The use of mathematical models in the characterization of ethylene oxide condensate surfactants by infrared and ultraviolet spectroscopy

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RÉSUMÉ

Utilisation de modèles mathématiques pour la caractérisation de surfactants à base d'oxyde d'éthylène par spectrométrie UV et IR.

Dans le présent travail, on a appliqué le traitement topologique aux molécules de produits tensioactifs. Le modèle DARC et le modèle de contribution des groupes ont été utilisés pour étudier la corrélation entre les structures des condensats d'oxyde d'éthylène, avec le nonylphénol et avec le ter-octylphénol, et leurs caractéristiques spectrales, telles que coefficient d'extinction *a* (exprimé en $l \cdot g^{-1} \cdot cm^{-1}$ pour la bande d'absorption à 275 nm) et le rapport h_2/h_1 des deux bandes dans l'infrarouge à 960 cm^{-1} (h_2) et 840 cm^{-1} (h_1). On peut déterminer le degré de condensation moyen d'un échantillon à partir de ses caractéristiques spectrales et des paramètres d'information déterminés à l'avance à partir du traitement mathématique d'une population clé.

Mots-clés : Tensioactifs. Condensats d'oxyde d'éthylène. Spectroscopie infrarouge. Spectroscopie ultraviolette. Description topologique des molécules.

SUMMARY

In the present paper, a topological treatment of the surfactant molecules (DARC system) and a group contribution model were applied to study the correlation between structures of ethylene oxide condensates with nonylphenol and tert-octylphenol and their spectral characteristics such as extinction coefficient a (expressed in $l \cdot g^{-1} \cdot cm^{-1}$ of the molecular absorption band at 275 nm) and the h_2/h_1 quotient of the IR bands at 960 cm^{-1} (h_2) and 840 cm^{-1} (h_1). Using the experimental values of the spectral characteristics of an unknown sample of an ethylene oxide condensate surfactant and the information parameters, previously determined by the mathematical treatment of a key population, it is possible to obtain their average condensation degree.

Key-words : Surfactants. Ethylene oxide condensates. Infrared and ultraviolet spectroscopy. Topological description of the molecules.

INTRODUCTION

The industry of condensation products generally supplies compounds with a given polydispersity degree, whose features depend on the average properties, determined by the reaction conditions. This demonstrates the importance of the development of analytical methods allowing a rapid characterization of these properties, both for quality control and for the analysis of commercial samples.

The condensates of ethylene oxide with different organic molecules (nonylphenol, tert-octylphenol, fatty alcohols, fatty acids, etc.) provide compounds with surfactant properties, which present numerous practical applications [1, 2].

Different methods for the caracterization of these compounds have been proposed in the literature, based on liquid chromatography [3], mass spectrometry [4], and nuclear magnetic resonance [5, 6].

We have recently found that some spectral properties of the nonylphenol and tert-octylphenol ethylene oxide condensates vary sistematically with increasing condensation degree (x). For instance, the extinction coefficient a, expressed as $l \cdot g^{-1} \cdot cm^{-1}$ of the absorption band at 275 nm increases as the condensation degree decreases [7]. On the other hand, the infrared (IR) spectra of these compounds shows two bands at about 960 (h_2) and 840 (h_1) cm^{-1} whose heights quotient h_2/h_1, increases with increasing condensation degree [8].

According to these properties, we have proposed two methods for the determination of the average properties of surfactants of this type by interpolation of the a and h_2/h_1 values of unknown samples in the regression plots of these properties versus x, obtained from compounds previously characterized by NMR. However, this procedure involves the use of different

equations for each type of condensates, even if their hydrophobic groups are very similar [9].

In a previous paper, we have presented the first results obtained using topological models to obtain relations between spectroscopic data and the chemical structure of surfactants [10].

The present paper describes in more detailed form, the characterisation of nonylphenol and tert-octylphenol ethylene oxide condensates by UV and IR spectroscopy, from the study of the topological description of the molecules by means of the DARC system, and of the use of a model based on the group contribution [11-16]. This allows us to establish the parameters relating the spectroscopic features of the surfactants with their structure. Also the accuracy of the characterization methods based on these data treatments and on the IR or UV measurements, has been evaluated.

EXPERIMENTAL

Apparatus

The spectrometers used were as follows : a Perkin-Elmer NMR R-12 spectrometer, with a magnetic field intensity of 14092 gauss and a resolution of 0.35 Hz, equipped with a double resonance accessory; a Shimadzu UV-240 spectrophotometer with a graphic printer PR-1, with 1-cm quartz cells and 2 nm slit-width; a Pye Unicam SP-2000 spectrophotometer, with sodium chloride cells; a HP-83 computer equipped with a disk unity 82901 M Hewlett Packard Flexide Disk Drive and a 82905 a Hewlett Packard Printer.

Reagents

— A 3.5 % (w/v) solution of tetramethylsilane (TMS) in distilled carbon tetrachloride.
— Samples of nonylphenol ethylene oxide condensates Nemol K-34, K-36, K-38, K-39, K-539, K-1030, K-1032, K-1033 and K-1035 (Masso & Carol S.A.); Renex 647, 697, 688, 690, 682 and 678 (ICI Pharmaceuticals); Arkopal 40, 60 and 80 (Hoechst).
— Samples of tert-octylphenol ethylene oxide condensates from the Triton X series (X-114 and X-100) manufactured by Serva Panreac, Merck and Fluka.

General procedure

Analysis by NMR

The surfactant (500 ± 1 mg) is weighed and dissolved in an equivalent amount of TMS solution and the NMR spectrum is recorded between 0 and 10 ppm. From the integrated values of the three hydrogen types, the degree of polymerization and the alkyl radical composition can be calculated, because each surfactant molecule contains hydrogens corresponding to the aromatic group, which can be used as an internal reference to calculate the number of hydrogens corresponding to the other peaks. From these calculated values, the molecular weight, condensation degree (x), hydrophilic-lipophilic balance (HLB) and percentage of ethylene oxide can be estimated.

Analysis by UV

Surfactant (0.1-0.2 g) was weighted out, dissolved in water-ethanol mixture (60/40 v/v) and diluted to 50 ml with this solvent. Several aliquots were taken from this solution and all were diluted to 50 ml in volumetric flasks. Their UV spectra were recorded and the values of absorbance at 275 nm determined. These data were plotted versus surfactant concentration in $g \cdot l^{-1}$ and the value of the slope a, determined from the regression by least squares fitting.

Analysis by IR

A drop of the surfactant to be analysed was placed between two sodium chloride windows and its IR spectrum recorded. The ratio between the heights of the bands at 960 and 840 cm^{-1} (h_2/h_1) was calculated.

Calculation methods

Topological model

For the description of molecules using the DARC model, the hydrophobic moiety and the first condensation molecule have been taken as the focus F_O (structure generating the properties of the molecule), the last molecule of ethylene oxide as the terminal group T, and the remaining ($x - 2$) molecules of ethylene oxide as the environment E (*Fig. 1*).

A topological vector (f_o, e, t) is defined for each compound. This vector contains three components related to each one of the different parts considered in the molecule.

As the families of compounds studied only contained one focus and terminal group, the corresponding components of the topological vector are the unity, and the component referring to the environment is $x - 2$, where x is the condensation degree. Therefore, the topological vector is (1, $x - 2$, 1).

One property of the molecule I, can be described by the equation :

$$I = I_{Fo} + e\,I_E + I_T \qquad (1)$$

or by :

$$\log I = I_{Fo} + e\,I_E + I_T \qquad (2)$$

that relate the property with the information parameters associated with the focus (I_{Fo}), with each unit of the environment (I_E) and the terminal group (I_T).

These parameters are obtained for each one of the surfactants series (nonylphenols and tert-octylphenols) for the IR and UV data.

In each case the determination of the information parameters has been made from the spectral characteristics experimentally measured of a number of compounds previously characterized, which provides a
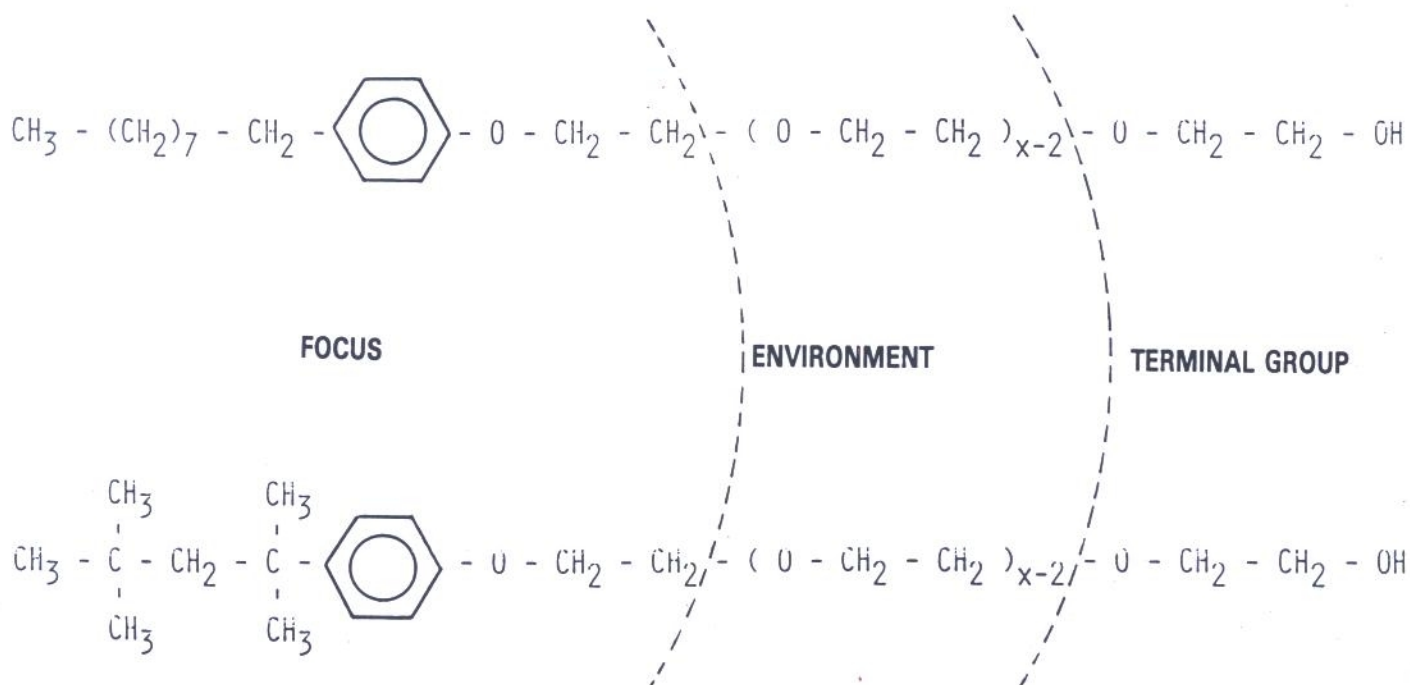
$$CH_3 - (CH_2)_7 - CH_2 - \bigcirc\!\!\!\!\bigcirc - O - CH_2 - CH_2 - (O - CH_2 - CH_2)_{x-2} - O - CH_2 - CH_2 - OH$$

FOCUS   **ENVIRONMENT**   **TERMINAL GROUP**

$$CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - CH_2 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - \bigcirc\!\!\!\!\bigcirc - O - CH_2 - CH_2 - (O - CH_2 - CH_2)_{x-2} - O - CH_2 - CH_2 - OH$$

FIG. 1. — *Topological description of the surfactants by the DARC model.*
FIG. 1. — *Description topologique des tensioactifs par le modèle DARC.*

system of equations of the type (1) or (2). Using a least square fitting, values of I_{Fo}, I_E and I_T could be obtained that minimizes the differences between spectroscopic data experimentally found and those calculated using these parameters.

Model of Group Contribution

For the use of the group contribution model, eight groups with different environments have been taken. These are shown in *Figure 2* for each one of the two types of surfactant considered.
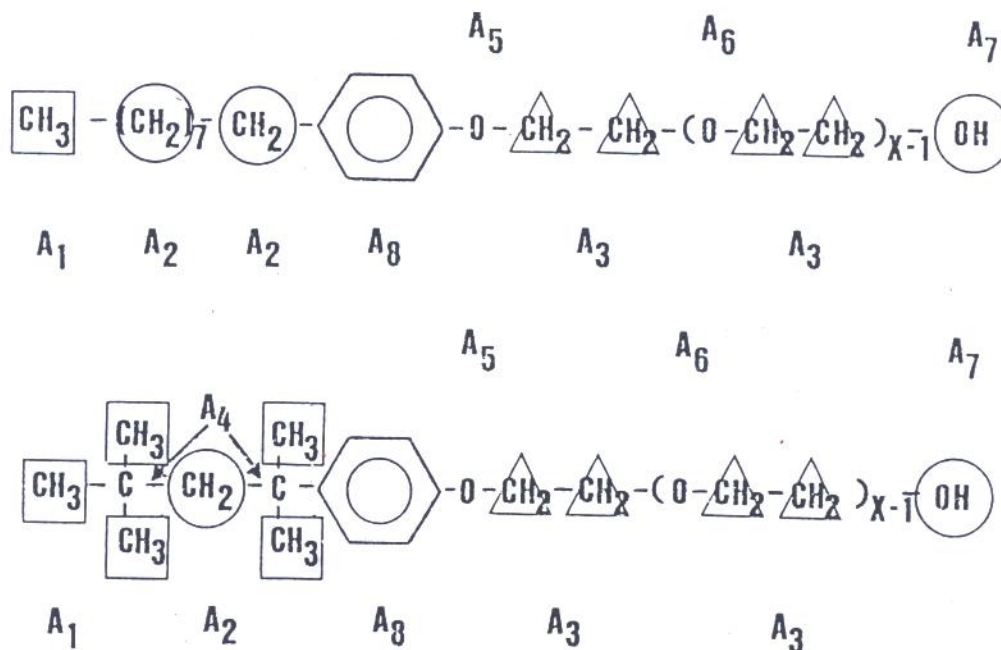
FIG. 2. — *Description of the surfactants by the group contribution model.*
FIG. 2. — *Description des tensioactifs par le modèle de contribution de groupes.*

Each molecule was decomposed in a series of functional groups (A_1, A_2, ... A_n). In this case, one spectral property of a molecule would be expressed in terms of an equation

$$I = \sum_{i=1}^{8} a_i I_{A_i} \qquad (3)$$

in which I is the value of property considered, a_i the number of times of a functional group (A_i) is contained in the molecule and I_{A_i} a parameter corresponding to the information associated with each group.

When treating a large series of compounds, a matritial notation is more appropriate to describe the system of equations of the type of (3) :

$$\begin{bmatrix} I_{\alpha 1} \\ I_{\alpha 2} \\ \cdot \\ \cdot \\ I_{\alpha n} \end{bmatrix} = \begin{bmatrix} a_{11} & a_{12} & \cdots & a_{18} \\ a_{21} & a_{22} & \cdots & a_{28} \\ & & \cdots & \\ & & \cdots & \\ a_{n1} & a_{n2} & \cdots & a_{n8} \end{bmatrix} \cdot \begin{bmatrix} I_{A_1} \\ I_{A_2} \\ \cdot \\ \cdot \\ I_{A_8} \end{bmatrix} \qquad (4)$$

Using a key population of previously characterized compounds, the I_{A_1}, I_{A_2} ... I_{A_8} parameters can be calculated by a least square fitting. From these parameters, and having measured the experimental I_α for an unknown sample, their average condensation degree could be determined.

In this case, a semilogarithmic relation between I_α and I_{A_i} could be employed.

RESULTS AND DISCUSSION

Description of the molecules studied based on the proposed models

The mathematical models employed consider the properties of the molecules as dependent on determined groups present in these. To determine the parameters that correspond to each one of these groups, it is necessary to use a number of previously characterized compounds, measure their properties and use the equations indicated in the experimental part.

In the next section we discuss the criteria employed for the description of the surfactant molecules, and the results obtained in the spectroscopic studies.

Topological description

For the topological description of the molecules considered, the previously indicated concepts were applied.

In *Table I*, we indicate the average condensation degree of a series of ethylene oxide condensates with nonylphenol and with tert-octylphenol determined by NMR; the topological vectors that describe these molecules according to the DARC system and the experimental values of h_2/h_1 and a determined by IR and UV spectroscopy respectively.

TABLE I. — *Topological description of surfactant molecules based on the DARC model and spectroscopic properties of these compounds.*
TABLEAU I. — *Description topologique des molécules de tensioactifs par le modèle DARC et propriétés spectroscopiques de ces composés.*

Sample	x_{NMR}	Topological vectors	h_2/h_1	a $1 \cdot g^{-1} \cdot cm^{-1}$
I a Nonylphenols				
Nemol K-34	4.6	(1, 2.6, 1)	0.8	3.57
Nemol K-36	7.2	(1, 5.2, 1)	1.02	2.90
Nemol K-38	10.0	(1, 8, 1)	1.10	2.41
Nemol K-39	10.7	(1, 8.7, 1)	1.11	2.271
Nemol K-539 (1)	12.0	(1, 10, 1)	1.130	2.214
Nemol K-539 (2)	10.5	(1, 8.5, 1)	1.10	2.29
Nemol K-1030	12.4	(1, 10.4, 1)	1.22	2.090
Nemol K-1032	13.4	(1, 11.4, 1)	1.21	1.894
Nemol K-1033	16.0	(1, 14.0, 1)	1.32	1.758
Nemol K-1035	17.8	(1, 15.8, 1)	1.23	1.70
Renex 647	5.1	(1, 3.1, 1)	0.87	3.31
Renex 697	6.4	(1, 4.4, 1)	0.96	3.090
Renex 688	9.8	(1, 7.8, 1)	1.11	2.44
Renex 690	11.9	(1, 9.9, 1)	1.11	2.13
Renex 682	12.8	(1, 10.8, 1)	1.16	2.1
Renex 678	16.5	(1, 14.5, 1)	1.17	1.69
Arkopal 40	4.3	(1, 2.3, 1)	0.83	3.68
Arkopal 60	6.0	(1, 4.0, 1)	0.95	3.07
Arkopal 80	8.9	(1, 6.9, 1)	1.09	2.41
I b Tert-octylphenols				
Triton X-114 (1) Serva	8.3	(1, 6.3, 1)	0.989	2.66
Triton X-114 (2) Serva	8.0	(1, 6.0, 1)	0.947	2.66
Triton X-114 Fluka	7.87	(1, 5.87, 1)	0.942	2.68
Triton X-100 Serva	10.3	(1, 8.3, 1)	1.031	2.25
Triton X-100 Panreac	11.3	(1, 9.3, 1)	1.069	2.19
Triton X-100 Fluka	10.2	(1, 8.2, 1)	1.019	2.308
Triton X-100 Merk	10.2	(1, 8.2, 1)	1.055	2.25

Group contribution

In order to carry out a description of the surfactant molecules based on the model of group contribution as we have indicated, a series of eight groups with different environments have been selected for each of the two types of surfactants considered.

In *Table II*, the values of coefficients a_1, a_2, ... a_8 are indicated for each compound. These parameters have been estimated from the determination of the average degree of condensation by NMR.

Obtention of the information parameters

As already indicated in the experimental part, in order to obtain the information parameters, two least square fitting have been tested, a linear one and a semilogarithmic one. In each case the model that allows us to obtain the minimum error of the spectroscopic properties considered has been chosen.

For the characterization of both series of surfactants studied from the values of a determined by UV spectroscopy, the best results were obtained using a semilogarithmic model for the adjustment of the results using both topological and groups approach.

TABLE II. — *Description of surfactant molecules based on the group contribution model.*

TABLEAU II. — *Description des molécules des tensioactifs par le modèle de contribution de groupes.*

2 *a* Nonylphenols								
Sample	A_1	A_2	A_3	A_4	A_5	A_6	A_7	A_8
Nemol K-34	1	8	9.2	0	1	3.6	1	1
Nemol K-36	1	8	14.4	0	1	6.2	1	1
Nemol K-38	1	8	20	0	1	9	1	1
Nemol K-39	1	8	21.4	0	1	9.7	1	1
Nemol K-539 (1)	1	8	24	0	1	11	1	1
Nemol K-539 (2)	1	8	21	0	1	9.5	1	1
Nemol K-1030	1	8	24.8	0	1	11.4	1	1
Nemol K-1032	1	8	26.8	0	1	12.4	1	1
Nemol K-1033	1	8	32	0	1	15	1	1
Nemol K-1035	1	8	35.6	0	1	16.8	1	1
Renex 647	1	8	10.2	0	1	4.1	1	1
Renex 697	1	8	12.8	0	1	5.4	1	1
Renex 688	1	8	19.6	0	1	8.8	1	1
Renex 690	1	8	23.8	0	1	10.9	1	1
Renex 682	1	8	25.6	0	1	11.8	1	1
Renex 678	1	8	33	0	1	15.5	1	1
Arkopal 40	1	8	8.6	0	1	3.3	1	1
Arkopal 60 ·	1	8	12	0	1	5	1	1
Arkopal 80	1	8	17.8	0	1	7.9	1	1
2 *b* Tert-octylphenols								
Sample	A_1	A_2	A_3	A_4	A_5	A_6	A_7	A_8
Triton X-114 (1) Serva	5	1	16.6	2	1	7.3	1	1
Triton X-114 (2) Serva	5	1	16	2	1	7	1	1
Triton X-114 Fluka	5	1	15.74	2	1	6.87	1	1
Triton X-100 Serva	5	1	20.6	2	1	9.3	1	1
Triton X-100 Panreac	5	1	22.6	2	1	10.3	1	1
Triton X-100 Fluka	5	1	20.4	2	1	9.2	1	1
Triton X-100 Merck	5	1	20.4	2	1	9.2	1	1

For the characterization of these compounds by IR spectroscopy from the values of h_2/h_1, the best results were obtained using a linear adjustment.

In *Table III* the values of I_{Fo}, I_E and I_T obtained for both surfactant series using both linear and semilogarithmic adjustment of the h_2/h_1 and *a* are given.

The quality of the adjustment has been estimated from the mean relative difference between calculated and experimentally measured values of both spectral characteristics.

It can be observed that for both series of compounds the values of the parameters are of the same order even though the topological system employed does not allow us to consider both simultaneously. These parameters have been obtained using all the compounds studied.

When the adjustment was carried out with only certain compounds, eg. those which have an odd number in the table, and then the values of these having an even number were predicted, slightly different values of the parameters and a higher error factor in the prediction were obtained.

In *Table IV* the relative differences obtained for *a* and h_2/h_1 data corresponding to the nonylphenol under the above mentioned conditions are indicated as an example.

Using the group contribution model, the values of the parameters I_{A_1}, I_{A_2}, ... I_{A_8} for all the surfactants considered have been obtained.

In *Table V* values found from both linear and semilogarithmic adjustments using a key population of 16 compounds are set out.

In his case too, linear adjustment provides better results in the h_2/h_1 estimation, while for the estimation of *a*, a semilogarithmic adjustment is preferable.

Having considered the contribution of 8 different groups it was necessary to use a key population of at

TABLE III. — *Information parameters corresponding to a topological description.*

TABLEAU III. — *Paramètres d'information obtenus à partir du traitement par le modèle DARC.*

Nonylphenols				
	I_{Fo}	I_A	I_T	$\bar{\varepsilon}$ (%)
h_2/h_1	0.8041	$3.217 \cdot 10^{-2}$	$6.33 \cdot 10^{-3}$	4
$\log h_2/h_1$	$- 6.807 \cdot 10^{-2}$	$1.345 \cdot 10^{-2}$	$- 1.498 \cdot 10^{-3}$	4.5
a	3.727	$- 0.1475$	$- 2.369 \cdot 10^{-2}$	5.6
$\log a$	0.6093	$- 2.568 \cdot 10^{-2}$	$- 1.413 \cdot 10^{-2}$	3.2
Tert-octylphenols				
	I_{Fo}	I_A	I_T	$\bar{\varepsilon}$ (%)
h_2/h_1	0.7633	$3.311 \cdot 10^{-2}$	$- 6.515 \cdot 10^{-3}$	0.9
$\log h_2/h_1$	$- 9.872 \cdot 10^{-2}$	$1.436 \cdot 10^{-2}$	$- 7.173 \cdot 10^{-3}$	0.9
a	3.657	$- 0.1576$	$- 4.384 \cdot 10^{-2}$	1.2
$\log a$	0.597	$- 2.805 \cdot 10^{-2}$	$- 2.895 \cdot 10^{-3}$	1.1

TABLE IV. — *Information parameters corresponding to nonylphenols and average errors obtained in the prediction of new values.*

TABLEAU IV. — *Paramètres d'information obtenus pour les nonylphénols et valeurs des erreurs moyennes obtenues dans la prédiction de nouvelles données.*

	I_{Fo}	I_A	I_T	ε^* (%)	ε^{**} (%)
h_2/h_1	0.6925	$4.307 \cdot 10^{-2}$	$4.363 \cdot 10^{-2}$	2.8	3.5
a	3.874	$- 0.1663$	$- 1.35 \cdot 10^{-2}$	5	7.9

* Relative difference between calculated and experimental values of the reference samples.
** Relative difference between calculated and experimental values obtained in the prediction of *a* and h_2/h_1 for new samples.

TABLE V. — *Information parameters corresponding to the use of the group contribution model.*

TABLEAU V. — *Paramètres d'information obtenus par l'emploi du modèle de contribution de groupes.*

	I_{A_1}	I_{A_2}	I_{A_3}	I_{A_4}	I_{A_5}	I_{A_6}	I_{A_7}	I_{A_8}	$\bar{\varepsilon}$ (%)
h_2/h_1	$- 0.7109$	$- 1.962 \cdot 10^{-3}$	$- 9.405 \cdot 10^{-4}$	1.382	3.588	4.381	256.7	$- 258.9$	2.3
$\log h_2/h_1$	$- 0.2171$	$5.245 \cdot 10^{-4}$	$4.871 \cdot 10^{-4}$	0.4246	1.562	1.675	$- 284$	282.5	2.7
a	4.923	$- 1.535 \cdot 10^{-2}$	$- 2.612 \cdot 10^{-2}$	$- 9.949$	$- 11.34$	$- 7.981 \cdot 10^{-2}$	1755	$- 1745$	4.4
$\log a$	0.5542	$7.014 \cdot 10^{-2}$	$1.634 \cdot 10^{-2}$	$- 0.8685$	$- 17.81$	$- 5.529 \cdot 10^{-2}$	4846	$- 4828$	3.8

least 16 compounds to estimate the information parameters and for this reason the tert-octylphenols have not been considered separately.

When the I_{A_1}, I_{A_2}, ... I_{A_8} parameters were determined for nonylphenols using a key population of all the 19 compounds studied the following relationship between these and the UV spectroscopy data was obtained :

$$\log a = -19.54\, a_1 + 1.689\, a_2 - 0.1259\, a_3$$
$$+ 2.289\, a_5 + 0.2289\, a_6 + 2.289\, a_7 + 2.289\, a_8$$

which is totally different from that obtained for all nonylphenols and tert-octylphenols considered simultaneously, due to the absence of the A_4 groups.

On the other hand, the error factor found in the prediction of a and h_2/h_1 for compounds not used as a part of a key population is 5.6 % for h_2/h_1 and 5.4 % for a, using a linear adjustment in both cases.

Accuracy of the results obtained using the proposed models

From an analytical point of view, the interest of the topological description of the surfactant molecules or the group contribution model, does not lie in the confirmation of the identity between experimentally found values and those obtained by a numerical calculation but in the possibility of estimating the average condensation degree of an unknown sample from the experimental a or h_2/h_1 values and the information parameters.

Using the coefficients obtained by linear adjustment, for h_2/h_1 data, and by semilogarithmic adjustment for the a data, the average degree of condensation of each compound from experimental values has been calculated. To determine the accuracy of the proposed methods, we have employed the regression between these data and those determined by NMR [17, 18].

In *Figures 3 and 4*, a comparison is made between the results obtained and the NMR data.
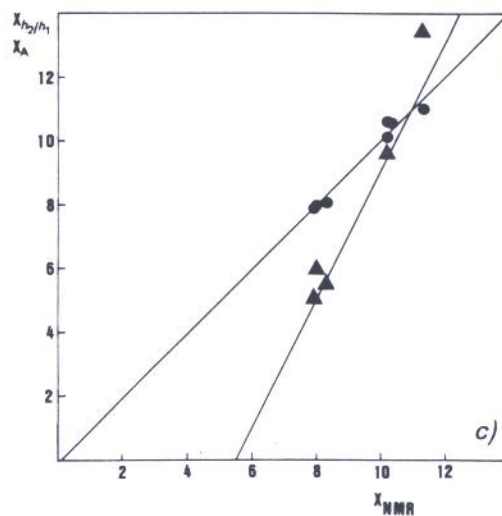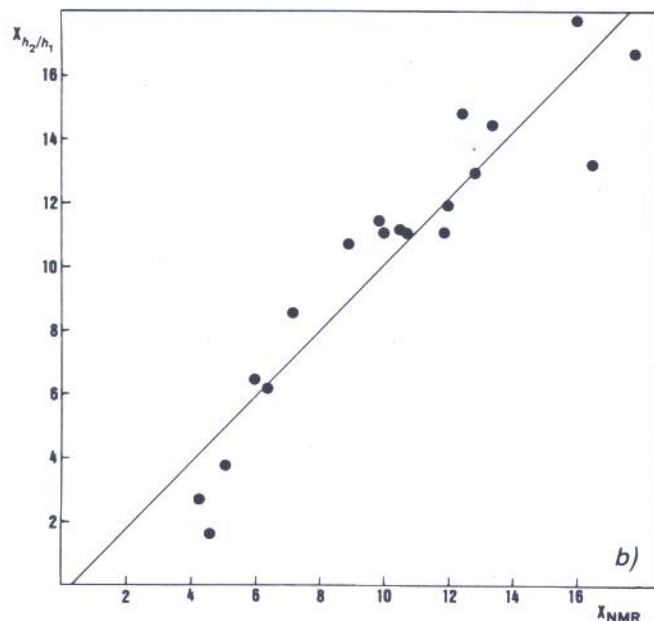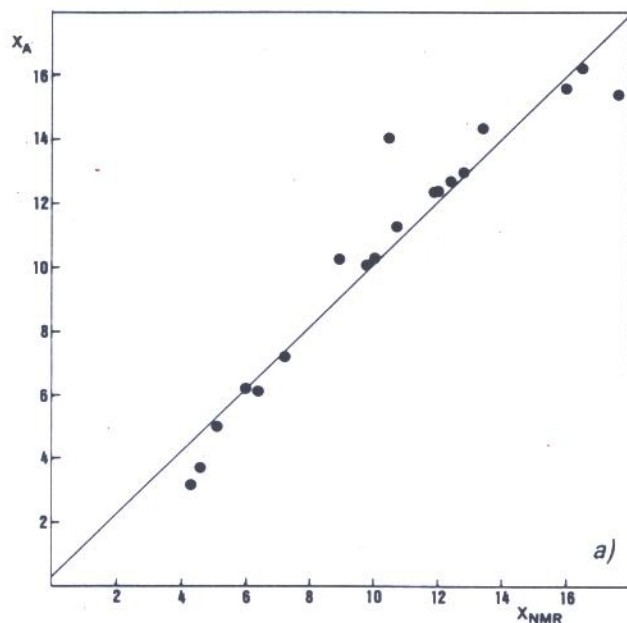

FIG. 3. — *Relationship between the average condensation degree values obtained by UV and IR spectroscopy, and NMR values employing the topological description of the molecule.*

1a. — Nonylphenol / UV data
1b. — Nonylphenol / IR data
1c. — Tert-octylphenol ● UV data ▲ IR data

1a : $x_a = 0.328 + 0.986\, x_{NMR}$ $r^2 = 0.92$
     $s_b = 0.0697$ $t_b = 0.2009$
     $s_a = 0.771$ $t_a = 0.425$ t_{teor} (95 %) = 2.11

1b : $x_{h_2/h_1} = -0.483 + 1.049\, x_{NMR}$ $r^2 = 0.88$
     $s_b = 0.0946$ $t_b = 0.518$
     $s_a = 1.046$ $t_a = 0.462$ t_{teor} (95 %) = 2.11

1c : $x_a = -0.153 + 1.020\, x_{NMR}$ $r^2 = 0.97$
     $s_b = 0.0791$ $t_b = 0.259$
     $s_a = 0.755$ $t_a = 0.203$ t_{teor} (95 %) = 2.571
     $x_{h_2/h_1} = -12.41 + 2.213\, x_{NMR}$ $r^2 = 0.96$
     $s_b = 0.416$ $t_b = 6.69$
     $s_a = 0.121$ $t_a = 87.27$ t_{teor} (95 %) = 2.776

FIG. 3. — *Relation entre le degré de condensation moyen obtenu par spectroscopie UV et IR et ceux obtenus par la NMR en employant le modèle DARC.*
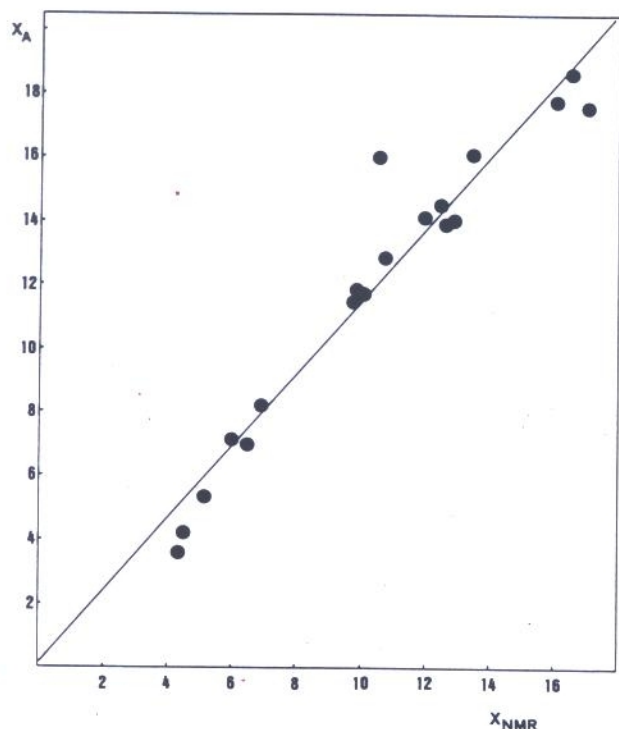
FIG. 4. — *Relationship between the average condensation degree values of nonylphenols obtained by UV and NMR values, employing the group contribution model.*

$$x_a = 0.0983 + 1.140\, x_{NMR} \qquad r^2 = 0.94$$
$$s_b = 0.0718 \qquad t_b = 1.95$$
$$s_a = 0.794 \qquad t_a = 0.123 \qquad t_{teor}\,(95\,\%) = 2.11$$

FIG. 4. — *Relation entre le degré de condensation moyen des nonylphénols obtenu par la spectroscopie UV et la RMN en employant le modèle de contribution de groupes.*

From these data, it can be deduced that both reference and proposed methods provide similar results. However, the errors corresponding to the average condensation degree of these molecules are higher than differences found between experimental values of a and h_2/h_1 and those calculated from the equations used.

The determination of the average condensation degree of tert-octylphenols from IR data using a topological description of these molecules presents constant relative errors and demands a blank correction (*Fig. 3c*).

The use of the group contribution model, despite its theoretical advantages, gives a higher error factor. It is particularly inapplicable to the determination of the average condensation degree of the compounds studied by IR, and although it does not present constant

relative errors or demand blank correction for the characterization of nonylphenols by UV spectroscopy (*Fig. 4*), it presents constant relative errors in the characterization of tert-octylphenols.

Consequently, the use of topological models to establish the relationship between the spectral properties of ethylene oxide condensates and their structure, allows us to obtain a good agreement between the measured values and the predicted values and can be used in the semiquantitative estimation of the average condensation degree of this type of compound from their spectra in the ultraviolet and infrared data.

These models allow a better description of the properties of condensation molecules from their structures than other simple models, such as linear, and could be employed in cases in which the variation with the condensation degree of certain properties can not be linearized.

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