Adsorption of Ethoxylated Sulfonates on Kaolinite and Alumina

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ABSTRACT

Ethoxylated surfactants have been reported to show improved interfacial tension and calcium tolerance properties, even though the mechanism by which ethoxylates influence interfacial phenomena are not completely understood. The impurities present in technical grade ethoxylated sulfonates place a major hurdle in studying this type of surfactants. A technique based on flash chromatography was therefore developed for separating them and the collected fractions were characterized using HPLC and NMR.

Adsorption studies showed the nonionic impurities to enhance the adsorption of as received and purified ethoxylated sulfonate on alumina in the premicellar region. The effect of variation in the structure of these compounds on adsorption was studied by comparing their adsorption with non-ethoxylated sulfonates. Also the effect of the degree of ethoxylation was studied using a series of ethoxylated sulfonates and ethoxylated alcohols. Interestingly, both ethoxylated alcohols and ethoxylated sulfonates exhibited increased adsorption in the premicellar region and lower adsorption in the micellar region with increase in ethoxylation, indicating increased hydrophobicity of the sulfonates with increase in ethoxylation. This is further supported by the HPLC behavior of these surfactants. The results are discussed in terms of molecular geometry and hydration of the ethoxy group.

INTRODUCTION

Surfactant depletion in micellar flooding is a complex process controlled by the multicomponent nature of the reservoir rock, the fluid, as well as the surfactants employed. Past studies have shown adsorption and precipitation to be the two major factors determining surfactant loss, and that these phenomena are markedly dependent on system variables such as pH, ionic strength, temperature, inorganic type, surfactant composition, and mineral type [1-12].

It has become clear that precipitation of alkylbenzenesulfonates can limit their use under the high brine and calcium levels of reservoir systems [13]. In

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order to circumvent this problem, modified surfactants have been developed for use in enhanced oil recovery [14,15]. Recently, ethoxylated surfactants have been reported to be superior to many others in salt tolerance [15]. Also, the hydrophilic lipophilic balance (HLB) of these surfactants can be altered conveniently by changing the degree of ethoxylation while keeping the main structure of the surfactant constant. However, the mechanisms by which ethoxylates influence interfacial phenomena, particularly adsorption, are not understood. A major problem in studying the basic phenomena underlying these chemicals has been the presence of 15 to 50% impurities present in the technical grade ethoxylated surfactants. In this paper we will present results on the characterization of polydispersed ethoxylated sulfonates by NMR and HPLC and their adsorption on sodium kaolinite and alumina.

MATERIALS AND METHODS

Kaolinite
Homoionic sodium kaolinite was prepared from kaolinite samples purchased from the clay repository of the University of Missouri. The procedure used for the preparation and characterization of homoionic sodium kaolinite was described elsewhere [8]. BET surface area of this kaolinite sample was 9.5 m^2 g^{-1}.

Alumina
Alumina was Linde (A) high purity sample purchased from Union Carbide Co. BET surface area of this sample was determined to be 15.0 m^2 g^{-1}.

Inorganic chemicals
Sodium chloride, sodium hydroxide, and potassium hydroxide used were of ultrapure grade and were purchased from Aldrich Chemical Co.

Alkylbenzenesulfonates
Isomerically pure 4-n-decylbenzenesulfonate (DBS) and 4-n-octylbenzenesulfonate (OBS) of 99% purity were synthesized in our laboratory. The synthesis and characterization procedures were described in detail elsewhere [5].

Ethoxylated sulfonates
The ethoxylated sulfonates used were Triton X-200 and Triton X-202 (Rohm and Haas), Alipal SE-463 (GAF Corporation), NES-1 (Diamond Shamrock), an TOPS-1 (synthesized [16] at Columbia University). In the absence of information on the nature of the alkyl chain and degree of ethoxylation, these surfactants were characterized using p-NMR and HPLC techniques.

Procedure for p-NMR

The proton-NMR spectra of the phenolic compounds were obtained by dissolving them in $CDCl_3$. The sulfonate solutions were obtained by dissolving them in trifluoroacetic acid followed by extraction with $CDCl_3$ and drying with anhydrous sodium sulfate. A Varian XL 200 FT spectrometer was used for p-NMR.

Procedure for HPLC

High performance liquid chromatography was used to characterize the ethoxylated sulfonates. The surfactants were dissolved in the HPLC solvent and a 20 μl sample was injected into a C-18 bonded silica column. The various components eluted from the column were analyzed using a variable wavelength UV detector set at 223 nm.
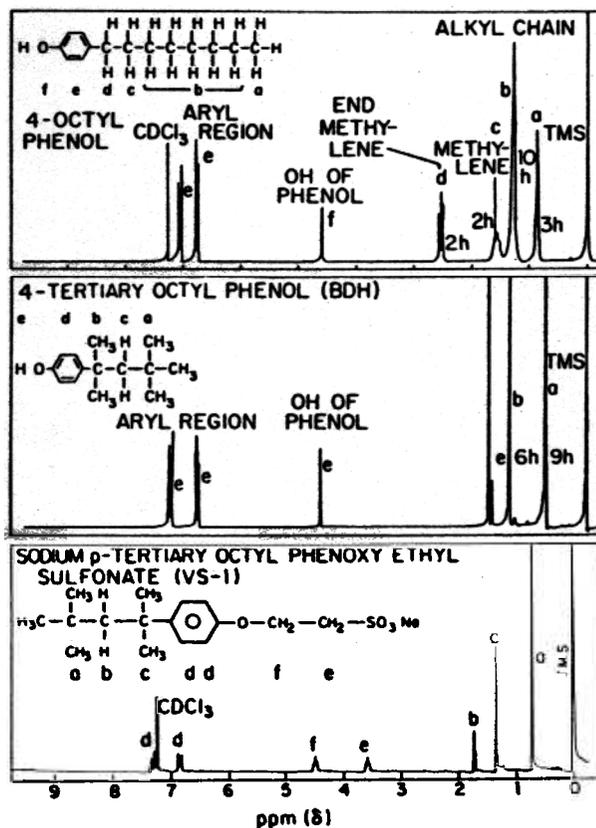
Fig. 1. p-NMR spectra of 4-n-octylphenol, 4-tertiaryoctylphenol, and TOPS-1.

Adsorption experiments

Adsorption tests were conducted in tightly capped 5 dram vials. Alumina and sodium kaolinite were preconditioned in NaCl solutions for 90 and 120 min, respectively, on a wrist-action shaker at the desired temperature. Surfactant solution was added and each sample was conditioned for a sufficient time to reach equilibrium (4 h for alumina and 72 h for sodium kaolinite). The solids were then separated from the liquid by centrifugation and the supernatant was analyzed for its surfactant concentration by two-phase titration technique [19] or HPLC.

RESULTS AND DISCUSSION

p-NMR characterization

The p-NMR spectra of the standards, 4-tertiaryoctylphenol and 4-n-octylphenol, isomerically pure 4-tertiaryoctylphenoxyethylsulfonate (TOPS-1), and the ethoxylated sulfonates are given in Figs 1 and 2. The assignment of the protons associated with the carbon atoms in the alkyl, aryl and ethoxylated regions for the standard compounds and for ethoxylated sulfonates (assigned by comparison with the standards) is schematically shown in each spectrum.
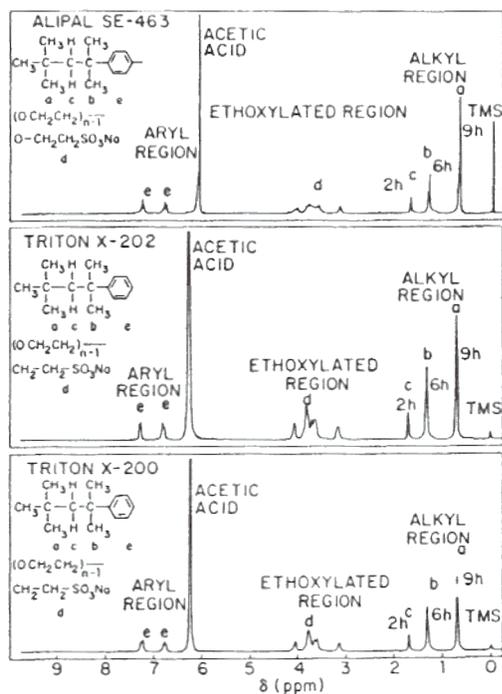
Fig. 2. p-NMR spectra of ethoxylated sulfonates.
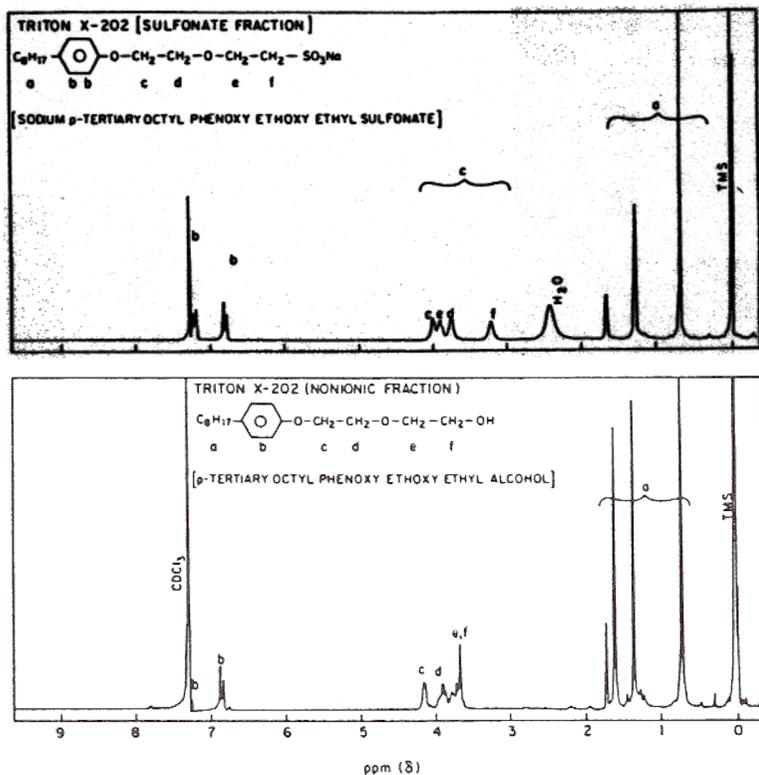
Fig. 3a. p-NMR spectra of sulfonates and nonionic fractions of Triton X-202.

A comparison of the alkyl regions of the ethoxylated sulfonates, 4-n-octyl-phenol and 4-tertiaryoctylphenol indicates all three sulfonates to have 4-tertiaryoctylphenyl structures rather than 4-n-octylphenyl structures. Furthermore, it can be concluded that the aromatic ring is *para* substituted because of the occurrence of the twin doublet peaks in the aryl region, characteristically obtained for such substitution. As suggested by the spectrum of Triton X-100 [17] (which is known to contain ethoxy groups) the proton peaks associated with ethoxy (EO) groups occur between 3 and 4 ppm. The number of EO groups can be calculated for the ethoxylated sulfonates from the integral value of the protons in this region.

Most of the commercial ethoxylated sulfonates used in the present study are polydispersed with respect to ethoxylation; the EO number specified by the company being an average value. In addition, they also contain a significant proportion of nonionic components. In order to determine the structure of these components, chromatographic mode sequencing techniques [18,23] (flash chromatography) was used to separate them and p-NMR was used to characterize each fraction. Typical NMR spectra of the sulfonate and the non-
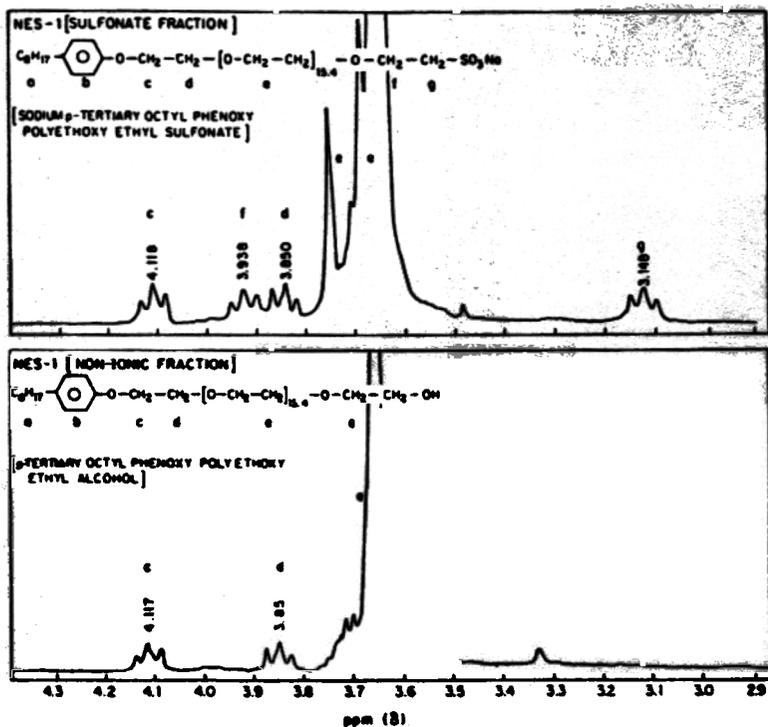
Fig. 3b. p-NMR spectra of ethoxylated region of sulfonate and nonionic fractions of NES-1.

TABLE 1

The ppm values of the peaks in the ethoxylated region of the NMR spectra

Surfactant		ppm Values				
Triton X-202						
(a)	Sulfonate fraction	3.194	3.755	3.894	3.990	
(b)	Alcohol fraction		3.6	3.8–3.9	4.15	
NES-						
(a)	Sulfonate fraction	3.148	3.6–3.75	3.8	3.938	4.118
(b)	Alcohol fraction		3.6–3.7	3.85		4.117
TOPS-1		3.5	4.4			

TABLE 2

Elution time in minutes of surfactants, alcohol and phenols obtained using HPLC technique at different solvent combinations

Surfactant	Elution time (min)[a]		
	CH₃CN:TBAP[b] 60:40	CH₃CN:TBAP 70:30	CH₃OH:H₂O[c] 70:30
n-OBS	3.08	1.25	1.31
n-DBS	5.54	1.29	1.70
n-DDBS	11.09	1.34	
n-TDBS	–	1.55	
4-n-Octylphenol	22.46		
4-Tertiary-octylphenol	12.15 13.48		
Triton X-100	1.84, 3.05, 3.30, 7.63, 8.50, 10.10, 13.97		2.51, 2.97, 19.68, 21.71, 23.53, 24.93, 26.39, 27.86, 29.29, 30.69, 32.16, 33.79, 37.59
Triton X-200	3.30, 3.50, 10.46, 10.85	.33, 5.5	1.20, 1.38, 1.69, 2.30, 5.87, 21.85, 23.75
Triton X-202	1.16, 1.43, 1.79, 2.01, 2.77, 3.27, 3.49, 10.72, 11.17, 12.11, 13.16	1.36, 1.77, 5.43	1.29, 1.68, 1.83, 19.06, 21.09
Alipal SE-463	1.26, 1.43, 1.65, 1.80, 2.13, 2.51, 3.01, 3.28, 3.48, 3.64, 10.77	.21, 5.53	1.29, 1.69, 1.85, 19.25, 21.25, 23.12
DDBS (EX-1)	1.47, 8.89, 9.22, 9.56, 10.32		

[a]Major peak of multi-isomers underlined.
[b]Acetonitrile:Tetrabutylammoniumphosphate solvent mixture.
[c]Methanol:water solvent mixture.

ionic fractions of two technical grade sulfonates (Triton X-202 and NES-1) are given in Figs 3a and 3b. From Fig. 3a it can be seen that both the sulfonate and the alcohol fraction of Triton X-202 have the same hydrophobe (p-ter-tiaryoctylphenoxy group). Similar results were obtained for NES-1. The p-NMR spectra expanded in the ethoxylated region of the sulfonate and alcohol fractions of NES-1 are given in Fig. 3b. Integration of the protons of the EO groups shows that Triton X-202 and NES-1 contain 2 and 17 EO groups, respectively, for both the sulfonate and alcohol fractions. The ppm values of the peaks in the ethoxylated region of the NMR spectra are shown in Table 1.

It is evident from Table 1 that the alkylphenoxypolyethoxyethyl alcohols have 3 major peaks around 3.6, 3.8–3.9 and 4.1–4.2 ppm. Introduction of the polar sulfonate group increases the number of peaks in the ethoxylated region to 4 in the case of Triton X-202 and to 5 in the case of NES-1. The most
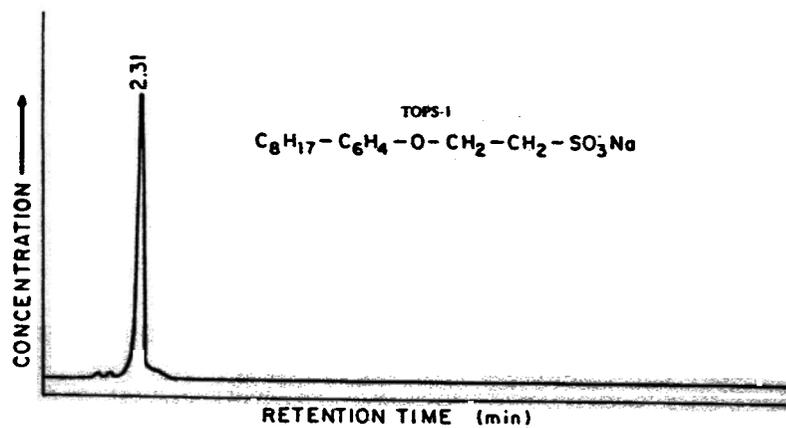
Fig. 4. HPLC chromatogram of TOPS-1.
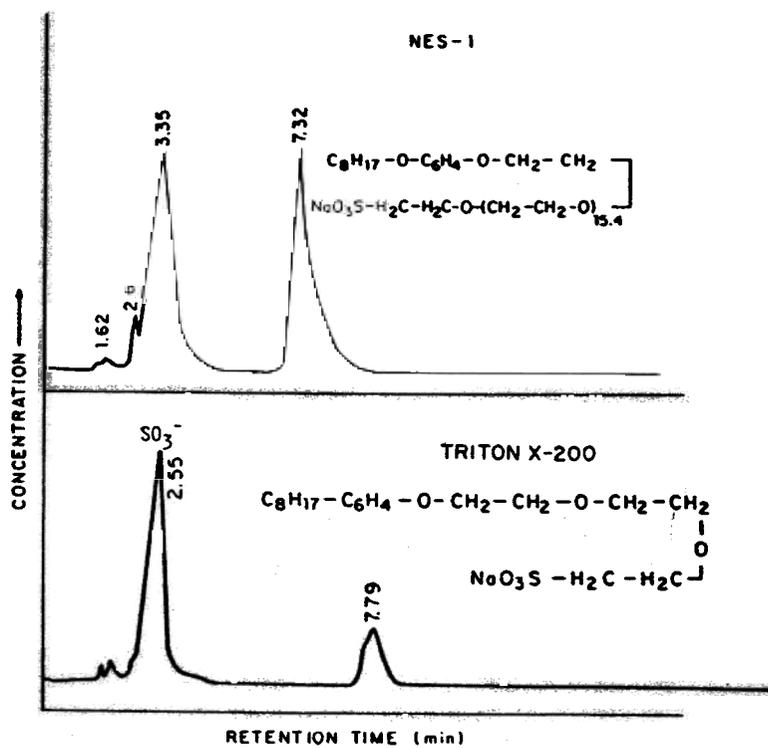
Fig. 5. HPLC chromatogram of Triton X-200 and NES-1

significant observation is the appearance of the peak at 3.1–3.2 ppm which is absent in the alcohol fraction. The number of protons associated with this peak at 3.1–3.2 ppm was found to be 2 (by integration). These protons are most likely to be the two CH_2 protons attached to the sulfonate group ($-CH_2-SO_3$). This was confirmed by synthesizing and analyzing monoisomeric TOPS-1 which has 1 EO group. The methylene protons attached to the sulfonate group are found to occur in this case at 3.5 and 4.4 ppm.

HPLC characterization

The HPLC chromatograms obtained for Triton X-200, NES-1, and TOPS-1 are given in Figs 4 and 5. It can be seen that while the chromatogram of the isomerically pure ethoxylated sulfonate, TOPS-1, shows only one major peak, the two technical grade sulfonates contain more than one peak, indicating the presence of impurities. There appears, however, to be two distinct fractions with widely differing elution times. The fast and slow eluting fractions were analyzed separately and only the former was found to contain the sulfonate. The high retention time of the latter fraction is characteristic of ethoxylated nonionic compounds (viz. Triton X-100) as indicated by HPLC data obtained for such compounds (see Table 2).

Salt tolerance of ethoxylated and nonethoxylated sulfonates

The tolerance of 10^{-2} kmol m^{-3} Triton X-200 solutions to sodium and calcium chlorides are shown in Figs 6a and 6b. It can be seen that at the specific surfactant level, precipitation occurs only above 14% NaCl and 7.4% $CaCl_2$. It is to be noted that the sodium and calcium tolerance of Triton X-200 is considerably higher than that of DBS (0.6% NaCl and 0.002% $CaCl_2$).

Adsorption of ethoxylated versus nonethoxylated sulfonates

The adsorption isotherms of Triton X-200, Triton X-202 and Alipal SE-463 on alumina and sodium kaolinite under medium salinity conditions are given in Fig. 7. For comparison adsorption/abstraction results of DBS on alumina and sodium kaolinite in the absence and presence of a soluble calcium mineral, gypsum, are given in Fig. 8. From Figs 7 and 8 we can see that the behavior of DBS in the presence of gypsum is totally different from the other systems. The vertical abstraction isotherms obtained with alumina and sodium kaolinite can be attributed to sulfonate precipitation by the calcium released from gypsum. The mechanism is shown below.

$$CaSO_4 \rightarrow Ca^{2+} + SO_4^{2-}$$

$$Ca^{2+} + 2\,RSO_3^- \rightarrow Ca(RSO_3)_2$$
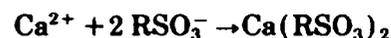
The solubility product of calcium disulfonate was determined experimentally [9] to be 7–8×10^{-12}. From the solubility product, the onset of precipitation
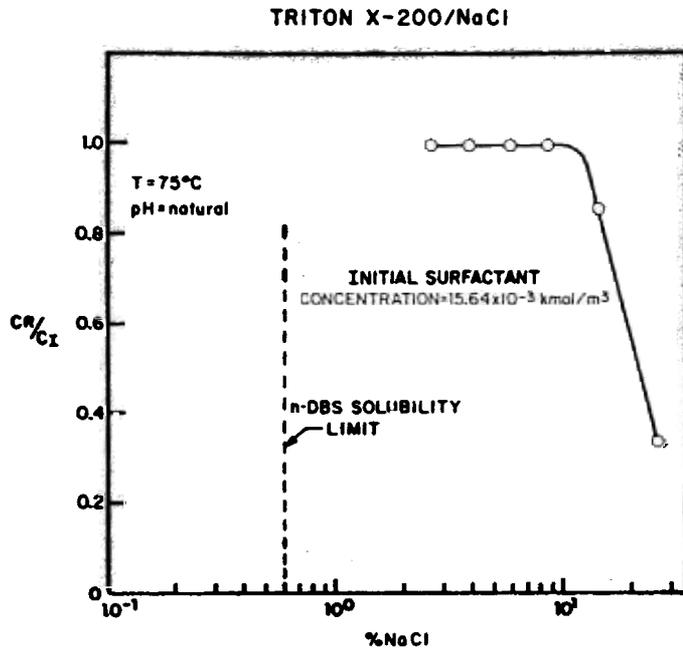
TRITON X-200/NaCl

Fig. 6a. The NaCl tolerance of 10^{-2} kmol m^{-3} Triton X-200 solutions
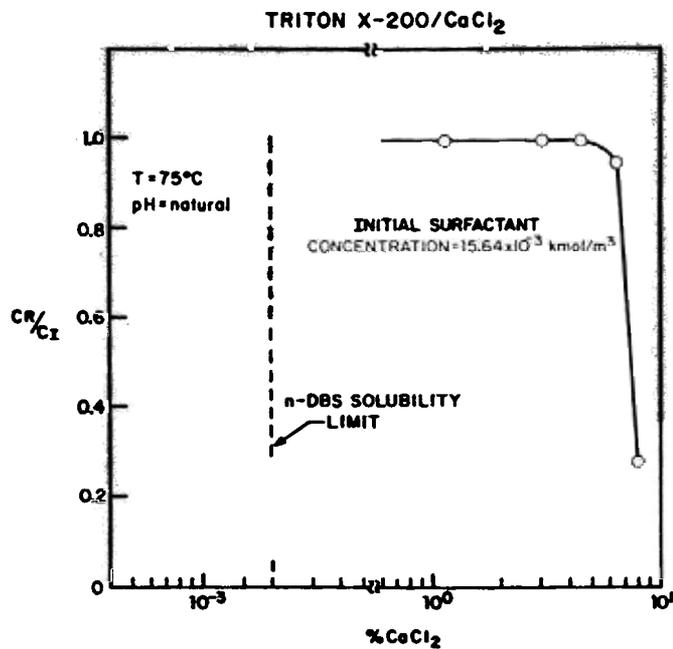
TRITON X-200/CaCl$_2$

Fig. 6b. The CaCl$_2$ tolerance of 10^{-2} kmol m^{-3} Triton X-200 solutions.
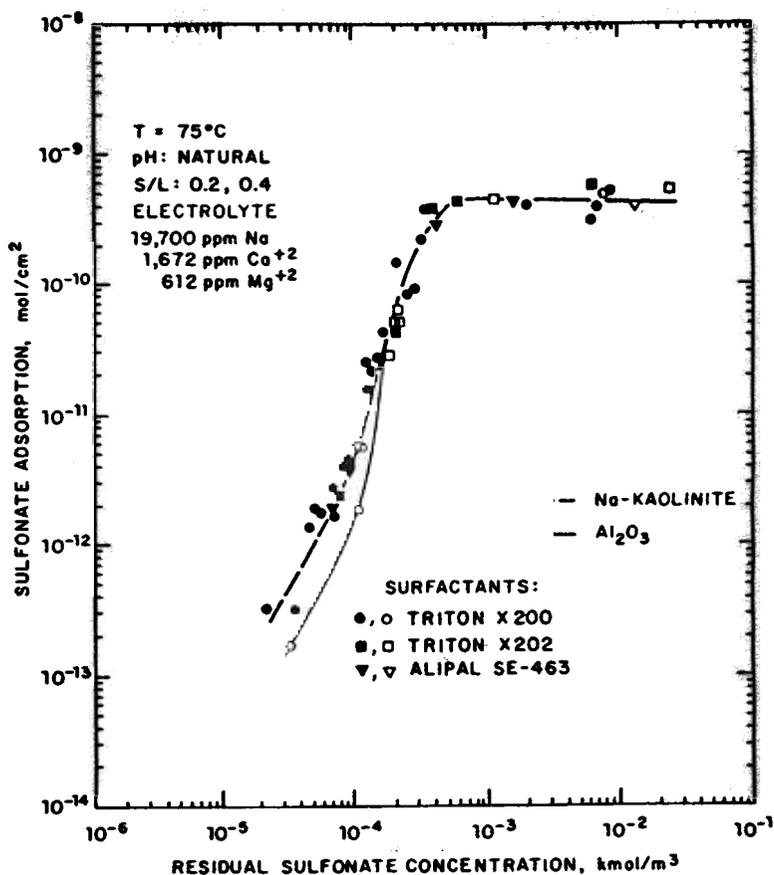
Fig. 7. Adsorption of ethoxylated sulfonates on alumina and sodium kaolinite under medium salinity conditions.

in the system can be determined from the residual sulfonate and calcium levels. The predicted onset of precipitation is shown in Fig. 8 to correlate with the abrupt increase in sulfonate depletion. In contrast, adsorption results of ethoxylated sulfonates on alumina and sodium kaolinite under harsher salinity conditions suggest that similar precipitation does not occur with these surfactants.

Clearly, the addition of ethoxylated groups affects significantly the solution behavior of sulfonate surfactants. In order to determine whether such effects are also manifested at the solid/liquid interface, systematic adsorption experiments were carried out using Triton X-200. In Fig. 9 the adsorption of Triton X-200 on alumina is compared with that of DBS and OBS. The isotherms are similarly shaped and characteristic of sulfonate adsorption on alumina. Upon comparing the magnitude of adsorption of these surfactants, it can be seen that the tendency of Triton X-200 to adsorb on alumina is less than that of DBS
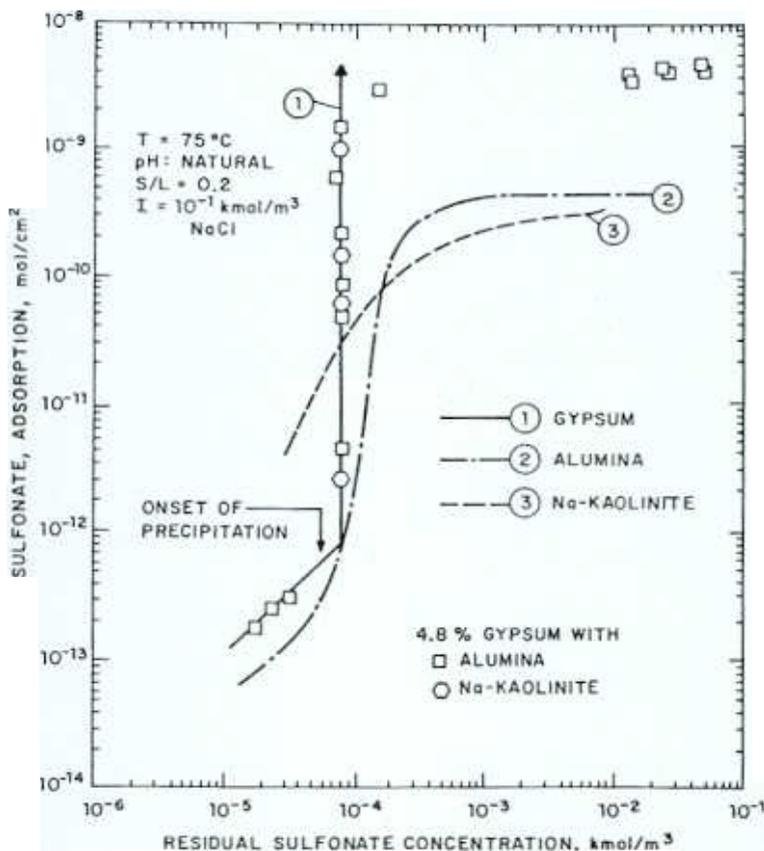
Fig. 8. Abstraction of decylbenzenesulfonate on reservoir minerals in the absence and presence of 4.8% gypsum.

but greater than that of OBS. Examination of the structures of these compounds and of the data obtained previously for the effects of chain length and branching on adsorption [20] suggests the following:

(1) The lower adsorption of Triton X-200 compared to that of DBS is expected on the basis of the longer and linear chain of the latter.

(2) On the same basis, however, the higher adsorption of Triton X-200 compared to OBS is not expected; linear C-8 chain of OBS should have a greater hydrophobic character (hemimicellization tendency) than the branched tertiaryoctyl chain of Triton X-200.

These observations suggest that the nature of the alkyl chain is not the only factor which determines the relative hydrophobicities of these surfactants. Structurally, Triton X-200 and alkylbenzenesulfonates differ because of the presence of the EO groups in the former as well as the position of the sulfonate
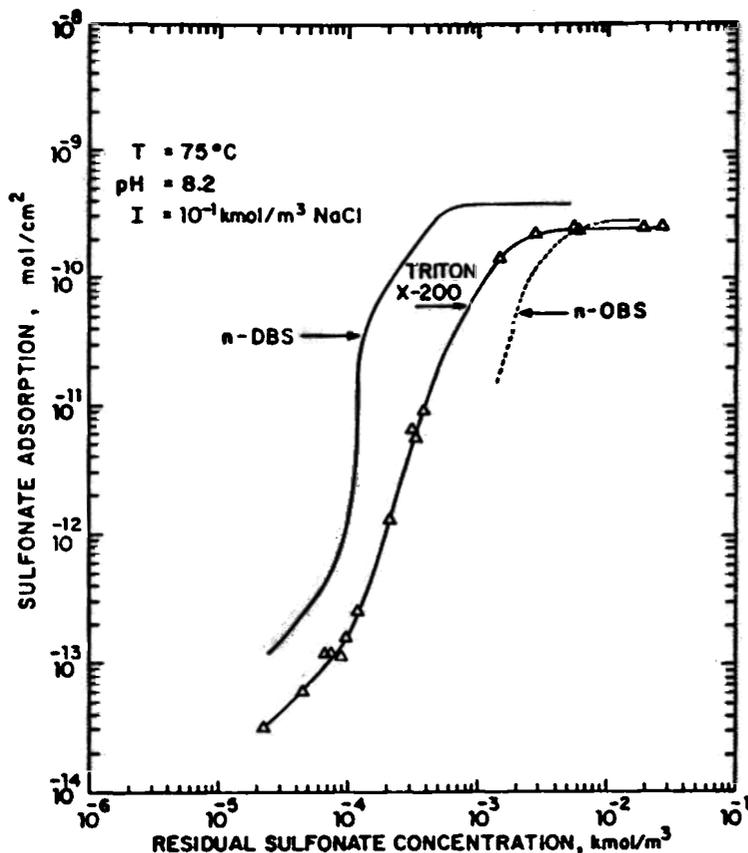
Fig. 9. Adsorption of Triton X-200, DBS and OBS on alumina at 75°C in 10^{-1} kmol m^{-3} NaCl.

group (the sulfonate group is attached to the benzene ring in the case of alkyl-benzenesulfonates, but in Triton X-200 it is attached to the EO chain). In order to understand the relative contributions of these differences on the hydrophobic character of these surfactants, HPLC studies were conducted using compounds having similar modifications in the structure. The elution time from a hydrophobic column (C_{18} bonded silica) in a polar solvent (acetonitrile-water) can be considered to be a measure of the relative hydrophobicities of the compounds studied; the more hydrophobic compounds are eluted at longer times. Table 2 summarizes the elution time of the compounds studied. The following conclusions can be drawn upon examining this data:

(1) The elution time of 4-n-octylphenol (22.46) is found to be greater than that of 4-tertiaryoctylphenol (12.15) suggesting that branching of the alkyl chain reduces hydrophobicity.

(2) The elution time for 4-tertiaryoctylphenol (12.15) is greater than that

hydrophobic than OBS. Indeed, HPLC results show the elution time of 4-n-octylphenol to be reduced from 22.46 to 3.08 when it is sulfonated to form OBS, while similar sulfonation of the 4-tertiaryoctylphenoxy ethoxylated alcohol to 4-tertiaryoctylphenoxy ethoxylated sulfonate (Triton X-200) reduces the elution time from 7.63 to 3.52. Clearly, the effect of the sulfonation in inducing hydrophilicity is markedly lower for the ethoxylated compound than for the nonethoxylated one. It is interesting to note that in the case of Triton X-200 the combined effect of branching, ethoxylation, and sulfonation in reducing hydrophobicity is still less than the effect of sulfonation alone for OBS.

While the above explanations based on the structural differences between Triton X-200 and OBS are reasonable and supported by HPLC studies, it is also possible that the observed differences in adsorption of these surfactants arise from either specific interaction of the EO groups with the surface or from the presence of impurities in Triton X-200. The alcohol impurities present in Triton X-200 are more hydrophobic than sulfonate and such impurities can coadsorb along with the sulfonate leading to enhancement of sulfonate adsorption [20,21]. Such enhancement can account for the higher adsorption of Triton X-200 when compared to that of OBS. However, the HPLC retention times and hence hydrophobicity of the sulfonates agree with the adsorption results on alumina; the order of increasing adsorption measured is suggested therefore
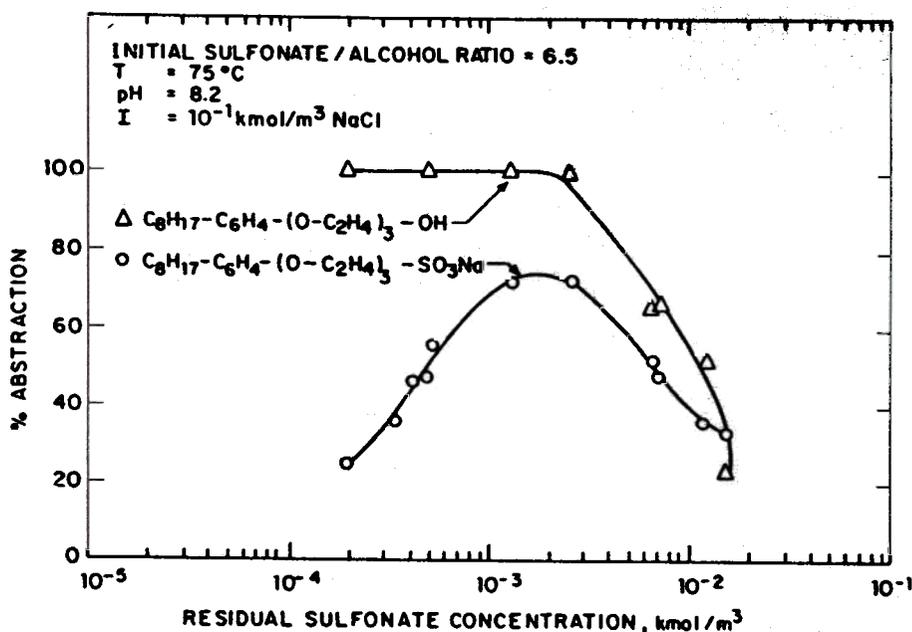
Fig. 11. Percentage adsorption of anionic and nonionic components from Triton X-200 on alumina computed from HPLC results as a function of residual sulfonate concentration.

to be predominantly the result of structural differences rather than the presence of impurities. However, the presence of impurities can be significant and this is discussed next.

Effect of impurities

In order to investigate the effect of impurities, adsorption experiments were carried out on alumina using both as received and purified [23] Triton X-200. The adsorption isotherm of the purified Triton X-200 on alumina is compared in Fig. 10 with that of the as-received sample. Examination of these isotherms suggest the following:

(1) Adsorption of purified Triton X-200 is up to an order of magnitude less than that of the impure sample in the premicellar region.

(2) Both the isotherms are S-shaped, indicating the absence of precipita-
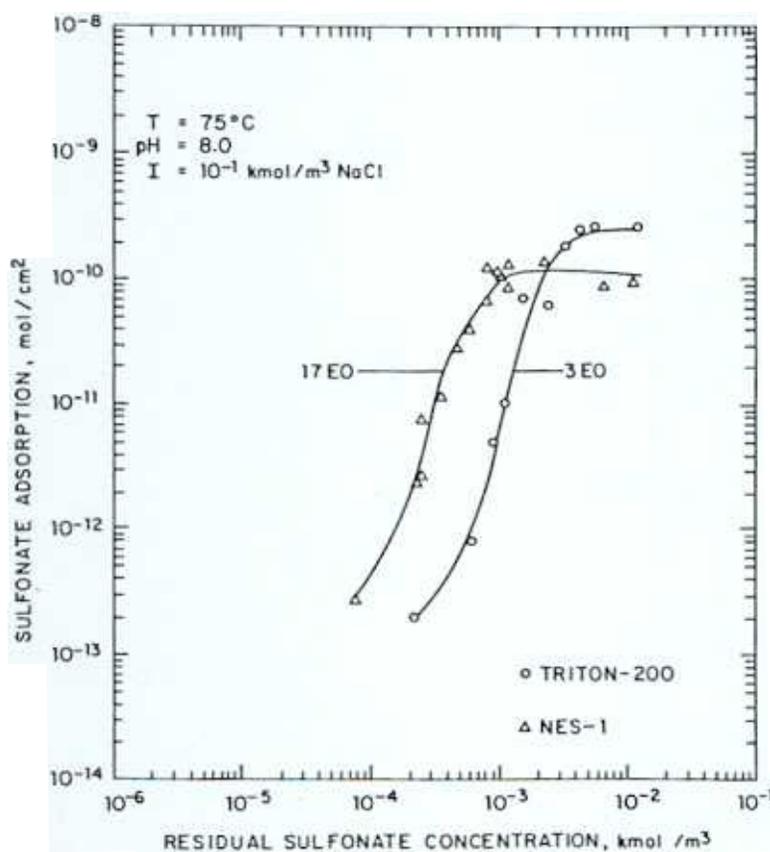
Fig. 12. Adsorption of purified Triton X-200 and NES-1 on alumina at 75°C in 10^{-1} kmol m^{-3} NaCl.

tion. Adsorption can thus be considered to be due to electrostatic, hemimicellar and micellar interactions.

(3) The CMCs as indicated by the onset of plateau are not markedly different.

The influence of ethoxylated alcohol, present as an impurity in this case, is to enhance the adsorption of sulfonate in the premicellar region. These results are in agreement with our previous work on the dodecane–decylbenzenesulfonate system [21] where the increased adsorption in the electrostatic and hemimicellar regions was considered to be due to synergistic effects of nonionic-sulfonate coadsorption.

HPLC data for typical mineral supernatants before and after adsorption allows quantitative determination of the adsorption of the sulfonate and the alcohol from the mixtures. These results are presented as percent adsorption
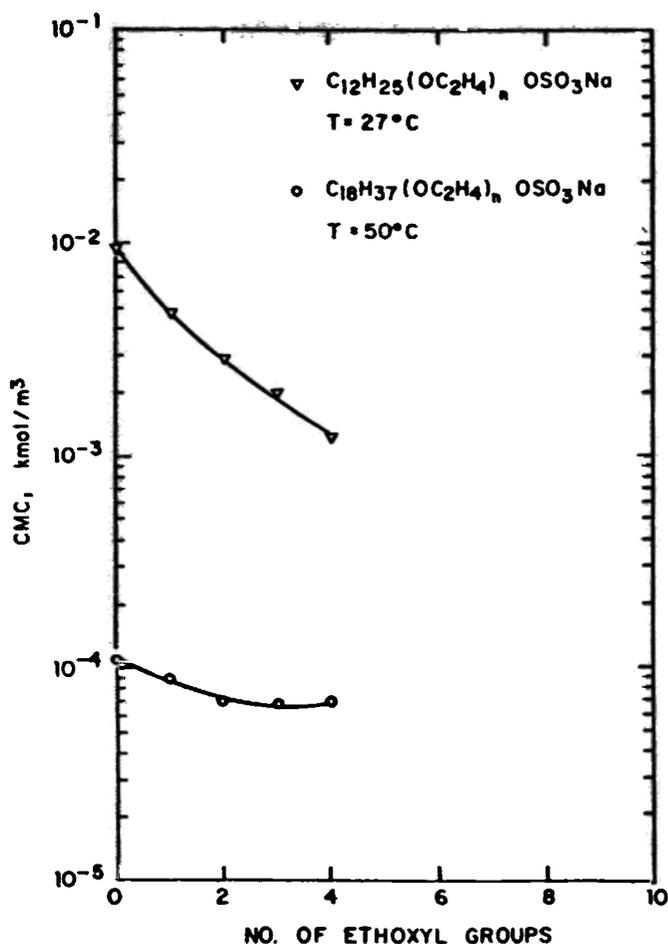
Fig. 13. Literature data on effect of ethoxylation on CMC of alkylethoxylated sulfates [25]

at various residual sulfonate levels in Fig. 11. It can be seen from this figure that almost all of the alcohol is preferentially abstracted from the solution in the premicellar region. In the plateau region alcohol adsorption is decreased substantially, possibly due to partitioning of the alcohol into the micellar pseudo-phase. Even though ethoxylated alcohol enhances the adsorption of sulfonate, examination of the magnitude of adsorption of purified Triton X-200 (Fig. 10) with that of DBS and OBS (Fig. 9) shows that the higher adsorption of Triton X-200 when compared to that of OBS cannot be due to impurities alone. The possible interaction of ethoxy group and the sulfonate group with the mineral surface cannot be ruled out.

Effect of ethoxylation

In order to understand the role of ethoxylation of sulfonates, we have selected two surfactants possessing the same alkyl chain but having a wide difference
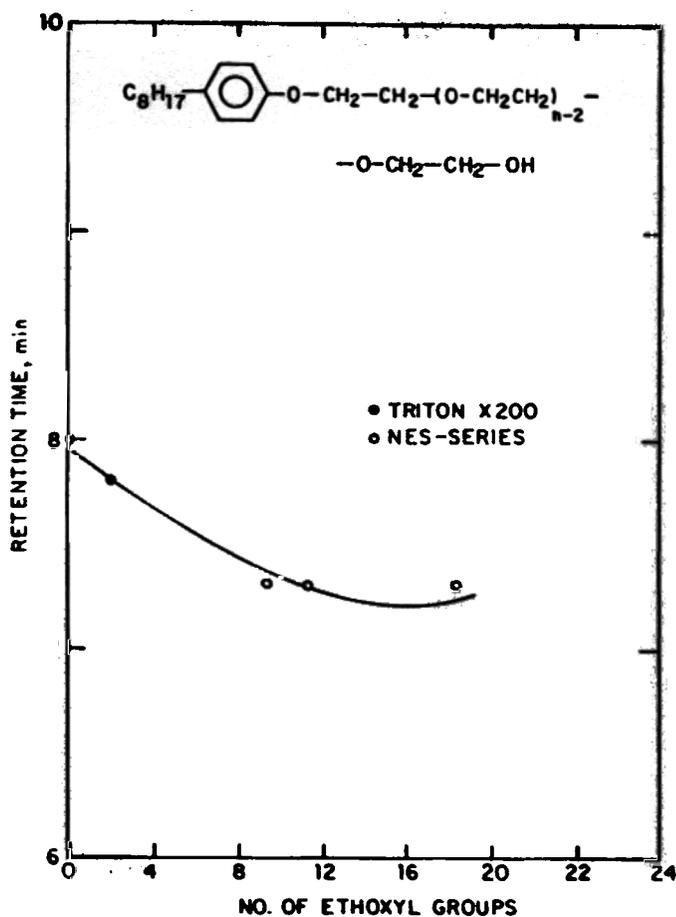
Fig. 14. Effect of ethoxylation on CMC of 4-tertiaryoctylphenoxyethyl alcohols.

in the degree of ethoxylation. Adsorption results using 4-tertiaryoctylphen-
oxyethylsulfonates with 3 and 17 EO groups on alumina are given in Fig. 12.
Although these sulfonates are polydispersed in EO groups, they are free from
nonionic impurities.

Examination of the isotherms in Fig. 12 shows the following:

(1) The isotherms for sulfonate with 3 EO groups (Triton X-200) and 17
EO groups (NES-1) are characteristic of the S-shaped isotherms for alkylben-
zenesulfonates on alumina.

(2) Adsorption in the hemimicellar region increases with increasing
ethoxylation.

(3) The CMC as indicated by the onset of plateau is lower for the more
ethoxylated surfactant (NES-1).

Fig. 15. Effect of ethoxylation on the retention time for 4-tertiaryoctylphenoxyethylsulfonates.

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The higher adsorption and lower CMC of the 17 EO surfactant compared to that of the 3 EO surfactant is interesting and not altogether in agreement with what is known about these compounds. It is generally thought that addition of EO groups to the structure increases the hydrophilicity of surfactants [24] and hence lowers the adsorption and raises the CMC. It is possible that EO groups interact specifically with the mineral surface leading to increased adsorption with increasing ethoxylation. However, the specificity of the EO groups with the surface cannot explain the lower CMC of the higher EO sulfonates. It is to be noted that our results for the changes in CMC are in agreement with those in the literature for ethoxylated sulfates [25] (Fig. 13) where increase in EO was indeed found to decrease the CMC. Interestingly, CMC measurements of 4-tertiaryoctylphenoxy ethoxylated alcohols using surface tension technique show an opposite trend, as seen in Fig. 14.

In order to compare the relative hydrophobicities of the two sulfonates, reversed phase ion-pair chromatography was used. As mentioned earlier, the retention time of these surfactants on a C_{18} bonded silica column is a measure of the hydrophobicity, with more hydrophobic compounds eluting at longer times. The data for 4-tertiaryoctylphenoxy ethoxylated sulfonates are pre-
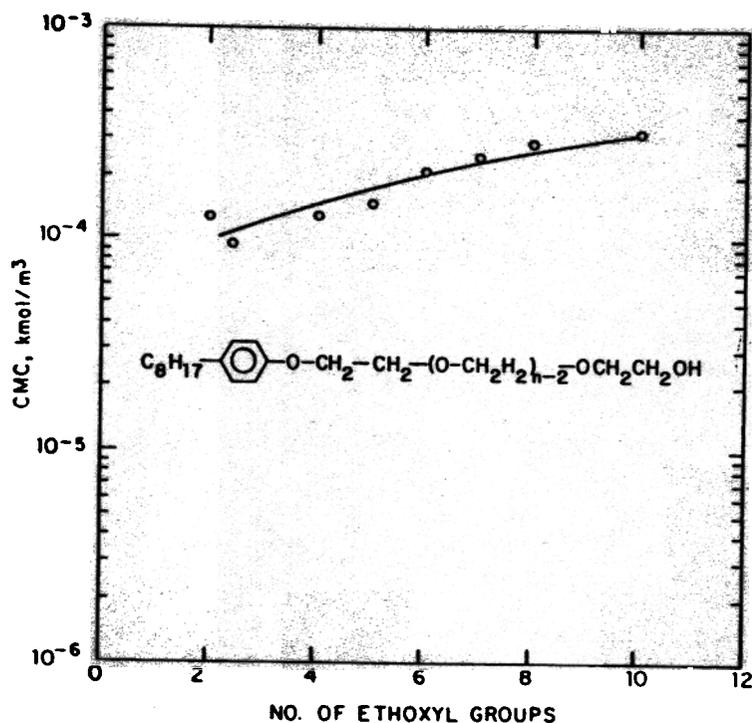
Fig. 16. Effect of ethoxylation on the retention time for 4-tertiaryoctylphenoxyethyl alcohols.

sented in Fig. 15, while the retention times of the 2-tertiaryoctylphenoxy ethoxylated alcohols are shown in Fig. 16. Again, as with the CMC data, the trend in retention times (hydrophobicity) versus EO number is totally different for each class of compounds, with the alcohols becoming more hydrophilic and the sulfonates more hydrophobic with increase in EO. It should also be noted that the replacement of the $-OH$ group with the $-SO_3$ group induces more hydrophilicity to the surfactant than does the addition of an EO group as evidenced by the range of retention times for the sulfonate (2 to 4 min) compared to that for the alcohols (7 to 8 min).

On the basis of these results, the following conclusions are offered for the effect of ethoxylation:

(1) EO group impart hydrophilicity to the molecule as a whole as seen in the decrease in retention times of the alcohols with increase in ethoxylation.

(2) For sulfonates with 1 to 17 EO groups, the hydrophilicity imparted by the sulfonate group is predominant, as indicated by the significantly different retention times of the alcohols and sulfonates, so that increase of the EO number does not have the same effect as in the case of alcohols. Indeed, in this case the EO groups appear to retard the effect of the sulfonate, making the surfactant more hydrophobic, possibly by effectively increasing its chain length.

The decrease in plateau adsorption for NES-1 (17 EO) compared to that for Triton X-200 (3 EO) can be expected on the basis of the lower CMC of the former. Since the monomer activity is constant at surfactant concentrations above CMC, adsorption is limited to the plateau value arrived at CMC. Thus the surfactant with lower CMC will also have a lower plateau value provided their adsorption levels do not differ by orders of magnitude in the premicellar region. However, there is increasing evidence that plateau values under conditions when the driving force for adsorption is sufficiently strong, correspond to saturated adsorption (monolayer). Therefore, the present result could also be interpreted in terms of a lower packing density for the surfactant with higher ethoxylation. This conclusion is supported by the literature surface tension data when ethoxylated surfactants with higher EO numbers were found to have a larger parking area [22]. These effects, explained on the basis of the highly hydrated nature of the ethoxy chain can also account for, to some extent partly, the differences in the plateau adsorption observed in the present studies.

CONCLUSIONS

(1) Ethoxylated sulfonates have higher salt tolerance for Na^+ and Ca^{2+} when compared to isomerically pure 4-n-decylbenzenesulfonate.

(2) Ethoxylated alcohol impurities present in the commercial ethoxylated sulfonates enhances adsorption of ethoxylated sulfonates in the premicellar region.

(3) Increasing the degree of ethoxylation increases the hydrophobicity of

ethoxylated sulfonates but decreases the hydrophobicity of ethoxylated alcohols.

(4) The CMC of ethoxylated alcohols increases with increase in ethoxylation.

(5) The CMC of ethoxylated sulfonates decreases with increase in ethoxylation.

(6) Increase in ethoxylation increases the adsorption of ethoxylated sulfonates in the premicellar region.

(7) Ethoxylation in general is found to decrease adsorption in micellar solutions.

(8) The results can be interpreted in terms of the hydrated nature of the ethoxy group and the molecular geometry dictating the parking areas.

ACKNOWLEDGEMENTS

REFERENCES

1 P. Somasundaran, T.W. Healy and D.W. Fuerstenau, Surfactant Adsorption at the Solid–Liquid Interface - Dependence of Mechanism on Chain Length, J. Phys. Chem., 68 (1964) 3562.
2 P. Somasundaran and D.W. Fuerstenau, Mechanism of Alkylsulfonate Adsorption at the Alumina-Water Interface, J. Phys. Chem., 70 (1966) 90.
3 J.B. Lawson and R.E. Dilgren, Adsorption of Sodium Alkylarylsulfonate on Sandstone, SPE preprint 6121, 1976.
4 H.S. Hanna and P. Somasundaran, Physico-Chemical Aspects of Adsorption at Solid/Liquid Interfaces, II. Mahogany Sulfonate/Berea Sandstone/Kaolinite, in D.O. Shah and R.S. Schechter (Eds), Improved Oil Recovery by Surfactant Polymer Flooding, Academic Press, New York, 1977, pp. 253-274.
5 P. Somasundaran, Adsorption from Flooding Solutions in Porous Media, Annual Report submitted to the DOE, NSF and a Consortium of Supporting Industrial Organizations, Columbia University, New York, 1981.
6 S. Stournas, Brine-Resistant Sulfonate Surfactants for Enhanced Oil Recovery, SPE preprint 11773, 1983.
7 K.P. Ananthapadmanabhan and P. Somasundaran, Mechanism for Adsorption Maximum and Hysteresis in a Sodium Dodecylbenzenesulfonate/Kaolinite System, Colloids Surfaces, 7 (1983) 105.
8 P. Somasundaran and H.S. Hanna, Adsorption of Sulfonates on Reservoir Rock, Soc. Pet. Eng. J., (1979) 221.
9 P. Somasundaran, K.P. Ananthapadmanabhan and K.V. Viswanathan, Adsorption of Sulfonate on Kaolinite and Alumina in the Presence of Gypsum, SPE paper 11780, 1983.

10 J. Scamehorn, R.S. Schechter and W.H. Wade, Adsorption of Isomerically Pure Alkylben-zenesulfonates on Alumina, J. Colloid Interface Sci., 85 (1982) 463.

11 P.E. Figdore, Adsorption of Surfactants on Kaolinite: NaCl versus $CaCl_2$, J. Colloid Interface Sci., 87 (1982) 500.

12 P. Somasundaran and P. Chandar, Interactions between Surfactants and Polymers with Reservoir Minerals, in Solid-Liquid Interactions in Porous Media, Colloque-Bilan, Nancy, February 1984, Editions Technip, Paris, France, 1985, pp. 411-427.

13 J. Novasad, B. Maini and J. Batycky, A Study of Surfactant Flooding at High Salinity and Harshness, J. Am. Oil Chem. Soc., 59 (1982) 833.

14 M.J. Rosen and Y. Nakamura, The Relationship of Structure to Properties in Surfactants – The Adsorption of Alpha and Omega Bis [Sodium p-sulfophenoxy] Alkanes on Alumina, J. Phys. Chem., 81 (1977) 873.

15 J.I. Di Stasio (Ed.), Chemicals for Oilfield Operations, Noyes Data Corporation. NJ, 1981, p. 157.

16 R.S. Schechter, W.H. Wade, V. Weerasooriya and W. Weerasooriya, Synthesis of Linear Monoisomeric Ethylene Oxide Surfactants, unpublished results, supplied by P. Lorenz, personal communications.

17 E.A. Dennis and A.A. Riberio, Use of Nuclear Magnetic Resonance Techiques to Study Nonionic Surfactant Micelles and Mixed Micelles with Phospholipids, ACS Symp. Ser., 34 (1976) 453.

18 Solid Phase Extraction Manual, Vol. I and II, J.T. Baker Chemical Co., 1984.

19 V.W. Reid, G.F. Longman and E. Heinerth, Determination of Anionic Active Detergents by Two-phase Titration, Tenside, 4 (1967) 292.

20 P. Somasundaran, R. Middleton and K.V. Viswanathan, Relationship between Surfactant Structure and Adsorption, ACS Symp. Ser., 253 (1984) 269.

21 K.V. Viswanathan and P. Somasundaran, Abstraction of Sulfonates and Dodecane by Alumina, SPE preprint 10602, 1982.

22 M.J. Rosen, Surfactants in Interfacial Phenomena, Wiley, New York, 1978, Ch. 3.

23 C. Still, Flash Chromatography, J. Org. Chem., 43 (1978) 2933.

24 P. Becher, Micelle Formation, in M.J. Schick (Ed.), Nonionic Surfactants, Marcel Dekker, New York, 1967, pp. 479-515.

25 K.J. Mysels and P. Mukerjee (Eds), Critical Micelle Concentrations in Aqueous Systems, NSRDS-NBS 36. US Government Printing Office, Washington, DC, 1971.