

## Relationship Between Surfactant Structure and Adsorption

P. SOMASUNDARAN, R. MIDDLETON, and K. V. VISWANATHAN

School of Engineering and Applied Science, Columbia University, New York, NY 10027

Adsorption of a surfactant on solids is dependent, among other things, on the structure of both the hydrophobic and hydrophilic portions of it. There are a number of mechanisms proposed for surfactant adsorption and an understanding of the effects of the structure of the surfactant can help in elucidating the role of these mechanisms. In this study, the effect on adsorption on alumina of some structure variations of sulfonates (chain length and the branching and the presence of ethoxyl, phenyl, disulfonate and dialkyl groups) is examined above and below CMC as a function of surfactant concentration, pH and salinity. Co-operative action between an ionic alkylsulfonate and a nonionic ethoxylated alcohol is also studied.

Surfactant adsorption on solids from aqueous solutions plays a major role in a number of interfacial processes such as enhanced oil recovery, flotation and detergency. The adsorption mechanism in these cases is dependent upon the properties of the solid, solvent as well as the surfactant. While considerable information is available on the effect of solid properties such as surface charge and solubility, solvent properties such as pH and ionic strength (1,2,3), the role of possible structural variations of the surfactant in determining adsorption is not yet fully understood.

Adsorption is governed by a number of forces: covalent bond formation or electrostatic attraction or hydrogen bond formation between the adsorbate and the adsorbent, electrostatic repulsion among the adsorbate species, lateral associative interaction among adsorbed species, solvation of adsorbate or adsorbent surface species. Structural modifications can affect one or more of the above interactions that might be predominant in different concentration regions, and it is the cumulative effect of all of these modifications on all interactions in various concentration regimes that will determine the overall adsorption behavior of a surfactant (4,5). Thus while in practice chain length or branching will affect only the lateral interactions in the hemi-micellar region,

presence of multifunctional groups (such as disulfonates with an ether linkage) can affect both electrostatic and lateral association interactions. Coadsorption between different surfactant species also can be expected to be influenced significantly by such structural variations.

In this paper the adsorption characteristics of a series of structurally modified surfactants will be analyzed. Figure 1 summarizes this series showing the following structural variations: aryl addition, chain length variation, branching, xylene alkyl addition, ether linkage and ethylene oxide addition, with alumina as the adsorbent. By understanding the effect of structural variations upon the adsorption mechanism a guideline may be established by which a surfactant may be tailored with specific structural modifications for certain situations.

### Experimental

**Surfactants.** n-sodium dodecylsulfonate specified to be 99.4% pure was purchased from Aldrich Chemicals.

n-sodium octyl, decyl, dodecyl and tetradecylbenzene sulfonates were synthesized and purified in our laboratory. Characterization of these chemicals using p-NMR, C-13 NMR, mass spectrometry and ALC showed these compounds to be isomerically pure. Branched hexadecyl benzene sulfonate was obtained from Conoco and used as received after characterization.

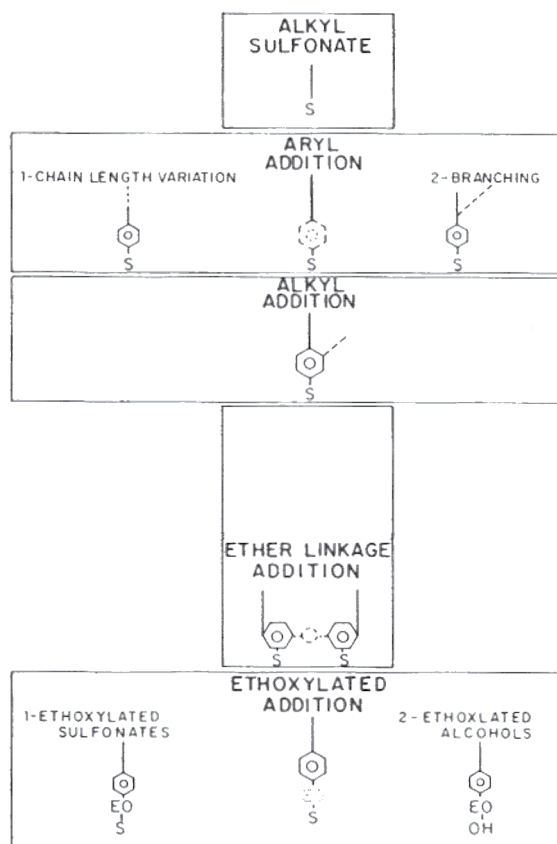
Alkyl aryl orthoxylenesulfonates were also investigated. The first being a linear nonyl orthoxylenesulfonate and the second being a branched dodecyl one. Both were supplied by the Exxon Corporation and contain known amounts of unsulfonated hydrocarbons (14% and 25.2% respectively).

The disulfonate, Dowfax 3B2, used was a didecylphenoxydisulfonate containing 10% monosulfonated impurities. HPLC analysis showed this surfactant to be a mixture of several compounds.

Triton X-200 was used to study the effects of ethoxylation on the sulfonates. Nonionic ethoxylated surfactants were investigated using Synfac 8216 obtained from the Milliken Corporation. This was stated to be 100% active with a molecular weight of 1100-1200. HPLC showed this surfactant to be a mixture of several components.

**Mineral.** Alumina used in this study was a high purity  $\alpha$ -Linde sample purchased from the Union Carbide Corporation. BET surface area was determined to be 15.0 m<sup>2</sup>/g.

**Procedure.** A gram of the mineral was preconditioned for 90 minutes with 5cc of a 0.2 kmol/m<sup>3</sup> sodium chloride solution at 75°C on a wrist action shaker. Then a 5cc solution of known surfactant concentration is added and allowed to shake for four hours. Four hours mixing was found to be sufficient to reach equilibrium from adsorption test conducted as a function of mixing time. The



**Figure 1. General overview.**

supernatant was obtained using a thermostated centrifuge at 4500 rpm. Analyzation of surfactant concentration was completed using a two-phase titration technique and U.V. spectroscopy.

### Results and Discussion

The adsorption isotherm obtained for dodecylsulfonate (DDS) on alumina is given in Figure 2. This isotherm is similar to that obtained in the past for sulfonate/alumina systems (4). This isotherm behaves in an s-shaped manner (6) revealing its four characteristic regions of adsorption: 1) Electrostatic interaction 2) Lateral association (hemimicellization), 3) Electrostatic hindrance and 4) micellization.

In Region 1, under low surfactant concentration conditions, adsorption occurs mainly due to the electrostatic attraction between the surfactant ion and the charged sites on the solid surface (3). The beginning of Region 2 is characterized by the onset of lateral association among the adsorbed surfactant species (4). This process is analogous to micellization but takes place at a lower surfactant concentration assisted by the electrostatic attractive forces between the hemi-micelle and the charged solid (7, 4). While sufficient surfactant ions have been adsorbed to neutralize the surface charge of the mineral, further adsorption progresses owing to continued hemimicellization. Charge reversal occurs and adsorption in this concentration region is hindered by the increasing electrostatic repulsion between the now similarly charged solid and surfactant species (Region 3) (4). Region 3 ends and a new region begins with the onset of micellization (8). In the micellar region, adsorption is nearly constant due to the absence of a marked increase in activity of the surfactant species in this region with an increase in its concentration (8). In this region apparent "adsorption" can, however, undergo drastic changes owing, among other things, to precipitation or micellar redissolution of the surface precipitate (5, 9), resulting in adsorption maxima and minima. While adsorption in the hemimicellar region, like that in the micellar region, is dependent on the hydrophobic properties of the surfactant, adsorption in the electrostatic region and alterations in adsorption owing to precipitation, redissolution and reprecipitation will depend upon solution properties such as pH, salinity and hardness. Thus factors to be considered while examining the effect of surfactant structure will include changes in the electrostatic attraction and repulsion of the adsorbate and adsorbent, solvent power of the medium for the surfactant and its precipitates, and lateral association as well as electrostatic repulsive interactions among the adsorbed species.

Aryl Addition. Surfactants having an aryl group added between the sulfonate and alkyl chain are studied using the standard adsorption procedure, and compared with an alkyl sulfonate. Figure

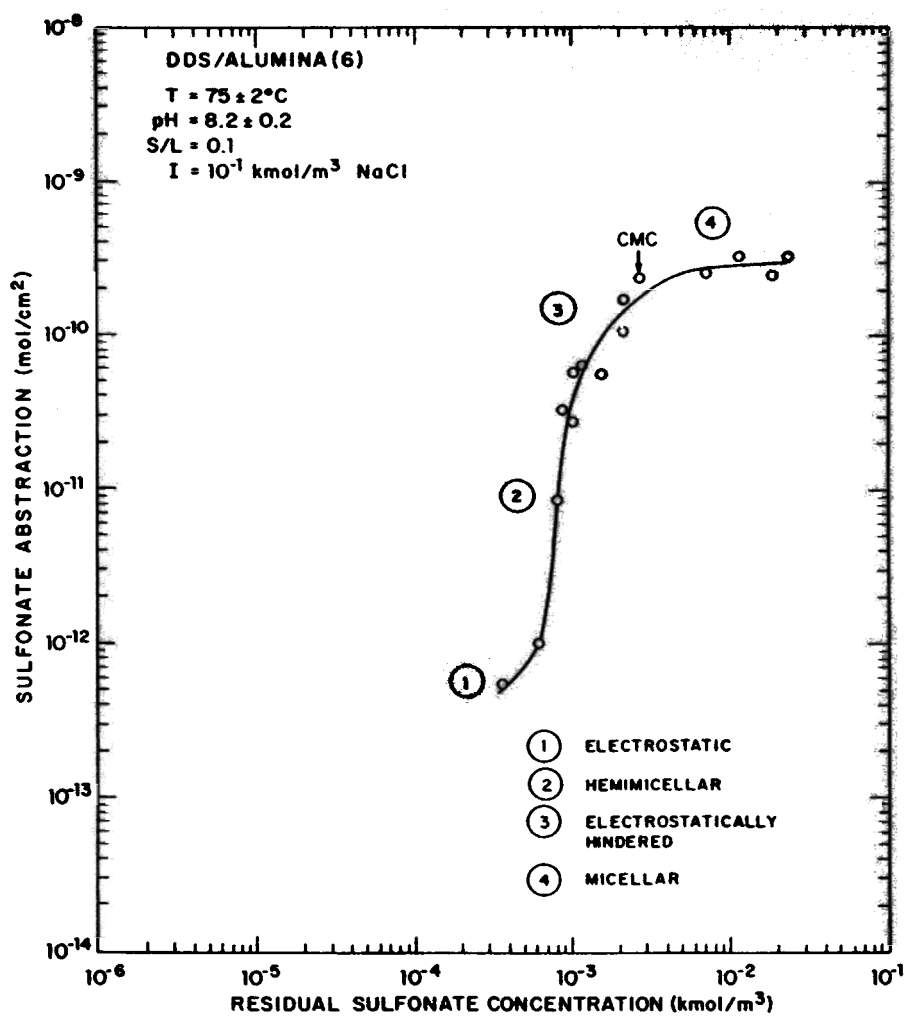
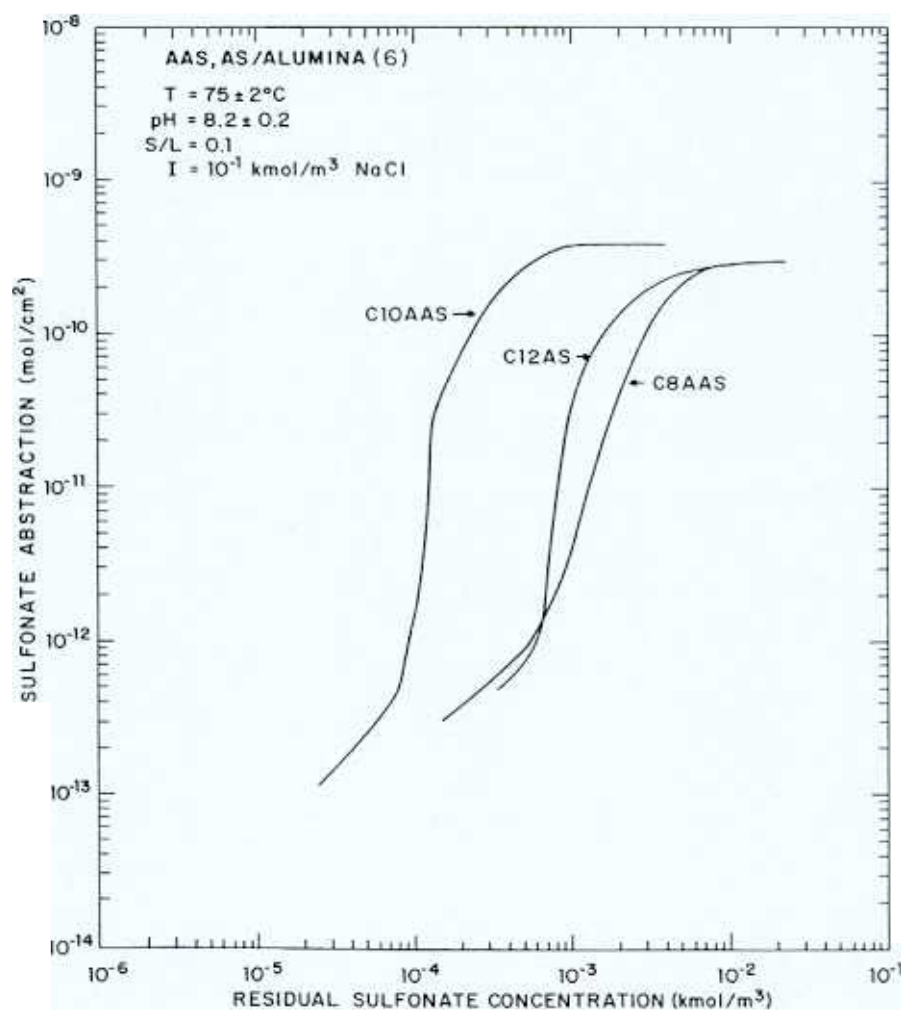


Figure 2. Alkyl sulfonate adsorption.

3 shows the adsorption isotherms of DDS, OBS and DDBS. Under the assumption that one benzene ring equals 3.5 alkyl units (10), the equivalent alkyl chain length of OBS and DDBS can be calculated: 11.5 and 13.5 respectively. DDS and OBS, both having similar equivalent alkyl chain lengths (.5 alkyl difference), do behave with similar adsorption characteristics. Comparison of DDS and DDBS shows the large increase in adsorption associated with the aryl addition.

Chain Length Variation. Adsorption isotherms obtained for alkylbenzene sulfonates of varying chain length are given in Figure 4. Adsorption clearly increases as the chain length of the alkyl group is increased from 8 to 14. This is found to be the case even in Region 1 where adsorption has been proposed to take place owing to electrostatic attraction only. Since in all cases, the charge of the sulfonate species is 1, adsorption in the electrostatic region should have been invariant with chain length. The fact that it is, to the contrary, dependent on the chain length suggests the possible influence of the reduced dielectric constant in the interfacial region(11). Transfer of the monomer chain into a less dielectric region should result in a lowering of free energy, with the reduction being larger for the longer chains. Adsorption of the long chain sulfonates in Region 1 should therefore be considered to be the result of electrostatic attraction as well as increased solvent power of the interfacial water. Increase in adsorption seen in the lower three regions (Figure 4) can be attributed to the increase in hydrophobicity with chain length resulting in stronger hemi-micellization as well as monomer transfer. The shift in the micellar regions of the AAS isotherms is in effect a measure of the increased hemimicellization versus micellization as the chain length is increased (12). When the hemi-micellization is essentially complete at the end of Region 3, the end methylene group of the peripheral chains in each hemimicelle is still exposed to bulk water; however, the fraction of exposed groups per chain will decrease with increase in chain length. Any such change in the case of micellization could be expected to be of a lower magnitude. Thus the higher adsorption of longer chains achieved at the beginning of the Region 4 can conceivably be the result of the greater energy of hemimicellization energy in relation to that of micellization.

Effect of Branching. The effect of branching was investigated by comparing the adsorption of various hexadecylbenzene sulfonates (Figure 5). The first had the benzene group occupying the number 2 position upon the alkyl chain and the second had it at the 8 position. Adsorption of the 2- $\phi$  HDBS is significantly higher than that of the 8- $\phi$  HDBS. In the low concentration region the former appears to adsorb almost an order of magnitude more than the latter; it is however to be noted that adsorption in this region borders upon the experimental limitations; even in the micellar region, adsorption of it is higher. 2- $\phi$  HDBS which is least branched



**Figure 3.** Structural comparison: AAS vs. AS.

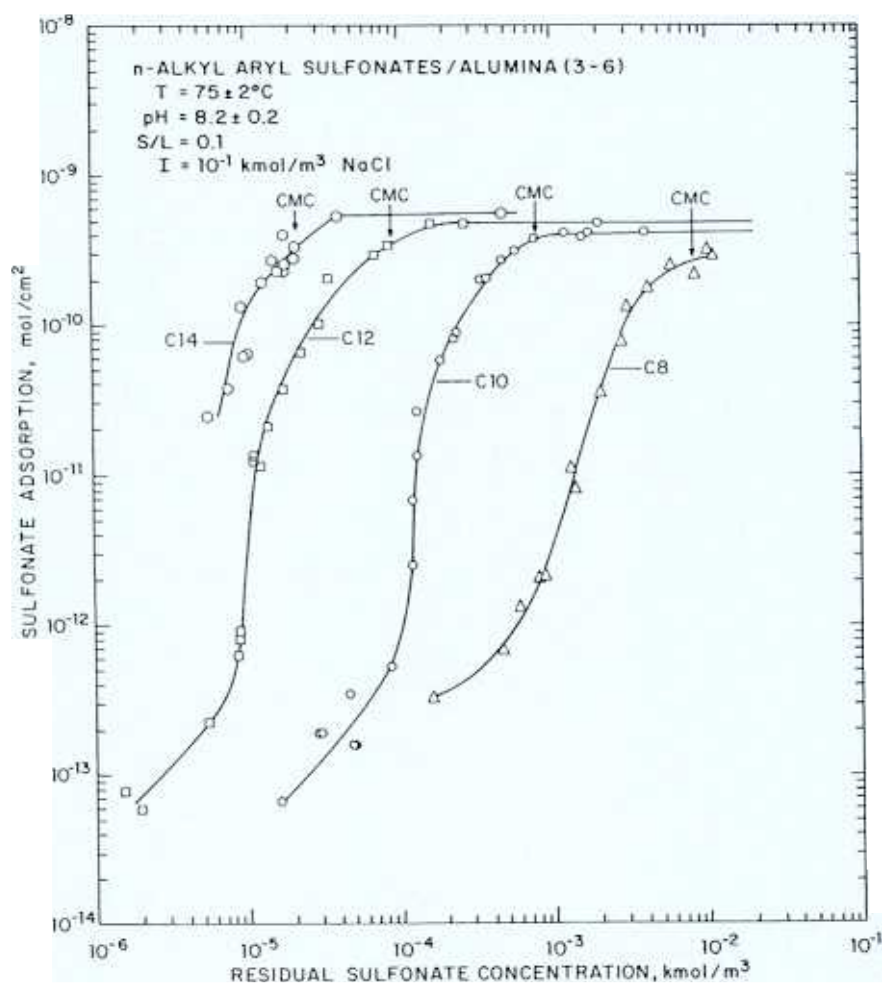


Figure 4. Effect of chain length.

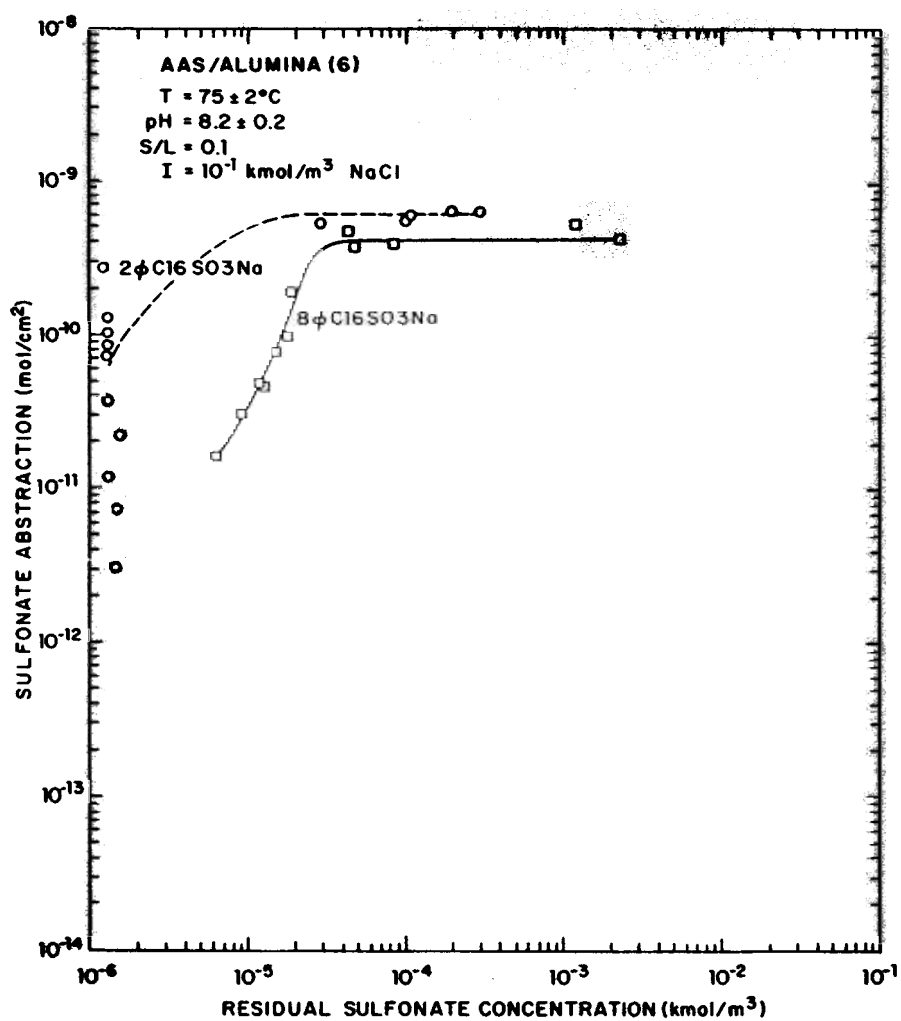


Figure 5. Effect of branching.

is considered to have a larger effective alkyl chain than the 6  $\phi$  HDBS (13), since the CMC of the former is considerably lower than that of the latter. It must, however, be pointed out that while formation of a spherical micelle might be more easily accomplished with the 2  $\phi$  HDBS than with the 8  $\phi$  HDBS, it is not fully evident as to why a planar hemi-micelle should be more easily achieved with the 2  $\phi$  HDBS.

Comparison of these adsorption isotherms with those obtained for the linear alkyl aryl sulfonates (Figure 6) reveals the behavior of the 2  $\phi$  HDBS to be close to that which would be expected for a 1  $\phi$  HDBS and that of the 8  $\phi$  HDBS to be equivalent to that of a tridecyl benzene sulfonate. Development of a quantitative model that can account for the effect of the position of the benzene group on the chain warrants additional data for a variety of surfactants with branched chains.

Alkyl Addition on the Aromatic Ring. The two surfactants chosen to be representative of this section were alkylaryl sulfonates having an additional alkyl groups substituted in the aromatic ring. These compounds were commercially named alkylaryl-orthoxylene sulfonates and referred to as such. The adsorption behavior of the following xylene sulfonates was examined: linear nonylorthoxylene sulfonate and branched dodecylorthoxylene sulfonate. Such orthoxylene sulfonates have been reported to be very effective in reducing interfacial tensions; however, adsorption characteristics of these compounds are not clearly known. Results obtained for the two alkylorthoxylene sulfonates are given in Figure 7. Since the position of the aryl group in the dodecyl chain was unknown for the branched orthoxylene sulfonate, an estimate of the relative hydrophobicity of the two compounds was obtained using HPLC. Two peaks were analyzed for both of the compounds giving retention times of 2.4 and 3.0 minutes for NXS and 2.8 and 3.74 minutes for DDXS. Therefore, DDXS, even though branched can be considered to possess an effective chain length longer than that of NXS; the larger adsorption of the former is in accord with the results of the above HPLC analysis. The above samples of the commercial xylene sulfonates were, however, reported to contain significant amounts of unsulfonated hydrocarbons (oil), NXS containing 14% and DDXS containing 25.2%. As oil is known to produce marked effects on adsorption, it becomes necessary to determine the adsorption behavior of the deoiled samples of the above sulfonates in order to more precisely identify the properties of xylene sulfonates. The adsorption isotherms of the deoiled xylene sulfonates are given in Figure 8 along with those of OBS and DBS for comparative purposes.

Firstly, deoiling is seen to produce lower adsorption; secondly, the isotherms for these deoiled sulfonates also show lower adsorption levels when compared with the straight chain alkylaryl sulfonates. In Figure 8, the nonylxylene sulfonate acts

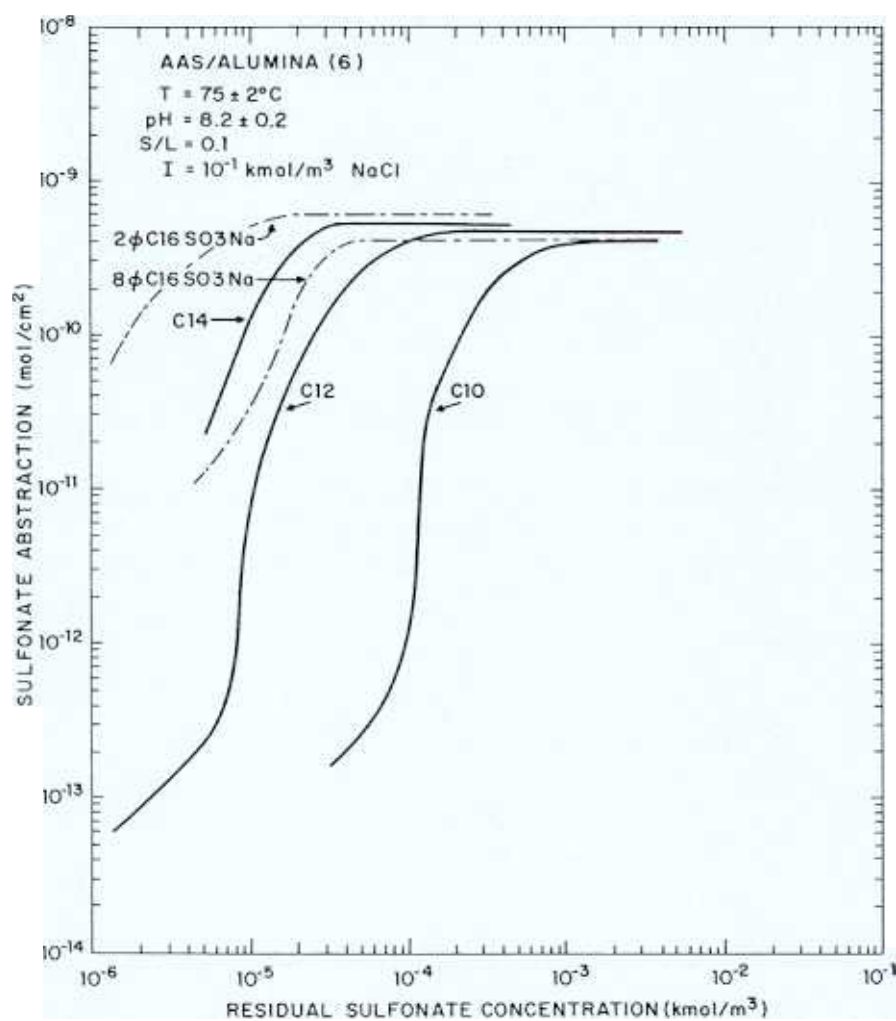


Figure 6. Structural comparison: branched vs. linear AAS.

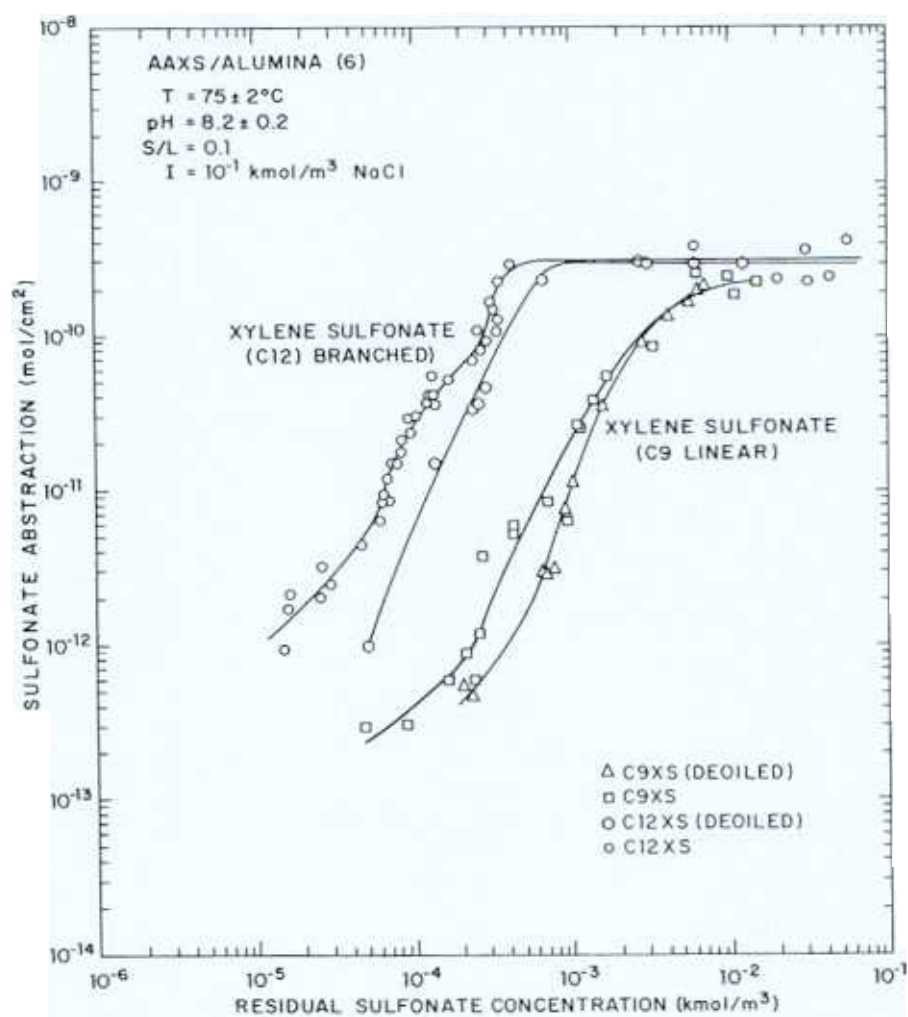


Figure 7. Alkylarylorthoxylene sulfonate adsorption.

SULFONATE ADSORPTION (mol/cm<sup>2</sup>)

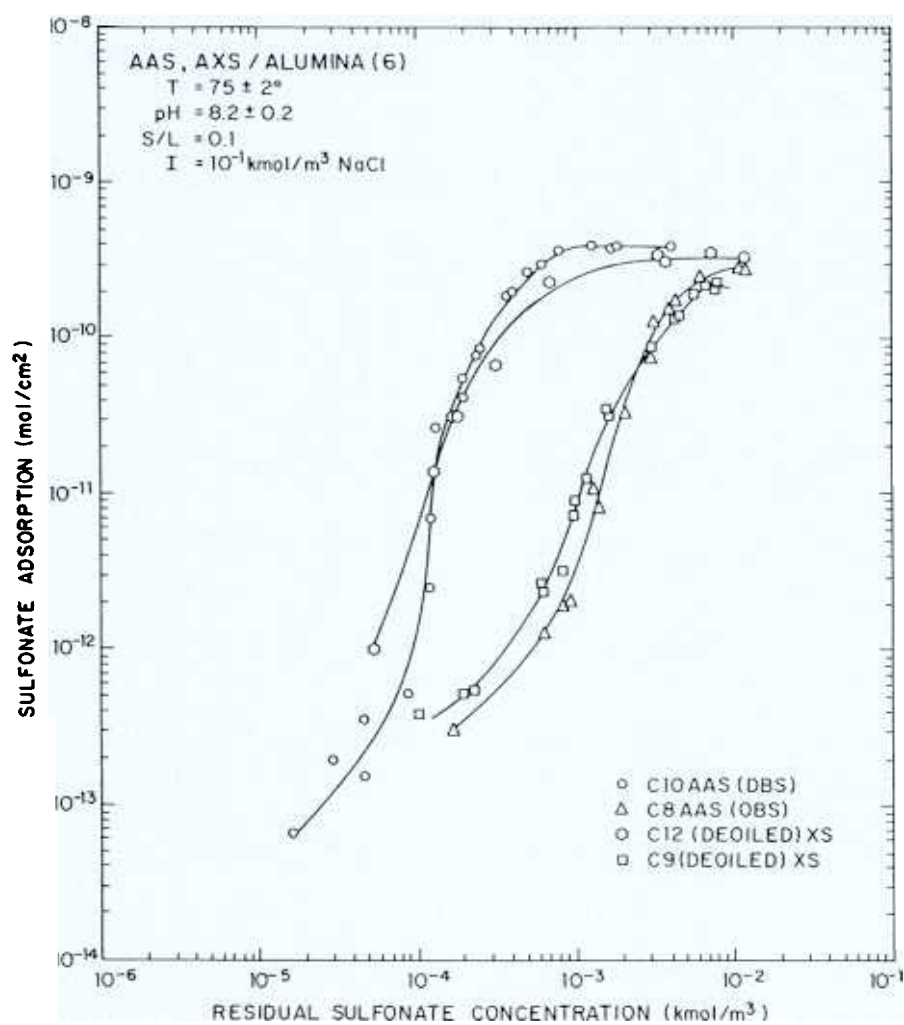


Figure 8. Structural comparison xylene sulfonate (deoiled) vs. AAS.

equivalently with the OBS and the branched dodecylxylene sulfonate approximates the behavior of DBS. Thirdly the slope of the hemi-micellar region did decrease without any measurable effect in the micellar region itself. Evidently the presence of the alkyl group on the benzene ring creates some steric hindrance in the two-dimensional packing of the surfactant species into the hemi-micelles. The factors responsible for these different effects of the xylene sulfonates in different regions could similarly yield different interfacial effects (interfacial tension vs. adsorption) and a full understanding of the mechanisms responsible for it should prove useful.

**Ether Linkage (Disulfonate).** The disulfonate used here is essentially two decylbenzene sulfonates connected through an oxygen (14). The isotherm obtained with the dodecylphenoxy sulfonate is compared in Figure 9 with that for the decylbenzene sulfonate. The disulfonates isotherm is characterized by the absence of multiple regions obtained in all other cases. Adsorption in the "Electrostatic region" is comparable, but at higher concentrations, adsorption of the disulfonate is markedly lower than that of the DBS. Importantly, there is an absence of the sharp rise in adsorption (attributed to hemi-micellization). Evidently, the disulfonate with the oxygen linkage in between the two AAS prevents the alkyl chains from packing tightly to form the two-dimensional aggregate. Also, a molecular model of the compound suggests the possibility of coiling of the two alkyl chains, even in the bulk, minimizing the driving force for aggregation on the surface (Figure 10). Adsorption under these conditions should be considered to be the result of electrostatic attraction only. The fact that the disulfonates adsorption was greater than the monosulfonates in the electrostatic attraction region helps prove these assumptions. Also, a value of  $1.1$  was obtained for the slope of the isotherm ( $3 \times 10^{-6} - 2 \times 10^{-3} \text{ kmol/m}^3$  range) further supports this consideration.

**Ethylene Oxide Addition.** Anionic and nonionic alkylaryl compounds containing amount of thylene oxide were used in this study. Addition of ethylene oxide groups is known to impart salt tolerance to the surfactant and therefore these compounds are of particular interest for micellar flooding purposes.

The anionic alkylarylpolyether sulfonate used in this study was Triton X-200. The chemical composition of this compound is such that the sulfonate is connected to a small alkyl group which in turn is connected to the ethylene oxide group. Then comes the aryl and alkyl groups. Due to the alkyl sulfonate link comparison with an alkyl sulfonate might prove more helpful than comparisons made with alkylaryl sulfonates. The isotherm obtained for Triton X-200 is similar in shape to that of the alkyl sulfonate, of equivalent chain length (Figure 11), with the electrostatic, hemi-micellar, electrostatic hindered and micellar regions all being comparable. When a  $10^{-2} \text{ kmol/m}^3$  solution of

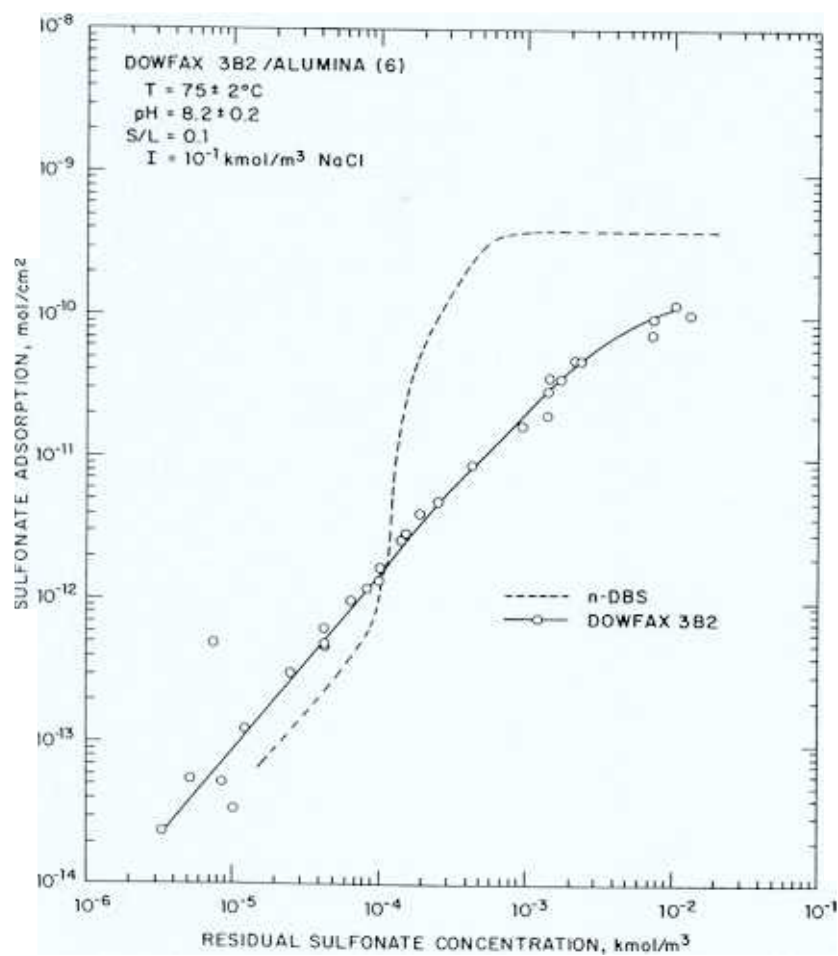
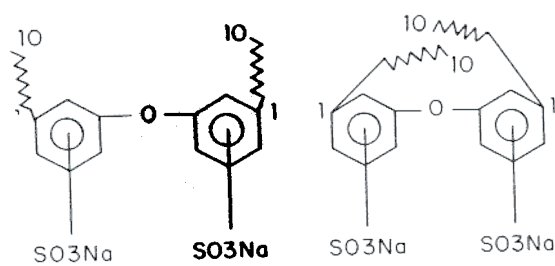


Figure 9. Structural comparison: disulfonate vs. AAS.



**Figure 10** Disulfonate adsorption model.

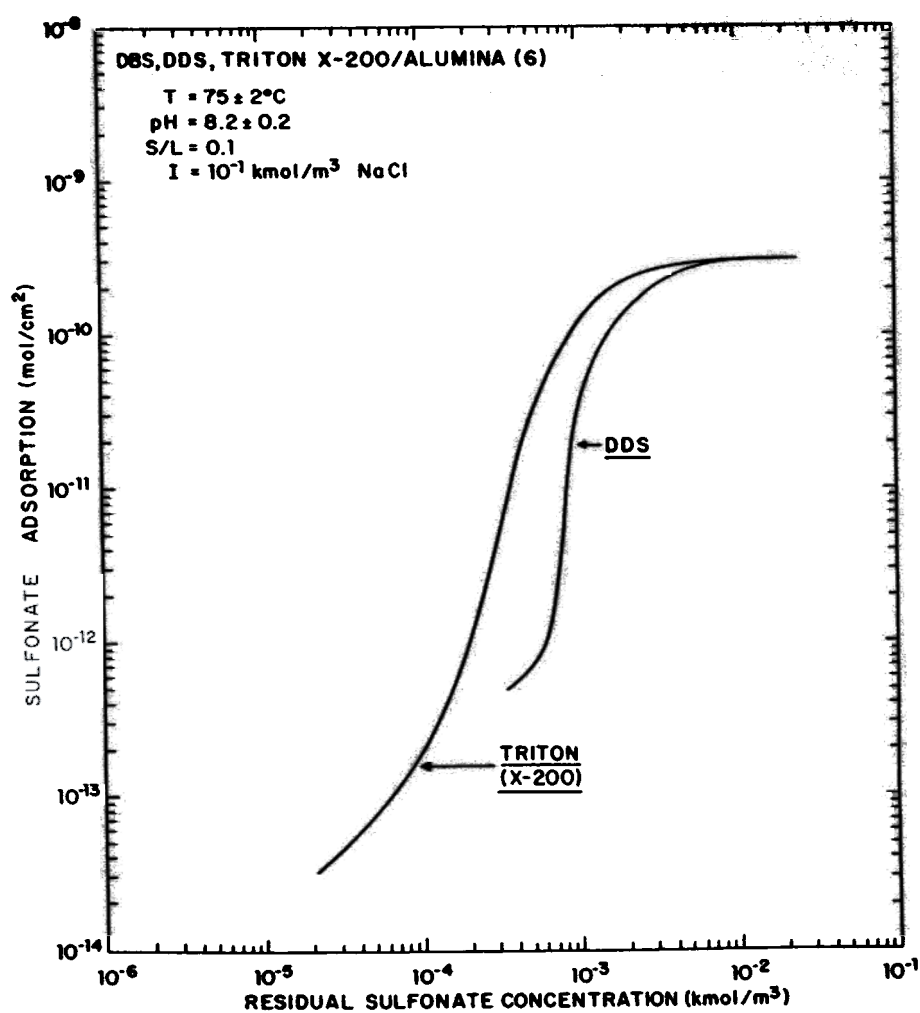


Figure 11. Structural comparison: ethoxylated sulfonate vs. AS.

calcium chloride was added to each of these systems the alkyl sulfonate precipitated while the Triton X-200 adsorption values remained relatively unchanged proving the salt tolerance of the ethylene oxide groups.

The nonionic surfactant used is Synfac 8216, an alkylaryl-ethoxylated alcohol. This compound did not adsorb by itself on alumina at a concentration of  $4.3 \times 10^{-4}$  kmol/m<sup>3</sup> even after a salt level of 30% at 27°C. At 75°C measurements were conducted in up to 5% NaCl and no significant adsorption was obtained. Synfac did however, undergo significant adsorption in the presence of dodecylsulfonate with maximum adsorption under the tested conditions at  $1.5 \times 10^{-3}$  kmol/m<sup>3</sup> DDS (see Figure 12). The adsorption of sulfonate was also enhanced by the addition of Synfac except in the micellar region (Figure 13). Synergetic interaction between Synfac and dodecylsulfonate suggests chain-chain interaction between the chains of the two reagents. Co-adsorption of nonionics can enhance hemi-micellization of ionic surfactants on account of the reduced lateral electrostatic repulsion between the ionic heads and thereby also increase the overall adsorption of both the compounds. Indeed, if most or all of the adsorption sites are occupied, the two species will have to share the sites, and under these conditions the individual adsorption of both the compounds will undergo a decrease unless multilayer adsorption can take place. It is clear from the results given in Figures 12 and 13 that interactions between various surfactants and co-surfactants can play a major role in determining the adsorption in the system depending particularly on their chemical structure.

### Conclusions

Structural variations of sulfonate surfactants in terms of chain length and branching, incorporation of phenyl, ethoxyl and multiple functional groups are found to produce specific effects in various adsorption regimes (electrostatic, hemimicellar, electrostatic hindered and micellar regions):

- a) Incorporation of the phenyl group between the  $\alpha$ -CH<sub>2</sub> and the sulfonate of the octyl and decyl sulfonate increased the effective chain length by 3 to 4 CH<sub>2</sub> groups with respect to its adsorption on alumina;
- b) Increase in the chain length of the alkyl groups increased the adsorption in all the regions except the micellar region. These effects suggest the role of hemi-micellization as well as the enhanced solvent power of the interfacial region for the longer chains;
- c) The position of the branching of the sulfonate has a measurable effect on adsorption. The nature of the effect of the positioning on adsorption, particularly in hemi-micellar region, is suggestive of the type of packing of the surfactant species in the two-dimensional aggregates;
- d) Presence of alkyl substitutions on the aromatic ring

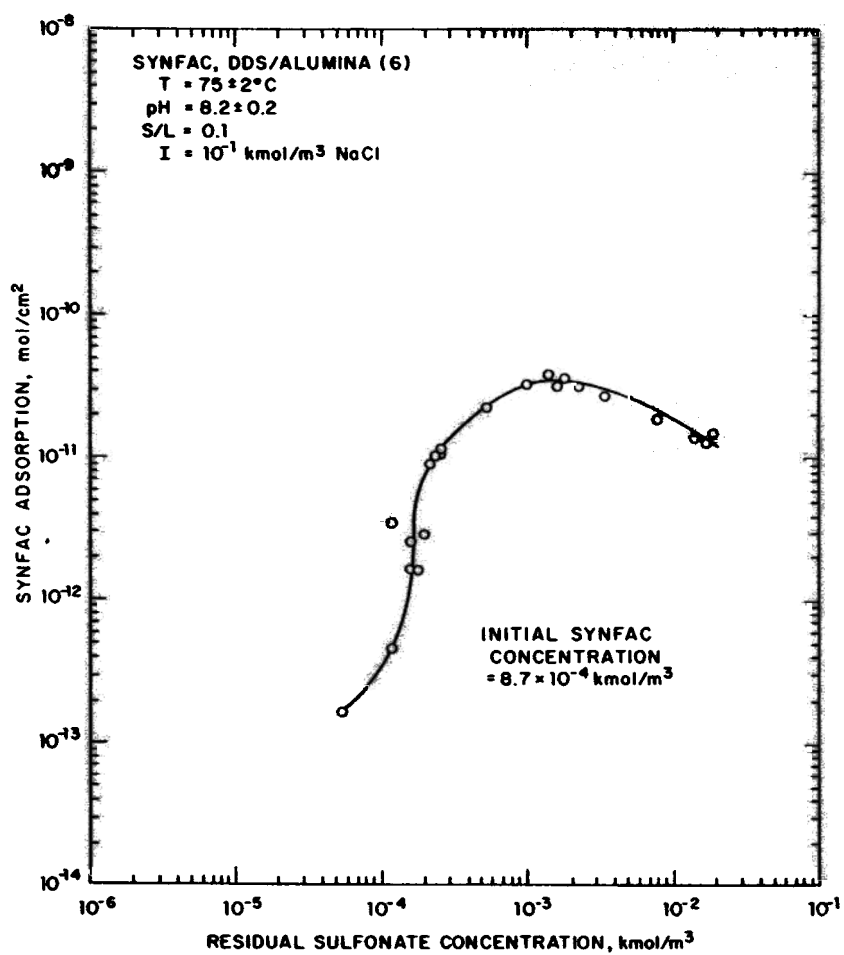


Figure 12. Ethoxylated alcohol coadsorption.

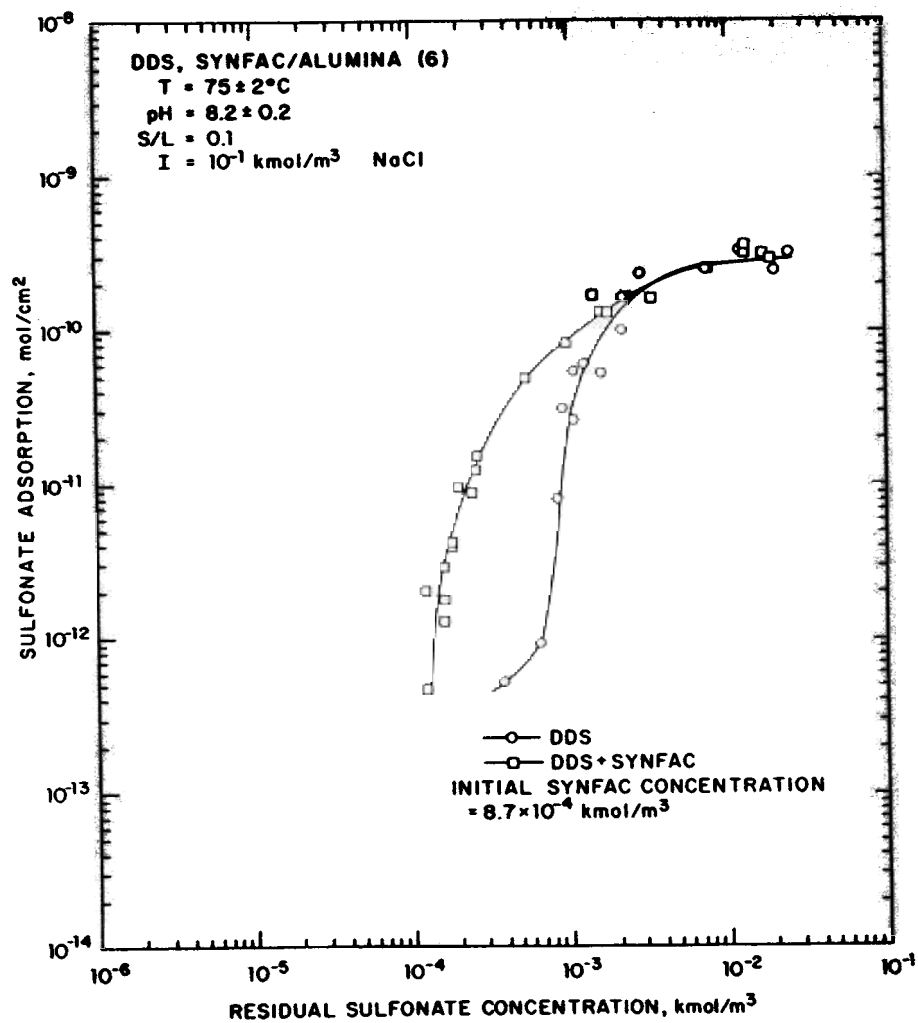


Figure 13. Effect of ethoxylated alcohol upon AS adsorption.

of the alkylaryl sulfonate decreased the adsorption. Furthermore, the hemi-micellization effect was also reduced apparently due to the steric hindrance produced by the xylene group.

e) Adsorption of the disulfonate, while comparable in the electrostatic region, was markedly lower at higher concentrations than that of the monosulfonate. Non-appearance of the sharp transition observed normally between Regions 1 and 2 suggests absence of hemi-micellization in the present case due to the head group bulkiness introduced by the ether linkage connecting the two sulfonates;

f) Adsorption characteristics of an anionic and a nonionic surfactant containing ethylene oxide groups were also studied. Even though salt (Ca) tolerance of the alkylarylpolyether sulfonate was markedly higher than that of the alkyl sulfonate of similar chain length, their adsorptions were not significantly different. The nonionic polyether alcohol, on the other hand, did not adsorb on alumina under the conditions studied. However, its adsorption was significant when the alkyl sulfonate was present in the system. This co-adsorption was also found to enhance the adsorption of the sulfonate.

The important role of the structure of the surfactants in determining adsorption is evident. Some of the surfactants discussed above can produce low interfacial tension and some others have excellent salt tolerance. A knowledge of the structure of such surfactants in adsorption can be helpful in developing surfactants that will meet different requirements simultaneously for special applications such as in enhanced oil recovery.

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