Experimental Conditions for HPLC Analysis of Ethoxylated Alkyl Phenol Surfactants in Microemulsion Systems. Part II. Gradient Mode for Extended EON Range as Found in the Analysis of Oligomer Fractionation

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ABSTRACT

The different oligomers of ethoxylated nonylphenols present in commercial sur-
factants can be separated by HPLC. While low ethylene oxide number (EON)
species may be separated by isocratic HPLC on silica, intermediate EONs require
gradient elution HPLC. The separation of higher oligomers can be carried out
with an intermediate polarity column of the NH_2 type and a solvent gradient. The
suggested experimental conditions allow a satisfactory single run separation of a
complex mixture with EONs ranging from 1 to 25 by using a linear gradient from
100% less polar solvent (n-heptane–chloroform–methanol 90/5/5) to its mixture
with up to 20% of a more polar solvent made of chloroform–methanol (50/50).
This method is used to analyze the EON distribution resulting from the mixing
of different commercial surfactants. When two surfactants with very different
EON distributions are mixed to produce a formulation scan, the occurrence of
three-phase behavior at the optimum formulation of the surfactant–oil–water sys-
tem is found to correlate with the absence of a gap in the overall EON distribution.
Both the fractionation of low EON species into the oil phase and the fractionation
of high EON oligomers into the water phase result in a depletion of the microemul-
sion phase.

INTRODUCTION

As pointed out in the first part of this study (1), it is now well established
that the phase behavior of surfactant–oil–water systems is closely related
to the properties of emulsions and foams. Most research was initially
dedicated to systems containing pure surfactants or mixtures behaving as
a pure surfactant, i.e., as a pseudocomponent.

However, most commercial surfactants are complex mixtures, and in
many cases each individual specie behaves on its own as far as its interfa-
cial adsorption and phase partitioning is concerned (2).

This so-called fractionation phenomenon may result in a discrepancy
between the composition of the overall surfactant mixture, i.e., the one
introduced into the system, and the actual active surfactant mixture, i.e.,
the one really adsorbed at the interface and responsible for the system
properties (3, 4).

The case of polyethoxylated nonionic surfactants is of utmost interest
because of their commercial importance; this type of surfactant generally
exhibits a Poisson distribution of ethylene oxide number (EON) because
of the polycondensation mechanism (5). This distribution may result in
severe fractionation and sometimes in paradoxical situations when widely
different commercial products are mixed (6, 7).

As in previous studies dealing with the formulation of surfac-
tant–oil–water systems, one of the variables is scanned until a three-
phase, e.g., microemulsion–oil–water, so-called optimum formulation

system is attained (8–11). The microemulsion middle-phase of such systems may be considered to be a folded interface, and its analysis through the pseudophase model may lead to the calculation of the interfacial composition, as shown recently by Graciaa and co-workers (3, 4, 6, 7).

In most previous reports dealing with ethoxylated alkylphenol surfactants in microemulsion systems, the oligomer distribution was analyzed only in the oil phase, generally by gas chromatography; however, this method is limited to low EON species, say EON ≤ 8.

In the first part of this report (1) we showed that the oligomer distribution can be analyzed not only in the oil phase but also in the microemulsion phase and excess water. We proposed a simple isocratic HPLC method with an optimized ternary solvent mixture which extended the EON measurable upper limit to 12.

This value of EON corresponds to a rather hydrophilic surfactant and may be high enough in some applications. However, some detergent and wetting agent formulations, as well as some emulsifiers, require a higher EON value, e.g., up to 20. Moreover, the formulation of complex commercial dispersing agents often involves a mixture of low EON and high EON nonionic surfactants to improve the stability or to produce multiple emulsions (12). In such cases the method of analysis should be able to separate species over a very wide range of EONs, that is, from very lipophilic to very hydrophilic surfactants. This challenge can be met only by gradient HPLC.

We report here the proper experimental conditions for gradient HPLC for the analysis of extended EON distribution, and how the technique can be used to prove oligomer fractionation in a complex mixture. The different steps in the attainment of these experimental conditions will be discussed elsewhere (13).

GRADIENT HPLC OF POLYETHOXYLATED SURFACTANTS

Isocratic and gradient HPLC have become the methods of choice to analyze the polyethoxylated surfactants because of the simplicity of the analytical procedure and its straightforward applicability to the separation of oligomers. Different columns and solvent gradients have been tested with more or less satisfactory results for short to medium range EON distributions (14–20); they are reviewed in detail in a companion article (13).

However, none of these publications dealt with a wide EON range, highly bimodal EON distributions, nor with surfactant separation in microemulsion systems, which are the conditions addressed in this paper.

EXPERIMENTAL PROCEDURES

HPLC Equipment

All the HPLC work was performed using two M6000A pumps and a
U6K injector from Waters, and a UV variable wavelength detector (from
Dupont) operated at 270 nm, connected to a Varian integrator model 4270.
Gradient elution was applied with a linear program using a Waters model
660 solvent programmer. All flow rates were set to 1 mL/min.

Two columns were used. The first was a high polarity silica column
with stainless steel tubing, 25 cm × 4.6 mm i.d., Lichrosorb Si 60, 10
μm, from Hibar, Merck; the second was an intermediate polarity column
with stainless steel tubing, 25 cm × 4.6 mm i.d., Adsorbosphere NH$_2$,
10 μm, from Alltech. The precolumns were filled with the same material
as the analytical columns.

Chemicals

Commercial polyethoxylated nonylphenols were provided by Stepan
Chemicals (Makon), Kao Atlas Japan (Emulgen), and Hoescht (Arkopal).
All these products were found to be similar, with an ethylene oxide num-
ber (EON) distribution very close to the expected Poisson's. They are
referred to as NPi, where i is a number which indicates the average number
of ethylene oxide group per nonyl phenol molecule, calculated on a mol
fraction basis, according to our HPLC data. These numbers are very simi-
lar to the manufacturers' claim in most cases.

The formation was varied by changing the proportion of two commercial
surfactants (nonyl phenol with different EON values). Generally, one of
them was lipophilic (NP4) while the other was hydrophilic (NP6 to NP13).

When an extremely hydrophilic surfactant was used (NP20), a ternary
mixture with an intermediate surfactant (NP10) might be required for the
attainment of three-phase behavior.

The water phase was distilled and deionized water, the oil phase was
HPLC grade n-heptane, and the overall surfactant concentration in the
whole system was 1.5 wt%, unless otherwise stated. The water-to-oil ratio
was unity.

The oil, water, and microemulsion middle phase samples were treated
as described in Part I (1) until a dry residue redissolved in methanol.
Aliquots (10 μL) of the methanol solution were injected for chromato-
graphic analysis. The concentration of the injected samples was set in the
0.05 mol/L range.

OPTIMIZING THE GRADIENT HPLC EXPERIMENTAL
CONDITIONS

In Part I (1) we showed that low to medium EON surfactants (up to EON = 8) could be separated in a silica column by using the ternary solvent mixture *n*-heptane/chloroform/methanol in a 70/10/20 proportion. Since the problem was to extend the separation to higher EON species, i.e., more hydrophilic surfactants, a polarity gradient was tested. The gradient starts with the previous solvent mixture (called A) which was then combined linearly with an increasing proportion of a more polar one, referred to as solvent B, which was chloroform/methanol (50/50) to avoid a baseline shift (13).

Figure 1 indicates the separation of a NP4 + NP10 equimolar mixture with a 15-minute ramp from 100% A to a 90/10 A/B combination. This chromatogram should be compared to Fig. 2(C) in part I (1) in which solvent A was used in an isocratic mode. It is seen that the introduction
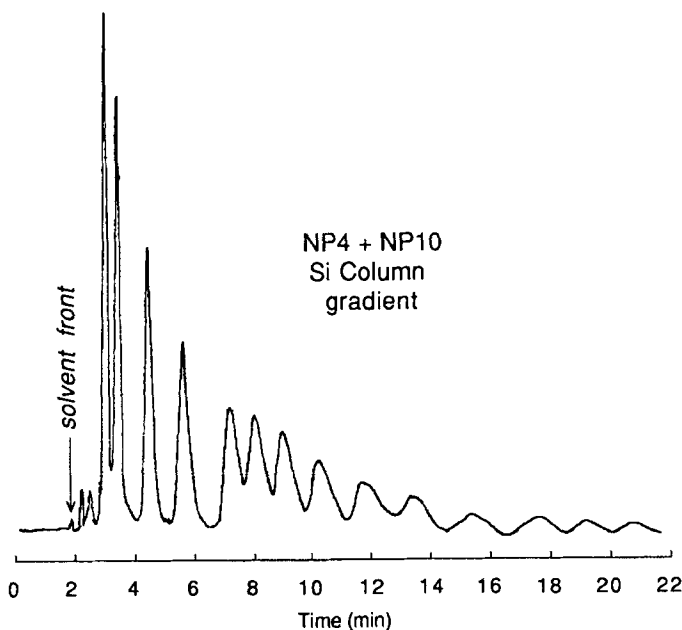
FIG. 1   Separation of NP4 + NP10 equimolar mixture using linear gradient elution from 0 to 10% of solvent B. Column, Lichrosorb Si 60, 250 × 4.6 mm i.d., 10 μm. UV detection at 270 nm.

of the gradient clearly increases the peak separation, especially at high EON.

Trials with a higher proportion of solvent B did not exhibit any improvement of separation nor a substantial reduction of the retention time of the high EON oligomers. As a consequence, a less polar column was selected, i.e., Adsorbosphere NH$_2$ (10 μm) from Alltech.

In order to test the entire EON range, a ternary equimolar mixture of NP4 + NP10 + NP20 commercial surfactants was analyzed so that all oligomers from EON = 1 to over 27 are present.

The optimization of the conditions, which is reported elsewhere (13), may be summed up as follows. The separation of a surfactant mixture with a wide EON range requires the use of gradient elution; the original solvent (A) must be of low polarity in order to separate the low EON species, while the added solvent (B) must be of higher polarity so that it can separate the high EON species. An appropriate solvent pair is found to be:

Base solvent (A): n-heptane/chloroform/methanol, 90/5/5
Additional solvent (B): chloroform/methanol, 50/50

The best compromise between separation and retention time is found with a linear gradient program from 0 to 20% of B in a 15-minute ramp.

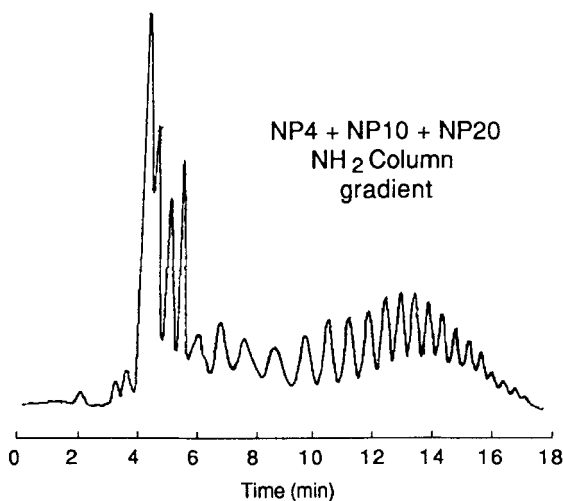NP4 + NP10 + NP20
NH $_2$ Column
gradient

Time (min)

FIG. 2   Separation of NP4 + NP10 + NP20 equimolar mixture using linear gradient elution from 0 to 20% of solvent B. Column, Adsorbosphere NH$_2$, 250 × 4.6 mm i.d., 10 μm. UV detection at 270 nm.

Figure 2 indicates the chromatogram of an equimolar mixture of NP4 + NP10 + NP20 in these conditions; it is seen that the separation is quite good over the entire EON range. A nonlinear gradient may be applied to improve the separation on either extreme, depending upon any special requirements. However, it is seen that the linear gradient is quite satisfactory and allows the three modes at EON = 4, 9, and 18 resulting from the ternary mixture to be visualized.

It should be noted that all three component distributions are actually Poissonlike, i.e., slightly skewed, with some tailing at high EON. However, the overlapping of the tail of the NP10 distribution with the lower EON part of the NP20 distribution turns the latter into an almost symmetrical form.

The above-mentioned gradient conditions are satisfactory for carrying out a single run analysis of broad spectrum mixtures of oligomers in a reasonable amount of time. They will be used to investigate the disappearance of the three-phase regime when the surfactant mixture components tend to behave on their own.

THREE-PHASE REGIME WITH SURFACTANT MIXTURES

A way to vary the formulation of a surfactant–oil–water system is to change the surfactant characteristic parameter, be it σ, α, or EON, depending on the kind of system (8–10). When two surfactants with similar characteristic parameter values are mixed, a linear mixing rule gives the mixture characteristic parameter. This rule can be extended to the mixing of two commercial surfactants, i.e., the mixing of mixtures (21–23). When the two surfactants or surfactant mixtures have similar molecular weights, it is not possible to be certain whether the mixing rule should be applied on a mole or weight fraction basis. A weight fraction was used in Griffin's original HLB mixing rule (12, 24), which is now recognized to lack accuracy in many instances. In the case of surfactants with similar interfacial area occupancies, a mole fraction mixing rule sounds more logical. Nevertheless, the matter is not settled because the difference is too small with similar surfactants. On the other hand, the mixing rule is no longer linear with widely different surfactants because of the fractionation phenomena.

As a consequence, a formulation scan can be carried out by mixing two surfactants only when these surfactants exhibit some kind of collective behavior, that is, when they are not too different, a concept which will become clear at the end of this section.

When a low (average) EON commercial ethoxylated nonylphenol is mixed with a high (average) EON one, the resulting formulation scan

produces the usual Winsor II → Winsor III → Winsor I phase behavior
transition (8–10, 22, 23, 25). It was shown that if the ethoxylated alkyl
phenols have similar EONs, a Winsor III three-phase behavior occurs at
optimum formulation, whereas a direct Winsor II → Winsor I transition
is found when the surfactant average EONs are very different (2). Similar
results were reported (26) with systems containing other nonionic surfac-
tants as well as alkyl aryl sulfonates. It was conjectured that no microe-
mulsion could form at optimum formulation when the fractionations were
too severe, with the most lipophilic surfactant partitioning into the oil
phase and the hydrophilic one partitioning into the water phase so that
not enough surfactant was left over at the interface.

Martínez (26) reported that a small amount of some intermediate surfac-
tant could bring back three-phase behavior, as if this intermediate surfac-
tant could trigger a collective behavior by the others.

Mixtures of NP4 with a higher EON surfactant were used to carry out
formulation scans with systems containing water and n-heptane. The
three-phase behavior is found at optimum EON* = 5.0 ± 0.1 when the
high EON surfactant is NP6 or NP8 (1). When NP10 is used as the high
EON surfactant, the calculated optimum EON* is slightly shifted to a
higher value (EON* = 5.15). This shift is explained by the change in the
acting surfactant mixture. According to the data shown in Part 1, it is
presumed that a part of the NP10 surfactant distribution (the high EON
tail) has partially partitioned into the water phase and is no longer present
at the interface, thus requiring a higher apparent EON to make up for the
loss.

When NP4 is combined with NP13 or NP20, no three-phase behavior is
found at optimum formulation, which is actually detected by the interfacial
tension minimum. However, three-phase behavior is exhibited at optimum
formulation if a certain amount of NP10 is added to the NP4 + NP20
mixture, as recommended by Martínez (26).

The previously discussed gradient HPLC method was used to analyze
the EON distribution in all the previous cases in order to correlate the
distribution shape and the phase behavior. Figure 2 of Part 1 (1) showed
that the EON distribution of the mixtures NP4 + NP6, NP4 + NP8, and
NP4 + NP10 are truly unimodal. Figures 3(A) and 3(B) show the EON
distributions of NP4 + NP13 and NP4 + NP20 equimolar mixtures, re-
spectively. In both cases the composed EON distribution is strongly bimo-
dal, with a wide gap between the two contributions in the NP4 + NP20
case (B) and a very slight overlapping in the NP4 + NP13 case (A).

These data indicate that the non-occurrence of three-phase behavior at
optimum seems to be related with the strong bimodality of the mixture,

A

**NP4 + NP13
mixture**

Time (min)

B

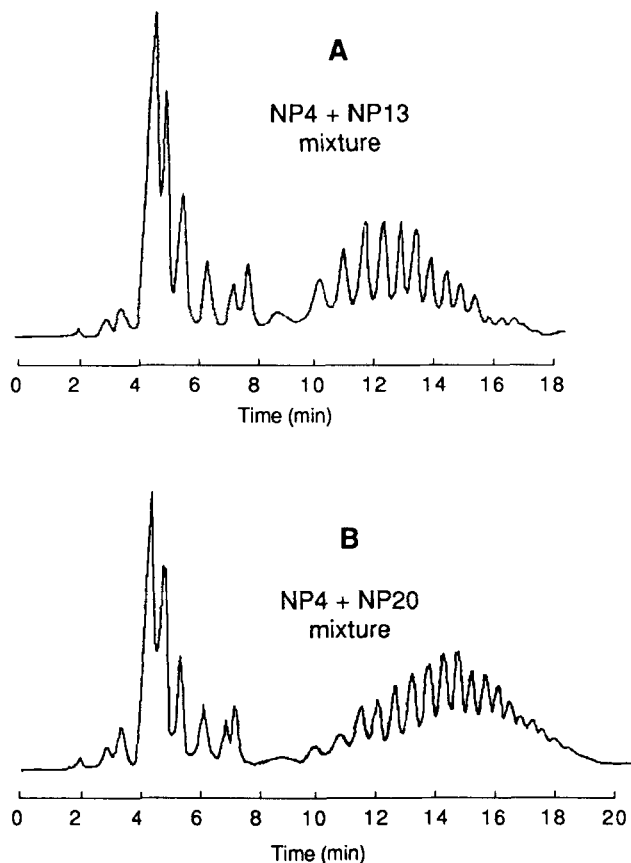**NP4 + NP20
mixture**

Time (min)

FIG. 3   Separation of NP4 + NP13 (A) and NP4 + NP20 (B) equimolar mixture using the same chromatographic conditions as in Fig. 2.

that is, with the fact that the two component distributions do not overlap significantly.

By adding NP10 to the NP4 + NP20 mixture, the "valley" between NP4 and NP20 distributions is filled by the NP10 species, as was shown previously in Fig. 2, and it can be said that the three distributions overlap substantially, with no gap between them.

It is found that such a ternary exhibits three-phase behavior at optimum, thus corroborating the previous statement linking the distribution shape with the occurrence of a three-phase regime at optimum formulation.

FRACTIONATION IN THREE-PHASE BEHAVIOR SYSTEMS

The phase behavior of a NPEON/water/*n*-heptane system was scanned by mixing NP4 + NP10 and NP20. Three-phase behavior was attained for EON = 5.22, a value slightly higher than the one required with a NP4 + NP6 mixture. Again, this slight increase is attributed to the preferential partitioning of the high EON specie into the water phase, a feature which does not occur in the NP4 + NP6 scan.

The microemulsion and the excess water and oil phases of the optimum formulation system were analyzed by gradient HPLC according to the previously described procedure. Figure 4 show the chromatograms of the oil (A), the microemulsion (B), and the water phase (C). Table 1 indicates the mole fraction distributions in all phases. The surfactant overall partitioning was 20 mol% in the oil phase, 76 in the microemulsion, and 4 in the water phase.

As in the case of the NP4 + NP6 mixture, the oil phase contains only low EON species coming from the NP4 contribution. The microemulsion phase contains a distribution similar to the overall mixture, that is, mainly NP4 + NP10 with a small amount of NP20 (Fig. 4B).

It is interesting to note that the water phase contains a higher proportion of the high EON species than the mixture. The effect is not very obvious at first glance because the peak height is the more striking information; however, it is the area that should be actually taken into account, and the area below the many high-EON small peaks turns out to be significant when compared to the area below the few low-EON large peaks.

The difference in average EON between the phases (see Table 1) indicates a strong preferential partitioning, not only of the low EON species in the oil phase, but also of the high EON species in the water phase. This partitioning in the water was not reported by Graciaa et al. (3), probably because these authors worked only with low EON species.

Of course, this dual selective partitioning in three-phase systems may be the basis of a separation process, as was remarked recently (27, 28).

However, the separation is not as simple as it may thought to be at first sight. In effect, Table 1 data show that the oil phase is actually extracting the low EON oligomers, but it also shows that the water phase contains a large amount of low EON species too. Since the water phase concentration at equilibrium with the microemulsion is generally assumed to be at about the mixture critical micelle concentration (29, 30), the low EON oligomers probably come from the first micelles, which are known to collect the most hydrophobic species (31). Thus, a separation process based upon fractionation of the surfactant in the water phase of an optimum three-phase system would be effective only if the micelles can be
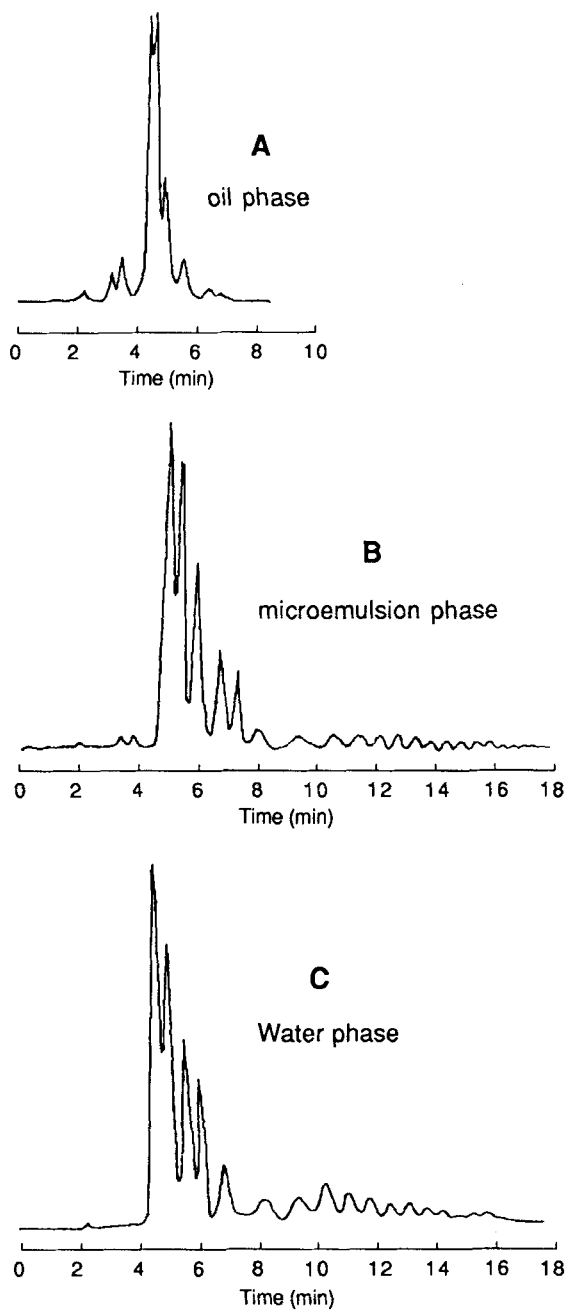
FIG. 4   Chromatograms of the oil (A), microemulsion (B), and water (C) phases at optimum formulation, attained with a surfactant mixture (NP4 + NP10 + NP20). Same conditions as in Fig. 3.

TABLE 1
Selective Partitioning of Surfactants between Oil/Water/Microemulsion Phases. Case of a
Type III System at Optimum Formulation

EON	Oil phase mol fraction × 100	Microemulsion phase mol fraction × 100	Water phase mol fraction × 100
1	3.71	1.38	—
2	5.30	1.98	—
3	29.46	28.41	26.62
4	31.73	22.16	19.03
5	17.87	16.19	13.89
6	7.95	10.28	9.78
7	2.70	6.41	6.16
8	1.27	3.12	0.26
9	—	2.42	4.10
10	—	2.07	4.43
11	—	1.73	4.75
12	—	1.04	3.11
13	—	0.69	1.86
14	—	0.35	1.43
15	—	0.27	1.28
16	—	0.24	1.00
17	—	0.21	0.71
18	—	0.17	0.57
19	—	0.14	0.43
20	—	0.10	0.28
21	—	0.069	0.029
22	—	0.034	0.025
Average	3.95	5.04	6.19

ultrafiltered in the excess water phase. It is worth remarking that if micelle filtration cannot be avoided, then the advantage of such a process over mixed micelle separation would probably vanish.

CONCLUSIONS

Gradient elution HPLC of a wide EON range of ethoxylated nonylphenol surfactants can be carried out with an intermediate polarity column of the NH_2 type, and a solvent gradient from less polar (to elute the low EON species) to more polar (to elute the high EON oligomers). The suggested experimental conditions allow a satisfactory single run separation of a complex mixture with EONs ranging from 1 to 25.

This method is used to analyze the EON distribution resulting from the mixing of more or less different commercial surfactants with average EONs ranging from 4 to 20.

The non-occurrence of a three-phase behavior at optimum formulation is found to correlate with a strong bimodality in the overall EON distribution. The addition of a small amount of intermediate surfactant eliminates the gap between the two main modes and makes the three-phase regime happen at optimum formulation.

Analysis of the three phases in equilibrium, when optimum formulation is attained by mixing two widely different surfactants, reveals a substantial fractionation of both the low EON oligomers toward the oil phase and the high EON species in the water phase. As a matter of fact, the water phase also contains low EON species, presumably in the first micelles. This observation may jeopardize the potential of such systems for separation purposes.

ACKNOWLEDGMENTS

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