.645 | 0.173 | 1.093 | 1.174 | 1.134 | 1095 | 1300 | 1414 | 1171 | 1246 | 974 |
| 333.65 | 0.576 | 0.051 | 0.745 | 0.087 | 1.091 | 1.694 | 1.128 | 1095 | 1300 | 1414 | 1171 | 1246 | 974 |
| 334.35 | 0.192 | 0.284 | 0.255 | 0.506 | 1.097 | 1.731 | 1.114 | 1089 | 1293 | 1404 | 1165 | 1240 | 969 |
| 334.75 | 0.301 | 0.189 | 0.414 | 0.355 | 1.120 | 1.808 | 1.083 | 1086 | 1289 | 1398 | 1161 | 1236 | 966 |
| 335.55 | 0.095 | 0.293 | 0.134 | 0.580 | 1.125 | 1.859 | 1.081 | 1079 | 1281 | 1387 | 1154 | 1229 | 960 |
| 336.85 | 0.047 | 0.273 | 0.071 | 0.609 | 1.139 | 2.011 | 1.031 | 1069 | 1267 | 1370 | 1143 | 1217 | 951 |
| 336.85 | 0.389 | 0.061 | 0.605 | 0.138 | 1.191 | 2.052 | 1.013 | 1069 | 1267 | 1370 | 1143 | 1217 | 951 |
| 337.85 | 0.297 | 0.092 | 0.480 | 0.224 | 1.204 | 2.139 | 1.003 | 1061 | 1257 | 1356 | 1134 | 1209 | 944 |
| 338.05 | 0.193 | 0.147 | 0.316 | 0.368 | 1.210 | 2.180 | 0.988 | 1060 | 1255 | 1354 | 1132 | 1207 | 943 |
| 339.05 | 0.092 | 0.179 | 0.157 | 0.473 | 1.220 | 2.248 | 1.000 | 1052 | 1246 | 1341 | 1124 | 1198 | 936 |
| 342.25 | 0.193 | 0.057 | 0.393 | 0.190 | 1.330 | 2.582 | 0.952 | 1028 | 1215 | 1300 | 1097 | 1171 | 914 |
| 343.25 | 0.092 | 0.093 | 0.192 | 0.326 | 1.326 | 2.645 | 0.971 | 1021 | 1206 | 1288 | 1089 | 1163 | 908 |
| 348.15 | 0.046 | 0.048 | 0.120 | 0.226 | 1.454 | 3.106 | 0.966 | 986 | 1162 | 1231 | 1051 | 1124 | 877 |

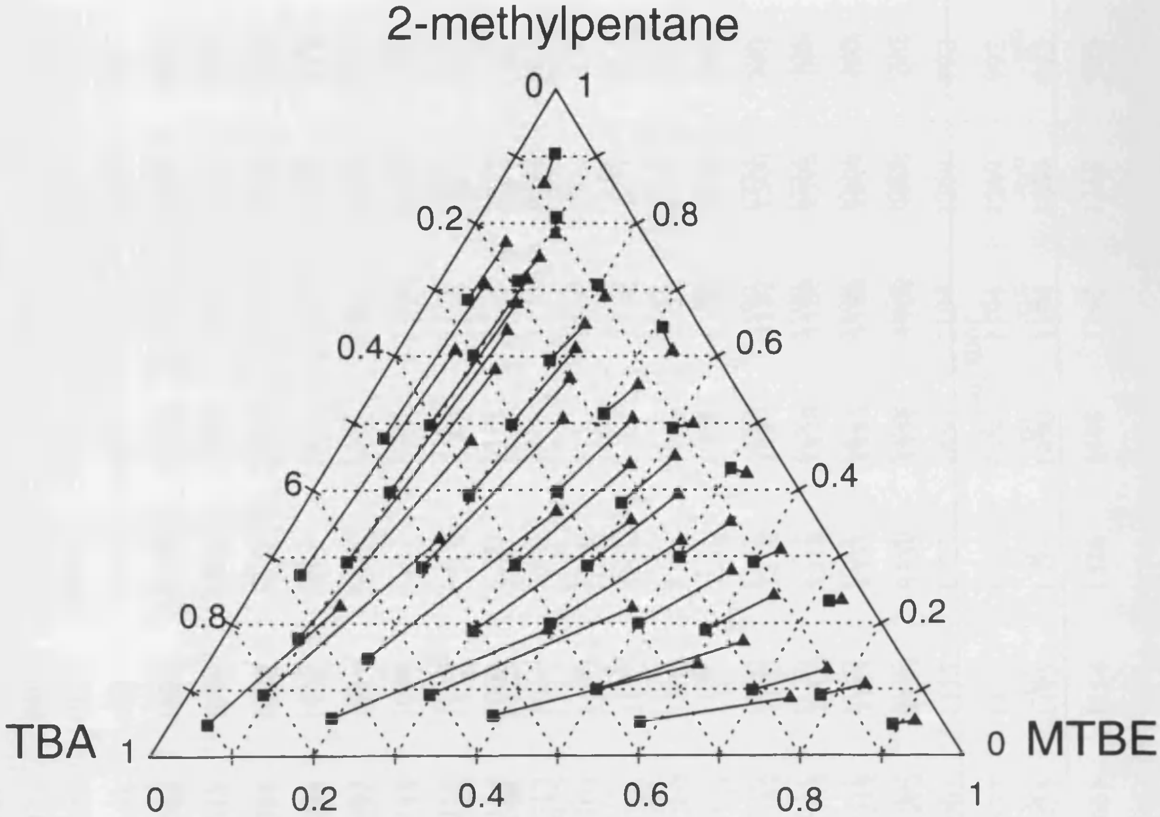

**Figure 3**. Diagram of VLE for the ternary system MTBE (1) + 2-methylpentane (2) + TBA (3) at 101.3 kPa: (■) liquid phase mole fractions; (▲) vapor phase mole fractions.

The activity coefficients $\gamma_i$ were calculated from eq 2 and the molar virial coefficients were estimated in the same way than the binary system. The ternary data were found to be thermodynamically consistent, as tested by the L-W method of Wisniak (1993) and the McDermott-Ellis method (1965) modified by Wisniak and Tamir (1977). The test requires that $D<D_{max}$ for every experimental point where the local deviation $D$ is given by:

$$D=\sum_{i=1}^{N}(x_{ia}+x_{ib})(\ln\gamma_{ia}-\ln\gamma_{ib}) \tag{5}$$

and $N$ is the number of components. The maximum deviation $D_{max}$ is given by:

$$
\begin{aligned}
D_{max} &= \sum_{i=1}^{N}(x_{ia}+x_{ib})\left(\frac{1}{x_{ia}}+\frac{1}{y_{ia}}+\frac{1}{x_{ib}}+\frac{1}{y_{ib}}\right)\Delta x \\
&+\sum_{i=1}^{N}(x_{ia}+x_{ib})\frac{\Delta P}{p}+2\sum_{i=1}^{N}\left|\ln\gamma_{b}-\ln\gamma_{ia})\right|\Delta x \\
&+\sum_{i=1}^{N}(x_{ia}+x_{ib})B_{j}\left\{(T_{a}+C_{j})^{-2}+(T_{b}+C_{j})^{-2}\right\}\Delta T
\end{aligned}
\tag{6}
$$

The error in the measurements $\Delta x$, $\Delta P$ and $\Delta T$ were as previously indicated.

Vapor-liquid equilibrium was correlated by using Wilson, NRTL, and UNIQUAC models for the activity coefficients of the components with the binary interaction parameters. The values of the binary interaction parameters for the binary 2-methylpentane (2) + TBA (3) were used from the data of Aucejo et al. (1999a), and corresponding parameters of the systems MTBE (1) + 2-methylpentane (2) and MTBE (1) + TBA (3) were calculated in this work and appear in Table 5. Table 7 shows the pertinent statistics of VLE interpolation. The three models yield similar deviations, representing the data successfully.

The boiling points of the systems were correlated by the equation proposed by Wisniak and Tamir (1976):

$$
\begin{aligned}
T/K &= \sum_{i=1}^{n}x_{i}T_{i}^{o}+\sum_{i,j=1}^{n}\left\{x_{i}x_{j}\sum_{k=0}^{m}C_{k}(x_{i}-x_{j})^{k}\right\} \\
&+x_{1}x_{2}x_{3}\{A+B(x_{1}-x_{2})+C(x_{1}-x_{3})+D(x_{2}-x_{3})\}
\end{aligned}
\tag{7}
$$

In this equation *n* is the number of components (*n*=2 or 3), $T_i^o$ is the boiling point of the pure component *i,* and *m* is the number of terms considered in the series expansion of ($x_i$-$x_j$). $C_k$ are the binary constants where A, B, C and D are ternary constants. The following equation, of the same structure, has been suggested by Tamir (1981) for the direct correlation of ternary data, without use of binary data:

**Table 7. Correlation of Experimental Ternary Data with Wilson, NRTL, and UNIQUAC Equations Using Binary Interaction Parameters**

| Model | $ij$ | $A_{ij}$ / J.mol$^{-1}$ | $A_{ji}$ / J.mol$^{-1}$ | $\alpha_{ij}$ | System | Buble-point pressures | | | Dew-point pressures | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | $\Delta P^{e}$ / % | 100 x $\Delta y_1{}^{f}$ | 100 x $\Delta y_2{}^{f}$ | $\Delta P^{e}$ / % | 100 x $\Delta x_1{}^{f}$ | 100 x $\Delta x_2{}^{f}$ |
| | 1-2$^{c}$ | 523.28 | 22.45 | | | | | | | | |
| $^{a}$Wilson | 1-3$^{c}$ | -687.80 | 2263.48 | | 1+2+3 | 0.59 | 0.24 | 0.77 | 1.35 | 0.57 | 0.73 |
| | 2-3$^{d}$ | -14.98 | 5658.90 | | | | | | | | |
| | 1-2$^{c}$ | 272.05 | 265.27 | 0.20 | | | | | | | |
| NRTL | 1-3$^{c}$ | 3080.07 | -1211.97 | 0.30 | 1+2+3 | 0.47 | 0.27 | 0.67 | 1.15 | 0.51 | 0.97 |
| | 2-3$^{d}$ | 4362.09 | 983.72 | 0.47 | | | | | | | |
| | 1-2$^{c}$ | -119.81 | 261.33 | | | | | | | | |
| $^{b}$UNIQUAC | 1-3$^{c}$ | 2267.27 | -1295.30 | | 1+2+3 | 0.72 | 0.32 | 0.77 | 1.08 | 0.41 | 0.87 |
| | 2-3$^{d}$ | 2844.32 | -1030.28 | | | | | | | | |

[a] Liquid volumes have been estimated from the Racket equation (Rackett, 1970). [b] Volume and surface parameters from DECHEMA (Gmehling and Onken, 1990). [c] Calculated in this work. [d] Aucejo et al. (1999a). [e] Average percentual deviation in bubble and dew pressure: $\Delta P = 100/N \Sigma \mid P_i^{expt} - P_i^{calc} \mid / P_i^{expt}$ ($N$: number of data points). [f] Average absolute deviation in composition $\Delta y = 1/N \Sigma \mid y_i^{expt} - y_i^{calc} \mid$ ; $\Delta x = 1/N \Sigma \mid x_i^{expt} - x_i^{calc} \mid$

$$
\begin{aligned}
T/K = \sum_{i=1}^{3} x_i T_i^o &+ x_1x_2\left[A_{12} + B_{12}(x_1 - x_2) + C_{12}(x_1 - x_2)^2 + \ldots\right] \\
&+ x_1x_3\left[A_{13} + B_{13}(x_1 - x_3) + C_{13}(x_1 - x_3)^2 + \ldots\right] \\
&+ x_2x_3\left[A_{23} + B_{23}(x_2 - x_3) + C_{23}(x_2 - x_3)^2 + \ldots\right]
\end{aligned}
\qquad (8)
$$

In eq 8 coefficients $A_{ij}$, $B_{ij}$, and $C_{ij}$ are not binary constants, they are multicomponent parameters determined directly from the data. Direct correlation of $T(x)$ for ternary mixtures can be very efficient as reflected by a lower percent average deviation and root mean square deviation (rmsd) and a smaller number of parameters than those for eq 7. The various constants of eqs 7 and 8 are reported in Table 8, which also contains information indicating the degree of goodness of the correlation. The values of the binary constants for MTBE (1) + 2-methylpentane (2) were recalculated from the data of Aucejo et al. (1998). For the binary system 2-methylpentane (2) + TBA (3), the binary constants were taken from Aucejo et al. (1999b). Corresponding parameters of the system MTBE (1) + TBA (3) were calculated from the data of this work. In Fig. 4 show the boiling isotherms for the ternary system calculated by direct fit which gives a better fit.

**Table 8. Coefficients in Correlation of Boiling Points, Eqs 7 and 8, Maximum, Average and Root Mean Square Deviations in Temperature (rmsd)**

**A. Equation 7 (fit from binary constants)**

| *A* | *B* | *C* | *D* | max dev. /K | avr dev /K | rmsd[a] /K |
|---|---|---|---|---|---|---|
| 12.85 | 2.74 | 4.06 | 0.00 | 0.57 | 0.15 | 0.032 |

Binary constants

| System | $C_0$ | $C_1$ | $C_2$ | max dev. /K | avr dev /K | rmsd[a] /K |
|---|---|---|---|---|---|---|
| MTBE (1) + 2-methylpentane (2)[b] | -6.69 | 1.90 | -0.75 | 0.08 | 0.02 | 0.007 |
| MTBE (1) + TBA (3) | -20.80 | 6.92 | -1.55 | 0.12 | 0.04 | 0.012 |
| 2-methylpentane (2) + TBA (3)[c] | -42.25 | 18.00 | -43.88 | 0.90 | 0.38 | 0.102 |

**B. Equation 8 (direct fit)**

| *ij* | $A_{ij}$ | $B_{ij}$ | $C_{ij}$ | max. dev. /K | avr. dev. /K | rmsd[a] /K |
|---|---|---|---|---|---|---|
| 1-2 | -5.59 | 1.89 | -7.63 | 0.44 | 0.13 | 0.026 |
| 1-3 | -18.49 | 8.89 | -4.55 | | | |
| 2-3 | -42.88 | 19.77 | -32.61 | | | |

[a] rmsd (T/K): Root mean square deviation, $\left\{\sum(T_{exp}-T_{cal})^2\right\}^{0.5}/N$. [b] Recalculated constants from data of Aucejo et al. (1998). [c] Constants from Aucejo et al. (1999b).

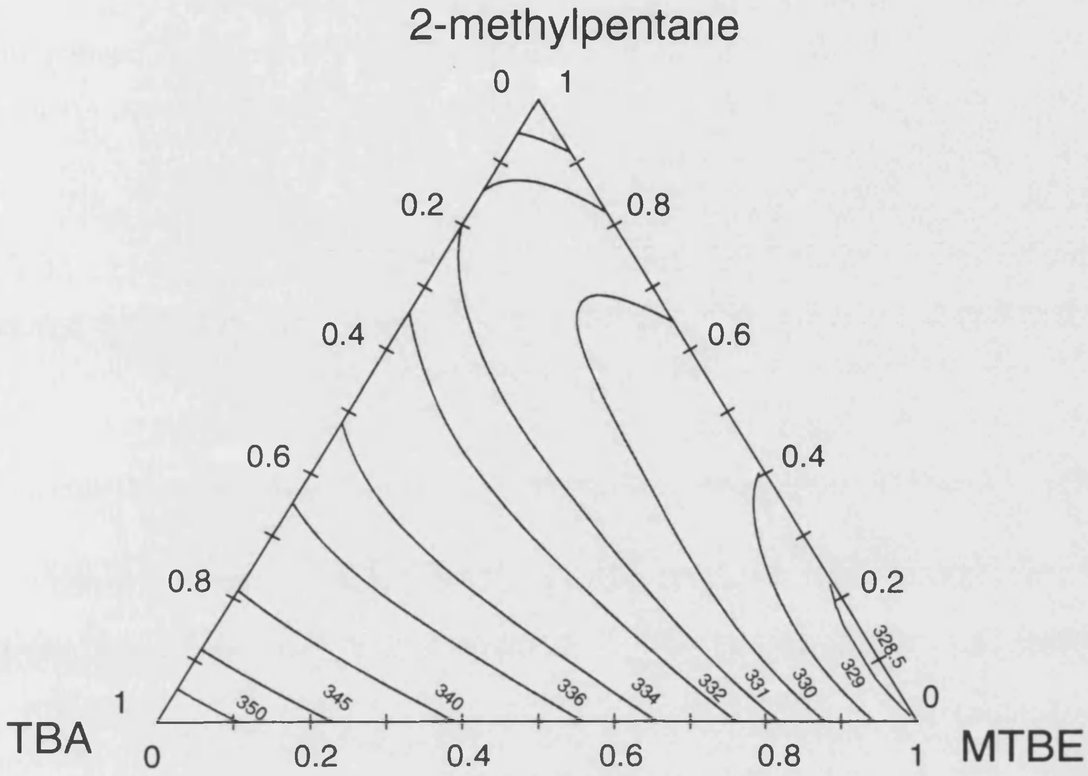

**Figure 4**. Isothermals (K) for the ternary system MTBE (1) + 2-methylpentane (2) + TBA (3) at 101.3 kPa, calculated with direct fit, eq 8.

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# 4.9. PHASE EQUILIBRIA IN THE SYSTEMS 2-METHYL-2-PROPANOL + METHYL 1,1-DIMETHYLPROPYL ETHER AND 2-METHYLPENTANE + 2-METHYL-2-PROPANOL + METHYL 1,1-DIMETHYLPROPYL ETHER

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## ABSTRACT

Consistent vapor-liquid equilibrium data for the binary and ternary systems 2-methyl-2-propanol (TBA) + methyl 1,1-dimethylpropyl ether (TAME) and 2-methylpentane + 2-methyl-2-propanol (TBA) + methyl 1,1-dimethylpropyl ether (TAME) are reported at 101.3 kPa. The results indicate that the systems deviate positively from ideality and that only the binary system presents an azeotrope. The ternary system is well predicted from binary data. The activity coefficients and boiling points of the solutions were correlated with its composition by Wilson, UNIQUAC, NRTL and Wisniak-Tamir equations.

## Introduction.

Ethers and alkanols used as gasoline additive are excellent antiknock quality and environmental protection substances. Light alkanols like methanol and ethanol are commonly used as oxygenating additives. 2-Methyl-2-propanol (TBA) is added in the oxygenated gasolines with ethanol to avoid the formation of two liquid phases in presence of small quantities of water. In other hand, Methyl 1,1-dimethylethyl ether (MTBE) is the primary oxygenated compound being used to reformulate gasolines. However, potential and documented contamination of water resources by MTBE has become a major public issue over the past few years, and restrictions in its use as additive are expected. This fact promotes further research with other ethers as potential additives. Methyl 1,1-dimethylpropyl ether (TAME) is effective at reducing automotive CO emissions and it has been considered a good alternative to MTBE as additive gasoline.

Phase equilibrium data of oxygenated mixtures are important for predicting the vapor-phase composition that would be in equilibrium with hydrocarbon mixtures, and the systems reported here constitute examples of such mixtures. The present work was undertaken to measure vapor-liquid equilibrium (VLE) data of the ternary system 2-methylpentane (1) + TBA (2) + TAME (3) and constituent binary system TBA (2) + TAME (3) at 101.3 kPa. For these systems no VLE data have been previously published. For the other binary constituent systems 2-methylpentane (1) + TAME (3) and 2-methylpentane (1) + TBA (2), VLE data at 101.3 kPa have already been reported by Aucejo et al. (1998) and Aucejo et al. (1999), respectively. Both systems present positive deviations from ideality: the first one presents a minimum boiling point azeotrope and the second one can be described as symmetric solutions and presents no azeotrope.

## Experimental Section

***Chemicals.*** 2-Methylpentane (99+ mass %, GC grade), TBA (99.5 mass %, HPLC grade) and TAME (97 mass %) were purchased from Aldrich Chemie Co. 2-Methylpentane and TBA were used without further purification after chromatography failed to show any significant impurities. TAME was purified to 99.9+ mass % by batch distillation in a Fischer SPALTROHR-column HMS-500, controlled by a Fischer System D301-C. The densities of the pure liquids were measured at 298.15 K using an Anton Paar DMA 55 densimeter. The refractive indexes of the pure liquids were measured at 298.15 K in an Abbe refractometer, Atago 3T. Temperature was controlled to ±0.01 K with a thermostated bath. The accuracies in density and refractive index measurements are ±0.01 kg m$^{-3}$ and ±0.0002, respectively. The experimental values of these properties and the boiling points are given in Table 1 together with those given in literature.

**Table 1. Density, $d$, Refractive Index, $n_D$, and Normal Boiling Point, $T_b$, of the Chemicals.**

| component | $d$(298.15K) /Kg m$^{-3}$ | | $n_D$ (298.15K) | | $T_b$ (101.3 kPa) /K | |
|---|---|---|---|---|---|---|
| | exptl. | lit. | exptl. | lit. | exptl. | lit. |
| 2-Methylpentane | 648.39 | 648.86[a] | 1.3689 | 1.3687[b] | 333.4 | 333.41[b] |
| 2-Methyl-2-propanol | 775.40[c] | 775.43[c,d] | 1.3851 | 1.3859[b] | 355.6 | 355.52[e] |
| Methyl 1,1-dimethylpropyl ether | 765.94 | 765.77[f] | 1.3858 | 1.3859[b] | 359.3 | 359.33[g] |

[a] Awwad and Pethrick (1983). [b] DIPPR (Daubert and Danner, 1998). [c] Measured to 303.15 K. [d] Hales et al. (1983). [e] Ambrose and Sprake (1970). [f] Linek (1987). [g] Martínez-Ageitos (1996).

***Apparatus and procedure.*** An all glass Fischer LABODEST vapor-liquid-equilibrium apparatus model 602/D, manufactured by Fischer Labor und Verfahrenstechnik (Germany), was used in the equilibrium determinations. The equilibrium vessel was a dynamic-recirculating still described by Walas (1985), equipped with a Cottrell circulation pump. The still is capable of handling pressures from 0.25 to 400 kPa, and temperature up to 523 K. The Cottrell pump ensures that both liquid and vapor phases are in intimate contact during boiling and also in contact with the temperature sensing element.

The equilibrium temperature was measured with a digital Fischer thermometer with an accuracy of ±0.1 K. The apparatus is equipped with two digital sensors of pressure: one for the low pressure zone with an accuracy of ±0.01 kPa, and another one for the high pressures with an accuracy of ±0.1 kPa. The temperature probe was calibrated against the ice and steam points of distilled water. The manometers were calibrated using the vapor pressure of ultrapure water. The still was operated under constant pressure until equilibrium was reached. Equilibrium conditions were assumed when constant temperature and pressure were obtained for 60 min or longer. Then, samples of liquid and condensate were taken for analysis. The sample extractions were carried out with special syringes that allowed one to withdraw small volume samples (1.0μL) in a system under partial vacuum or under overpressure conditions.

***Analysis.*** Compositions of the liquid and condensed vapor phase samples were determined using a Hewlett-Packard 5890 S-II gas chromatograph (GC), after calibration with gravimetrically prepared standard solutions. A flame ionization detector was used together with a 60 m, 0.2 mm i.d., fused silica capillary column, SUPELCOWAX 10. The GC response peaks were integrated with a Hewlett-Packard 3396 integrator. Column, injector and detector temperatures were 343, 423, 473 K for the two systems. Very good separation was achieved under these conditions, and calibration analyses were carried out to convert the peak ratio to the mass composition of the sample. At least three analyses were made of each composition; the standard deviation in the mole fraction was usually less than 0.001.

## Results and Discussion

Vapor pressures $P_i^o$ were calculated with the Antoine equation whose parameters $A_i$, $B_i$, and $C_i$ are reported in Table 2.

$$\ln(P_i^\circ/\mathrm{kPa}) = A_i - \frac{B_i}{(T/\mathrm{K}) - C_i} \tag{1}$$

The Antoine constants for 2-methylpentane and TAME were taken from Aucejo et al. (1998). For TBA, the values given in Aucejo et al. (1999) were used.

**Table 2. Antoine Coefficients, Equation 1**

| compound | $A_i$ | $B_i$ | $C_i$ |
|---|---|---|---|
| 2-methylpentane[a] | 14.0614 | 2791.52 | 37.75 |
| 2-methyl-2-propanol[b] | 14.8533 | 2649.89 | 96.69 |
| methyl 1,1-dimethylpropyl ether[a] | 14.3501 | 3111.28 | 39.52 |

[a] Aucejo et al. (1998). [b] Aucejo et al. (1999).

***Binary System.*** The temperature $T$, the liquid-phase $x_i$ and vapor-phase $y_i$ mole fractions at 101.3 kPa are reported in Table 3 and are shown in Figure 1. Figure 2 shows the activity coefficients $\gamma_i$ that were calculated from the following equation (Van Ness and Abbott, 1982):

$$\ln\gamma_i = \ln\frac{y_i P}{x_i P_i^0} + \frac{\left(B_{ii} - V_i^L\right)\left(P - P_i^0\right)}{RT} + \frac{P}{2RT}\sum\sum y_i y_k \left(2\delta_{ji} - \delta_{jk}\right) \qquad (2)$$

where $T$ and $P$ are the boiling point and the total pressure, $V_i^L$ is the molar liquid volume of component i, $B_{ii}$ and $B_{jj}$ are the second virial coefficients of the pure gases, $P_i^0$ is the vapor pressure, $B_{ij}$ the cross second virial coefficient and

$$\delta_{ij} = 2\,B_{ij} - B_{jj} - B_{ii} \qquad (3)$$

The standard state for calculation of activity coefficients is the pure component at the pressure and temperature of the solution. Equation 2 is valid at low and moderate pressures when the virial equation of state truncated after the second coefficient is adequate to describe the vapor phase of the pure components and their mixtures, and liquid volumes of the pure components are incompressible over the pressure range under consideration. The molar virial coefficients $B_{ii}$ and $B_{ij}$ were estimated by the method of Hayden and O'Connell (1975) using the molecular parameters suggested by Prausnitz et al. (1980) and are shown in Table 3.

**Table 3. Experimental Vapor-Liquid Equilibrium Data for TBA (2) + TAME (3) at 101.3 kPa**

| $T$/K | $x_2$ | $y_3$ | $\gamma_2$ | $\gamma_3$ | $B_{22}$/ cm$^3$ mol$^{-1}$ | $B_{33}$/ cm$^3$ mol$^{-1}$ | $B_{23}$/ cm$^3$ mol$^{-1}$ |
|---|---|---|---|---|---|---|---|
| 359.30 | 0.000 | 0.000 | | 1.000 | | | |
| 358.25 | 0.021 | 0.043 | 1.821 | 1.006 | -1125 | -1366 | -1229 |
| 357.15 | 0.052 | 0.098 | 1.794 | 1.010 | -1136 | -1377 | -1238 |
| 356.15 | 0.099 | 0.172 | 1.700 | 1.005 | -1146 | -1387 | -1247 |
| 355.15 | 0.149 | 0.234 | 1.602 | 1.014 | -1156 | -1397 | -1255 |
| 354.55 | 0.198 | 0.282 | 1.483 | 1.027 | -1162 | -1403 | -1261 |
| 353.95 | 0.248 | 0.328 | 1.410 | 1.043 | -1168 | -1410 | -1266 |
| 353.55 | 0.297 | 0.367 | 1.336 | 1.065 | -1172 | -1414 | -1269 |
| 353.25 | 0.347 | 0.406 | 1.282 | 1.084 | -1175 | -1417 | -1272 |
| 353.05 | 0.395 | 0.444 | 1.237 | 1.104 | -1177 | -1419 | -1274 |
| 352.95 | 0.440 | 0.475 | 1.195 | 1.128 | -1179 | -1420 | -1274 |
| 352.85 | 0.491 | 0.507 | 1.147 | 1.169 | -1180 | -1421 | -1275 |
| 352.85 | 0.541 | 0.549 | 1.127 | 1.187 | -1180 | -1421 | -1275 |
| 352.85 | 0.581 | 0.576 | 1.102 | 1.221 | -1180 | -1421 | -1275 |
| 352.95 | 0.645 | 0.627 | 1.076 | 1.265 | -1179 | -1420 | -1274 |
| 353.15 | 0.696 | 0.665 | 1.050 | 1.316 | -1176 | -1418 | -1273 |
| 353.35 | 0.745 | 0.710 | 1.037 | 1.357 | -1174 | -1416 | -1271 |
| 353.65 | 0.793 | 0.755 | 1.026 | 1.394 | -1171 | -1413 | -1268 |
| 353.95 | 0.842 | 0.805 | 1.018 | 1.440 | -1168 | -1410 | -1266 |
| 354.35 | 0.892 | 0.859 | 1.010 | 1.505 | -1164 | -1406 | -1262 |
| 354.85 | 0.943 | 0.924 | 1.007 | 1.522 | -1159 | -1400 | -1258 |
| 355.25 | 0.974 | 0.964 | 1.002 | 1.566 | -1155 | -1396 | -1254 |
| 355.60 | 1.000 | 1.000 | 1.000 | | | | |

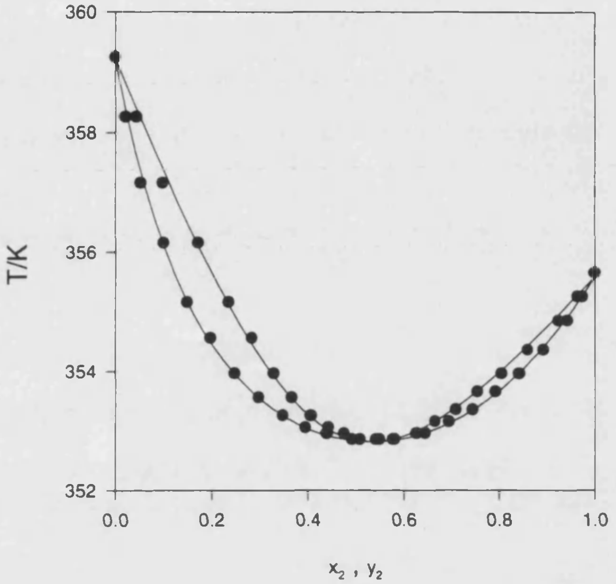

**Figure 1.** Boiling temperature diagram for the system TBA (2) + TAME (3) at 101.3 kPa. Experimental data (●); smoothed with the Legendre polynomial used in consistency test (—).

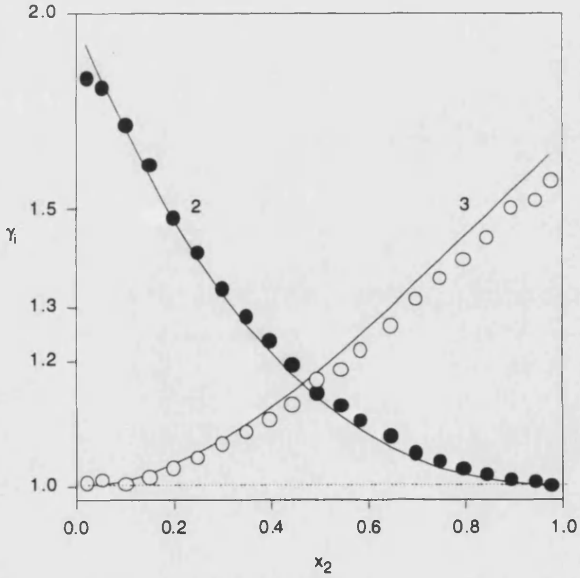

**Figure 2.** Activity coefficient plot for the system TBA (2) + TAME (3) at 101.3 kPa. $\gamma_2$ (●); $\gamma_3$ (○); smoothed with the Legendre polynomial used in consistency test (—).

Critical properties of all components were taken from DIPPR (Daubert and Danner, 1989). The last two terms in eq 2, particularly the second one that expresses the correction due to the non ideal behavior of the vapor phase, contributed less than 2.5% for the system TBA + TAME. The calculated activity coefficients reported in Table 3 are estimated to be accurate to within ± 3%. The results reported in that Table indicate that the measured system positive deviation from ideal behavior and an azeotrope composition is present at $x_1 \approx 0.54$ and $T = 352.85$ K.

The VLE data reported in Table 3 were found to be thermodynamically consistent by the point-to-point method of Van Ness et al. (1973), as modified by Fredenslund et al. (1977). The pertinent statistics required by the Fredenslund test together with the number of parameters of the Legendre polynomial used for consistency are shown in Table 4.

**Table 4. Consistency Test for the Binary Mixture TBA (2) + TAME (3)**

| $n$ | $100 \times \mathrm{MAD}y_2$[a] | MAD$P$[b] /kPa |
|---|---|---|
| 2 | 0.44 | 0.19 |

[a] Mean absolute deviation in vapor phase composition. [b] Mean absolute deviation in pressure.

The parameters of the Wilson, NRTL and UNIQUAC equations were obtained by minimizing the following objective function (OF):

$$\mathrm{OF} = \sum_{i=1}^{N} 100 \times \left( \left| \frac{P_i^{\mathrm{exptl}} - P_i^{\mathrm{calc}}}{P_i^{\mathrm{exptl}}} \right| + \left| y_i^{\mathrm{exptl}} - y_i^{\mathrm{calc}} \right| \right) \tag{4}$$

and are reported in Table 5, together with the pertinent statistics of VLE interpolation, for the data of the system 2-methylpentane (1) + TAME (3) reported in Aucejo et al. (1998), and for the data of the system TBA (2) + TAME (3) reported in this work. Inspection of the results given in Table 5 shows that all models are adequate to predict the binary data.

**Table 5. Parameters and Deviations between Experimental and Calculated Values for Different $G^E$ Models for the Binary Systems 2-Methylpentane (1) + TAME (3) and TBA (2) + TAME (3)**

| model | $A_{ij}$/ J mol$^{-1}$ | $A_{ji}$/ J mol$^{-1}$ | $\alpha_{ij}$ | bubble-point pressures $\Delta P$ [a] /% | bubble-point pressures $100 \times \Delta y$ [b] | dew-point pressures $\Delta P$ [a] /% | dew-point pressures $100 \times \Delta x$ [b] |
|---|---|---|---|---|---|---|---|
| | | | 2-methylpentane (1) + TAME (3)[e] | | | | |
| [c]Wilson | -575.18 | 1112.85 | | 0.24 | 0.81 | 0.90 | 0.90 |
| NRTL | -504.22 | 953.38 | 0.2 | 0.21 | 0.88 | 0.88 | 1.00 |
| [d]UNIQUAC | -377.67 | 509.97 | | 0.21 | 0.87 | 0.87 | 0.99 |
| | | | TBA (2) + TAME (3) | | | | |
| [c]Wilson | 2634.43 | -646.82 | | 0.23 | 0.40 | 0.20 | 0.44 |
| NRTL | -163.00 | 2120.81 | 0.3 | 0.24 | 0.39 | 0.21 | 0.43 |
| [d]UNIQUAC | -937.11 | 1774.84 | | 0.20 | 0.42 | 0.20 | 0.47 |

[a] Average percentual deviation in pressure $\Delta P = 100 / N \sum_{i}^{N} \left| P_i^{exptl} - P_i^{calc} \right| / P_i^{exptl}$ (N : number of data points); [b] Average absolute deviation in vapor and liquid phase composition; [c] Liquid volumes have been estimated from the Rackett equation (Rackett, 1970); [d] Volume and surface parameters from DECHEMA (Gmehling and Onken, 1990). [e] Parameters calculated from data of Aucejo et al. (1998).

***Ternary System.*** The VLE data for the ternary system are shown in Table 6 and Figure 3. The activity coefficients $\gamma_i$ were calculated from eq 2 and the molar virial coefficients were estimated as well as for the binary system. The ternary data were found to be thermodynamically consistent, as tested by the L-W method of Wisniak (1993) and the McDermott-Ellis method (1965) modified by Wisniak and Tamir (1977). The test requires that $D < D_{max}$ for every experimental point, where the local deviation $D$ is given by:

**Table 6. Experimental Vapor-Liquid Equilibrium Data for 2-Methylpentane (1) + TBA (2) + TAME (3) at 101.3 KPa**

| T (K) | $x_1$ | $x_2$ | $y_1$ | $y_2$ | $\gamma_1$ | $\gamma_2$ | $\gamma_3$ | $-B_{11}$ | $-B_{22}$ | $-B_{33}$ | $-B_{12}$ | $-B_{13}$ | $-B_{23}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | ($cm^3\ mol^{-1}$) | | | | | |
| 331.95 | 0.928 | 0.048 | 0.901 | 0.090 | 1.013 | 5.182 | 0.966 | 1318 | 1438 | 1672 | 986 | 1463 | 1483 |
| 335.85 | 0.726 | 0.048 | 0.816 | 0.081 | 1.044 | 3.876 | 0.949 | 1277 | 1383 | 1620 | 958 | 1418 | 1440 |
| 340.45 | 0.522 | 0.046 | 0.698 | 0.074 | 1.086 | 3.022 | 0.942 | 1232 | 1323 | 1562 | 926 | 1368 | 1392 |
| 345.85 | 0.319 | 0.045 | 0.521 | 0.074 | 1.139 | 2.428 | 0.955 | 1182 | 1257 | 1498 | 891 | 1312 | 1339 |
| 353.35 | 0.108 | 0.030 | 0.234 | 0.058 | 1.239 | 2.100 | 0.976 | 1118 | 1174 | 1416 | 845 | 1241 | 1271 |
| 350.05 | 0.151 | 0.090 | 0.308 | 0.142 | 1.269 | 1.977 | 0.952 | 1145 | 1210 | 1451 | 865 | 1271 | 1300 |
| 349.85 | 0.145 | 0.109 | 0.295 | 0.164 | 1.272 | 1.887 | 0.960 | 1147 | 1212 | 1453 | 866 | 1273 | 1302 |
| 344.95 | 0.292 | 0.106 | 0.487 | 0.144 | 1.192 | 2.096 | 0.946 | 1190 | 1268 | 1508 | 897 | 1321 | 1348 |
| 342.15 | 0.386 | 0.103 | 0.584 | 0.136 | 1.171 | 2.289 | 0.927 | 1216 | 1302 | 1541 | 915 | 1350 | 1375 |
| 339.35 | 0.497 | 0.101 | 0.669 | 0.130 | 1.128 | 2.528 | 0.927 | 1243 | 1337 | 1575 | 934 | 1379 | 1404 |
| 336.85 | 0.602 | 0.105 | 0.735 | 0.130 | 1.101 | 2.726 | 0.926 | 1267 | 1370 | 1607 | 951 | 1407 | 1430 |
| 334.55 | 0.710 | 0.101 | 0.792 | 0.127 | 1.077 | 3.059 | 0.938 | 1291 | 1401 | 1637 | 967 | 1433 | 1454 |
| 332.85 | 0.801 | 0.099 | 0.835 | 0.125 | 1.059 | 3.332 | 0.934 | 1308 | 1425 | 1659 | 980 | 1452 | 1473 |
| 332.95 | 0.710 | 0.189 | 0.799 | 0.162 | 1.140 | 2.244 | 0.909 | 1307 | 1423 | 1658 | 979 | 1451 | 1472 |
| 335.05 | 0.608 | 0.191 | 0.743 | 0.170 | 1.163 | 2.121 | 0.925 | 1286 | 1394 | 1630 | 964 | 1427 | 1449 |
| 337.35 | 0.501 | 0.194 | 0.675 | 0.180 | 1.198 | 1.991 | 0.940 | 1262 | 1363 | 1600 | 948 | 1401 | 1424 |
| 339.95 | 0.399 | 0.200 | 0.600 | 0.194 | 1.241 | 1.845 | 0.934 | 1237 | 1329 | 1568 | 930 | 1373 | 1397 |
| 342.85 | 0.297 | 0.198 | 0.506 | 0.207 | 1.294 | 1.752 | 0.939 | 1209 | 1293 | 1533 | 910 | 1342 | 1368 |
| 347.65 | 0.157 | 0.200 | 0.322 | 0.239 | 1.362 | 1.642 | 0.968 | 1166 | 1236 | 1477 | 880 | 1294 | 1322 |
| 351.45 | 0.048 | 0.271 | 0.125 | 0.328 | 1.581 | 1.426 | 1.010 | 1133 | 1194 | 1436 | 857 | 1258 | 1288 |

| $T$ (K) | $x_1$ | $x_2$ | $y_1$ | $y_2$ | $\gamma_1$ | $\gamma_2$ | $\gamma_3$ | $-B_{11}$ | $-B_{22}$ | $-B_{33}$ | $-B_{12}$ | $-B_{13}$ | $-B_{23}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | (cm$^3$ mol$^{-1}$) | | | | | |
| 348.85 | 0.099 | 0.293 | 0.238 | 0.316 | 1.544 | 1.408 | 1.001 | 1156 | 1223 | 1464 | 872 | 1283 | 1311 |
| 344.95 | 0.194 | 0.302 | 0.395 | 0.281 | 1.459 | 1.428 | 0.992 | 1190 | 1268 | 1508 | 897 | 1321 | 1348 |
| 341.55 | 0.294 | 0.304 | 0.520 | 0.252 | 1.396 | 1.471 | 0.977 | 1222 | 1309 | 1548 | 919 | 1356 | 1381 |
| 338.55 | 0.391 | 0.311 | 0.615 | 0.233 | 1.350 | 1.519 | 0.972 | 1251 | 1347 | 1585 | 939 | 1388 | 1412 |
| 335.85 | 0.490 | 0.315 | 0.690 | 0.218 | 1.309 | 1.585 | 0.983 | 1277 | 1383 | 1620 | 958 | 1418 | 1440 |
| 332.55 | 0.635 | 0.316 | 0.781 | 0.198 | 1.263 | 1.676 | 0.976 | 1312 | 1429 | 1663 | 982 | 1456 | 1476 |
| 334.55 | 0.495 | 0.405 | 0.722 | 0.232 | 1.408 | 1.394 | 1.007 | 1291 | 1401 | 1637 | 967 | 1433 | 1454 |
| 337.15 | 0.390 | 0.424 | 0.651 | 0.255 | 1.493 | 1.299 | 1.006 | 1264 | 1366 | 1603 | 949 | 1403 | 1427 |
| 340.25 | 0.294 | 0.418 | 0.555 | 0.282 | 1.544 | 1.269 | 1.013 | 1234 | 1325 | 1564 | 928 | 1370 | 1394 |
| 343.45 | 0.210 | 0.394 | 0.438 | 0.310 | 1.559 | 1.288 | 1.027 | 1204 | 1286 | 1526 | 906 | 1336 | 1362 |
| 350.05 | 0.059 | 0.386 | 0.162 | 0.391 | 1.713 | 1.259 | 1.059 | 1145 | 1210 | 1451 | 865 | 1271 | 1300 |
| 347.75 | 0.094 | 0.494 | 0.260 | 0.415 | 1.848 | 1.147 | 1.111 | 1165 | 1235 | 1476 | 879 | 1293 | 1321 |
| 343.25 | 0.191 | 0.496 | 0.440 | 0.351 | 1.734 | 1.176 | 1.089 | 1206 | 1288 | 1528 | 908 | 1338 | 1364 |
| 339.45 | 0.290 | 0.501 | 0.575 | 0.304 | 1.658 | 1.182 | 1.070 | 1242 | 1336 | 1574 | 933 | 1378 | 1403 |
| 334.65 | 0.442 | 0.508 | 0.720 | 0.256 | 1.568 | 1.221 | 1.050 | 1290 | 1400 | 1635 | 967 | 1432 | 1453 |
| 337.85 | 0.299 | 0.600 | 0.620 | 0.320 | 1.821 | 1.115 | 1.147 | 1257 | 1356 | 1594 | 944 | 1396 | 1419 |
| 342.35 | 0.194 | 0.601 | 0.487 | 0.373 | 1.938 | 1.063 | 1.147 | 1214 | 1299 | 1539 | 914 | 1348 | 1373 |
| 349.05 | 0.061 | 0.600 | 0.201 | 0.497 | 2.122 | 1.071 | 1.207 | 1154 | 1221 | 1462 | 871 | 1281 | 1309 |
| 346.45 | 0.101 | 0.701 | 0.331 | 0.497 | 2.263 | 1.020 | 1.279 | 1177 | 1250 | 1491 | 887 | 1306 | 1334 |
| 339.05 | 0.248 | 0.705 | 0.606 | 0.363 | 2.070 | 1.021 | 1.213 | 1246 | 1341 | 1579 | 936 | 1383 | 1407 |
| 345.85 | 0.106 | 0.797 | 0.386 | 0.526 | 2.566 | 0.973 | 1.366 | 1182 | 1257 | 1498 | 891 | 1312 | 1339 |
| 349.25 | 0.057 | 0.894 | 0.266 | 0.679 | 2.973 | 0.974 | 1.526 | 1152 | 1218 | 1460 | 870 | 1279 | 1308 |

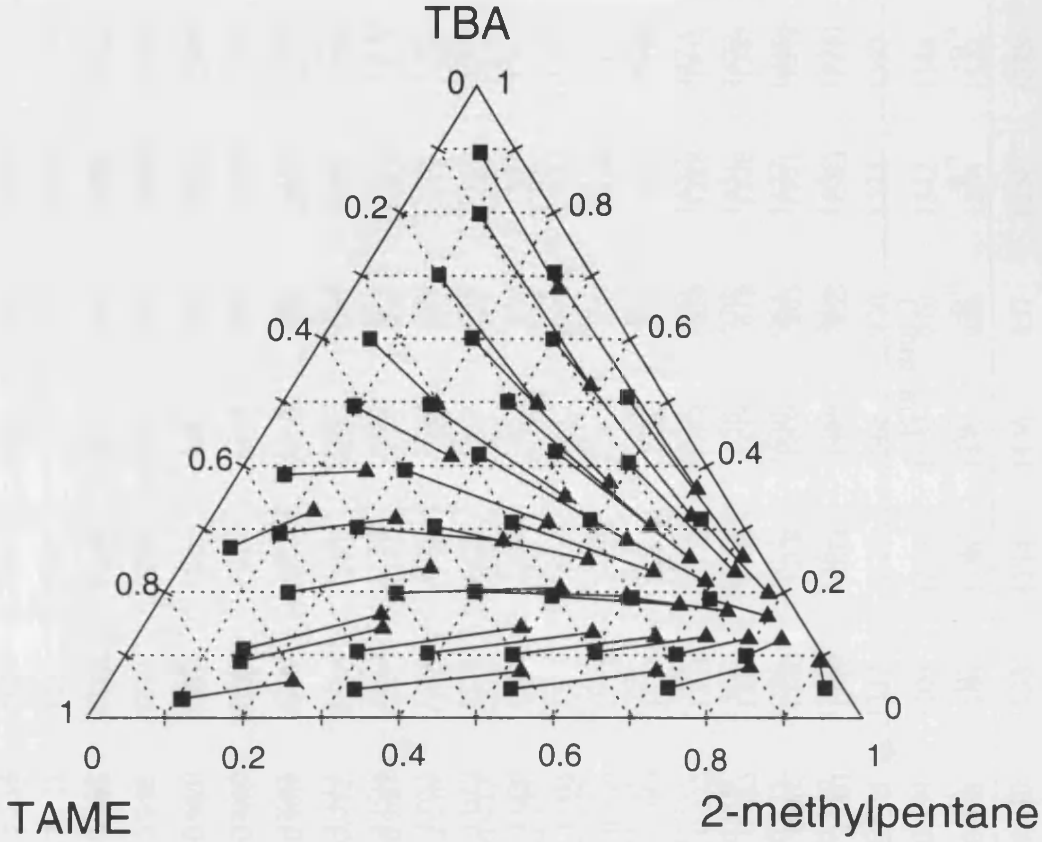

**Figure. 3**. Diagram of VLE for the ternary system 2-methylpentane (1) + TBA (2) + TAME (3) at 101.3 kPa: (■) liquid phase mole fractions; (▲) vapor phase mole fractions.

$$D = \sum_{i=1}^{N} (x_{ia} + x_{ib})(\ln \gamma_{ia} - \ln \gamma_{ib}) \tag{5}$$

and $N$ is the number of components. The maximum deviation $D_{\max}$ is given by:

$$\begin{aligned} D_{max} = {} & \sum_{i=1}^{N} (x_{ia} + x_{ib}) \left( \frac{1}{x_{ia}} + \frac{1}{y_{ia}} + \frac{1}{x_{ib}} + \frac{1}{y_{ib}} \right) \Delta x \\ & + \sum_{i=1}^{N} (x_{ia} + x_{ib}) \frac{\Delta P}{p} + 2 \sum_{i=1}^{N} \left| \ln \gamma_{b} - \ln \gamma_{ia} \right| \Delta x \\ & + \sum_{i=1}^{N} (x_{ia} + x_{ib}) B_j \left\{ (T_a + C_j)^{-2} + (T_b + C_j)^{-2} \right\} \Delta T \end{aligned} \tag{6}$$

The error in the measurements $\Delta x$, $\Delta P$ and $\Delta T$ were as previously indicated.

Vapor-liquid equilibrium was correlated by using Wilson, NRTL, and UNIQUAC models for the activity coefficients of the components with the binary interaction parameters. The values of the binary interaction parameters for the binary 2-methylpentane (1) + TBA (2) were used from the data of Aucejo et al. (1999) and corresponding parameters of the systems 2-methylpentane (1) + TAME (2) and TBA (2) + TAME (3) were calculated in this work. Table 7 shows the pertinent statistics of VLE interpolation. The three models yield similar deviations, representing the data successfully.

***Boiling isotherms correlation.*** The boiling points of the systems were correlated by the equation proposed by Wisniak and Tamir (1976):

$$\begin{aligned} T/K = \sum_{i=1}^{n} x_i T_i^o + \sum_{i,j=1}^{n} \left\{ x_i x_j \sum_{k=0}^{m} C_k (x_i - x_j)^k \right\} \\ + x_1 x_2 x_3 \{A + B(x_1 - x_2) + C(x_1 - x_3) + D(x_2 - x_3)\} \end{aligned} \tag{7}$$

In this equation $n$ is the number of components ($n$=2 or 3), $T_i^o$ is the boiling point of the pure component $i$, and $m$ is the number of terms considered in the series expansion of ($x_i$-$x_j$). $C_k$ are the binary constants where $A$, $B$, $C$ and $D$ are ternary constants. Tamir (1981) has suggested the following equation, of the same structure, for the direct correlation of ternary data, without use of binary data:

$$\begin{aligned} T/K = \sum_{i=1}^{3} x_i T_i^o + x_1 x_2 \left[ A_{12} + B_{12}(x_1 - x_2) + C_{12}(x_1 - x_2)^2 + \ldots \right] \\ + x_1 x_3 \left[ A_{13} + B_{13}(x_1 - x_3) + C_{13}(x_1 - x_3)^2 + \ldots \right] \\ + x_2 x_3 \left[ A_{23} + B_{23}(x_2 - x_3) + C_{23}(x_2 - x_3)^2 + \ldots \right] \end{aligned} \tag{8}$$

**Table 7. Correlation of Experimental Ternary Data with Wilson, NRTL, and UNIQUAC Equations Using Binary Interaction Parameters**

| Model | $ij$ | $A_{ij}$ / J.mol$^{-1}$ | $A_{ji}$ / J.mol$^{-1}$ | $\alpha_{ij}$ | System | Buble-point pressures | | | Dew-point pressures | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | $\Delta P^e$ / % | 100 x $\Delta y_1$[f] | 100 x $\Delta y_2$[f] | $\Delta P^e$ / % | 100 x $\Delta x_1$[f] | 100 x $\Delta x_2$[f] |
| [a]Wilson | 1-2[c] | -14.98 | 5658.90 | | 1+2+3 | 0.60 | 1.46 | 0.80 | 1.18 | 1.40 | 0.96 |
| | 1-3[c] | -575.18 | 1112.85 | | | | | | | | |
| | 2-3[d] | 2634.43 | -646.82 | | | | | | | | |
| NRTL | 1-2[c] | 4362.09 | 983.72 | 0.47 | 1+2+3 | 0.48 | 1.56 | 0.74 | 1.39 | 1.62 | 0.91 |
| | 1-3[c] | -504.22 | 953.38 | 0.20 | | | | | | | |
| | 2-3[d] | -163.00 | 2120.81 | 0.30 | | | | | | | |
| [b]UNIQUAC | 1-2[c] | 2844.32 | -1030.28 | | 1+2+3 | 1.18 | 1.60 | 0.86 | 1.02 | 1.50 | 1.00 |
| | 1-3[c] | -377.67 | 509.97 | | | | | | | | |
| | 2-3[d] | -937.11 | 1774.84 | | | | | | | | |

[a] Liquid volumes have been estimated from the Racket equation (Rackett, 1970). [b] Volume and surface parameters from DECHEMA (Gmehling and Onken, 1990). [c] Aucejo et al. (1999). [d] Calculated in this work. [e] Average percentual deviation in bubble and dew pressures: $\Delta P = 100/N\,\Sigma|P_i^{expt} - P_i^{calc}|/P_i^{expt}$ ($N$: number of data points). [f] Average absolute deviation in composition $\Delta y = 1/N\,\Sigma|y_i^{expt} - y_i^{calc}|$ ; $\Delta x = 1/N\,\Sigma|x_i^{expt} - x_i^{calc}|$

In eq 8 coefficients $A_{ij}$, $B_{ij}$, and $C_{ij}$ are not binary constants, they are multicomponent parameters determined directly from the data. Direct correlation of $T(x)$ for ternary mixtures can be very efficient as reflected by a lower percent average deviation and root mean square deviation (rmsd) and a smaller number of parameters than those for eq 7. The various constants of eqs 7 and 8 are reported in Table 8, which also contains information indicating the degree of goodness of the correlation. The values of the binary constants for the two binaries 2-methylpentane (1) + TAME (3) and 2-methylpentane (1) + TBA (2) were recalculated in this work from the data of Aucejo et al. (1998) and Aucejo et al. (1999), respectively. Corresponding parameters of the system TBA (2) + TAME (3) were calculated from the data of this work. In Figure 4 show the boiling isotherms for the ternary system calculated by direct fit which gives a better fit.

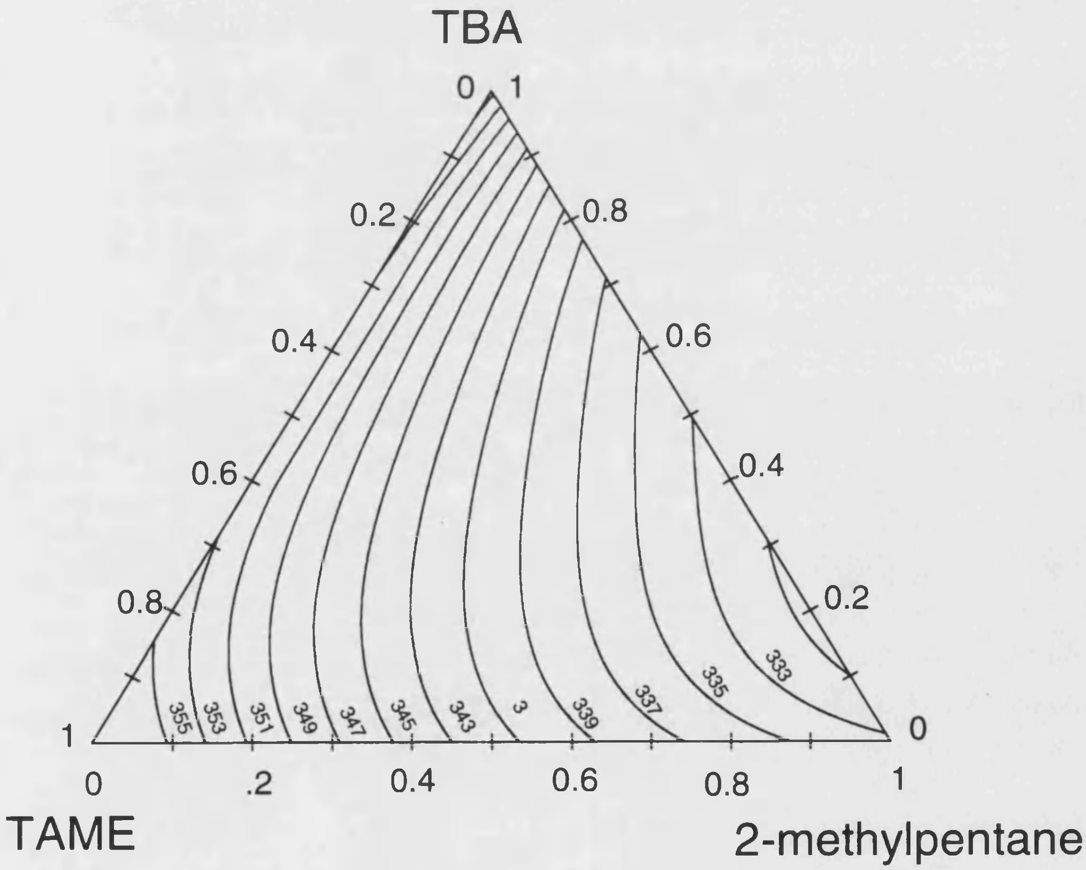

**Figure. 4**. Isothermals (K) for the ternary system 2-methylpentane (1) + TBA (2) + TAME (3) at 101.3 kPa, calculated with direct fit, eq 8.

**Table 8. Coefficients in Correlation of Boiling Points, Equations 7 and 8, Maximum, Average and Root Mean Square Deviations in Temperature (rmsd)**

**A. Equation 7 (fit from binary constants)**

| $A$ | $B$ | $C$ | $D$ | max dev. /K | avr dev /K | rmsd[a] /K |
|---|---|---|---|---|---|---|
| -43.42 | 0.00 | 0.00 | 0.00 | 0.42 | 0.20 | 0.034 |

Binary constants

| System | $C_o$ | $C_1$ | $C_2$ | max dev. /K | avr dev /K | rmsd[a] /K |
|---|---|---|---|---|---|---|
| 2-methylpentane (1) + TBA (2)[b] | -42.25 | 18.00 | -43.88 | 0.90 | 0.38 | 0.102 |
| 2-methylpentane (1) + TAME (3)[c] | -13.42 | 5.13 | -1.22 | 0.11 | 0.04 | 0.012 |
| TBA (2) + TAME (3) | -17.36 | 10.51 | -13.78 | 0.55 | 0.23 | 0.061 |

**B. Equation 8 (direct fit)**

| $ij$ | $A_{ij}$ | $B_{ij}$ | $C_{ij}$ | max. dev. /K | avr. dev. /K | rmsd[a] /K |
|---|---|---|---|---|---|---|
| 1-2 | -45.75 | 18.65 | -31.98 | 0.40 | 0.13 | 0.025 |
| 1-3 | -18.30 | 4.43 | -0.50 | | | |
| 2-3 | -19.96 | 7.44 | -6.92 | | | |

[a] rmsd (T/K): Root mean square deviation, $\left\{\sum\left(T_{exp}-T_{cal}\right)^2\right\}^{0.5}/N$. [b] Recalculated constants from data of Aucejo et al. (1999). [c] Recalculated constants from data of Aucejo et al. (1998).

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# 5. RESUMEN Y DISCUSIÓN DE RESULTADOS

# 5. RESUMEN Y DISCUSIÓN DE RESULTADOS

## 5.1. SISTEMAS BINARIOS

### 5.1.1. Azeotropía

En la Tabla 1 se resumen las composiciones y las temperaturas azeotrópicas de aquellos sistemas binarios en los que se ha encontrado un azeótropo, todos ellos de temperatura de ebullición mínima.

Los dos sistemas formados por un hidrocarburo (2-metilpentano) y un alcohol (etanol o TBA), presentan un azeótropo. En la bibliografía se pueden encontrar numerosos ejemplos de sistemas azeotrópicos formados por uno de estos dos alcoholes (etanol o TBA) y un alcano, lineal, cíclido o ramificado, con un número de átomos de carbono ente seis y ocho: Deshpande y Lu (1963), Hwang y Robinson (1977), Janaszewski y col. (1982), Oracz (1986), Hongo y col. (1994), Tripathi y col. (1976), Govindaswamy y col. (1977), Weidlich y col. (1986), Rodríguez y col. (1993), Gabaldón y col. (1999), etc.

En los sistemas formados por un hidrocarburo y un éter solamente se ha encontrado un azeótropo en los sistemas 2-metilpentano + MTBE, 3-metilpentano + THF y 2,3-dimetilpentano + TAME. No es habitual observar comportamiento azeotrópico en estos sistemas (Vijayaraghavan, 1967; Mößner y col. 1997; Wisniak y col., 1997b; Reich y col., 1999) dada su gran idealidad.

Por último en los sistemas formados por dos compuestos oxigenados (éter + alcohol) se han encontrado puntos azeotrópicos en los sistemas TAME + TBA y MTBE + metanol.

**Tabla 1. Puntos azeotrópicos de los sistemas binarios**

| Sistema | $P$ / kPa | $T$ / K | $x_1$[a] |
|---|---|---|---|
| 2-metilpentano (1) + MTBE (2) | 101.3 | 328.2 | 0.08 |
| 2-metilpentano (1) + etanol (2) | 101.3 | 326.2 | 0.75 |
| 2-metilpentano (1) + TBA (2) | 101.3 | 331.1 | 0.85 |
| 3-metilpentano (1) + THF (2) | 101.3 | 333.4 | 0.59 |
| TAME (1) + 2,3-dimetilpentano (2) | 101.3 | 359.2 | 0.93 |
| TBA (1) + TAME (2) | 101.3 | 352.9 | 0.54 |
| MTBE (1) + metanol (2) | 94.0 | 322.5 | 0.69 |
| MTBE (1) + metanol (2) | 78.4 | 317.6 | 0.71 |
| MTBE (1) + metanol (2) | 50.0 | 306.5 | 0.76 |

[a] valores aproximados, obtenidos a partir de las tablas de datos experimentales *T-x-y*

### 5.1.2. Consistencia termodinámica

Como se ha comentado anteriormente, la bondad de los datos experimentales de los sistemas binarios ha sido evaluada mediante el test de consistencia termodinámica de Fredenslund, cuyos resultados se muestran en la Tabla 2 y en las Figuras 2 a 18. En dicha tabla aparece las desviaciones medias entre los valores experimentales y calculados para la presión y la composición de la fase vapor, obtenidas en la aplicación de dicho test. Asimismo, se indica el número de parámetros ($n$) utilizado en el polinomio de Legendre. En la Tabla 2 también aparece el valor del parámetro $A$ de la ecuación [61] para aquellos sistemas en los que el modelo de Porter ($n = 1$) es el más adecuado para representar la tendencia de los coeficientes de actividad. Cabe hacer notar que el parámetro $A$ indicado en la Tabla 2 y en los artículos correspondientes, está expresado en forma adimensional, es decir, aparece dividido por el módulo $RT$.

**Tabla 2. Resultados del test de consistencia termodinámica de Fredenslund**

| Sistema | $P$ / kPa | $\Delta P$ / kPa | $100 \cdot \Delta y_1$ | $n$ | $A$ |
|---|---|---|---|---|---|
| 2-metilpentano (1) + MTBE (2) | 101.3 | 0.13 | 0.09 | 1 | 0.186 |
| 2-metilpentano (1) + TAME (2) | 101.3 | 0.25 | 0.32 | 1 | 0.115 |
| 2-metilpentano (1) + ETBE (2) | 101.3 | 0.16 | 0.13 | 1 | 0.122 |
| 2-metilpentano (1) + etanol (2) | 101.3 | 0.42 | 0.72 | 5 | — |
| 2-metilpentano (1) + TBA (2) | 101.3 | 0.21 | 0.86 | 4 | — |
| MTBE (1) + 3-metilpentano (2) | 101.3 | 0.13 | 0.12 | 1 | 0.183 |
| 3-metilpentano (1) + TAME (2) | 101.3 | 0.29 | 0.15 | 1 | 0.095 |
| 3-metilpentano (1) + ETBE (2) | 101.3 | 0.29 | 0.35 | 1 | 0.097 |
| 3-metilpentano (1) + DIPE (2) | 101.3 | 0.27 | 0.49 | 1 | 0.108 |
| 3-metilpentano (1) + THF (2) | 101.3 | 0.15 | 0.34 | 1 | 0.548 |
| MTBE (1) + 2,3-dimetilpentano (2) | 101.3 | 0.53 | 0.33 | 2 | — |
| DIPE (1) + 2,3-dimetilpentano (2) | 101.3 | 0.49 | 0.23 | 2 | — |
| TAME (1) + 2,3-dimetilpentano (2) | 101.3 | 0.08 | 0.08 | 2 | — |
| etanol (1) + TBA (2) | 101.3 | 0.10 | 0.17 | 2 | — |
| MTBE (1) + TBA (2) | 101.3 | 0.23 | 0.69 | 2 | — |
| TBA (1) + TAME (2) | 101.3 | 0.19 | 0.44 | 2 | — |
| metanol (1) + MTBE (2) | 94.0 | 1.12 | 0.96 | 1 | 1.229 |
| metanol (1) + MTBE (2) | 78.4 | 0.91 | 0.54 | 1 | 1.229 |
| metanol (1) + MTBE (2) | 50.0 | 0.25 | 0.59 | 1 | 1.172 |

A continuación se presenta la distribución de los residuos para los valores de presión y para los correspondientes a las composiciones del vapor, obtenida en la aplicación del test de consistencia.

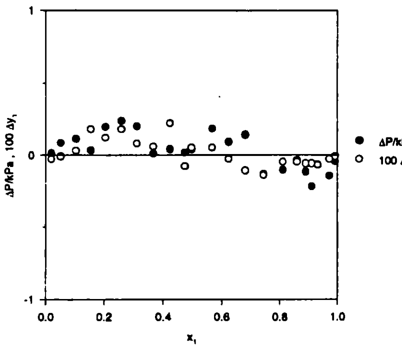


**Figura 2.** Residuales del test de consistencia. 2-metilpentano (1) + MTBE (2) a 101.3 kPa.

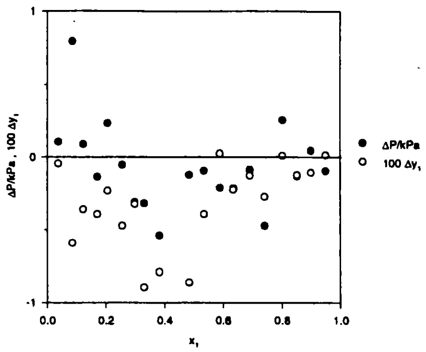


**Figura 3.** Residuales del test de consistencia. 2-metilpentano (1) + TAME (2) a 101.3 kPa.

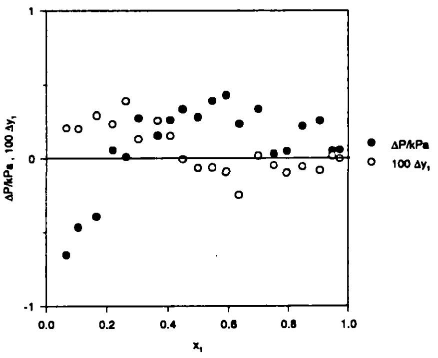


**Figura 4.** Residuales del test de consistencia. 2-metilpentano (1) + ETBE (2) a 101.3 kPa.

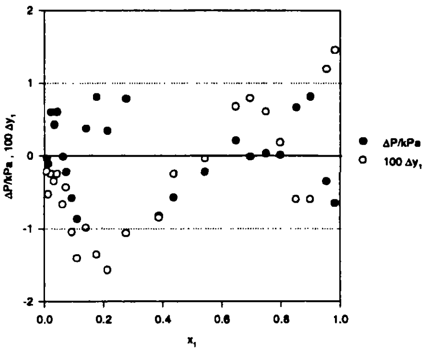


**Figura 5.** Residuales del test de consistencia. 2-metilpentano (1) + etanol (2) a 101.3 kPa.

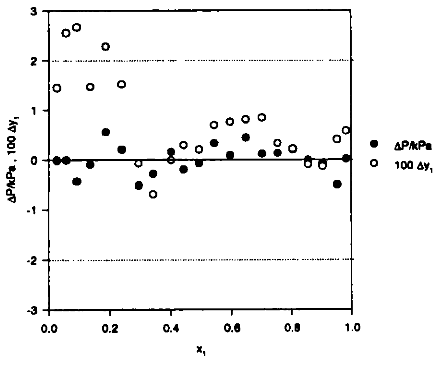


**Figura 6.** Residuales del test de consistencia. 2-metilpentano (1) + TBA (2) a 101.3 kPa.

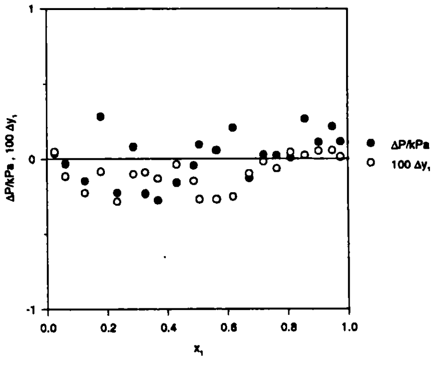


**Figura 7.** Residuales del test de consistencia. MTBE (1) + 3-metilpentano (2) a 101.3 kPa.

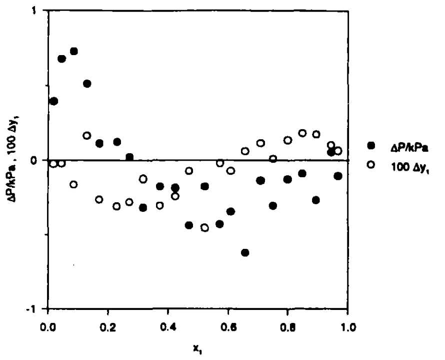


**Figura 8.** Residuales del test de consistencia. 3-metilpentano (1) + TAME (2) a 101.3 kPa.

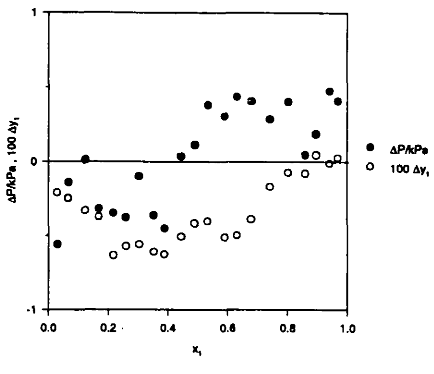


**Figura 9.** Residuales del test de consistencia. 3-metilpentano (1) + ETBE (2) a 101.3 kPa.

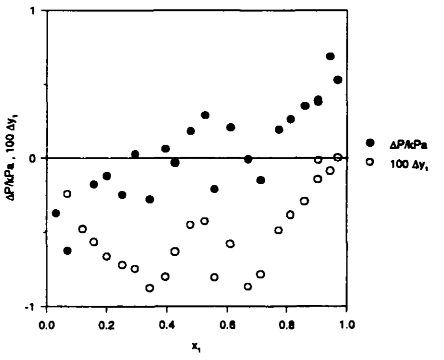


**Figura 10.** Residuales del test de consistencia. 3-metilpentano (1) + DIPE (2) a 101.3 kPa.

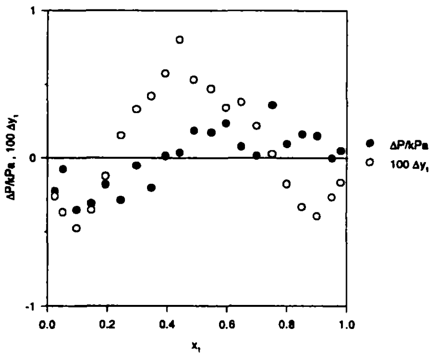


**Figura 11.** Residuales del test de consistencia. 3-metilpentano (1) + THF (2) a 101.3 kPa.

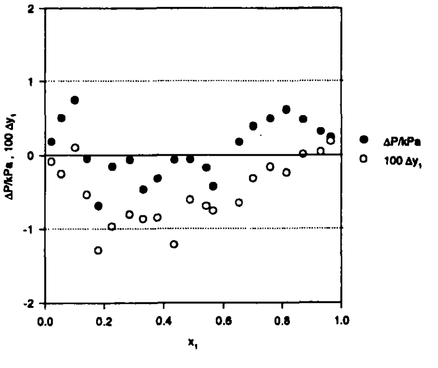


**Figura 12.** Residuales del test de consistencia. MTBE (1) + 2,3-dimetilpentano (2) a 101.3 kPa.

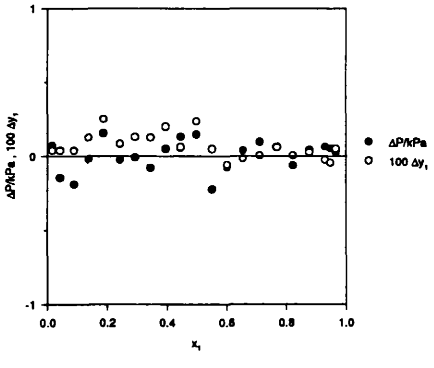


**Figura 13.** Residuales del test de consistencia. TAME (1) + 2,3-dimetilpentano (2) a 101.3 kPa.

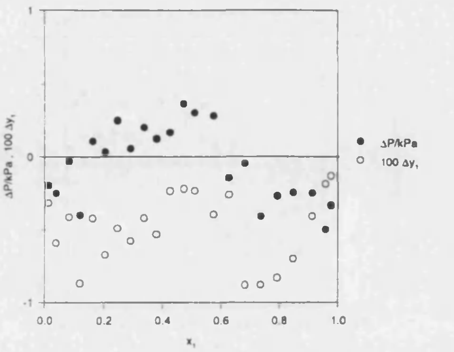


**Figura 14.** Residuales del test de consistencia. DIPE (1) + 2,3-dimetilpentano (2) a 101.3 kPa.

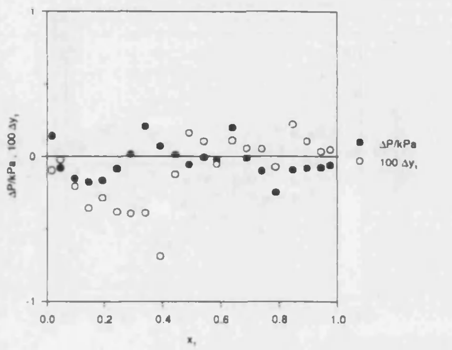


**Figura 15.** Residuales del test de consistencia. etanol (1) + TBA (2) a 101.3 kPa.

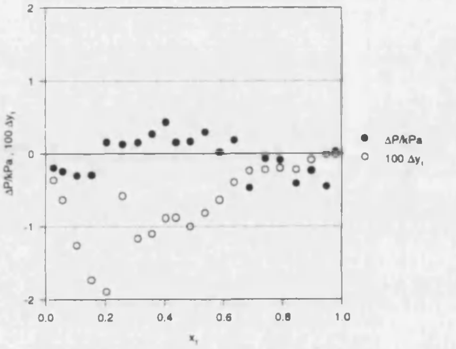


**Figura 16.** Residuales del test de consistencia. MTBE (1) + TBA (2) a 101.3 kPa.

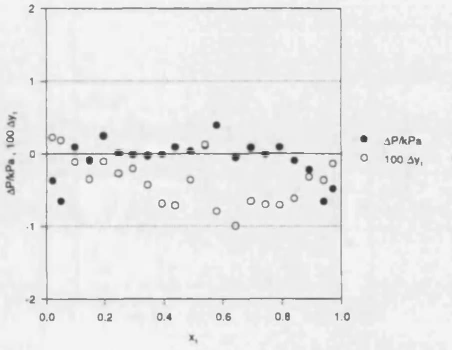
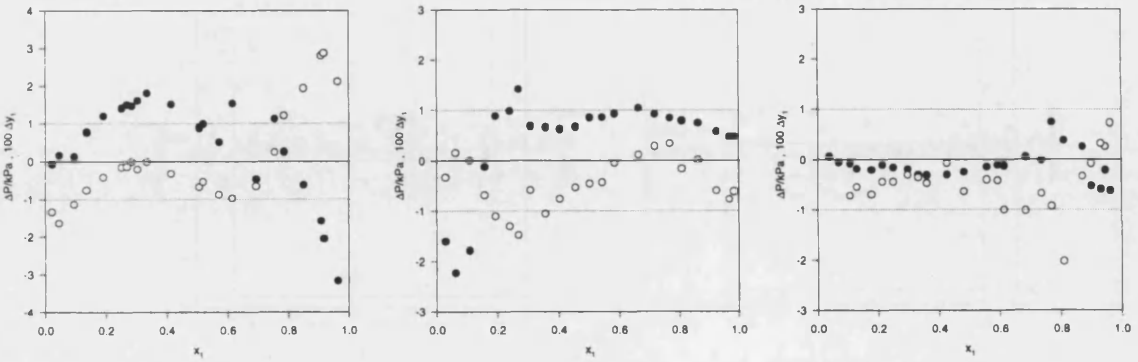


**Figura 17.** Residuales del test de consistencia. TBA (1) + TAME (2) a 101.3 kPa.



(a) (b) (c)

**Figura 18.** Residuales del test de consistencia: (●) ΔP/kPa; (o) 100 $\Delta y_1$. Sistema metanol (1) + MTBE (2): (a) 94.0 kPa; (b) 78.4 kPa; (c) 50.0 kPa

El test de consistencia termodinámica refleja en general excelentes resultados para las mezclas binarias consideradas, especialmente para los sistemas hidrocarburo + éter. Sin embargo, las mezclas en donde uno de los componentes es un alcohol presentan mayores desviaciones medias, existiendo además algunos datos que no cumplen el criterio de consistencia impuesto por el test de Fredenslund ($\Delta y_1 \leq 0.01$).

Es bien conocido que los alcoholes muestran tendencia a la asociación (formación de polímeros) y por tanto sus moléculas se distribuyen en disolución de forma no aleatoria. El fenómeno de la asociación se da de forma más intensa en alcoholes de menor peso molecular y se ve favorecida al aumentar la presión, ya que la cercanía entre moléculas aumenta. Se puede distinguir dos tipos de asociación dependiendo del tipo de moléculas que interaccionen: cuando se asocian moléculas del mismo componente se habla de autoasociación, mientras que cuando la asociación tiene lugar entre moléculas de compuestos diferentes se denomina heteroasociación o asociación cruzada.

Como se comentó anteriormente, los ajustes polinomiales de la curva de $G^E$ no tienen en cuenta este tipo de interacciones en las que la distribución de las moléculas no es aleatoria, y por tanto en sistemas con sustancias asociantes el test de Fredenslund, que utiliza polinomios de Legendre para ajustar la energía de Gibbs de exceso, puede resultar inadecuado. Este hecho dependerá de la importancia que tengan tales fuerzas de asociación frente a otras fuerzas moleculares de efectos opuestos. Asimismo, en estos sistemas la corrección del virial para el cálculo del coeficiente de fugacidad puede no ser suficiente, ya que la asociación en la fase vapor suele ser la principal causa del comportamiento no ideal de dicha fase a presiones moderadas. En estos casos se podría haber aplicado la teoría química para el cálculo de los coeficientes de fugacidad, sin embargo en el caso de los alcoholes el efecto de la asociación sólo es importante para concentraciones elevadas de alcohol (ver figuras 5 y 6 para $x_1 \leq 0.25$). El método de Hayden y O'Connell es adecuado para el resto del intervalo de composiciones, y es el que se ha utilizado en el tratamiento de la no idealidad en la fase vapor.

De esta forma, la presencia de asociación en los sistemas con alcoholes permite explicar los resultados obtenidos en el test de consistencia. Además, se puede ver que el sistema metanol + MTBE a mayor presión está al límite de la consistencia, hecho que concuerda con lo comentado anteriormente.

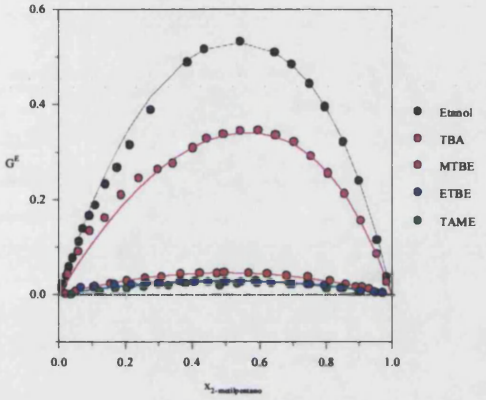
En resumen, es de suma importancia disponer de una buena expresión correctiva del comportamiento de la fase vapor, ya que una ecuación inadecuada para expresar la no idealidad de dicha fase induce a errores sistemáticos en el análisis de consistencia.

Por otra parte, tan importante es el hecho de que el método utilizado en el cálculo de coeficientes de fugacidad esté bien expresado (es decir, que represente adecuadamente las interacciones moleculares), como contar con buenos parámetros para su aplicación. De este modo, el método de Hayden y O'Connell estima los valores de los segundos coeficientes del virial a partir de propiedades físicas y parámetros moleculares de los compuestos puros.

En los sistemas hidrocarburo + ETBE o + TAME, se obtuvieron peores resultados en los análisis de consistencia si teníamos en cuenta la corrección de la fase vapor. Este mismo hecho también ha sido observado por otros grupos de investigación, y se ha propuesto una revisión de los parámetros moleculares de dichos éteres (Martínez-Ageitos, 1996; Reich y col., 1999). Por tanto, se ha optado por considerar un comportamiento ideal de la fase vapor en estos sistemas, utilizando la ley de Raoult modificada [21] para el cálculo de los coeficientes de actividad.

### 5.1.3. Desviación de los sistemas respecto al comportamiento de una disolución ideal

En las Figuras 19 a 26 se representa la variación de la energía de Gibbs en función de la composición, con el fin de mostrar la desviación respecto a la idealidad de los diferentes sistemas binarios, y realizar una comparación adecuada entre ellos. Los valores experimentales de $G^E$ se han obtenido mediante la ecuación [24] (los valores que aparecen en las figuras corresponden a: $G^E = g^E/RT$), y las líneas continuas representan la función de ajuste utilizada en el test de consistencia.



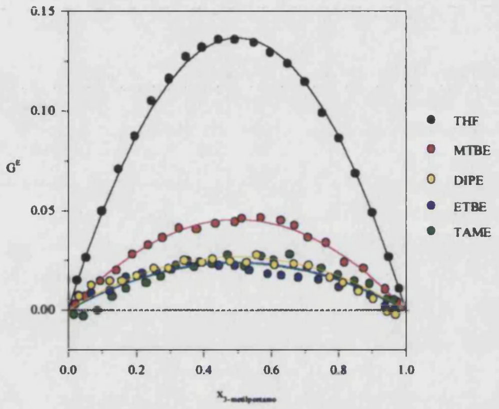
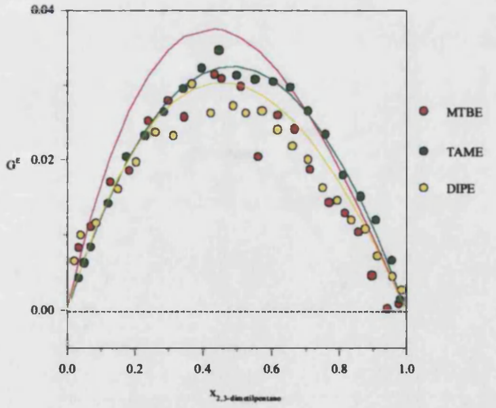


**Figura 19.** Variación de $G^E$ con la composición de la fase líquida de 2-metilpentano para el ELV a 101.3 kPa con etanol, TBA, MTBE, ETBE y TAME.

**Figura 20.** Variación de $G^E$ con la composición de la fase líquida de 3-metilpentano para el ELV a 101.3 kPa con THF, MTBE, DIPE, ETBE y TAME.



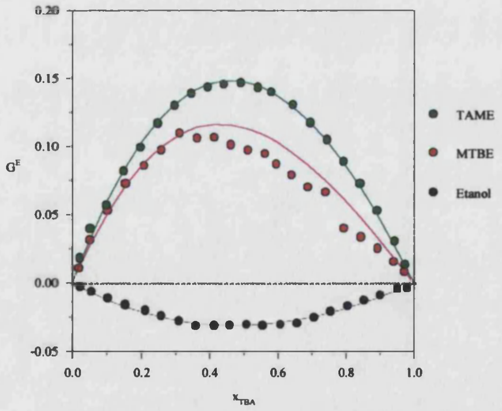


**Figura 21.** Variación de $G^E$ con la composición de la fase líquida de 2,3-dimetilpentano para el ELV a 101.3 kPa con MTBE, TAME y DIPE.

**Figura 22.** Variación de $G^E$ con la composición de la fase líquida de TBA para el ELV a 101.3 kPa con TAME, MTBE y etanol.

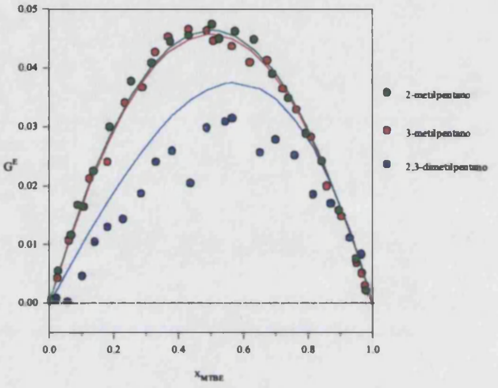


**Figura 23.** Variación de $G^E$ con la composición de la fase líquida de MTBE para el ELV a 101.3 kPa con 2-metilpentano, 3-metilpentano y 2,3-dimetilpentano.

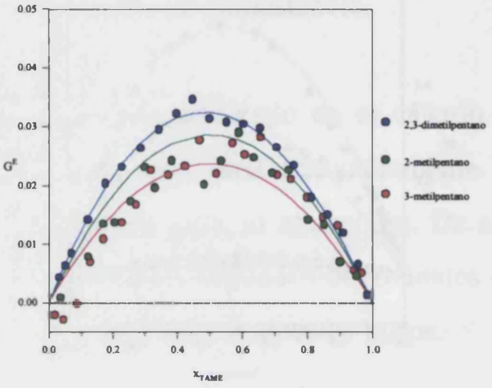


**Figura 24.** Variación de $G^E$ con la composición de la fase líquida de TAME para el ELV a 101.3 kPa con 2-metilpentano, 3-metilpentano y 2,3-dimetilpentano.

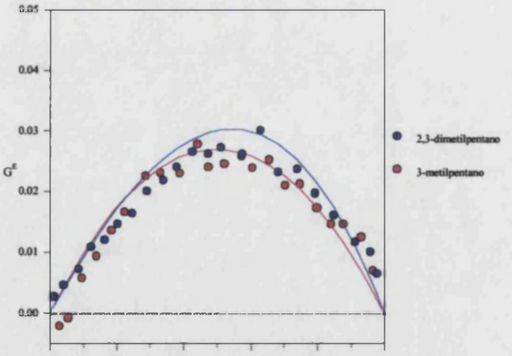


**Figura 25.** Variación de $G^E$ con la composición de la fase líquida de DIPE para el ELV a 101.3 kPa con 3-metilpentano y 2,3-dimetilpentano.

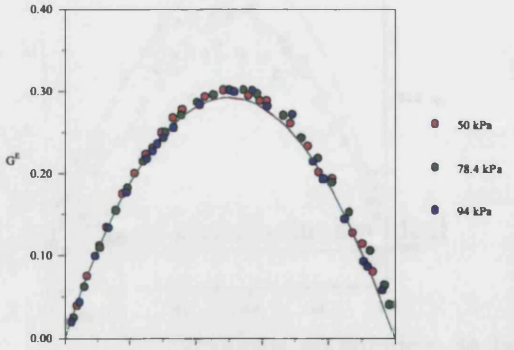


**Figura 26.** Variación de $G^E$ con la composición de la fase líquida de metanol para el ELV a 101.3 kPa con MTBE a 50.0, 78.4 y 94.0 kPa.

Todos los sistemas estudiados, excepto el etanol + TBA, presentan desviaciones positivas respecto a la ley de Raoult. Los sistemas hidrocarburo + alcohol muestran grandes desviaciones (elevados valores de $G^E$ y de $\gamma_i$) que dan lugar a un azeótropo de temperatura de ebullición mínima, característico de sistemas formados por un componente apolar y otro que presenta autoasociación.

En las mezclas entre compuestos oxigenados tienen lugar dos interacciones competitivas: la autoasociación de los alcoholes y la asociación cruzada entre alcoholes distintos (etanol + TBA) o entre alcohol y éter. Según la teoría química, Prausnitz y col. (1986), deben aparecer desviaciones positivas cuando los componentes de una mezcla muestran tendencia a la autoasociación (interacción entre moléculas iguales), mientras las desviaciones negativas son frecuentes cuando se da asociación cruzada (interacción entre moléculas distintas). En el caso de los sistemas alcohol + éter, predomina el efecto de la autoasociación del alcohol (metanol o etanol) frente a la asociación cruzada, y los sistemas muestran desviaciones positivas (ver figuras 22 y 26). Se observa como el sistema metanol + MTBE se desvía con igual magnitud del comportamiento ideal para las tres presiones de trabajo (ver figura 26). Por otra parte, en el sistema etanol + TBA es dominante la asociación cruzada, y por tanto el sistema presenta desviación negativa (ver figura 22). Esta competitividad entre los dos tipos de asociación con efectos opuestos conduce a pequeñas desviaciones, de ahí que los sistemas se comporten de forma prácticamente ideal a pesar de la asociación.

Por último, los sistemas hidrocarburo + éter presentan pequeñas desviaciones respecto a la idealidad, y parecen comportarse como soluciones regulares. El modelo de Porter [59] representa adecuadamente el comportamiento de los coeficientes de actividad y de la energía de Gibbs de exceso para los sistemas con isómeros del hexano. Sin embargo, para las mezclas 2,3-dimetilpentano + éter se consigue consistencia termodinámica con el modelo de Porter (ver Tabla 3) pero sin ajustar adecuadamente los coeficientes de actividad. Estos sistemas muestran un comportamiento asimétrico, de ahí que mejore la consistencia con un polinomio de Legendre de dos parámetros. Si se utiliza el modelo de Van Laar se obtienen mejores resultados, especialmente en el sistema MTBE + 2,3-dimetilpentano. Este hecho indica que se mantiene el comportamiento regular en dichas mezclas, pero al tratarse de componentes con mayor diferencia entre sus tamaños moleculares presentan un comportamiento asimétrico.

**Tabla 3. Consistencia termodinámica para los sistemas éter (1) + 2,3-dimetilpentano (2) a 101.3 kPa utilizando diferentes modelos de $G^E$**

| | Legendre $n$=1 | | Legendre $n$=2 | | Van Laar | |
|---|---|---|---|---|---|---|
| Éter | $\Delta P$ / kPa | 100·$\Delta y_1$ | $\Delta P$ / kPa | 100·$\Delta y_1$ | $\Delta P$ / kPa | 100·$\Delta y_1$ |
| MTBE | 0.51 | 0.71 | 0.33 | 0.53 | 0.34 | 0.42 |
| TAME | 0.08 | 0.08 | 0.08 | 0.08 | 0.08 | 0.09 |
| DIPE | 0.30 | 0.54 | 0.23 | 0.49 | 0.22 | 0.43 |

En las Figuras 2 a 18 se observa para algunos de estos sistemas cierta dispersión en el ajuste debido al pequeño intervalo de variación en los valores de $\gamma_i$ dada la gran idealidad de los sistemas, y en todos los casos las diferencias entre los valores calculados con el modelo correspondiente y los experimentales, están dentro del error cometido en la determinación experimental. Por esta misma razón, en estos sistemas es difícil sacar conclusiones acerca del comportamiento termodinámico de las mezclas.

Tusel-Langer y col. (1991) han determinado experimentalmente entalpías de exceso de mezclas hidrocarburo + éter. Los valores obtenidos para $h^E$ son positivos y del mismo orden de magnitud que $g^E$, y lo atribuyen a un efecto de "desempaquetamiento" del orden en una solución de cadenas hidrocarbonadas al introducir una molécula de éter. Recordando la ecuación [23]:

$$g^E = h^E - Ts^E \qquad [23]$$

parece razonable esperar que el valor de la entropía de exceso, $s^E$, sea muy pequeño y casi despreciable. Este hecho está de acuerdo con el comportamiento regular de estos sistemas observado a partir de los datos de ELV.

Los hidrocarburos y los éteres son compuestos que difieren en cuanto a sus propiedades moleculares: forma, estructura, polaridad, naturaleza química, etc. Por esta razón sus moléculas presentan dificultades para mezclarse: esto provocaría una desviación positiva respecto al comportamiento ideal. Por otra parte, las diferencias apreciables de tamaño dan lugar a desviaciones negativas, como se comentó anteriormente. El resultado global es que estas mezclas se desvían positivamente de la idealidad, por tanto parecen tener menor importancia los efectos derivados de las diferencias de tamaño. Ahora bien, la presencia en las soluciones de estos dos efectos opuestos explica el hecho de comportarse de forma más o menos ideal si se trata de un éter u otro, o de un hidrocarburo u otro. Realizando una comparación adecuada de los sistemas, se tiene:

- Serie hidrocarburo + diferentes éteres. Se observa que para el mismo hidrocarburo se obtiene el siguiente orden en los valores de $G^E$ (ver figuras 19-21), o del parámetro regular $A$ (ver Tabla 2), dependiendo del éter en disolución:

$$\text{THF} > \text{MTBE} > \text{DIPE} \approx \text{TAME} \approx \text{ETBE}$$

Si se ordenan éstos éteres según su volumen o peso molecular creciente se obtiene la misma secuencia. El tetrahidrofurano es el de menor peso molecular, además tiene estructura cíclica, y por tanto es el de menor tamaño. Los éteres más pequeños presentan mayores dificultades para "desempaquetar" el orden de las cadenas hidrocarbonadas, de ahí que se comporten menos idealmente.

- Serie éter + diferentes hidrocarburos. En este caso, la secuencia que se obtiene es diferente según se trate de un éter u otro (ver figuras 23-25).

MTBE: 2-metilpentano ≈ 3-metilpentano > 2,3-dimetilpentano

TAME: 2,3-dimetilpentano > 2-metilpentano > 3-metilpentano

DIPE: 2,3-dimetilpentano > 3-metilpentano

El sistema MTBE + isómero de hexano presenta mayores desviaciones que el sistema con el isómero de heptano. Ésto se debe a que el efecto volumétrico es mayor para el 2,3-dimetilpentano que para los isómeros del hexano, ya que la diferencia de tamaños es mayor en el primer caso. Dicho efecto hace disminuir las desviaciones (positivas) debidas al reordenamiento del sistema éter + hidrocarburo, ya que una diferencia apreciable de tamaño da lugar a desviaciones negativas. Este mismo hecho se observa en los sistemas MTBE + hexano y MTBE + heptano, determinados por Wisniak y col. (1997b).

La secuencia del MTBE se invierte para los éteres TAME y DIPE. En este caso se trata de éteres más grandes (ambos con el mismo peso molecular) y las diferencias de tamaño ya no son tan apreciables y en este caso el efecto volumétrico es similar. Por tanto el hecho de que el sistema 2,3-dimetilpentano presente mayores desviaciones respecto a los sistemas con metilpentanos, se debe a que los efectos de reordenamiento son más importantes cuanto mayor es la cadena hidrocarbonada, es decir a un éter le cuesta más mezclarse con hidrocarburos de mayor peso molecular. Reich y col. (1999) obtuvieron el ELV de los sistemas binarios ETBE + hexano y ETBE + heptano; en dicho trabajo el sistema con heptano se desvía más del comportamiento ideal, concordando con los resultados aquí obtenidos ya que ETBE, TAME y DIPE son éteres de tamaños moleculares similares.

### 5.1.4. Correlación

Los datos de ELV de los diferentes sistemas binarios han sido correlacionados utilizando modelos de energía de exceso de composición local: Wilson, NRTL y UNIQUAC. Los parámetros de estos modelos se han obtenido minimizando la siguiente función objetivo:

$$FO = \sum_{i=1}^{N} 100 \times \left( \left| \frac{P_i^{\mathrm{exptl}} - P_i^{\mathrm{calc}}}{P_i^{\mathrm{exptl}}} \right| + \left| y_i^{\mathrm{exptl}} - y_i^{\mathrm{calc}} \right| \right) \qquad [85]$$

En las Tablas 4, 5 y 6 se muestra un resumen de la correlación, indicando los parámetros de interacción y las desviaciones medias de la presión de burbuja para cada uno de los modelos.

En general, los sistemas más ideales (hidrocarburo + éter y etanol + TBA) presentan menores desviaciones que el resto de los sistemas. Para este tipo de mezclas los tres modelos utilizados representan adecuadamente los datos de ELV experimentales, siendo muy similares las desviaciones obtenidas en las tres correlaciones.

Para los sistemas formados por un hidrocarburo y un alcohol las ecuaciones propuestas en los modelos de Wilson y NRTL proporcionan mejores resultados que UNIQUAC. Los modelos NRTL y UNIQUAC pueden predecir inmiscibilidad de fases, aún cuando no exista, en sistemas que estén al límite de la inmiscibilidad, dando lugar a una correlación errónea. No obstante, en el modelo NRTL se puede evitar seleccionando un valor adecuado del parámetro $\alpha_{ij}$, mientras que en el modelo UNIQUAC no, de ahí que este último proporcione peores resultados que NRTL, especialmente en el sistema 2-metilpentano + etanol, ya que la curva de burbuja presenta una zona prácticamente plana que es característica de sistemas al límite de la inmiscibilidad.

**Tabla 4. Parámetros y desviaciones entre los valores experimentales y calculados para el modelo de Wilson**

| Sistema | $P$ | $A_{12}$[a] | $A_{21}$[a] | Presión de burbuja | |
|---|---|---|---|---|---|
| | kPa | J/mol | J/mol | $\Delta P$[b] / % | $100 \cdot \Delta y_1$[c] |
| MTBE (1) + 2-metilpentano (2) | 101.3 | 523.28 | 22.45 | 0.11 | 0.05 |
| 2-metilpentano (1) + TAME (2) | 101.3 | -575.18 | 1112.85 | 0.24 | 0.81 |
| 2-metilpentano (1) + etanol (2) | 101.3 | 1187.08 | 9489.34 | 0.69 | 0.44 |
| 2-metilpentano (1) + TBA (2) | 101.3 | -14.98 | 5658.90 | 0.45 | 0.69 |
| MTBE (1) + 3-metilpentano (2) | 101.3 | 309.33 | 225.19 | 0.17 | 0.08 |
| 3-metilpentano (1) + TAME (2) | 101.3 | -213.68 | 528.20 | 0.21 | 0.12 |
| 3-metilpentano (1) + ETBE (2) | 101.3 | -337.50 | 701.81 | 0.38 | 0.30 |
| 3-metilpentano (1) + DIPE (2) | 101.3 | -126.76 | 472.68 | 0.31 | 0.47 |
| 3-metilpentano (1) + THF (2) | 101.3 | -189.70 | 1882.85 | 0.17 | 0.09 |
| MTBE (1) + 2,3-dimetilpentano (2) | 101.3 | -992.62 | 2001.60 | 0.44 | 0.48 |
| DIPE (1) + 2,3-dimetilpentano (2) | 101.3 | -823.78 | 1336.27 | 0.22 | 0.49 |
| TAME (1) + 2,3-dimetilpentano (2) | 101.3 | 31.77 | 369.78 | 0.08 | 0.07 |
| etanol (1) + TBA (2) | 101.3 | -343.43 | 784.63 | 0.11 | 0.16 |
| MTBE (1) + TBA (2) | 101.3 | -687.80 | 2263.48 | 0.56 | 0.84 |
| TBA (1) + TAME (2) | 101.3 | 2634.43 | -646.82 | 0.23 | 0.40 |
| metanol (1) + MTBE (2) | 94.0 | 4843.70 | -687.62 | 1.03 | 0.71 |
| metanol (1) + MTBE (2) | 78.4 | 4772.06 | -925.77 | 0.51 | 0.36 |
| metanol (1) + MTBE (2) | 50.0 | 4758.19 | -1117.82 | 0.39 | 0.46 |

[a] $A_{ij} = \Delta\lambda_{ij}$. [b] Desviación media porcentual en la presión de burbuja $\Delta P = 100/N \sum_{i}^{N} \left| P_i^{exptl} - P_i^{calc} \right| / P_i^{exptl}$ ($N$: número de datos puntuales). [c] Desviación media absoluta en la composición de vapor $\Delta y = 1/N \sum_{i}^{N} \left| y^{exptl} - y^{calc} \right|$

**Tabla 5. Parámetros y desviaciones entre los valores experimentales y calculados para el modelo NRTL**

| Sistema | $P$ | $A_{12}$[a] | $A_{21}$[a] | $\alpha_{12}$ | Presión de burbuja | |
|---|---|---|---|---|---|---|
| | kPa | J/mol | J/mol | | $\Delta P$[b] / % | $100 \cdot \Delta y_1$[c] |
| MTBE (1) + 2-metilpentano (2) | 101.3 | 272.05 | 265.27 | 0.2 | 0.11 | 0.05 |
| 2-metilpentano (1) + TAME (2) | 101.3 | -504.22 | 953.38 | 0.2 | 0.21 | 0.88 |
| 2-metilpentano (1) + etanol (2) | 101.3 | 6356.65 | 3990.00 | 0.47 | 0.70 | 0.68 |
| 2-metilpentano (1) + TBA (2) | 101.3 | 4362.09 | 983.72 | 0.47 | 0.74 | 0.68 |
| MTBE (1) + 3-metilpentano (2) | 101.3 | 675.98 | -139.21 | 0.3 | 0.17 | 0.09 |
| 3-metilpentano (1) + TAME (2) | 101.3 | -29.74 | 331.11 | 0.3 | 0.24 | 0.13 |
| 3-metilpentano (1) + ETBE (2) | 101.3 | 1933.52 | -1340.45 | 0.3 | 0.48 | 0.25 |
| 3-metilpentano (1) + DIPE (2) | 101.3 | -138.44 | 460.00 | 0.3 | 0.26 | 0.50 |
| 3-metilpentano (1) + THF (2) | 101.3 | -227.56 | 1870.29 | 0.2 | 0.13 | 0.10 |
| MTBE (1) + 2,3-dimetilpentano (2) | 101.3 | 1293.69 | -717.96 | 0.3 | 0.38 | 0.61 |
| DIPE (1) + 2,3-dimetilpentano (2) | 101.3 | 161.58 | 185.733 | 0.3 | 0.25 | 0.56 |
| TAME (1) + 2,3-dimetilpentano (2) | 101.3 | 318.15 | 76.19 | 0.3 | 0.08 | 0.07 |
| etanol (1) + TBA (2) | 101.3 | 714.30 | -989.00 | 0.3 | 0.13 | 0.15 |
| MTBE (1) + TBA (2) | 101.3 | 3080.07 | -1211.97 | 0.3 | 0.13 | 0.76 |
| TBA (1) + TAME (2) | 101.3 | -163.00 | 2120.81 | 0.3 | 0.24 | 0.39 |
| metanol (1) + MTBE (2) | 94.0 | 2839.93 | 852.48 | 0.2 | 1.13 | 0.83 |
| metanol (1) + MTBE (2) | 78.4 | 2410.05 | 1036.14 | 0.2 | 0.54 | 0.43 |
| metanol (1) + MTBE (2) | 50.0 | 1935.94 | 1288.10 | 0.2 | 0.54 | 0.49 |

[a] $A_{ij} = \Delta g_{ij}$. [b] Desviación media porcentual en la presión de burbuja $\Delta P = 100/N \sum_i^N \left| P_i^{exptl} - P_i^{calc} \right| / P_i^{exptl}$ ($N$: número de datos puntuales). [c] Desviación media absoluta en la composición de vapor $\Delta y = 1/N \sum_i^N \left| y^{exptl} - y^{calc} \right|$

**Tabla 6. Parámetros y desviaciones entre los valores experimentales y calculados para el modelo UNIQUAC**

| Sistema | $P$ kPa | $A_{12}$[a] J/mol | $A_{21}$[a] J/mol | Presión de burbuja $\Delta P$[b] / % | Presión de burbuja $100 \cdot \Delta y_1$[c] |
|---|---|---|---|---|---|
| MTBE (1) + 2-metilpentano (2) | 101.3 | -119.81 | 261.33 | 0.10 | 0.05 |
| 2-metilpentano (1) + TAME (2) | 101.3 | -377.67 | 509.97 | 0.21 | 0.87 |
| 2-metilpentano (1) + etanol (2) | 101.3 | 4271.12 | -475.03 | 2.12 | 1.66 |
| 2-metilpentano (1) + TBA (2) | 101.3 | 2844.32 | -1030.28 | 0.97 | 0.71 |
| MTBE (1) + 3-metilpentano (2) | 101.3 | 141.87 | -11.48 | 0.17 | 0.08 |
| 3-metilpentano (1) + TAME (2) | 101.3 | -121.45 | 194.90 | 0.22 | 0.13 |
| 3-metilpentano (1) + ETBE (2) | 101.3 | -1299.15 | 410.93 | 0.37 | 0.14 |
| 3-metilpentano (1) + DIPE (2) | 101.3 | -214.89 | 305.57 | 0.26 | 0.49 |
| 3-metilpentano (1) + THF (2) | 101.3 | 796.32 | -230.81 | 0.15 | 0.10 |
| MTBE (1) + 2,3-dimetilpentano (2) | 101.3 | 664.88 | -487.67 | 0.38 | 0.56 |
| DIPE (1) + 2,3-dimetilpentano (2) | 101.3 | 92.33 | -670.09 | 0.28 | 0.33 |
| TAME (1) + 2,3-dimetilpentano (2) | 101.3 | 62.28 | 21.82 | 0.08 | 0.07 |
| etanol (1) + TBA (2) | 101.3 | -195.04 | 194.90 | 0.13 | 0.16 |
| MTBE (1) + TBA (2) | 101.3 | 2267.27 | -1295.30 | 0.32 | 0.61 |
| TBA (1) + TAME (2) | 101.3 | -937.11 | 1774.84 | 0.20 | 0.42 |
| metanol (1) + MTBE (2) | 94.0 | -409.22 | 3316.82 | 1.05 | 0.80 |
| metanol (1) + MTBE (2) | 78.4 | -471.30 | 3297.00 | 0.52 | 0.41 |
| metanol (1) + MTBE (2) | 50.0 | -523.50 | 3262.68 | 0.55 | 0.50 |

[a] $A_{ij} = \Delta u_{ij}$. [b] Desviación media porcentual en la presión de burbuja $\Delta P = 100/N \sum_{i}^{N} \left| P_i^{exptl} - P_i^{calc} \right| / P_i^{exptl}$ ($N$: número de datos puntuales). [c] Desviación media absoluta en la composición de vapor $\Delta y = 1/N \sum_{i}^{N} \left| y^{exptl} - y^{calc} \right|$

## 5.2. SISTEMAS TERNARIOS

En ninguno de los tres sistemas ternarios se observa azeotropía. Las líneas que unen puntos en equilibrio muestran una tendencia hacia los azeótropos binarios de los sistemas constituyentes. Al existir dos azeótropos binarios en cada uno de los sistemas ternarios, las composiciones en equilibrio tenderán a uno u a otro dependiendo de la diferencia de volatilidad entre la mezcla ternaria y el azeótropo binario.

El análisis de consistencia termodinámica de los datos de ELV para los sistemas ternarios se ha realizado con el test de McDermott-Ellis (1965) modificado por Wisniak y Tamir (1977) y con el método L-W de Wisniak (1993). Los dos métodos han confirmado la consistencia termodinámica de los puntos experimentales.

Los sistemas MTBE + 2-metilpentano + TBA y 2-metilpentano + TBA + TAME presentan desviaciones positivas respecto a la idealidad ($\gamma_i > 1$), puesto que todos los sistemas binarios constituyentes se desvían positivamente. Sin embargo, el sistema 2-metilpentano + etanol + TBA presenta desviaciones positivas y negativas, debido a la presencia del sistema binario etanol + TBA con desviaciones negativas.

Las isolíneas de temperaturas se han calculado con las ecuaciones de Wisniak y Tamir para los sistemas MTBE + 2-metilpentano + TBA y 2-metilpentano + TBA + TAME, obteniéndose en los dos casos mejores resultados con el modelo directo de Tamir. Para obtener los parámetros correspondientes se ha minimizado la siguiente expresión:

$$\sum \left(T^{exptl} - T^{calc}\right)^2 \qquad [86]$$

Por último, en los tres sistemas ternarios se consigue una buena estimación de los datos con los modelos de correlación Wilson, NRTL y UNIQUAC utilizando los parámetros binarios.

# 6. CONCLUSIONES

# 6. CONCLUSIONES

1. Se ha llevado a cabo la determinación experimental del equilibrio líquido-vapor (ELV) a 101.3 kPa de sistemas binarios y ternarios formados por hidrocarburos constituyentes de las gasolinas (2-metilpentano, 3-metilpentano y 2,3-dimetilpentano) y compuestos oxigenados (MTBE, TAME, ETBE, DIPE, THF, TBA y etanol), por ser mezclas de interés práctico no suficientemente estudiadas.

2. El ELV del sistema MTBE + metanol se ha realizado a tres presiones diferentes: 50, 78.4 y 94 kPa, con el fin de mejorar la técnica de separación de la mezcla por destilación.

   El sistema presenta un azeótropo de temperatura de ebullición mínima que se enriquece en MTBE al disminuir la presión. Estos resultados indican que eligiendo un valor adecuado de la presión, se puede mejorar los resultados del actual proceso mixto de destilación-pervaporación utilizado en la separación de la mezcla MTBE + metanol.

3. Se han determinado las presiones de vapor de los siguientes componentes puros: 2-metilpentano, 3-metilpentano, 2,3-dimetilpentano, MTBE, TAME, DIPE, TBA y etanol. En todos los casos los datos experimentales se ajustan perfectamente a la ecuación de Antoine y a los valores encontrados en la bibliografía.

4. El análisis de consistencia con el test de Fredenslund refleja en general buenos resultados para las mezclas binarias consideradas. En los sistemas con alcoholes se obtienen algunos puntos inconsistentes que pueden deberse a una aplicación incorrecta del test de Fredenslund. Se propone para un futuro, la aplicación de la teoría química para el cálculo de los coeficientes de fugacidad con un modelo que represente adecuadamente la asociación entre alcoholes.

Por otra parte, el hecho de que los sistemas que contienen TAME o ETBE presenten desviaciones mayores en el test de consistencia en comparación con las otras mezclas hidrocarburo + éter, sugiere una revisión de los parámetros moleculares de este componente (radio de giro, momento dipolar, parámetro de solvatación, etc.) empleados en el método de Hayden y O'Connell para el cálculo de los coeficientes de fugacidad. En estos sistemas el análisis de consistencia presentado es el realizado considerando el comportamiento de la fase vapor como ideal, obteniéndose excelentes resultados.

5. En todos los sistemas se puede considerar una buena aproximación para el cálculo de los coeficientes de actividad la ley de Raoult modificada, ya que la contribución de la no idealidad de la fase vapor supone menos de un 5.5 % del valor total de $\gamma_i$. Esta contribución es mayor en los sistemas hidrocarburo + alcohol que en las mezclas con éteres, debido a la autoasociación de los alcoholes.

6. Los sistemas hidrocarburo + alcohol muestran grandes desviaciones positivas y un azeótropo de temperatura de ebullición mínima. Las formas de las curvas de equilibrio para estos sistemas son características de sistemas altamente no ideales, como era de suponer, debido a la diferencia de volatilidad entre los componentes de las mezclas y a la fuerte asociación que se espera en mezclas con alcoholes.

7. Los sistemas hidrocarburo + éter son prácticamente ideales y se comportan como soluciones regulares. La introducción de una molécula de éter en una solución de cadenas hidrocarbonadas provoca un "desempaquetamiento" del orden, dando lugar a desviaciones positivas.

   La determinación experimental del ELV de estos sistemas requiere mayor minuciosidad dada su gran idealidad, ya que cualquier error experimental se ve magnificado en el cálculo de los coeficientes de actividad debido al pequeño intervalo de variación de dichos valores.

8. En la mezcla entre compuestos oxigenados tienen lugar dos interacciones competitivas: la autoasociación y la asociación cruzada. El primer tipo de asociación da lugar a desviaciones positivas, mientras que la asociación cruzada provoca desviaciones negativas. La competitividad entre estos dos tipos de asociación explica el comportamiento prácticamente ideal de estos sistemas a pesar de la asociación.

   El sistema etanol + TBA presenta desviaciones negativas, puesto que predomina la asociación cruzada entre alcoholes diferentes. Sin embargo, en los sistemas alcohol + éter predomina el efecto de la autosociación del alcohol, y por esta razón muestran desviaciones positivas.

9. Los modelos de composición local utilizados resultan adecuados para la correlación de los datos de ELV de los sistemas binarios. Los parámetros de interacción se han considerado independientes de la temperatura al tratarse de sistemas con entalpías de mezcla relativamente bajas.

   En todos los casos se obtienen muy buenos resultados, con desviaciones medias entre los valores experimentales y los calculados inferiores al 1 %, a excepción de la correlación del sistema 2-metilpentano + etanol con UNIQUAC debido a las dificultades que encuentra este modelo en sistemas al límite de la inmiscibilidad.

10. Ningún sistema ternario presenta azeótropos. Las composiciones de las fases en equilibrio tienden a los azeótropos binarios de los sistemas constituyentes.

    Los sistemas MTBE + 2-metilpentano + TBA y 2-metilpentano + TBA + TAME se desvían positivamente respecto de la idealidad, al igual que todas las mezclas binarias constituyentes. No obstante, en el sistema 2-metilpentano + etanol + TBA no todas las mezclas binarias constituyentes se desvían con el mismo signo, de ahí que el sistema ternario muestre una combinación de desviaciones positivas y negativas.

11. Se ha comprobado que los parámetros de interacción obtenidos en la correlación de los sistemas binarios pueden utilizarse para estimar los sistemas ternarios con muy buenos resultados con cualquiera de los tres modelos empleados. Este hecho permite concluir que no es imprescindible estudiar directamente sistemas multicomponentes formados por gasolinas reales y aditivos, ya que ésto complicaría enormemente tanto los análisis químicos como el tratamiento termodinámico.

# 7. NOMENCLATURA

# 7. NOMENCLATURA

## 7.1. SIMBOLOGÍA

| | |
|---|---|
| $A'$ | Parámetro regular, ecuaciones [57], [60] y [61] |
| $A_{wi}$ | Área molecular (Bondi, 1968) |
| $A, B, C$ | Parámetros de Antoine, ecuación [17] |
| $A, B, C, D$ | Constantes para un sistema ternario de la ecuación de Wisniak-Tamir [52] |
| $A_{ij}$, $B_{ij}$, $C_{ij}$ | Párametros multicomponentes de la ecuación de Tamir [53] |
| $a_k$ | Coeficientes del polinomio de Legendre, ecuación [63] |
| $B$ | Segundo coeficiente del Virial |
| $B'$ | Parámetro regular, ecuaciones [58] y [60] |
| $B_{ij}$ | Segundos coeficientes del Virial cruzados |
| $C$ | Constante de la ecuación [3] |
| $C_k$ | Constantes de los sistemas binarios de la ecuación Wisniak-Tamir [50] y [52] |
| $c_{ij}$ | Energía cohesiva, ecuación [54] |
| $D$ | Desviación del test de Wisniak, ecuación [82] |
| $D_i$ | Desviación local del test de McDermott-Ellis, ecuación [72] |
| $D_{max}$ | Desviación máxima del test de McDermott-Ellis |
| $d$ | Densidad |
| $f_i^o$ | Fugacidad de referencia del componente *i* |
| $\hat{f}_i^{\alpha}$ | Fugacidad del componente *i* en la fase $\alpha$ |
| $\hat{f}_i^{L}$ | Fugacidad del componente *i* en la fase líquida |
| $\hat{f}_i^{V}$ | Fugacidad del componente *i* en la fase vapor |
| $G$ | Energía de Gibbs |
| $G^{E}$ | Energía de Gibbs (adimensional) |
| $G_{ji}$ | Parámetro de la ecuación NRTL |
| $g^{E}$ | Energía de Gibbs molar de exceso |
| $g^{id}$ | Energía de Gibbs molar de una disolución ideal |

| | |
|---|---|
| $\Delta g_{ij}$ | Parámetros energéticos de la ecuación NRTL |
| $h^{\mathrm{E}}$ | Entalpía molar de exceso |
| $\Delta h_i^o$ | Entalpía de vaporización del componente *i* puro |
| $L$ | Parámetro del test de Wisniak en forma global, ecuación [81] |
| $L_i$ | Parámetro del test de Wisniak en forma puntual, ecuación [80] |
| $L_k$ | Polinomio de Legendre de orden *k* |
| $l_i$ | Parámetro de la ecuación UNIQUAC, ecuación [48] |
| $m$ | Número de fases en la mezcla, ecuaciones [2] y [4] |
| $m$ | Número de términos en la serie de expansión de $(x_1 - x_2)$, ecuación [50] |
| $N$ | Número de componentes del sistema |
| $n_D$ | Índice de refracción |
| $n_i$ | Número de moles del componente *i* |
| $n_T$ | Número total de moles |
| $P$ | Presión |
| $P_c$ | Presión crítica |
| $P_i^o$ | Presión de vapor del componente *i* puro |
| $PM$ | Peso molecular |
| $q_i$ | Parámetro estructural de área del componente *i* |
| $R$ | Constante universal de los gases |
| $RD$ | Radio medio de giro |
| $r_i$ | Parámetro estructural de volumen del componente *i* |
| $s^{\mathrm{E}}$ | Entropía molar de exceso |
| $\Delta s$ | Parámetro definido en la ecuación [78] |
| $\Delta s_i^o$ | Entropía de vaporización del componente *i* puro |
| $T$ | Temperatura absoluta |
| $T_{\mathrm{b}}$ | Temperatura de ebullición normal |
| $T_{\mathrm{c}}$ | Temperatura crítica |
| $T_i^o$ | Temperatura de ebullición del componente *i* puro |
| $u^{\mathrm{E}}$ | Energía interna molar de exceso |
| $u_{ij}$ | Parámetros de interacción en la ecuación UNIQUAC |
| $\bar{V}$ | Volumen molar parcial |

| | |
|---|---|
| $\bar{V}_i$ | Volumen molar parcial del componente *i* |
| $V_i^L$ | Volumen molar del líquido puro *i* |
| $V_{wi}$ | Volumen molecular (Bondi, 1968) |
| $v^E$ | Volumen molar de exceso |
| $W$ | Parámetro del test de Wisniak en forma global, ecuación [81] |
| $W_i$ | Parámetro del test de Wisniak en forma puntual, ecuación [80] |
| $w$ | Parámetro definido en la ecuación [51] |
| $x_i$ | Fracción molar del componente *i* en la fase líquida |
| $x_{ji}$ | Fracción molar local del componente *j* alrededor del componente *i* |
| $y_i$ | Fracción molar del componente *i* en la fase vapor |
| $Z$ | Factor de compresibilidad |
| $Z_c$ | Factor de compresibilidad crítico |
| $z$ | Número de coordinación ($z$=10) |

## *SÍMBOLOS GRIEGOS*

| | |
|---|---|
| $\alpha_{ij}$ | Parámetro de desorden de la ecuación NRTL |
| $\delta_{ij}$ | Parámetro definido en la ecuación [19] |
| $\Phi_i$ | Fracción molecular de volumen |
| $\hat{\phi}_i$ | Coeficiente de fugacidad del componente *i* en la fase vapor |
| $\phi_i^o$ | Coeficiente de fugacidad del componente *i* en las condiciones de saturación |
| $\gamma_i$ | Coeficiente de actividad del componente *i* en la fase líquida |
| $\eta$ | Parámetro de asociación |
| $\Lambda_{ij}$ | Parámetro de la ecuación de Wilson, ecuación [29] |
| $\lambda_{ij}$ | Parámetros energéticos de la ecuación de Wilson |
| $\mu$ | Momento dipolar |
| $\mu_i$ | Potencial químico del componente *i* |
| $\theta_i$ | Fracción molecular de área |
| $\tau_{ji}$ | Parámetro de energía en las ecuaciones NRTL y UNIQUAC |

| | |
|---|---|
| $\xi_i$ | Fracción de volumen molar local del componente *i* |

## *SUBÍNDICES*

| | |
|---|---|
| *i*, *j*, *k* | Componente *i*, *j*, *k* respectivamente. |

## *SUPRAÍNDICES*

| | |
|---|---|
| ^ | Propiedad de un componente en disolución |
| $^o$ | Propiedad de un componente puro |
| — | Propiedad molar parcial |
| *calc* | Variable calculada |
| E | Propiedad de exceso |
| *exptl* | Variable obtenida experimentalmente |
| id | Propiedad de disolución ideal |
| *L* | Referente a la fase líquida |
| *V* | Referente a la fase vapor |
| *C* | Referente a la contribución combinatorial en UNIQUAC |
| *R* | Referente a la contribución residual en UNIQUAC |

## 7.2. ABREVIATURAS

| | |
|---|---|
| ASOG | Analitical Solution Of Groups |
| CAA | Clean Air Act |
| DIPE | Diisopropil éter: $CH_3CH(CH_3)OCH(CH_3)CH_3$ |
| ELV | Equilibrio líquido-vapor |
| EPA | Environmental Protection Agency |
| ETBE | Etil *terc*-butil éter: $(CH_3)_3COCH_2CH_3$ |

| | |
|---|---|
| IBA | Isobutil alcohol: $HC(CH_3)_2CH_2OH$ |
| MTBE | Metil *terc*-butil éter: $H_3COC(CH_3)_3$ |
| NRTL | Non-Random Two Liquids |
| RFG | Gasolina reformulada |
| RVP | Presión de vapor de Reid |
| TBA | *terc*-Butil alcohol: $C(CH_3)_3OH$ |
| TAEE | *terc*-Amil etil éter: $CH_3CH_2OC(CH_3)_2CH_2CH_3$ |
| TAME | *terc*-Amil metil éter: $CH_3OC(CH_3)_2CH_2CH_3$ |
| THF | Tetrahidrofurano: $-CH_2CH_2CH_2CH_2O-$ |
| VOC | Compuestos orgánicos volátiles |
| UNIFAC | Uniquac Functional-group Activity Coeficients |
| UNIQUAC | Universal Quasi-Chemical theory |

# 8. BIBLIOGRAFÍA

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# APÉNDICE 1.- (Parámetros)

**Componente:** 2-METILPENTANO

| Parámetro | Unidades | Valor | Referencia |
|---|---|---|---|
| $PM$ | u.m.a | 86.177 | Daubert y Danner (1989) |
| $d$(298.15 K) | Kg/m$^3$ | 648.39 | este trabajo |
| $n_\mathrm{D}$ | — | 1.3689 | este trabajo |
| $T_\mathrm{b}$ | K | 333.4 | este trabajo |
| $T_c$ | K | 497.50 | Daubert y Danner (1989) |
| $P_c$ | bar | 30.103 | Daubert y Danner (1989) |
| $Z_c$ | — | 0.267 | Daubert y Danner (1989) |
| $RD$ | m | $3.784 \cdot 10^{-10}$ | Daubert y Danner (1989) |
| $\mu$ | Deb. | 0 | Daubert y Danner (1989) |

**Parámetros de la ecuación de Antoine [17]** (este trabajo)

$A = 6.10678$

$B = 1212.34$

$$\log\left(P_i^\circ / \mathrm{kPa}\right) = A - \frac{B}{(T/\mathrm{K}) + C}$$

$C = -37.75$

**Parámetros UNIQUAC** (Gmehling y Onken, 1990)

$r = 4.4990$

$q = 3.8520$

**Componente:** 3-METILPENTANO

| Parámetro | Unidades | Valor | Referencia |
|---|---|---|---|
| $PM$ | u.m.a | 86.177 | Daubert y Danner (1989) |
| $d$(298.15 K) | Kg/m$^3$ | 659.51 | este trabajo |
| $n_D$ | — | 1.3738 | este trabajo |
| $T_b$ | K | 336.3 | este trabajo |
| $T_c$ | K | 504.43 | Daubert y Danner (1989) |
| $P_c$ | bar | 31.240 | Daubert y Danner (1989) |
| $Z_c$ | — | 0.273 | Daubert y Danner (1989) |
| $RD$ | m | $3.695 \cdot 10^{-10}$ | Daubert y Danner (1989) |
| $\mu$ | Deb. | 0 | Daubert y Danner (1989) |

**Parámetros de la ecuación de Antoine [17]** (este trabajo)

$A = 6.24116$

$B = 1302.78$

$$\log\left(P_i^\circ / \mathrm{kPa}\right) = A - \frac{B}{(T/\mathrm{K}) + C}$$

$C = -28.69$

**Parámetros UNIQUAC** (Gmehling y Onken, 1990)

$r = 4.4990$

$q = 3.8520$

**Componente:** 2,3-DIMETILPENTANO

| Parámetro | Unidades | Valor | Referencia |
|---|---|---|---|
| $PM$ | u.m.a | 100.204 | Daubert y Danner (1989) |
| $d$(298.15 K) | Kg/m$^3$ | 690.80 | este trabajo |
| $n_D$ | — | 1.3894 | este trabajo |
| $T_b$ | K | 363.0 | este trabajo |
| $T_c$ | K | 537.35 | Daubert y Danner (1989) |
| $P_c$ | bar | 29.080 | Daubert y Danner (1989) |
| $Z_c$ | — | 0.256 | Daubert y Danner (1989) |
| $RD$ | m | $3.917 \cdot 10^{-10}$ | Daubert y Danner (1989) |
| $\mu$ | Deb. | 0 | Daubert y Danner (1989) |

**Parámetros de la ecuación de Antoine [17]** (este trabajo)

$A = 6.10469$

$B = 1323.67$

$$\log\left(P_i^{\circ} / \mathrm{kPa}\right) = A - \frac{B}{(T / \mathrm{K}) + C}$$

$C = -40.11$

**Parámetros UNIQUAC** (Gmehling y Onken, 1990)

$r = 5.1726$

$q = 4.3880$

**Componente:** METANOL

| Parámetro | Unidades | Valor | Referencia |
|---|---|---|---|
| $PM$ | u.m.a | 32.042 | Daubert y Danner (1989) |
| $d$(298.15 K) | Kg/m$^3$ | 787.32 | este trabajo |
| $n_D$ | — | 1.3270 | este trabajo |
| $T_b$ | K | 337.84 | este trabajo |
| $T_c$ | K | 512.64 | Daubert y Danner (1989) |
| $P_c$ | bar | 80.970 | Daubert y Danner (1989) |
| $Z_c$ | — | 0.224 | Daubert y Danner (1989) |
| $RD$ | m | $1.552 \cdot 10^{-10}$ | Daubert y Danner (1989) |
| $\mu$ | Deb. | 1.70 | Daubert y Danner (1989) |

**Parámetros de la ecuación de Antoine [17]** (Tablas TRC, a-5030)

$A = 7.8975$

$B = 1474.08$

$$\log\left(P_i^{\circ} / \mathrm{mmHg}\right) = A - \frac{B}{\left(T / {}^{\circ}\mathrm{C}\right) + C}$$

$C = 229.13$

**Parámetros UNIQUAC** (Prausnitz y col., 1980)

$r = 1.43$

$q = 1.43$

**Componente:** ETANOL

| Parámetro | Unidades | Valor | Referencia |
|---|---|---|---|
| *PM* | u.m.a | 46.069 | Daubert y Danner (1989) |
| $d$(298.15 K) | Kg/m$^3$ | 785.04 | este trabajo |
| $n_D$ | — | 1.3592 | este trabajo |
| $T_b$ | K | 351.6 | este trabajo |
| $T_c$ | K | 516.25 | Daubert y Danner (1989) |
| $P_c$ | bar | 63.835 | Daubert y Danner (1989) |
| $Z_c$ | — | 0.248 | Daubert y Danner (1989) |
| *RD* | m | $2.2590 \cdot 10^{-10}$ | Daubert y Danner (1989) |
| $\mu$ | Deb. | 1.69 | Daubert y Danner (1989) |

**Parámetros de la ecuación de Antoine [17]** (este trabajo)

$A = 16.4298$

$B = 3545.95$

$$\ln\left(P_i^{\circ} / \mathrm{kPa}\right) = A - \frac{B}{(T/\mathrm{K}) + C}$$

$C = -51.36$

**Parámetros UNIQUAC** (Gmehling y Onken, 1990)

$r = 2.1055$

$q = 1.9720$

**Componente:** TBA

| Parámetro | Unidades | Valor | Referencia |
|---|---|---|---|
| $PM$ | u.m.a | 74.123 | Daubert y Danner (1989) |
| $d$(303.15 K) | Kg/m$^3$ | 775.40 | este trabajo |
| $n_D$ | — | 1.3851 | este trabajo |
| $T_b$ | K | 355.6 | este trabajo |
| $T_c$ | K | 506.20 | Daubert y Danner (1989) |
| $P_c$ | bar | 39.719 | Daubert y Danner (1989) |
| $Z_c$ | — | 0.260 | Daubert y Danner (1989) |
| $RD$ | m | $3.0670\cdot10^{-10}$ | Daubert y Danner (1989) |
| $\mu$ | Deb. | 1.67 | Daubert y Danner (1989) |

**Parámetros de la ecuación de Antoine [17]** (este trabajo)

$A = 14.8533$

$B = 2649.89$

$$\ln\left(P_i^{\circ}/\mathrm{kPa}\right) = A - \frac{B}{(T/\mathrm{K}) + C}$$

$C = -96.69$

**Parámetros UNIQUAC** (Gmehling y Onken, 1990)

$r = 3.4528$

$q = 3.1280$

**Componente:** THF

| Parámetro | Unidades | Valor | Referencia |
|---|---|---|---|
| $PM$ | u.m.a | 72.107 | Daubert y Danner (1989) |
| $d$(298.15 K) | Kg/m$^3$ | 881.91 | este trabajo |
| $n_\mathrm{D}$ | — | 1.4046 | este trabajo |
| $T_\mathrm{b}$ | K | 339.1 | este trabajo |
| $T_c$ | K | 540.15 | Daubert y Danner (1989) |
| $P_c$ | bar | 51.878 | Daubert y Danner (1989) |
| $Z_c$ | — | 0.259 | Daubert y Danner (1989) |
| $RD$ | m | $2.694 \cdot 10^{-10}$ | Daubert y Danner (1989) |
| $\mu$ | Deb. | 1.63 | Daubert y Danner (1989) |

**Parámetros de la ecuación de Antoine [17]** (Wu y Sandler, 1988)

$A = 6.44102$

$B = 1384.21$

$$\log\left(P_i^\circ / \mathrm{kPa}\right) = A - \frac{B}{(T/\mathrm{K}) + C}$$

$C = -27.00$

**Parámetros UNIQUAC** (Gmehling y Onken, 1990)

$r = 2.9415$

$q = 2.7200$

**Componente:** MTBE

| Parámetro | Unidades | Valor | Referencia |
|---|---|---|---|
| $PM$ | u.m.a | 88.15 | Daubert y Danner (1989) |
| $d$(298.15 K) | Kg/m$^3$ | 735.20 | este trabajo |
| $n_D$ | — | 1.3664 | este trabajo |
| $T_b$ | K | 328.2 | este trabajo |
| $T_c$ | K | 497.10 | Daubert y Danner (1989) |
| $P_c$ | bar | 34.300 | Daubert y Danner (1989) |
| $Z_c$ | — | 0.273 | Daubert y Danner (1989) |
| $RD$ | m | $3.179 \cdot 10^{-10}$ | Daubert y Danner (1989) |
| $\mu$ | Deb. | 1.36 | Daubert y Danner (1989) |

**Parámetros de la ecuación de Antoine [17]** (este trabajo)

$A = 6.34991$

$B = 1312.52$ $\quad \log\left(P_i^\circ / \text{kPa}\right) = A - \dfrac{B}{(T/\text{K}) + C}$ $\quad$ Ref.: este trabajo

$C = -26.03$

$A = 6.7359$

$B = 1032.99$ $\quad \log\left(P_i^\circ / \text{mmHg}\right) = A - \dfrac{B}{(T/^\circ\text{C}) + C}$ $\quad$ Ref.: Reich y col., 1999

$C = 213.27$

**Parámetros UNIQUAC** (Gmehling y Onken, 1990)

$r = 4.0678$

$q = 3.6320$

**Componente:** TAME

| Parámetro | Unidades | Valor | Referencia |
|---|---|---|---|
| $PM$ | u.m.a | 102.177 | Daubert y Danner (1989) |
| $d$(298.15 K) | Kg/m$^3$ | 765.94 | este trabajo[a] |
| | | 765.98 | |
| $n_D$ | — | 1.3858 | este trabajo[a] |
| | | 1.3862 | |
| $T_b$ | K | 359.3 | este trabajo[a] |
| | | 359.2 | |
| $T_c$ | K | 534.00 | Daubert y Danner (1989) |
| $P_c$ | bar | 30.400 | Daubert y Danner (1989) |
| $Z_c$ | — | 0.262 | Daubert y Danner (1989) |
| $RD$ | m | $3.465 \cdot 10^{-10}$ | Daubert y Danner (1989) |
| $\mu$ | Deb. | 1.43 | Martínez-Ageitos (1996) |

[a] Se realizaron dos medidas durante el tiempo transcurrido en la realización de la parte experimental al tratarse de un producto purificado.

**Parámetros de la ecuación de Antoine [17]** (este trabajo)

$A = 6.23218$

$B = 1351.21$

$C = -39.52$

$$\log\left(P_i^{\circ} / \text{kPa}\right) = A - \frac{B}{(T/\text{K}) + C}$$

**Parámetros UNIQUAC** (Martínez-Ageitos, 1996)

$r = 4.7422$

$q = 4.1720$

## **Componente:** ETBE

| Parámetro | Unidades | Valor | Referencia |
|---|---|---|---|
| $PM$ | u.m.a | 102.177 | Daubert y Danner (1989) |
| $d$(298.15 K) | Kg/m$^3$ | 735.62 | este trabajo |
| $n_D$ | — | 1.3730 | este trabajo |
| $T_b$ | K | 345.8 | este trabajo |
| $T_c$ | K | 514.00 | Daubert y Danner (1989) |
| $P_c$ | bar | 30.400 | Daubert y Danner (1989) |
| $Z_c$ | — | 0.272 | Daubert y Danner (1989) |
| $RD$ | m | $3.825 \cdot 10^{-10}$ | Daubert y Danner (1989) |
| $\mu$ | Deb. | 1.20 | Rodil (1999) |

**Parámetros de la ecuación de Antoine [17]** (Reich y col., 1999)

$A = 5.96651$

$B = 1151.73$

$$\log\left(P_i^{\circ} / \mathrm{kPa}\right) = A - \frac{B}{(T/\mathrm{K}) + C}$$

$C = -55.06$

**Parámetros UNIQUAC** (Calculados por UNIFAC-Dortmund: Gmehling y col., 1993)

$r = 4.3059$

$q = 5.4927$

**Componente:** DIPE

| Parámetro | Unidades | Valor | Referencia |
|---|---|---|---|
| $PM$ | u.m.a | 102.177 | Daubert y Danner (1989) |
| $d$(298.15 K) | Kg/m$^3$ | 718.14$^a$<br>718.13$^b$ | este trabajo |
| $n_D$ | — | 1.3656$^a$<br>1.3658$^b$ | este trabajo |
| $T_b$ | K | 341.4$^a$<br>341.6$^b$ | este trabajo |
| $T_c$ | K | 500.05 | Daubert y Danner (1989) |
| $P_c$ | bar | 28.776 | Daubert y Danner (1989) |
| $Z_c$ | — | 0.267 | Daubert y Danner (1989) |
| $RD$ | m | $3.906 \cdot 10^{-10}$ | Daubert y Danner (1989) |
| $\mu$ | Deb. | 1.13 | Daubert y Danner (1989) |

[a] DIPE con una pureza del 99.8+ % en masa. [b] DIPE con una pureza del 99 % en masa.

**Parámetros de la ecuación de Antoine [17]**

$$\log\left(P_i^\circ / \text{kPa}\right) = A - \frac{B}{(T/\text{K}) + C}$$

$A = 6.05151$
$B = 1185.74$
$C = -48.54$

Ref.: este trabajo

$A = 6.22201$
$B = 1257.61$
$C = -43.15$

Ref.: Reid y col., 1977

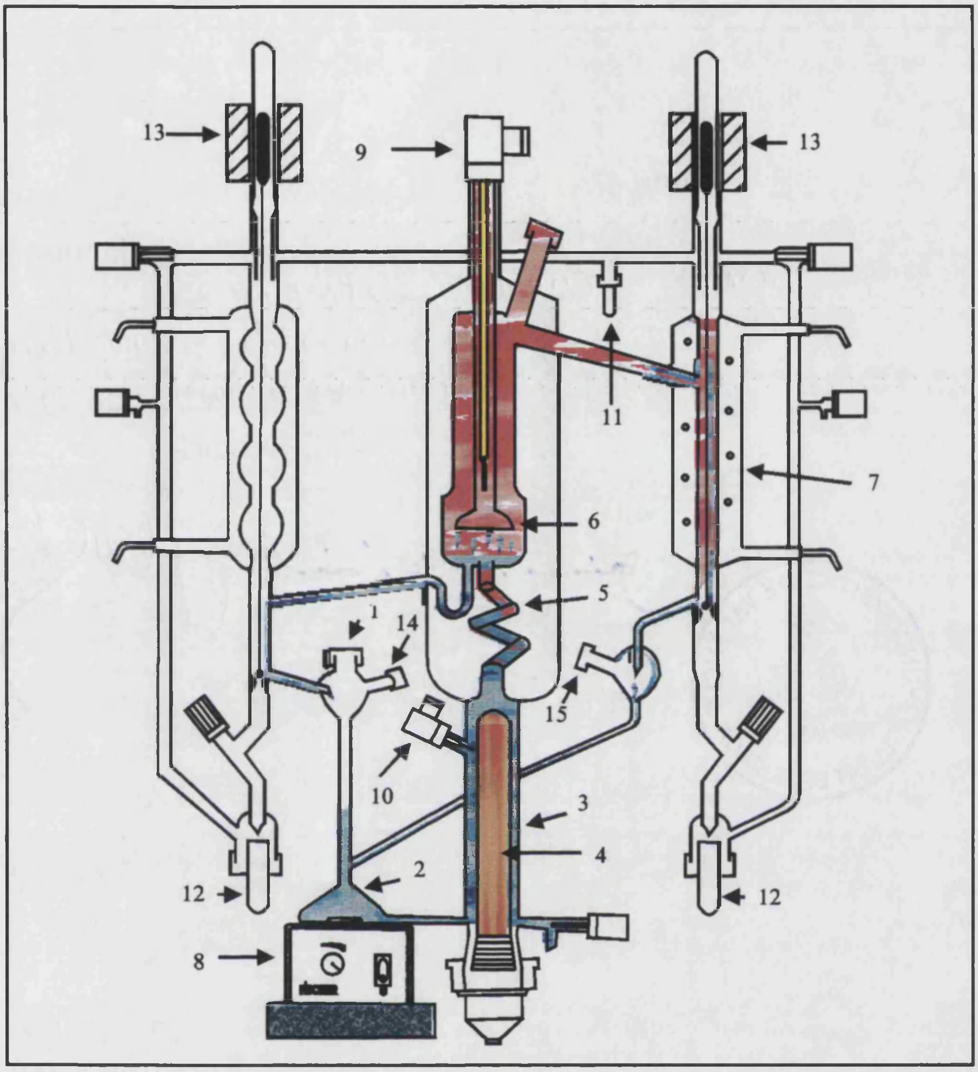
**Parámetros UNIQUAC** (Gmehling y Onken, 1990)

$r = 4.7421$
$q = 4.0880$

## Parámetros de asociación y solvatación (Prausnitz y col., 1980)

| η | Hidrocarburo | Metanol | Etanol | TBA | Éteres |
|---|---|---|---|---|---|
| **Hidrocarburo** | 0.00 | | | | |
| **Metanol** | — | 1.63 | | | |
| **Etanol** | 0.00 | — | 1.40 | | |
| **TBA** | 0.00 | — | 1.55 | 1.00 | |
| **Éteres** | 0.00 | 0.50 | — | 0.50 | 0.00 |

# APÉNDICE 2.- (Destilador de equilibrio)



*1. Entrada de alimentación*

*2. Matraz mezclador*

*3. Calderín*

*4. Calentador eléctrico*

*5. Bomba Cottrell*

*6. Pantalla deflectora*

*7. Condensador*

*8. Agitador magnético*

*9 y 10. Termorresistencias*

*11. Conexión al dispositivo de presión*

*12. Tubos para recoger muestras*

*13. Válvulas magnéticas*

*14. Entrada para coger fase líquida*

*15. Entrada para coger fase vapor*

**Figura 26.** Destilador de equilibrio: modelo Labodest de Fischer

UNIVERSIDAD DE VALENCIA FACULTAD DE CIENCIAS QUIMICAS

Reunido el Tribunal que suscribe, en el día de la fecha, acordó otorgar, por unanimidad, a esta Tesis doctoral de D. SONIA LORAS GIMÈNEZ

la calificación de Sobresaliente "cum Laude"

Valencia, a 27 de Septiembre de 1999.

El Secretario,

El Presidente