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N. Marquez[ab]; R. E. Anton[a]; A. Usubillaga[c]; J. L. Salager[d]
[a] LABORATORIO FIRP INGENIERíA QUíMICA FACULTAD DE INGENIERíA, UNIVERSIDAD DE LOS ANDES, MéRIDA, VENEZUELA [b] FACULTAD DE CIENCIAS, UNIVERSIDAD DEL ZULIA, MARACAIBO, VENEZUELA [c] INSTITUTO DE INVESTIGACIONES QUíMICAS FACULTAD DE FARMACIA UNIVERSIDAD DE LOS ANDES, MéRIDA, VENEZUELA [d] LABORATORIO FIRP INGENIERíA QUíMICA FACULTAD DE. INGENIERíA, UNIVERSIDAD DE LOS ANDES, MéRIDA, VENEZUELA

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N. MARQUEZ
LABORATORIO FIRP
INGENIERÍA QUÍMICA
FACULTAD DE INGENIERÍA
UNIVERSIDAD DE LOS ANDES
MÉRIDA, VENEZUELA

FACULTAD DE CIENCIAS
UNIVERSIDAD DEL ZULIA
MARACAIBO, VENEZUELA

R. E. ANTON
LABORATORIO FIRP
INGENIERÍA QUÍMICA
FACULTAD DE INGENIERÍA
UNIVERSIDAD DE LOS ANDES
MÉRIDA, VENEZUELA

A. USUBILLAGA
INSTITUTO DE INVESTIGACIONES QUÍMICAS
FACULTAD DE FARMACIA
UNIVERSIDAD DE LOS ANDES
MÉRIDA, VENEZUELA

J. L. SALAGER
LABORATORIO FIRP
INGENIERÍA QUÍMICA
FACULTAD DE INGENIERÍA
UNIVERSIDAD DE LOS ANDES
MÉRIDA, VENEZUELA

ABSTRACT

In surfactant–oil–water phase behavior studies, especially those related to enhanced oil recovery, each of the oligomers of commercial polyethoxylated nonionic surfactants partitions in a different pattern into the two or three phases in equilibrium, and a simple, fast, and accurate method is required to analyze all phases. Up to now, only oil-phase GC was relied upon to determine the partitioning without closing the surfactant inventory. Isocratic normal phase HPLC with a ternary mobile phase (*n*-heptane–chloroform–methanol 70–10–20) is shown to comply with these requirements to analyze the oligomer distribution in microemulsion, excess oil, and excess water phases of an optimum formulation system.

INTRODUCTION

In the mid-seventies much research was carried out on surfactant science because of interest in enhanced oil recovery. Industrial research groups as well as university teams tried to understand the basics of phase behavior, interfacial tension, and solubilization in systems containing surfactant, oil, and water. The systems are much more complex than the so-called Winsor's ternary (1) because each of the three components is a mixture itself which may contain scores of different chemicals. By the end of the seventies a good understanding was attained for pure surfactant–oil–brine systems (2). Later on, this knowledge was used to understand the relationship between physicochemical formulations and the properties of such dispersed systems as emulsions (3–7) and foams (8, 9). At the same time, deeper research was carried out in order to understand complex multicomponent systems, especially the behavior of mixtures.

In the past 10 years, surfactant mixtures have been dealt with for two reasons: 1) because real systems are mixtures, generally for commercial reasons, and 2) mixtures allow the attainment of some average effect or some synergy, i.e., the enhancement of a property. It must be recalled that in the surfactant business an impurity may be the cause, the culprit, or the savior of a problem, i.e., "a friend or a foe." In many applications it is of primary importance to know the composition of an effective mixture of surfactants. It has been shown that changes in the behavior of surfactant mixtures with concentration or the water-to-oil ratio (10–16) are due to a phenomenon, the so-called fractionation, which is a differential partitioning of the surfactant between the oil, water, and microemulsion phase (17). A few years ago a model was proposed to interpret the partitioning of ethoxylated nonionic surfactants (18–20). This model was recently extended to the case of complex mixtures containing not only polydistributed nonionic surfactants but also anionics (21) and cationics (22).

The application of the model requires a great deal of information, especially on the critical micelle concentration (CMC) of the mixtures and on the partitioning of pure surfactant species between oil and water. It has been shown that fractionation depends not only upon the partition coefficient but also upon the water-to-oil ratio (WOR), the total surfactant concentration, and the physicochemical formulation. Actually, the formulation is a set of ten or so variables which describe the nature of the different components of the system in addition to the effects of temperature and pressure (11, 23).

Progress in this area has been slow because of the difficulty in analyzing surfactant isomeric species in complex mixtures. Of particular interest is the separation of polyethoxylated nonionic oligomers. In the next section, our review on the current literature on this topic will show that analytical chromatography (GC or HPLC) techniques have been applied mostly to organic solvents. However, the fractionation data require the surfactant species to be analyzed in all the (two or three) phases in equilibrium. The present article addresses this problem.

We optimize the solvent mixture so that good separation can be reached in the isocratic mode. As an application of our technique, we studied the complex fractionation of a polyethoxylated alkyl phenol surfactant system along an EON formulation scan.

ANALYSIS OF POLYETHOXYLATED NONIONICS

Most nonionic surfactants are of the polyether-type synthesized by the addition of ethylene oxide to substances with a reactive hydrogen atom, such as alkylphenols (24). During the ethoxylation process, adduction randomness results in a mixture of oligomers with a variable degree of ethoxylation, which is often Poisson distributed.

Some previous research has been dedicated to the determination of the ethylene oxide number (EON) distribution of polyethoxylated nonylphenol surfactants by various analytical procedures (25, 26), mainly of the chromatographic type.

The application of thin layer chromatography (TLC) (27–30) seems to be limited to qualitative analysis (31), whereas gas–liquid chromatography (GLC) techniques fail to separate higher molecular weight oligomers (EON > 8) because of their low volatility (27, 32–36). High performance liquid chromatography (HPLC) has recently become a method of choice because of the simplicity of the analytical procedure and its straightforward applicability to the separation of higher ethoxymers. Ethoxylated alkylphenols are readily traced by UV and fluorescence detectors. UV detection of ethoxylated alkylphenols at the aromatic ring absorbance wavelength (about 275 nm) has been found to be independent of the EON (37–39), a useful feature indeed.

As far as the separation method is concerned, isocratic HPLC exhibits several attractive features such as its simplicity, its reproducibility, and its relatively low cost. It has been reported to be quite useful for the analysis of ethoxylated alkylphenol organic solutions (40–44). We applied it to the analysis of this kind of surfactants (in the 4–10 average EON range) in real surfactant–oil–water systems with two or three coexisting phases at equilibrium.

Up to now the partitioning (13, 20, 45, 46) of surfactant in oil–water–microemulsion systems has been deduced mostly from the GC or reversed phase HPLC analysis of the oil phases, without closing the total surfactant mass inventory.

In this article we describe a fast and reliable isocratic HPLC method to analyze the polyethoxylated nonylphenol oligomer species in the oil, aqueous, and microemulsion phases of a ternary system.

EXPERIMENTAL PROCEDURES

HPLC Equipment

The HPLC equipment was set up with a M600 pump, a U6K injector (both from Waters Associates), and a UV variable wavelength detector (from Du Pont) operated at 276 nm, connected to a Varian integrator model 4270. The column is a stainless steel, 25 cm × 4.6 mm i.d., Lichrosorb Si 60-10 m, with a precolumn (stainless steel, 5 cm × 3.8 mm i.d.) for normal phase chromatography packed in the laboratory with Corasil. All flow rates were set at 1 mL/min.

Chemicals

n-Heptane, chloroform, and methanol, used in the mobile phase, were HPLC-grade solvents from Baker. They were filtered with a Millipore nonaqueous 0.45-μm filter before use. The mobile phases were degassed by ultrasonication and by continuous stripping with helium. The mobile phase was composed of *n*-heptane, chloroform, and methanol in various volume proportions referred to as (a) 90–5–5, (b) 60–20–20, and (c) 70–10–20.

Commercial polyethoxylated nonylphenols (Makon 4, 6, 8, and 10, where the index indicates the average EON), were provided by Stepan Chemicals Co.

Procedures

All surfactant solution samples were dissolved in anhydrous methanol so that a single phase was obtained whatever the solution composition. Reference solutions for chromatographic analysis contain 2 wt% surfactant. The injected aliquot volume was 10 μL, unless otherwise stated.

The physicochemical formulation change through the three-phase transition was provided by an EON scan, the principle of which is described elsewhere (2, 11). The water phase was pure distilled water which does not contain any electrolyte, the oil phase was *n*-heptane, and the surfactants were Makon family nonionics. The water-to-oil ratio was unity. From one system to the next, the only difference was the average EON of the ethoxylated nonylphenol surfactant, whose effective value was the actual formulation variable.

The average EON is changed by mixing two nearest commercial surfactants, e.g., Makon 4 with Makon 6 (both dissolved in heptane at 3 wt%). The EON increase results in the II → III → I transition of the phase behavior (11). The tubes are closed with a screw cap and placed in a vertical position in a constant temperature enclosure (25°C). They are gently stirred once a day for a period of 1 week in order to improve the phase contact; then they are left to fully equilibrate for at least 2 weeks. After equilibration, the oil and aqueous phase samples are evaporated to dryness in a convection oven at 60°C or using a Rotavapor under vacuum. The microemulsion dissolution in methanol is helped by ultrasonic stirring; the methanol is then evaporated, together with the traces of water or oil, until a dry surfactant residue is left. The surfactant residue is then redissolved in methanol, and 10 μL aliquots of this solution are analyzed by HPLC.

RESULTS AND DISCUSSION

HPLC Analysis

Most commercially available nonionic surfactants are polyethoxylated alcohols or alkyl phenols with a wide distribution in their ethylene oxide chain length. According to published data (47), nonionic surfactants exhibit a greater affinity toward the oil than toward the water when they contain less than eight ethylene oxide groups per molecule.

As a consequence if *n*-heptane is used as a mobile phase to fractionate a mixture of surfactant species, the lipophilic ones (EON < 8) elute with the solvent front while the hydrophilic ones are strongly retained by the column. On the other hand, if pure methanol is used, the hydrophilic surfactant species elute with the solvent front.

Thus, the practical problem of isocratic HPLC lays in finding an appropriate mobile phase so that the hydrophilic and lipophilic species can be fully separated. This difficulty has curtailed the application of this method, and many researchers have turned to gradient elution HPLC, a more fashionable and sophisticated technique. It is, however, a more time-consuming, more expensive and less reproducible alternative.

In this report an optimized mobile phase is investigated in an attempt to retain the user-friendly features of routine isocratic HPLC versus gradient HPLC, which will be dealt with in Part II of this series.

This normal phase separation is based on the difference in affinity of the polyether chain of the surfactant species with respect to the stationary phase (silica) and the mobile phase, which must be less polar.

At first, it may be thought that a mixture of an apolar solvent, such as *n*-heptane, with a polar one, such as methanol, would produce a proper polarity compromise. Unfortunately these two solvents, and many others with the same characteristics, are not miscible, as may be deduced from their large difference in solubility parameters (48). The miscibility gap may be reduced by the addition of a third component with an intermediate polarity, as is well known from regular solution theory. In the present case chloroform, which is miscible with both heptane and methanol, is a choice candidate to attain a single-phase elution solvent.

Different ternary mixture proportions were tried in order to find out the optimum one. With mixture (a), which contains *n*-heptane–chloroform–methanol with respective 90:5:5 volume fractions, the hydrophilic surfactants are strongly retained in the column. On the other hand, mixture (b), which contains a 60:20:20 composition, produces the quick elution of all surfactant species with poor resolution. The optimum mixture (c) is found to be composed of *n*-heptane–chloroform–methanol in 70:10:20 volume fractions.

Figure 1 shows the chromatograms obtained with methanol solutions of Makon 4 (A), Makon 6 (B), Makon 8 (C), and Makon 10 (D), and the optimum mobile phase (c). It is seen that the surfactant oligomers can be separated very effectively by isocratic normal HPLC with a very short elution time, i.e., a few minutes.

Since UV absorbance has been found to be independent of the polyether chain, peak areas can used to calculate the mole fraction of each ethoxylated alkylphenol oligomer. These results are shown in Tables 1 and 2 for Makon 4 and 6, whose average EON are found to be, respectively, 3.95 and 5.2, a close agreement with 4, and a not-so-close fit with 6. When the EON experimental values are compared with the theoretical Poisson distribution, a more or less accurate agreement is exhibited, as mentioned by other authors (49).

Since surfactant mixing is the experimental way to reach an intermediate value of average EON, the HPLC fingerprints of these mixtures are evaluated prior to analysis of the partitioning data.

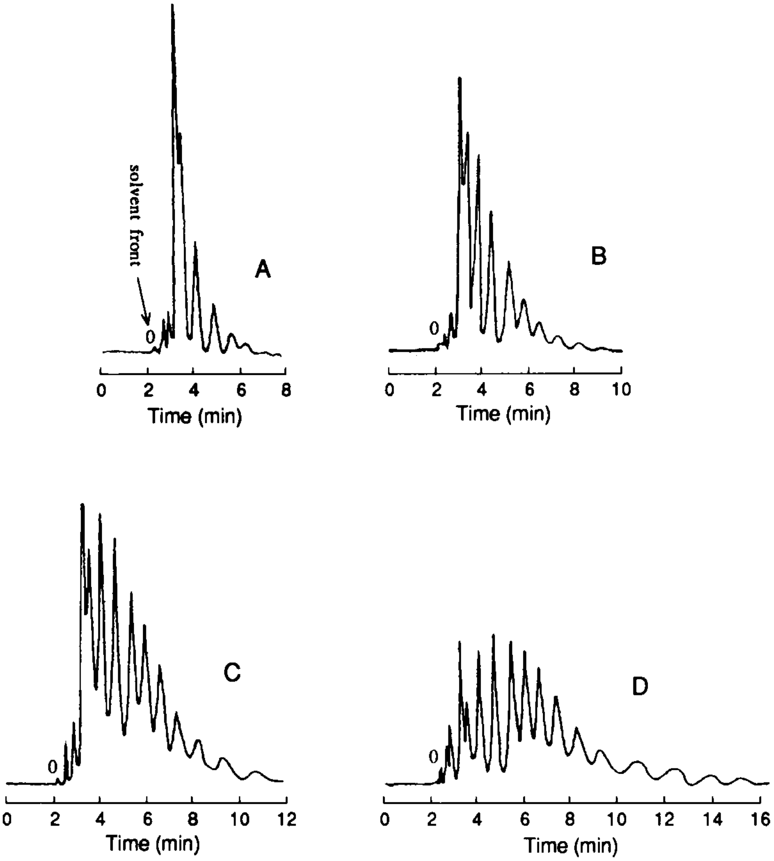

FIG. 1 Normal phase chromatograms of Makon 4 (A), Makon 6 (B), Makon 8 (C), and Makon 10 (D). Column, Lichrosorb Si 60, 250 × 4.6 mm i.d., 10 μm particle size; precolumn, Corasil, 50 × 3.8 mm; mobile phase, *n*-heptane–chloroform–methanol (70:10:20); UV detection at 276 nm. Concentration of each surfactant, 2 g in 100 mL methanol.

The different commercial surfactants are mixed two at a time (Makon 4 + Makon 6, Makon 4 + Makon 8, and Makon 4 + Makon 10) to obtain intermediate EON, assuming a linear mixing rule on a mole fraction basis. The three cases exhibit an increasing difference of hydrophilicity between the two surfactants of the mixture. This feature will be used later to interpret the partitioning according to the mono- or bimodality of the EON distribution.

TABLE 1
EO Distribution of Makon 4

EON	Peak area	Mole fraction × 100%	Mole fraction × EON
1	3,286	5.03	0.0503
2	3,990	6.10	0.122
3	22,066	33.78	1.014
4	14,016	21.46	0.858
5	11,656	17.85	0.890
6	6,344	9.71	0.580
7	2,828	4.32	0.300
8	1,131	1.73	0.138
	65,316	99.98	Av EON = 3.95

As seen in Fig. 2, the three chromatograms (for 50 wt% of each surfactant in the mixture) share a general appearance with those shown in Fig. 1 for the base surfactants alone. Because of the smaller molecular weight of Makon 4, the 50 wt% mixture results in a higher molar fraction of Makon 4 and a dominance of its peak pattern at low EON. However, the resolution is kept at a satisfactory level up to EON = 12; beyond this value a higher amount of surfactant is needed to insure the proper detection. As shown in Fig. 1, the maximum EON which may be detected is about 16,

TABLE 2
EO Distribution of Makon 6

EON	Peak area	Mole fraction × 100%	Mole fraction × EON
1	353	0.61	0.0061
2	898	1.56	0.0131
3	10,482	18.25	0.55
4	12,311	21.43	0.86
5	11,217	19.53	0.98
6	8,990	15.65	0.94
7	6,555	11.41	0.80
8	3,942	6.86	0.55
9	1,007	1.75	0.16
10	803	1.40	0.14
11	531	0.92	0.10
12	350	0.61	0.073
	57,439	99.98	Av EON = 5.19

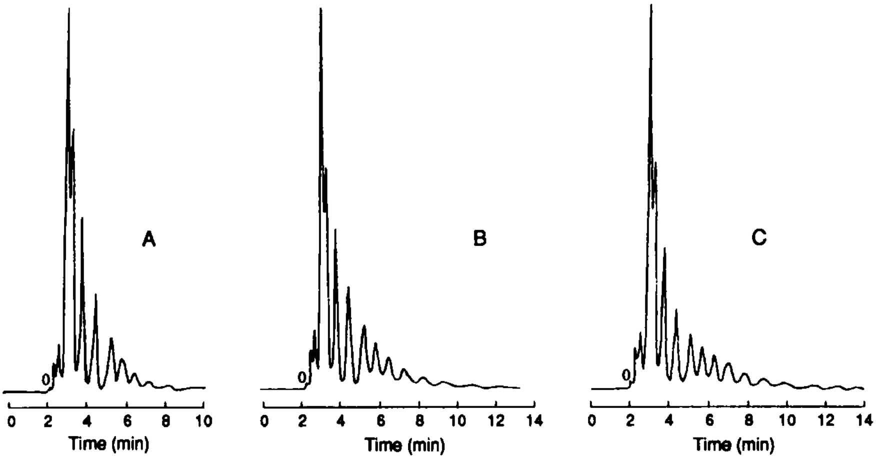

FIG. 2 Normal phase chromatograms of mixture of surfactants. Makon 4 + Makon 6 (A); Makon 4 + Makon 8 (B), and Makon 4 + Makon 10 (C). Conditions as in Fig. 1. Concentration of each surfactant, 1 g in 100 mL methanol.

a value which is, in any case, higher than the maximum detectable by GC.

Surfactant Partitioning

When an EON formulation scan is carried out, some of the systems exhibit a three-phase behavior in which a surfactant-rich microemulsion is in equilibrium with excess oil and water phases (11). Previous research has shown that the nonionic oligomers tend to be present in different amounts and to have different compositions in the three phases (20).

As an application of the proposed isocratic method, the ethoxylated nonylphenol distribution between the three phase of such a system was studied. The EON scan was carried out by mixing Makon 4 and Makon 6 in different proportions, according to Bourrel et al. (11, 13), who found that mixing two nonionic surfactants to obtain a product having an intermediate average should only be done with surfactants whose individual averages are closest to the sought after mixture average.

Three-phase behavior is exhibited in the range from 0.76 to 0.96 mol fraction of Makon 4 in the Makon 4–Makon 6 mixture. The optimum formulation is for the system with a 0.84 Makon 4 mol fraction, i.e., at the center of the three-phase range where the microemulsion contains equal solubilized amounts of oil and water. After carrying out the extraction procedure reported in a previous section, the surfactant contents in the oil, microemulsion, and water phases were determined by HPLC.

As expected, the excess oil phase contains a much higher concentration of surfactant than the excess aqueous phase. The surfactant overall mole inventory in the three-phase optimum system is 21% in the oil phase, 77% in the microemulsion, and 2% in the aqueous phase.

Figure 3 shows chromatograms of the oil (A), microemulsion (B), and aqueous (C) phases reduced to a similar concentration level in order to appreciate the composition difference and the selective partitioning of the oligomers. The actual concentration of each species is calculated by multiplying the peak area by the respective inventory percentage.

The oil-phase chromatogram (A) looks like the Makon 4 one (see Fig. 1A) while the aqueous-phase chromatogram has flattened low EON peaks as does the Makon 10 one (see Fig. 1D).

The chromatogram of microemulsion is similar to the chromatogram of the overall mixture, an expected result since 77% of the surfactant is in it. Nevertheless, it is different because 20% of the surfactant species which partition into the oil phase are more lipophilic than the average. As a consequence, the microemulsion surfactant EON, the so-called real or interfacial $\mathrm{EON}^*_{\mathrm{int}}$, is higher than the overall one.

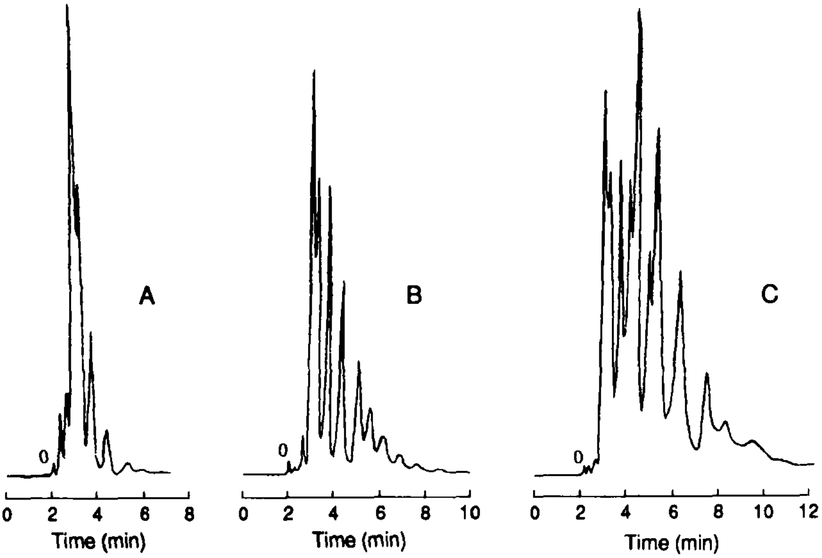

FIG. 3 Normal phase chromatograms of surfactant mixture (Makon 4 + Makon 6, at optimum formulation) in the oil (A), microemulsion (B), and water (C) phases. Conditions as in Fig. 1.

Table 3 shows the mole fraction of different oligomers in the three phases. The average EON in each phase agrees with the values computed by the Graciaa et al. (11) mathematical model.

By using the optimum formulation correlation (31), the EON* (EON at optimum formulation) is calculated to be 5.6 for this system (polyethoxylated nonylphenol, ACN = 7, S = 0, no alcohol, 25°C). As far as the experimental EON* is concerned, it may be calculated by assuming a linear mixing rule on a molar basis:

$$\mathrm{EON}^* = x_1\mathrm{EON}_1 + x_2\mathrm{EON}_2$$

where EON_i is the EON average value of each mixture component and x_i is its pseudomole fraction.

The result depend on whether the EON_i are taken as the manufacturer's data or as the HPLC average values. If Makon 4 and 6 are assumed to contain exactly 4 and 6 EO groups, respectively, EON* is found to be 5.7. Using the EON average calculated from HPLC data (3.95 and 5.2, respectively), the EON* of the mixture is found to be 5.0, which is in agreement with the overall inventory calculated from Table 3 data:

$$21\% \times 3.52 + 77\% \times 5.43 + 2\% \times 7.19 = 5.06$$

Summing up, it can be said that the correlation for optimum formulation (EON* = 5.6) and the experimental result using the manufacturer data

TABLE 3
Selective Partitioning of Surfactants between Oil/Water/Microemulsion Phases. Type III System at Optimum Formulation

EON	Oil phase mol fraction × 100	Microemulsion phase mol fraction × 100	Water phase mol fraction × 100
1	2.68	0.27	0.063
2	4.10	1.37	0.18
3	50.10	21.97	9.21
4	29.55	15.46	8.62
5	8.98	17.82	10.05
6	3.39	14.79	7.39
7	0.94	11.04	20.17
8	0.23	7.12	9.03
9	—	4.18	14.05
10	—	2.74	13.74
11	—	1.98	5.65
12	—	1.06	2.08
	Av EON = 3.52	Av EON = 5.43	Av EON = 7.19

(EON* = 5.7) are in close agreements. These label values are the ones used in practice.

However, it has been shown that HPLC analysis leads to more accurate, although lower values (5.0 from optimum formulation data and 5.06 from inventory), for the overall EON*.

Furthermore, it has been shown that the real or effective EON (that is, the interfacial value $\mathrm{EON}^*_{\mathrm{int}}$) is higher (5.4) because of the partitioning.

Recent knowledge about mixture partitioning and interfacial composition allows the experimenter to forecast the effect of slight variations in the formulation, an improvement made possible by better accuracy in the analytical data.

When it is remembered that a difference of 0.2 EON units can change the phase behavior of the system or the emulsion type, or affect its stability by several orders of magnitude, it is clear that a precise method to determine the exact EON distribution, whether overall or interfacial, will be welcome.

CONCLUSIONS

Although isocratic HPLC has been considered by some authors as not flexible enough to analyze complex surfactant mixtures, optimization of the mobile phase may turn it into the simplest method to determine the ethoxylated nonylphenol partitioning into all the phases of surfactant–oil–water systems, including the microemulsion. In the present study, normal-phase HPLC with an *n*-heptane–chloroform–methanol mobile phase results in an excellent compromise between accuracy and simplicity.

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REFERENCES

1. P. Winsor, *Solvent Properties of Amphiphilic Compounds*, Butterworths, London, 1954.
2. M. Bourrel and R. S. Schechter, *Microemulsion and Related Systems*, Dekker, New York, 1988.
3. J. L. Salager, J. L. Grosso, and M. A. Eslava, *Rev. Tecn. INTEVEP*, 2, 149 (1982).
4. J. L. Salager, L. Maldonado, M. Miñana, and F. Silva, *J. Dispersion Sci. Technol.*, *3*, 279 (1982).
5. J. L. Salager, M. Miñana, J. Andérez, J. Grosso, C. Rojas, and I. Layrisse, *Ibid.*, *4*, 161 (1983).
6. J. L. Salager, M. Miñana, M. Pérez, M. Ramirez, and C. Rojas, *Ibid.*, *4*, 313 (1983).
7. J. L. Salager, "Phase Transformation and Emulsion Inversion on the Basis of Catastrophe Theory," in *Encyclopedia of Emulsion Technology*, Vol. 3 (P. Becher, Ed.), Dekker, New York, 1988, p. 79.
8. J. Lachaise, T. Breul, A. Graciaa, G. Marion, A. Monsalve, and J. L. Salager, *J. Dispersion Sci. Technol.*, *11*(5), 443 (1990).
9. J. Lachaise, S. Sahnoun, C. Dicharry, B. Mendiboure, and J. L. Salager, *Prog. Colloid Polym. Sci.*, *84*, 253 (1991).
10. W. H. Wade, J. Morgan, J. Jacobson, J. L. Salager, and R. S. Schechter, *Soc. Pet. Eng. J.*, *18*, 242 (1978).
11. M. Bourrel, J. L. Salager, R. S. Schechter, and W. H. Wade, *Colloid Interface Sci.*, *75*, 451 (1980).
12. J. M. Andérez, J. L. Salager, A. Graciaa, and J. Lachaise, *Influence of Surfactant Concentration on Microemulsion Formation*, Presented at the 8th Symposium on Surfactants in Solution, Gainsville, Florida, June 10–15, 1990.
13. M. Bourrel, C. Koukounis, R. S. Schechter, and W. H. Wade, *J. Dispersion Sci. Technol.*, *1*, 13 (1980).
14. H. Kunieda and K. Shinoda, *J. Colloid Interface Sci.*, *107*, 107 (1985).
15. H. Kunieda and N. Ishikawa, *Ibid.*, *107*, 122 (1985).
16. H. Kunieda, K. Hanno, S. Yamaguchi, and K. Shinoda, *Ibid.*, *107*, 129 (1985).
17. C. Koukounis, "Phase Partitioning and Fractionation of Anionic and Nonionic Surfactant Mixtures," M.Sc. Thesis, University of Texas, 1979.
18. J. G. Sayous, "Etude du partage de tensioactifs non-ioniques entre les phases de systèmes de Winsor," Thèse Dr., Université de Pau P.A., 1983.
19. M. Ben Ghoulam, "Etude du partage de mélanges de tensioactifs nonioniques et anioniques entre les phases des systèmes de Winsor," Thèse Dr., Université de Pau P.A., 1984.
20. A. Graciaa, J. Lachaise, J. G. Sayous, P. Grenier, S. Yiv, R. S. Schechter, and W. H. Wade, *J. Colloid Interface Sci.*, *93*, 474 (1983).
21. A. Graciaa, J. Lachaise, M. Bourrel, I. Osborne-Lee, R. S. Schechter, and W. H. Wade, *SPE Reservoir Eng.*, *2*, 305 (1984).
22. A. Graciaa, M. Ben Ghoulam, G. Marion, and J. Lachaise, *J. Phys. Chem.*, *93*, 4167 (1989).
23. J. L. Salager, J. Morgan, R. S. Schechter, W. H. Wade, and E. Vasquez, *Soc. Pet. Eng. J.*, *19*, 107 (1979).
24. M. J. Schick (Ed.), *Non-ionic Surfactants*, Dekker, New York, 1966, p. 45.
25. A. E. Johnson Jr., P. R. Geissier, and L. D. Talley, *J. Am. Oil Chem. Soc.*, *67*, 123 (1990).

26. P. Jones and G. Nickless, *J. Chromatogr.*, *156*, 87 (1978).
27. K. Konishi and S. Yamaguchi, *Anal. Chem.*, *38*, 1755 (1966).
28. R. N. McCoy and A. B. Bullock, *J. Am. Oil Chem. Soc.*, *46*, 289 (1969).
29. L. Favretto, G. P. Marletta, and I. F. Gabrielli, *J. Chromatogr.*, *46*, 255 (1970).
30. B. Stancher, I. F. Gabrielli and L. Favretto, *Ibid.*, *111*, 459 (1975).
31. L. Farkas, J. Morgos, P. Sallay, I. Rosznak, B. Bartha, and G. Veres, *J. Am. Oil Chem. Soc.*, *58*, 650 (1981).
32. L. Favretto and B. Stancher, *J. Chromatogr.*, *108*, 183 (1975).
33. L. Farkas, J. Morgos, P. Sallay, I. Rosznan, B. Bartha, and G. Veres, *J. Am. Oil Chem. Soc.*, *58*, 650 (1981).
34. H. G. Nadeau, D. M. Oaks, A. W. Nichols, and L. P. Carr, *Anal. Chem.*, *36*, 1914 (1964).
35. L. Glindenberg and J. R. Trowbridge, *J. Am. Oil Chem. Soc.*, *42*, 69 (1965).
36. J. Tornquist, *Acta Chem. Scand.*, *20*, 283 (1966).
37. A. M. Rothman, *J. Chromatogr.*, *253*, 283 (1982).
38. M. Ahel and W. Giger, *Anal. Chem.*, *57*, 2584 (1985).
39. R. H. Scheuder and A. Martijin, *J. Chromatogr.*, *73*, 435 (1988).
40. I. Zeeman, M. Bares, and J. Silha, *Tenside Deterg.*, *23*, 181 (1986).
41. I. Zeeman, *J. Chromatogr.*, *363*, 223 (1986).
42. P. Jandera, J. Urbanek, B. Prokes, and J. Churacek, *Ibid.*, *504*, 297 (1990).
43. R. E. A. Escott, S. J. Brinkworth, and T. A. Steedman, *Ibid.*, *282*, 655 (1983).
44. A. Nozawa and T. Ohnuma, *Ibid.*, *187*, 261 (1980).
45. Ch. Koukounis, W. H. Wade, and R. S. Schechter, *Soc. Pet. Eng. J.*, *23*, 301 (1983).
46. D. R. Zornes, G. P. Willhite, and J. M. Michnick, *Ibid.*, *207*, 301 (1978).
47. M. J. Schick (Ed.), *Non-ionic Surfactants*, Dekker, New York, 1966, p. 485.
48. A. Barton, *CRC Handbook of Solubility Parameters and Other Cohesion Parameters*, CRC Press, 1983.
49. A. M. Rothman, *J. Chromatogr.*, *253*, 283 (1982).

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