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Effect of Alkylate Isomerism upon Surfactant Retention in an HPLC Column and Partitioning between Water and Oil

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ABSTRACT

The degree of isomerization in the alkyl chain of ethoxylated alkylphenol surfactants influences the retention time in a HPLC silica column and the partitioning coefficient between *n*-heptane and water. HPLC analysis of isomer species with different alkyl groups allows the deduction of some general trends in the influence of isomerization and branching on the surfactant properties. The alkyl group interaction with the solvent and the heptane–water partitioning data show that direct interaction between the surfactant "tail" and the solvent is also of importance.

INTRODUCTION

Nonionic surfactants of the polyether type were synthesized by adding ethylene oxide to substances with a reactive hydrogen atom, such as alkylphenols (1). During the ethoxylation process, the adduction randomness results in a mixture of oligomers with different degrees of ethoxylation. The characteristic of each oligomer specie is the number of ethylene oxide groups per alkylphenol molecule, the so-called ethylene oxide number (EON).

Some previous research has been dedicated to the determination of the EON distribution in polyethoxylated nonylphenol surfactants by various analytical procedures (2, 3), mainly of the chromatographic type. Gas chromatography (4–9) has been used only for low average EON mixtures since it fails to separate higher oligomers (EON > 8) because of their low volatility and because of the risk of thermal degradation above 270°C. High performance liquid chromatography (HPLC) has become the method of choice because of the simplicity of the analytical procedure and its straightforward applicability to the separation of higher ethoxymers. Ethoxylated alkylphenol surfactants have been separated by both reversed and normal phase HPLC. Octadecyl or octyl-silane columns have been used for such separations (10–14). Silica gel (10, 15, 16) and silica with chemically bonded nitrile (15, 17), diol (16), and amino phases (16–24) have also been tested as column packings in normal phase HPLC separation. Several column packing materials used for normal phase separation were tested with aliphatic alcohols and hydrocarbon solvents (25) in order to compare the chromatographic behavior of un-derivatized ethoxylated nonylphenols on different stationary phases. A normal phase HPLC separation of ethoxylated nonylphenol oligomers has been described by Zhou et al. (26), who used a silica-diol column and a nonpolar solvent gradient elution. HPLC of an ethoxylated alkylphenol mixture having a low average EON was selected for interlaboratory testing, using a diol-bonded phase column under isocratic and gradient conditions (27, 28).

In recent articles we have shown how to tune up both isocratic and gradient elution HPLC methods to separate ethoxylated alkylphenol surfactants (29–31). These methods were used to determine a general expression for the partitioning coefficient of commercial alkylphenol surfactants (32) between water and hydrocarbon. It is worth remarking that these surfactants generally contain an alkylate group that comes from the polymerization of a short olefin, e.g., propylene, with the corresponding branching due to Markovnikov's rule. Recently a simple way to separate the polyethylene glycol (PEG) oligomer species by isocratic elution with

reversed-phase columns was reported (33). A rapid reversed-phase HPLC method was developed for the separation and characterization of individual oligomers in polyethoxylated octylphenol (PEOP) surfactants, using a C1 trimethylsilyl (TMS) column (34). In a recent paper an analysis by HPLC was proposed as a method to determine the isomeric purity of acids and esters (35) that could be completely resolved on a reversed-phase HPLC column using water–methanol–trifluoroacetic acid elution.

On the other hand, a relationship was recently reported between the capacity factor (on a reversed-phase column) and the octanol–water partition coefficient for a variety of aromatic substances (36). Although none of these substances was a surfactant, the study indicated that the chromatographic hydrophobicity can be estimated from HPLC data.

The partitioning of surfactant species between the water and oil phases in the water/oil/surfactant system is an important phenomenon that must be closely monitored when dealing with surfactant mixtures. In effect, a significant part of the surfactant species can fractionate into one of the phases and thus disappear from the interface (37, 38) with sometimes striking results as in the so-called retrograde transition, in which the addition of a lipophilic surfactant mixture results in a hydrophilic effect (39, 40).

The partition coefficients of surfactants between oil and water have been reported in several papers (41–43). It seems that the partition coefficient, defined as the ratio of the surfactant concentration in the water phase to that in the oil phase, is nearly unity at the optimal conditions for oil recovery. The fractionation of anionic surfactants between oil and water phases was found to be rather small unless disulfonate species are involved (44), while the opposite applied for nonionic surfactant systems (45). This is thought to be due to the large variation of hydrophilicity exhibited by the oligomer species in a typical commercial ethoxylated nonionic surfactant compared with the much smaller difference found in anionic surfactants that only differ from one another by their hydrophobe group length. As a matter of fact, the more critical type of partitioning takes place with polyethoxylated nonionic surfactants.

Partitioning has been studied in high concentration systems by determining the concentration of each oligomer in the excess water and oil phases of a three-phase system at optimum formulation (46). The standard procedures and the pseudophase model used to calculate the interface composition are discussed elsewhere (37, 38). The calculation of the interface composition allows the formulator to know which specie is most important and which is not, quite important information as far as cost is concerned. For instance, it is not uncommon that 30% of the surfactant

mixture that is introduced in a detergent, foaming, or cleaning product does not contribute to the sought property because it is not present at the interface.

The application of this model has been severely impaired by the lack of partitioning data, a consequence of the limitation of early analytical techniques, particularly gas chromatography, that cannot analyze oligomers with EON > 8 because of their low volatility (47–52). Enhanced HPLC methods are used in this paper to determine the partition coefficients of ethoxylated alkylphenol surfactants with different kinds of alkylate groups: linear, branched, and multiple.

APPARATUS

All HPLC separations were performed by using one or two M6000 pumps, a U6K injector, a Model 660 solvent programmer, and a UV detector Lambda-max model 481LC operated at 270 nm (all from Waters Associates) connected to a personal computer loaded with Data BaseLine 810 software. The column used was stainless steel, 25 cm × 4.6 mm ID, Lichrosorb Si 60, 10 μm (Hibar-Merck).

A stainless steel, 5 cm × 3.8 mm ID precolumn was used; it was packed in the laboratory with Corasil for normal phase chromatography. All flow rates were set at 1 mL/min.

CHEMICALS

N-Heptane, chloroform, and methanol used in the mobile phase for chromatographic analysis, as well as *n*-heptane used as the oil phase in partitioning studies, were all HPLC grade from Baker. The dissolved gas was scavenged from the mobile phase by ultrasonic stirring and by continuous stripping with helium. The water was redistilled and deionized.

Commercial polyethoxylated alkylphenols were provided by Stepan Chemicals and Hoechst Gmbh. They are symbolically written as CxØEOy where "x" is the number of carbon atoms in the alkyl group (or Surfactant Alkyl Carbon Number so-called SACN) and "y" is the average number of ethylene oxide groups per molecule, i.e., average EON. The alkyl groups of these surfactants are believed to exhibit the typical branching resulting from polymerization of olefins which is, for instance, a methyl group every two carbons for the propylene trimer and tetramer.

Ethoxylated tri-terbutyl phenols provided by Hoechst are symbolized tri-ter-C4ØEOy, while the ethoxylated linear alkylphenols provided by Hüls are noted as LCxØEOy, with the same meanings for "x" and "y."

SAMPLE PREPARATION

The physicochemical formulation change through the three-phase transition is provided by an EON scan, the principle of which is described elsewhere (32, 46).

The EON scan for the oil/water/surfactant system is carried out by preparing several oil–water (WOR = 1) systems that contain a surfactant mixture of varying hydrophilicity. Typically, a lipophilic commercial surfactant dissolved in heptane (e.g., C9ØEO4) is mixed in different proportions with a hydrophilic one dissolved in water (e.g., C9ØEO10), so that the average EON of the surfactant mixture changes from one system to the next. The increasing average EON results in the so-called Winsor II-III-I transition of the phase behavior (32, 46, 53, 54). The test tubes containing the surfactant–oil–water systems 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.

The optimum formulation corresponds to the system that exhibits a three-phase behavior in which a microemulsion is in equilibrium with excess water and excess oil. The excess phases of these systems contain the highest possible concentrations in the absence of micelles, so that they can be used to determine the partition coefficient defined as $K_i = C_{iw}/C_{io}$ where "i" indicates the species (i.e., the oligomer rank EON), and "w" and "o" stand for water and oil phases, respectively.

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 surfactant residue is then redissolved in methanol, and 10 μL aliquots of this solution are analyzed by HPLC.

HPLC SETTINGS

Normal phase separation is based on the difference in EON, i.e., in the difference in polarity of the polyether chain of the surfactant molecule with respect to the stationary phase (silica) and to the mobile phase, which must be less polar.

The separation on a silica column on an isocratic mode with an optimized mobile phase containing a mixture *n*-heptane/chloroform/methanol 70/10/20 (vol) is found to be limited to oligomer species with up to 12 ethylene oxide groups.

Whenever the EON distribution extends beyond the EON = 12 oligomer, a gradient mode is used. The optimal separation of ethoxylated nonyl-

and dodecylphenol oligomers, both with linear or branched alkylates, is carried out with a gradient mode on a silica column. Starting with base solvent A, which is an *n*-heptane/chloroform/methanol 70/10/20 mixture, solvent B (chloroform/methanol 50/50 mixture) is added linearly in order to attain a 10% proportion of B after 15 minutes.

EXPERIMENTAL RESULTS AND DISCUSSION

HPLC Separation

The HPLC separation was carried out for both a commercial ethoxylated octylphenol with an average EON = 9 (C8ØEO9) and the equivalent linear alkyl octylphenol mixture (LC8ØEO9). Figure 1 shows the two chromatograms resulting from the same conditions of analysis. Figure 2 indicates the corresponding calculated EON distributions.

Figure 1 indicates that the distribution of the branched species is spread over a slightly wider range than for their linear counterparts. However,

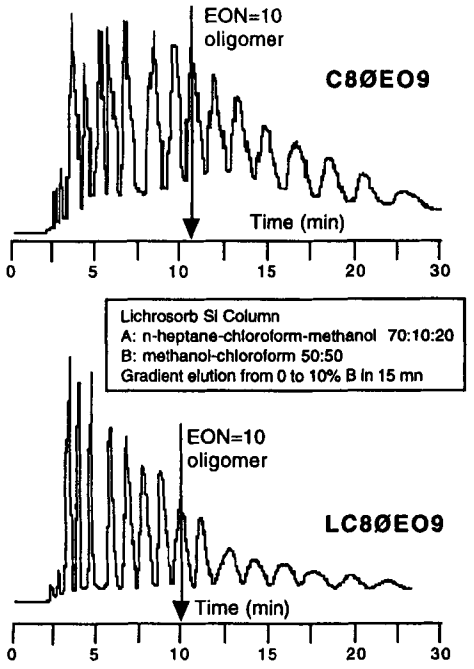

FIG. 1 Chromatograms resulting from the analysis of branched (top) and linear (bottom) octylphenol mixtures having the same average EON = 9.

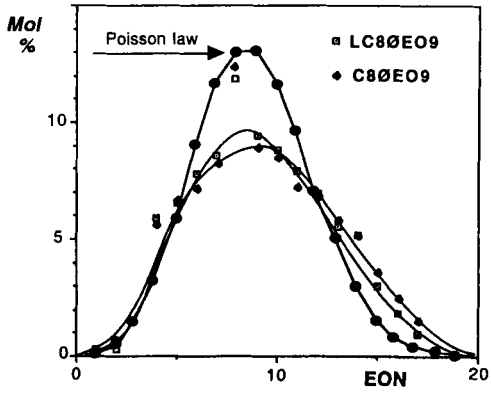

FIG. 2 Comparison between the oligomer distributions for linear and branched ethoxylated alkylphenol surfactants (EON = 9) with the corresponding Poisson's law.

the difference is not very significant, and it is not far away from the corresponding Poisson distribution with average EON = 9, as can be seen in Fig. 2.

The comparison between the residence times of isomeric oligomers in the two chromatograms indicates clearly that the linear alkylate species are retained for a shorter time in the column. For instance, oligomer LC8EO10 gets out of the column after 10 minutes while C8EO10 lasts 11.5 minutes, as indicated by the arrows in Fig. 1.

Since adsorption on the silica column is due to a polyether chain that is the same in both series, the difference in retention time must be linked to the alkyl chain structure. It is conjectured that the linear alkyl chain exhibits a stronger interaction with the solvent mobile phase that mainly contains *n*-heptane than with the branched species.

This explanation is based on the well-known tendency of more branched hydrocarbons to be more water soluble, i.e., less hydrophobic, as is corroborated in the next section by quantitative estimations.

A similar comparison was carried out with three types of C12 alkylphenol ethoxylates that exhibit different branching characteristics, i.e., linear alkylate (LC12ØEO9), regular branched alkylate (C12ØEO9), i.e., the one made from propylene tetramer alkylate, and the multiple chain specie (tri-ter-C4ØEO9)

The peak corresponding to the EON = 10 oligomers is indicated in all three Fig. 3 chromatograms by an arrow. The shift indicates that the retention time increases when passing from the linear isomer to the branched

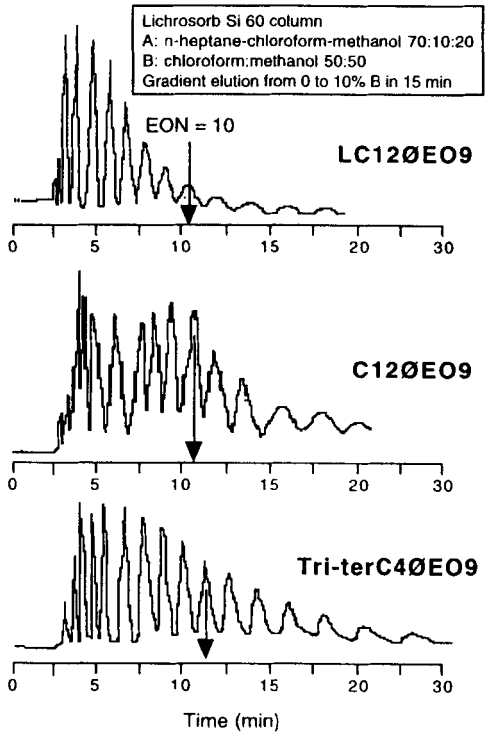

FIG. 3 Chromatograms resulting from the analysis of linear, single-branched chain, and multiple chain dodecylphenol oligomer mixtures.

one, as seen in the previous case. Moreover the retention increases again when passing to the even more branched *tert*-butyl phenol isomers. This corroborates that the more branched species exhibit a lower interaction with the solvent, since everything is identical on the hydrophilic chain side.

Partitioning

The partitioning was measured between the excess oil and excess water phase of three-phase systems with a variety of ethoxylated alkylphenol surfactants, pure water, and *n*-heptane at 25°C. In recent publications (32, 39) it has been shown that the partition coefficient K_i (i.e., the ratio of the "ith" specie concentration in water to its concentration in oil) depends upon the degree of ethoxylation "i" according to the following rela-

tionship:

$$\text{Log } K_i = \log K_0 + 0.45i \quad (1)$$

where i is the number of ethylene oxide groups per alkylphenol molecule (i.e., EON), and K_0 is the partition coefficient value extrapolated to $i = 0$, which depends upon the surfactant hydrophobe as well as the nature of the water and oil phases and temperature. For branched species it was found that log K_0 decreases linearly when the number of carbon atoms in the alkyl group SACN increases (32) according to

$$\text{Log } K_0 = -3.54 - 0.0425\text{SACN} \quad (2)$$

Because of the accuracy of this relationship, log K_0 is a good yardstick to estimate the relative hydrophobicity of a surfactant "tail" in a given oil/water/temperature physicochemical environment.

Figure 4 indicates the variation of the logarithm of the partition coefficient for branched C12Ø ethoxylates and multichain tri-ter-C4Ø counterparts. In both cases the linear variation is perfectly obeyed with a slope of 0.45 according to the linear regression data. On the other hand, it is seen that the log K_0 value is larger for the trialkyl family than for the branched alkyl one. Thus, the more branched one (tri-ter-C4Ø) has significantly more affinity for the water phase (or less affinity for the oil phase), a result that corroborates the previous discussion.

It is worth noting that the linear LC12Ø species data points lie very slightly below the C12Ø points (exactly at log $K_0 = -4.15$); they are not indicated in Fig. 4 for the sake of clarity.

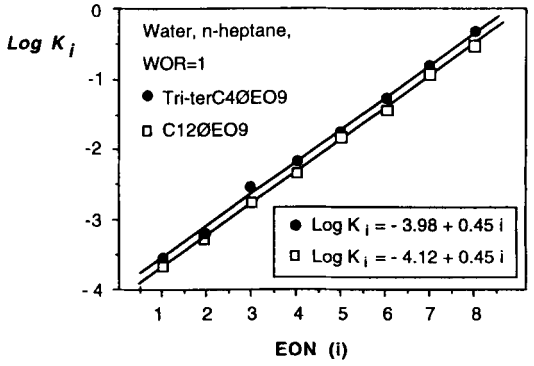

FIG. 4 Partition coefficient of multichain and branched single chain dodecylphenol oligomers.

The same comparison was carried out with linear and branched octylphenol ethoxylates, and as in the previous case, a very slight difference was found. It can be translated by the respective values of K_0:

$$\text{for LC8ØEON:} \quad \text{Log } K_0 = -3.95 \tag{3}$$

$$\text{for C8ØEON:} \quad \text{Log } K_0 = -3.88 \tag{4}$$

In this case the difference is just at the limit of the estimated experimental error, but since it is systematic, it may be taken as slightly significant.

The change in log K_0 can be interpreted in terms of equivalent length of linear chain. Equation (2) indicates that each additional methylene group results in a decrease $\Delta \log K_0 = 0.0425$.

The difference between the linear LC12 ($\log K_0 = -4.15$) and the multichain tri-ter-C4 ($\log K_0 = -3.98$) alkylate moiety is 0.17, which is exactly equivalent to $0.17/0.0425 = 4$ methyl or methylene groups.

This means that the 12 alkyl carbon atoms of the tri-ter-butyl phenol ethoxylates are equivalent to 8 carbon atoms located in a linear chain. In other words tri-ter-C4ØEON oligomers have the same hydrophilicity as LC8ØEON oligomers with an equal EON.

This change may seem to be very significant in terms of alkyl group carbon number SACN. However, it is not considerable in term of hydrophilicity. In effect, it is worth noting that according to Eq. (1), a change to $\Delta \log K_i = 0.17$ is equivalent to $0.17/0.45 = 0.37$ additional EO group. This remark points out a known but not well-publicized fact: It is much more effective to alter hydrophilicity by changing EON than by modifying the lipophilic chain length.

CONCLUSION

HPLC analysis of ethoxylated alkylphenol surfactants with different alkyl groups indicates some general trends in the influence of isomerization and branching on the surfactant's properties.

The linear alkyl tail species are less retained than the branched one on the silica column. This is probably due to the better interaction of the linear chain with the solvent which is mainly *n*-heptane. The multichain tri-ter-butyl species are retained longer than the branched counterparts, probably for the same reason.

The change in partitioning corroborates this trend by showing that the relative affinity of the alkylphenol oligomers (at constant EON) for the oil phase decreases with branching.

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