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ADSORPTION FROM FLOODING SOLUTIONS IN POROUS MEDIA
Final Report

By
P. Somasundaran
C. C. Gryte

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ADSORPTION FROM FLOODING SOLUTIONS IN POROUS MEDIA

A Study of Interactions of Surfactants
and Polymers with Reservoir Minerals

Final Report

P. Somasundaran, Principal Investigator
C. C. Gryte, Co-Investigator

Research Staff

P. Chander	R. Middleton
E. Fu	V. Pereira
Y. Huang	P. Siracusa
A. Kebaili	K. V. Viswanathan
L. T. Lee	E. Williams

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

Work performed for the Department of Energy
Under Contract No. DE-AC19-79BC10082

Dr. Fred Burtch, Technical Project Officer
Bartlesville Project Office
P. O. Box 1398
Bartlesville, Oklahoma 74005

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c: Flotation and adsorption activation of quartz/dodecylsulfonate system using cationic polymer.

ABSTRACT

The loss of surfactants from systems relevant to micellar flooding, including the influence of oils, alcohols and polymers, was investigated. Our work has demonstrated the critical role of rock mineralogy in determining the type and extent of surfactant loss. The presence of as little as 1% gypsum in samples of kaolinite, silica and alumina caused decylbenzene sulfonate depletion to shift from adsorption-controlled to precipitation-controlled. However, in gypsum-magnesite mixtures, the influence of gypsum was greatly reduced because calcium activity was controlled by carbonate equilibria. The precipitation phenomena has been studied extensively, and a thermodynamic model developed. It has been shown that above the CMC, redissolution of the precipitate occurs due to adsorption of precipitating ions on micelles, which reduces its activity in the bulk. Modifications to surfactant structure were found to greatly enhance salt tolerance. Through addition of ethoxy groups to alkylbenzenesulfonates, salt tolerance can be improved by more than one order of magnitude for Na^+ and three orders of magnitude for Ca^{2+} . Future work will focus on such surfactants as a means to minimize surfactant loss in micellar flooding.

1. INTRODUCTION

Loss of surfactants during micellar flooding is considered to be a major factor that determines the efficiency of tertiary oil production. Our studies have shown surfactant depletion due to adsorption and precipitation to be markedly influenced by mineralogical heterogeneity, in addition to surfactant structure, fluid properties (salinity, hardness, pH), and the presence of other materials such as polymers and alcohols. The overall surfactant loss is the result of many complex interactions that occur between minerals, surfactants, inorganics, oils, alcohols, and polymers. Clearly, it is necessary to develop a full understanding of these interactions in order to design fluid systems that will be compatible with different reservoir mineralogy.

The objective of this project was to identify the effects of some of the major system variables on the depletion of surfactants, and to elucidate the mechanisms governing the adsorption loss in selected mineral surfactant systems under different physico-chemical conditions. The preliminary phase of the project consisted of studying adsorption behavior of commercial grade surfactants on sandstones and limestones in order to identify major parameters governing the adsorption process. Analysis of the isotherms in these cases were in general complicated by the impure nature of the surfactants employed as well as the lack of knowledge of the relevant mineral

characteristics. These studies clearly showed the need for using well-characterized mineral-surfactant systems in order to interpret the isotherms mechanistically. Considerable emphasis was therefore placed on preparing and characterizing minerals and synthesizing isomerically pure (as characterized by p-NMR, ^{13}C NMR, mass spectrometry, HPLC, and elemental analysis) sulfonates. The overall approach of our research was to first study well-characterized mineral-surfactant systems, and then to extend them to systems of increasing complexity and relevance to EOR by varying mineralogy, electrolyte mixtures, temperature, surfactant type and composition.

This report summarizes the major research findings of the Department of Energy project¹ "Adsorption from Flooding Solutions in Porous Media: A Study of Interactions of Surfactants and Polymers with Reservoir Minerals", DE-AC19-79 BC 10082. The role of major system parameters are discussed in relation to adsorption and precipitation behavior of surfactants in micellar flooding systems.

2. MINERALOGY AND SURFACTANT LOSS

Surfactant depletion has been shown to be markedly affected by mineralogical and morphological characteristics. Studies conducted on selected minerals indicate that the type and

1. Co-funded by the National Science Foundation and eight oil companies.

magnitude of abstraction can vary, in general, according to the electrochemical nature of the solid (surface charge), degree of dissolution of the mineral (solubility and kinetics of dissolution), as well as the morphological aspects of the surface (porosity).

2.1 Electrochemical Nature of Solid

Adsorption of ionic surfactants on minerals is controlled primarily by the electrical nature of the interface. Earlier studies, conducted on the adsorption of sulfonates on alumina, Biosil A and quartz, clearly indicated adsorption of these surfactants occur only under conditions when the surface is positively charged. In such systems, as pH is decreased away from the point of zero charge, the surface potential increases due to the potential - determining effect of H^+ ions. Consequently, the adsorption of anionic sulfonate increases with decrease in pH. In the case of Biosil A and quartz, which are negatively charged above pH=3, no sulfonate adsorption occurs even at very high surfactant concentrations (Figure 1). On clay minerals such as kaolinite, the pH of the system also primarily controls the surface potential, so that a similar increase in adsorption with decrease in pH is observed for these cases (Fig.2). Similar results have been obtained with limestone.

In addition to pH, the ionic strength of the system can affect the potential at the solid-liquid interface and in turn alter the adsorption of ionic surfactants. This effect is

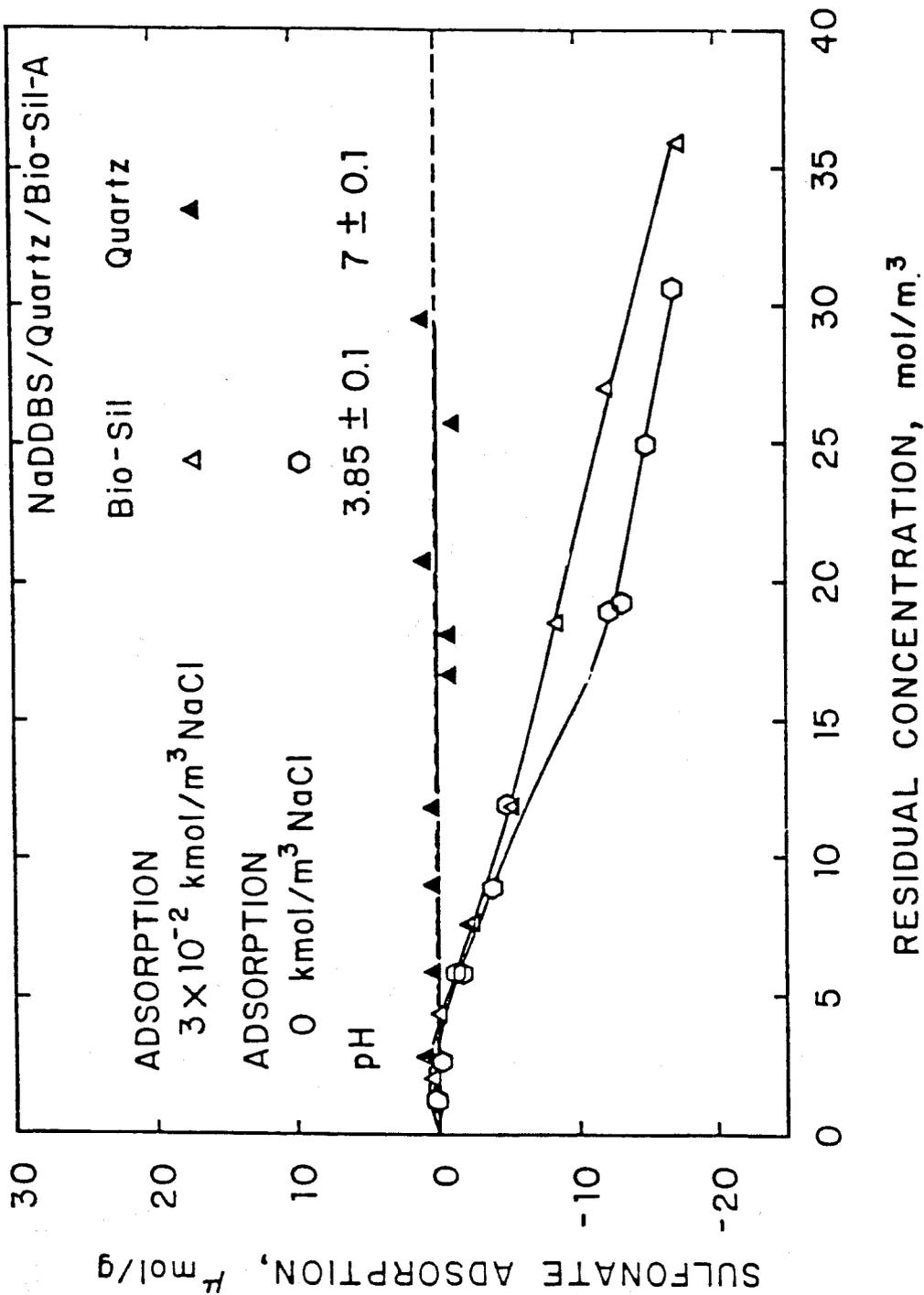


Figure 1: Adsorption of sodium dodecylbenzenesulfonate on quartz and Biosil A in 10^{-1} kmol/m³ NaCl at 27 degrees C.

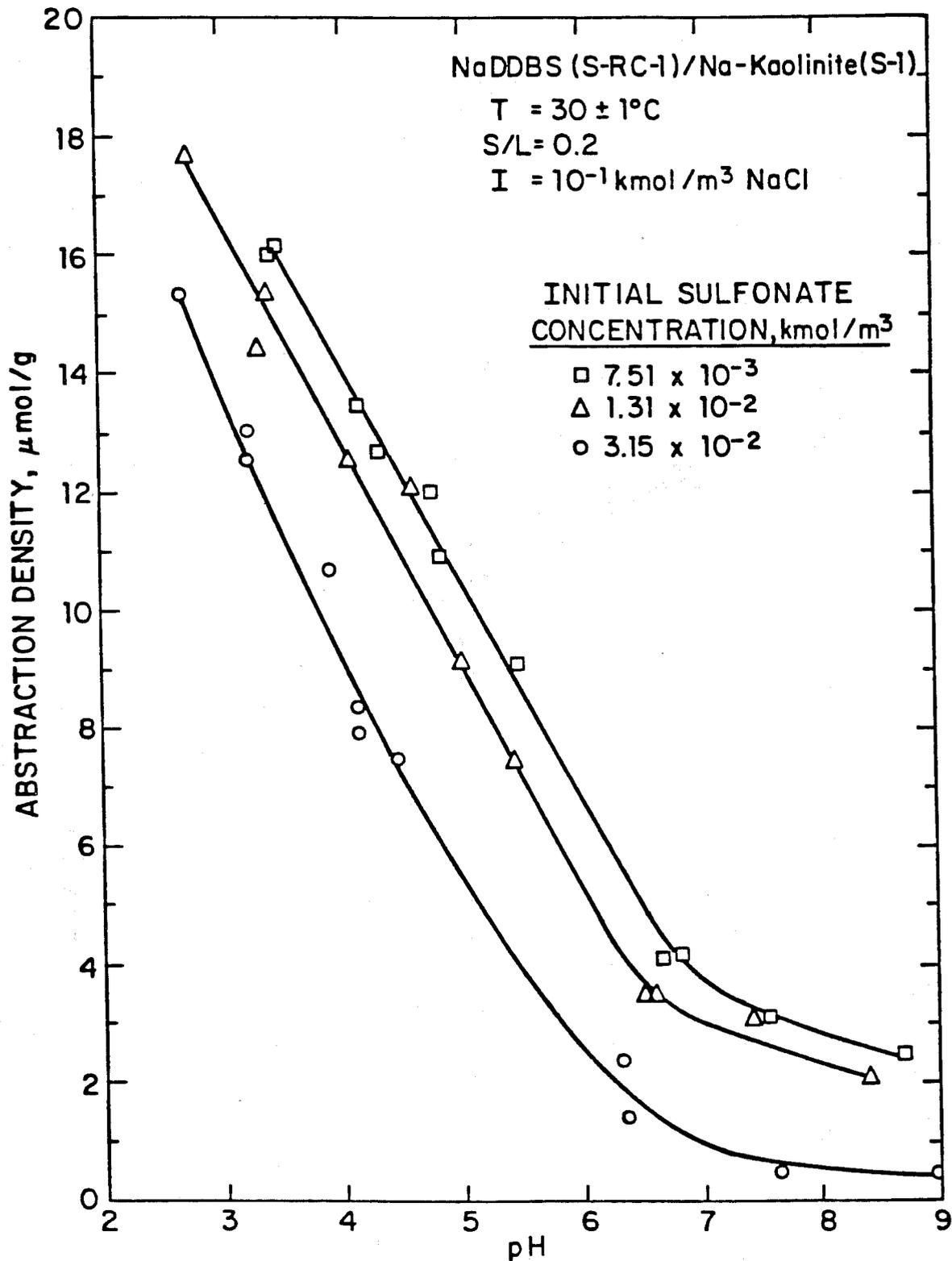


Figure 2: Abstraction density vs pH for three initial sodium dodecylbenzenesulfonate concentrations on Na-kaolinite in 10⁻¹ kmol/m³ NaCl and at 30 degrees C.

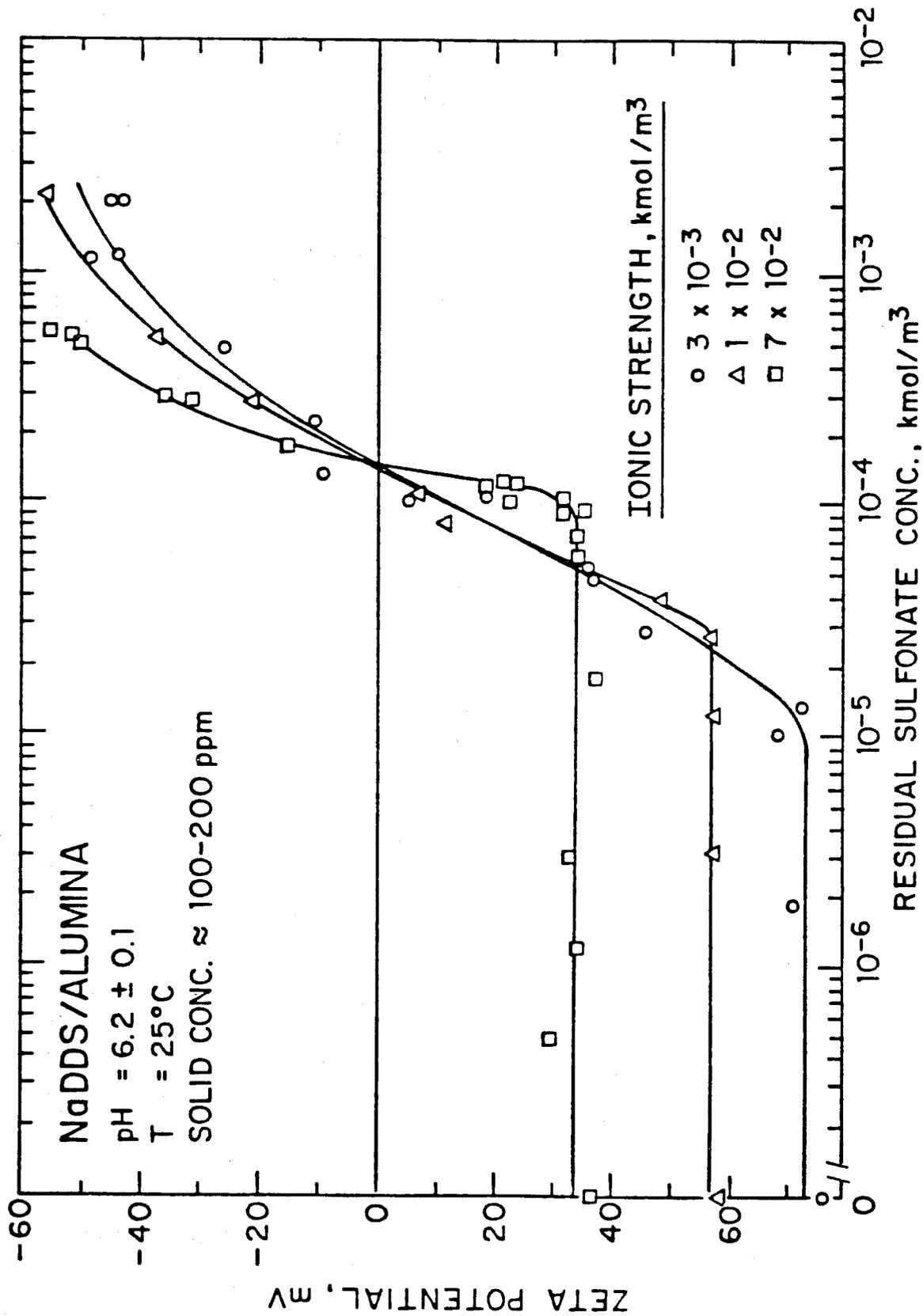


Figure 3: Zeta potential of alumina at different ionic strength levels in the presence of sodium dodecylsulfonate.

clearly evident in the results given in Figures 3 where an increase in ionic strength of the medium is seen to decrease the zeta potential of alumina, resulting in decreased adsorption (Fig.4) under conditions where the electrostatic interaction governs the adsorption process (ie. low surface coverage).

These results demonstrated the important role of the electrochemical nature of the solid, which is in turn influenced by such variables as pH and salinity. There is sufficient evidence which indicates that electrostatic adsorption is a necessary prerequisite for physically adsorbing systems, so that adsorption can be totally prevented under conditions when adsorbate and substrate are similarly charged. Since most minerals are negatively charged under high pH conditions, the use of anionic surfactants under alkaline conditions becomes desirable in flooding processes.

While a great deal of attention has been paid to adsorption controlled by electrostatic attraction, the role of electrostatic repulsion has not been examined. Our results show that the overall adsorption process can be affected by such repulsion, for example, between micelles and negatively charged substrates, and that such interactions can lead to negative adsorption. Adsorption of surfactants measured by conventional techniques represents the excess concentration in the interfacial region over that in the bulk. The exclusion of species from the interfacial region will thus report as negative adsorption. In

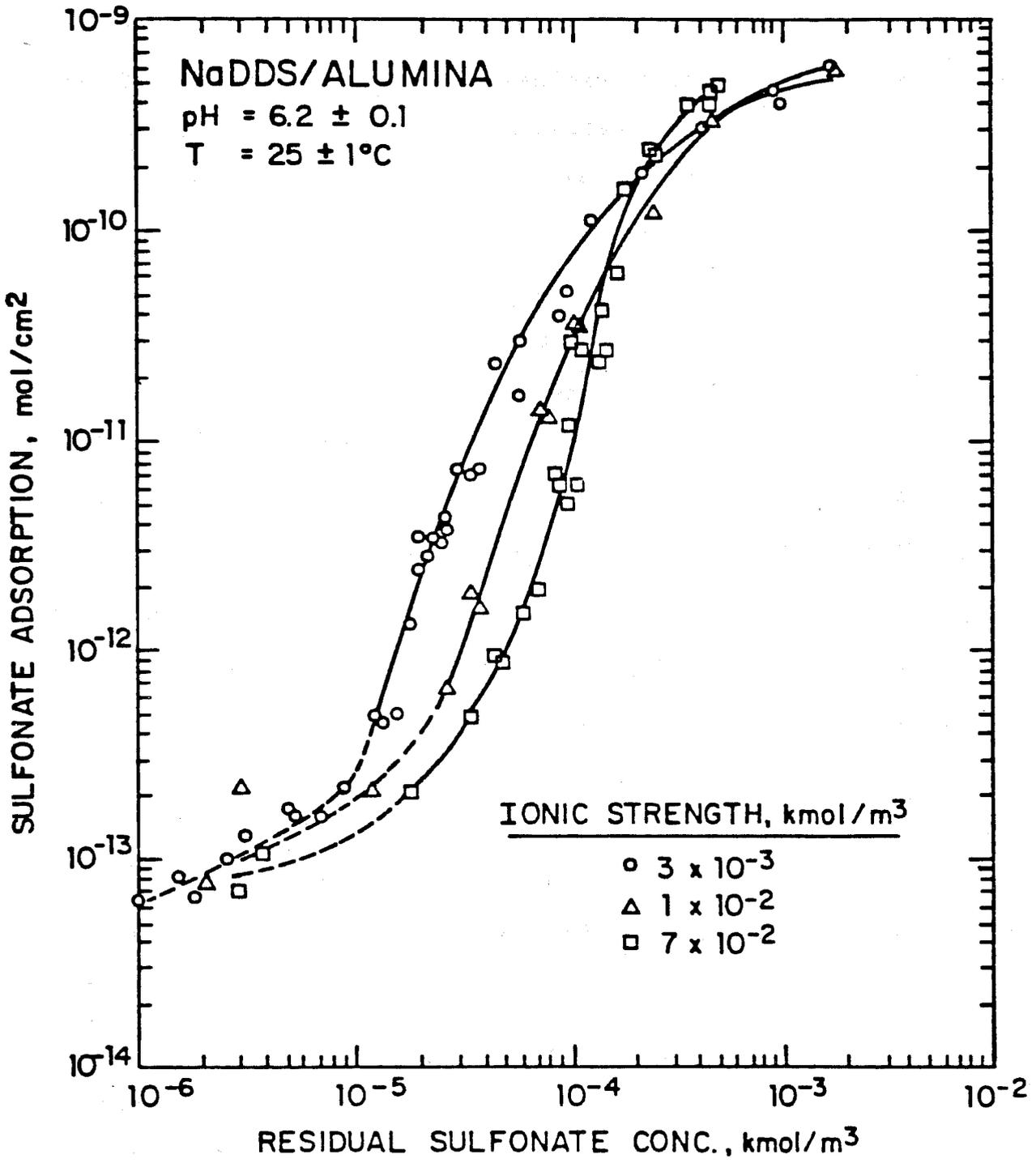


Figure 4: Adsorption isotherms of sodium dodecylsulfonate on alumina at different ionic strengths.

the micellar region a negative adsorption of micelles can result in a maximum in surfactant adsorption around CMC (since the adsorption of monomers can be expected to remain almost constant in this region). Micellar exclusion is therefore one of the possible reasons for the existence of an adsorption maximum observed in some systems in the region of CMC. In adsorption tests using nonporous solids of relatively low surface area, the extent of negative adsorption may not be measurable. However, for samples with large surface areas, enough exclusion may take place to affect the shape of the isotherm. This is illustrated in Figure 1 which shows the adsorption of sodium dodecylbenzenesulfonate on Biosil and quartz. As can be seen, no negative adsorption was detected on quartz, a mineral with a surface area of 5-6 m²/g. In contrast, negative adsorption (Fig.5) was detected at pH 11 for a high surface area alumina (75-90 m²/g). The negative adsorption measured in the alumina system was found to be in excellent agreement with that predicted on the basis of an electrostatic exclusion model developed by analogy to particle-particle interaction theories. The exclusion of micelles can also result from physical size considerations (steric) with highly porous mineral samples such as Biosil [350-400 m²/g, 0.7-0.8 c.c./g pore volume](Fig.1). In this case, the calculated exclusion of micelles from the pores (micelle diameter 5 nm, pore diameter 5 nm) was in agreement with the measured negative adsorption. It is evident from the effect of sodium chloride in reducing the extent of negative adsorption in

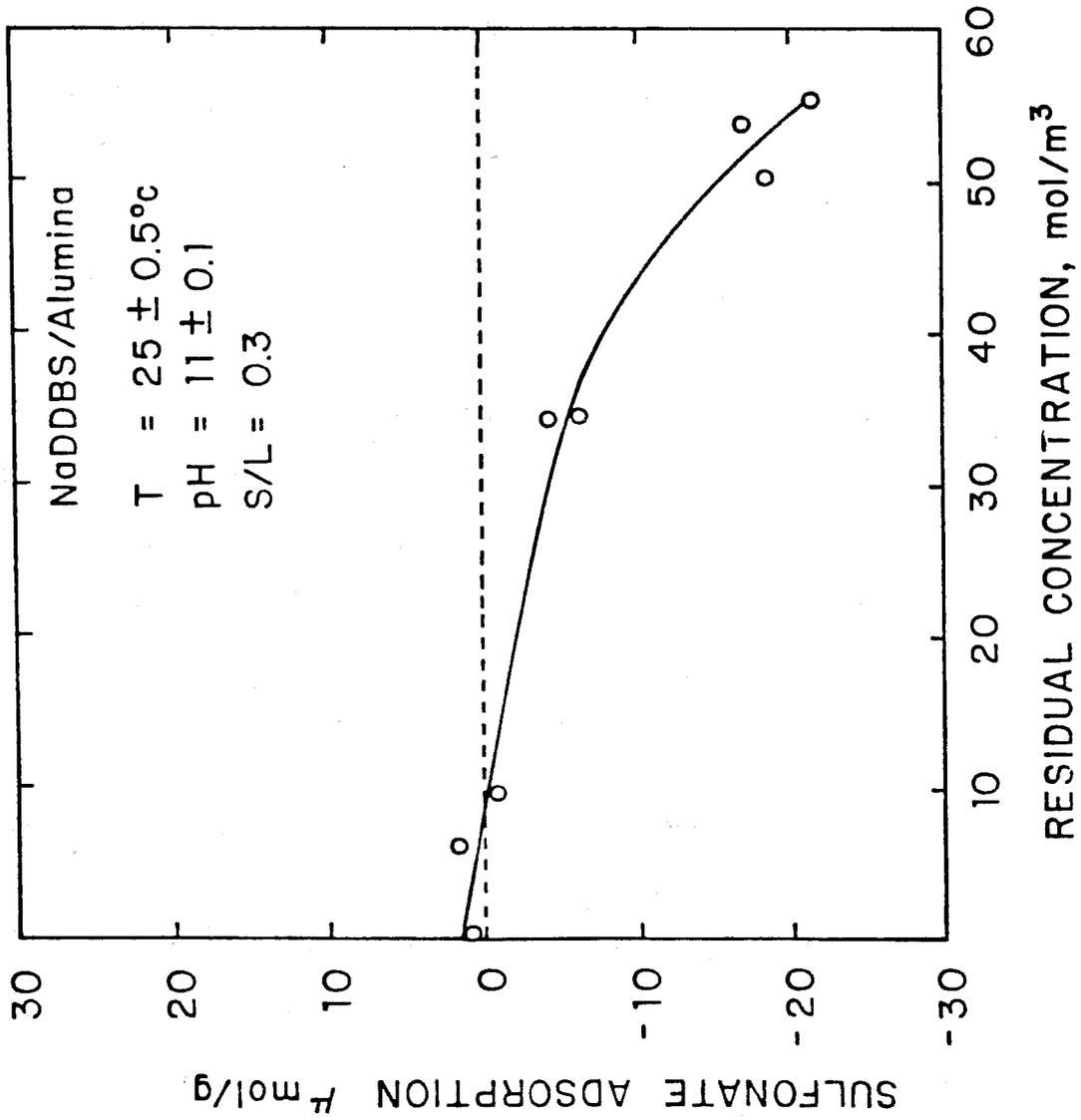


Figure 5: Adsorption of sodium dodecylbenzenesulfonate on alumina at 27 degrees C and at pH 11.0.

the Biosil system (Fig.1), that in addition to physical exclusion (small pore size compared to micelle size), electrostatic exclusion was also active in this system. Thus, in dealing with adsorption in micellar systems, a consideration of the roles of both the electrochemical and morphological aspects of the substrate in governing these processes is needed. It is to be emphasized that such knowledge is limited at present.

2.2 Role of Mineral Solubility

Reservoir rock systems consist of minerals of variable solubility, a property that is affected by temperature, pH, salinity etc. Therefore, major emphasis was placed on studying the role of rock mineralogy and dissolved species on the depletion of surfactant. Tests were designed using minerals such as clays, oxides (alumina, silica) and salt-type minerals (gypsum, calcite, magnesite), as well as mixtures of these minerals.

Adsorption studies with sulfonates and kaolinite, alumina, gypsum, magnesite and calcite, have clearly shown that the type and magnitude of adsorption can be significantly different depending on the mineralogical composition of the substrate. Alumina, magnesite, and to some extent kaolinite, were found to exhibit four region isotherms (see Fig. 6) characterized by electrostatic, hemimicellar, electrostatically hindered, and micellar interactions. In contrast to this, sulfonate loss in the presence of gypsum is characterized by a sharp rise in

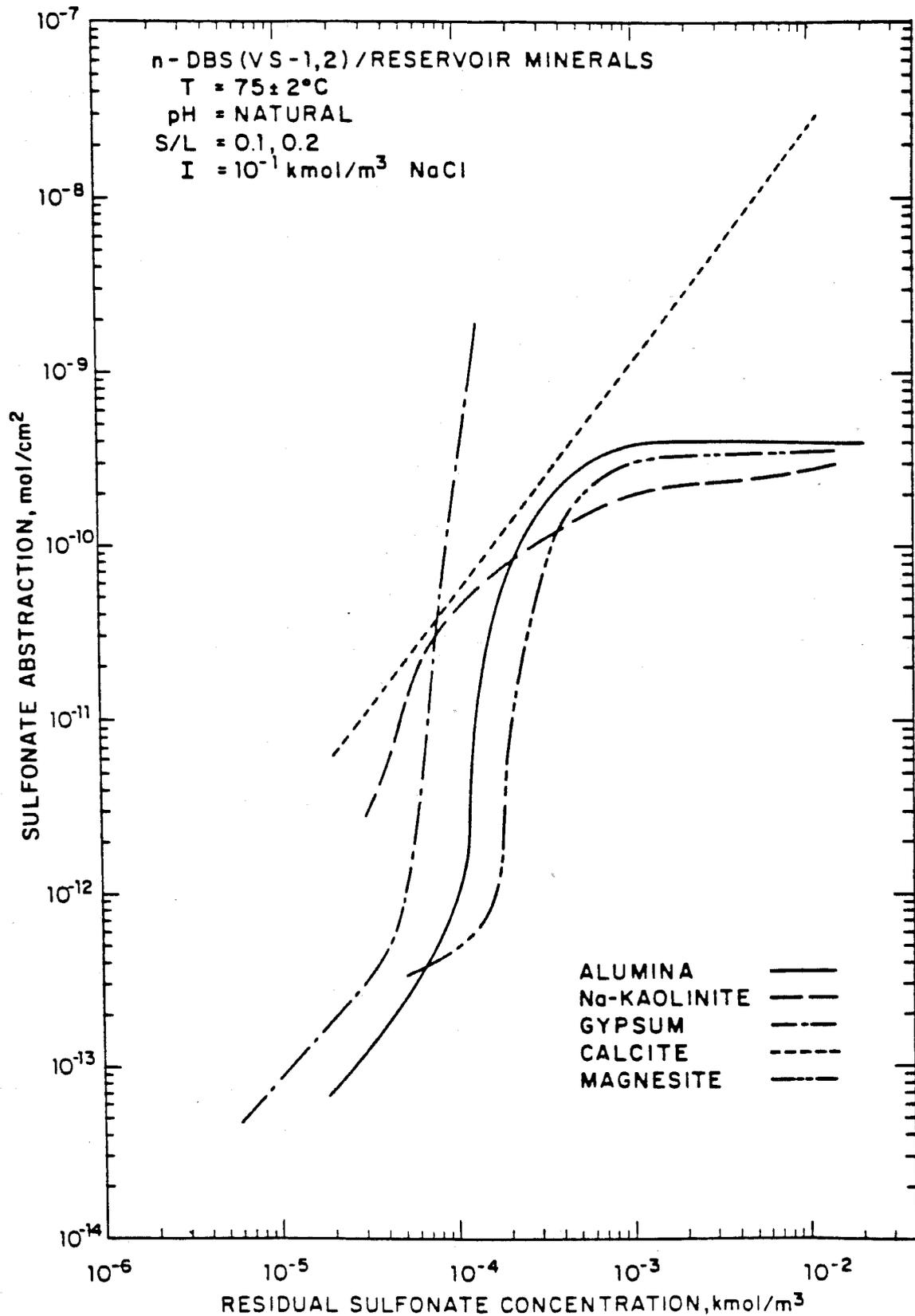


Figure 6: Adsorption of n-DBS (Sodium n-decylbenzenesulfonate) on selected reservoir minerals at 75 degrees C in 10⁻¹ kmol/m³ NaCl.

abstraction, at a concentration that has been correlated with the estimated precipitation of calcium disulfonate $[\text{CaR}_2]$. Calcite, another semisoluble mineral, exhibited, unlike gypsum, a linear sulfonate abstraction isotherm. However, blank tests in the absence of the mineral showed that precipitation of sulfonate, due to dissolved calcium from calcite, contributed significantly to the overall sulfonate depletion. It should be noted that precipitation of CaR_2 results in a vertical abstraction line only if the calcium-controlling solid phase is present in excess and is in equilibrium with the solution. If the solid is unable to replenish the solution with Ca^{+2} as quickly as it is being depleted by precipitation, the increase in abstraction would be less sharp. Thus in the case of calcite, dissolution kinetics of this mineral was considered to determine the overall shape of the isotherm.

The presence of dissolved multivalent species of the mineral does not always lead to precipitation. Magnesite, which releases substantial quantities of magnesium species into solution [$3.9 \times 10^{-4} \text{ kmol/m}^3$], exhibits a four-region adsorption isotherm characteristic of non-precipitating systems. Supporting tests with magnesium chloride and sulfonate showed that precipitation does not occur in this system (Fig. 7). The reason for the high magnesium tolerance of sulfonate in this system is not clear at present. Tests are currently in progress to understand the complexing properties of magnesium, as opposed to calcium, in

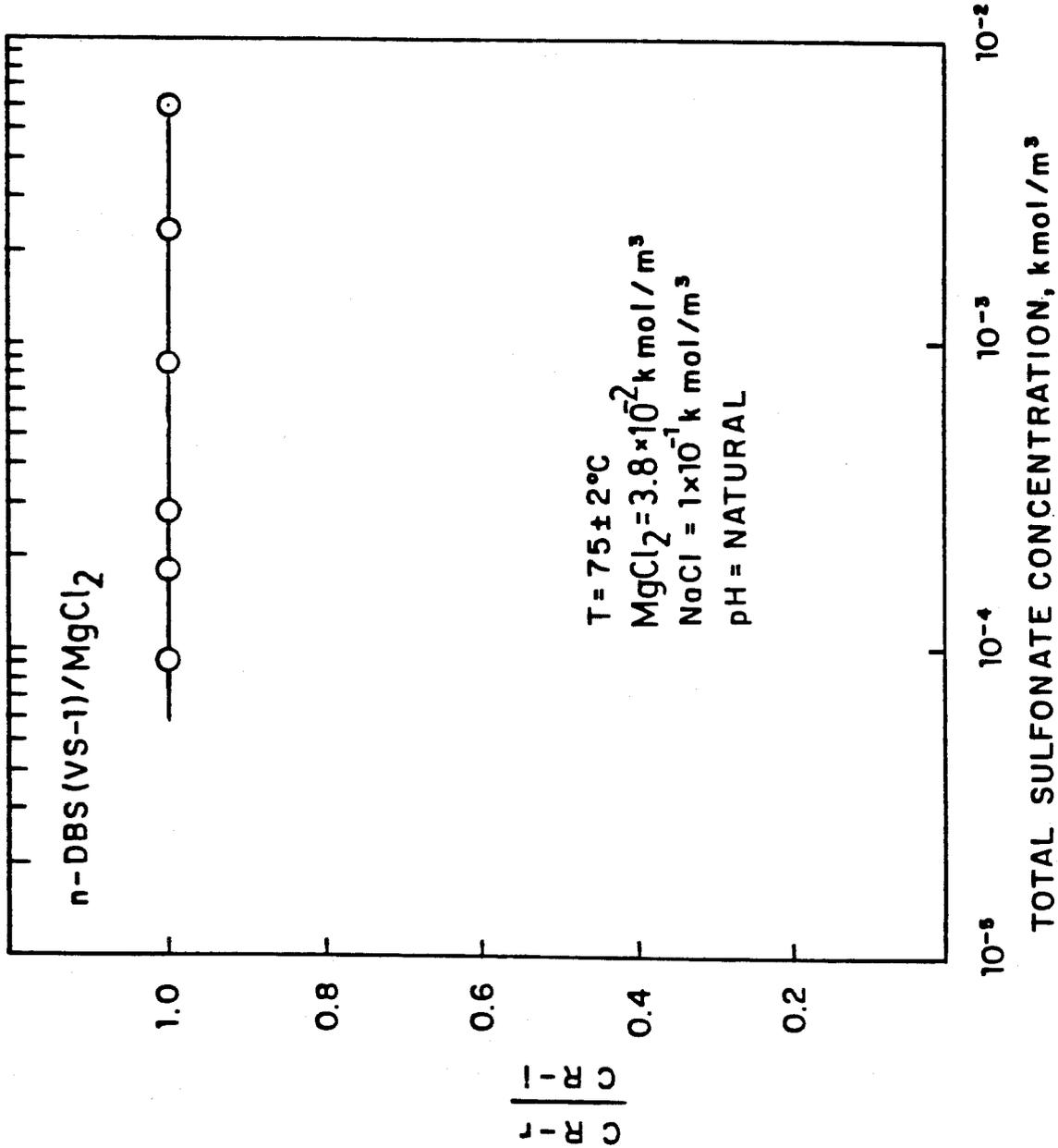


Figure 7: Ratio of residual to initial n-decylbenzenesulfonate concentrations as a function of total sulfonate concentration for MgCl₂/DBS (Sodium n-decylbenzenesulfonate) system in 10⁻¹ kmol/m³ NaCl and at 75 degrees C.

sulfonate solutions in order to better understand this phenomenon.

Even though clay minerals are considered to have limited solubility, studies show that measurable amounts of aluminum species are released by kaolinite and that the dissolution is dependent on pH (Fig. 8). The amount of aluminum in solution was found to be sufficient to precipitate aluminum sulfonate, although four-region isotherms are generally obtained with kaolinite-sulfonate systems. It is to be recalled that a precipitating system in which the mineral can continuously and rapidly dissolve to release multivalent ions, should result in a vertical depletion isotherm (as in the case of gypsum) with the activity of the multivalent species remaining constant. Interestingly, measured aluminum in solution during abstraction tests on kaolinite-sulfonate systems (Fig. 9) shows that this is not the case. Kaolinite in the presence of surfactant behaves like a system with a limited amount of dissolved multivalents. This is further evidenced by the minimum in the aluminum concentration around CMC, indicating a precipitation-redissolution process occurring in the system. Such behaviour is only possible for a system that does not continuously release aluminum ions into solution.

A major conclusion that arises from the study of these isotherms, is that only in the absence of precipitation is an isotherm with electrostatic, hemimicellar, electrostatically

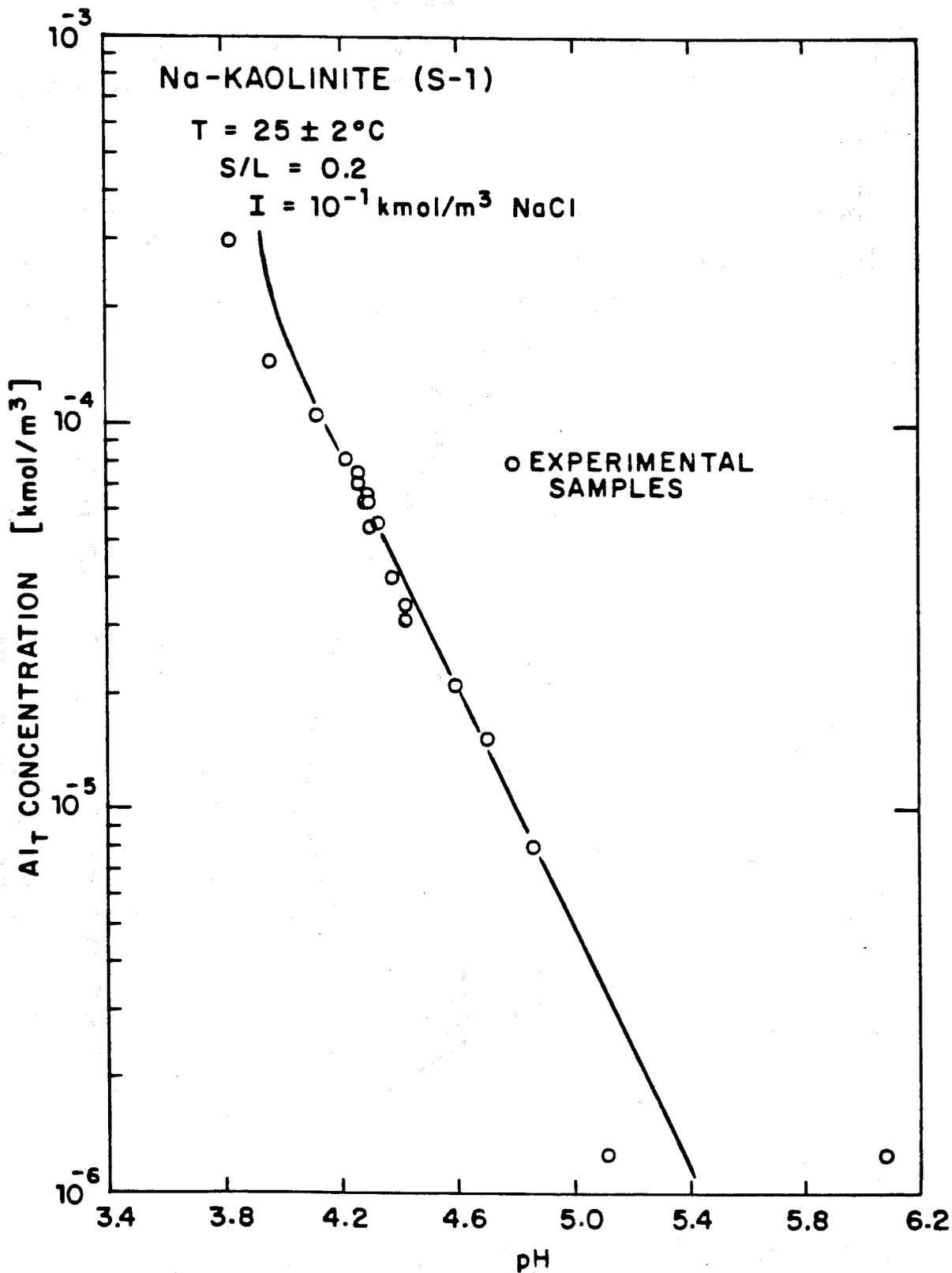


Figure 8: Total aluminum concentration as a function of pH for Na-kaolinite contacted in 10⁻¹ kmol/m³ NaCl for 72 hours.

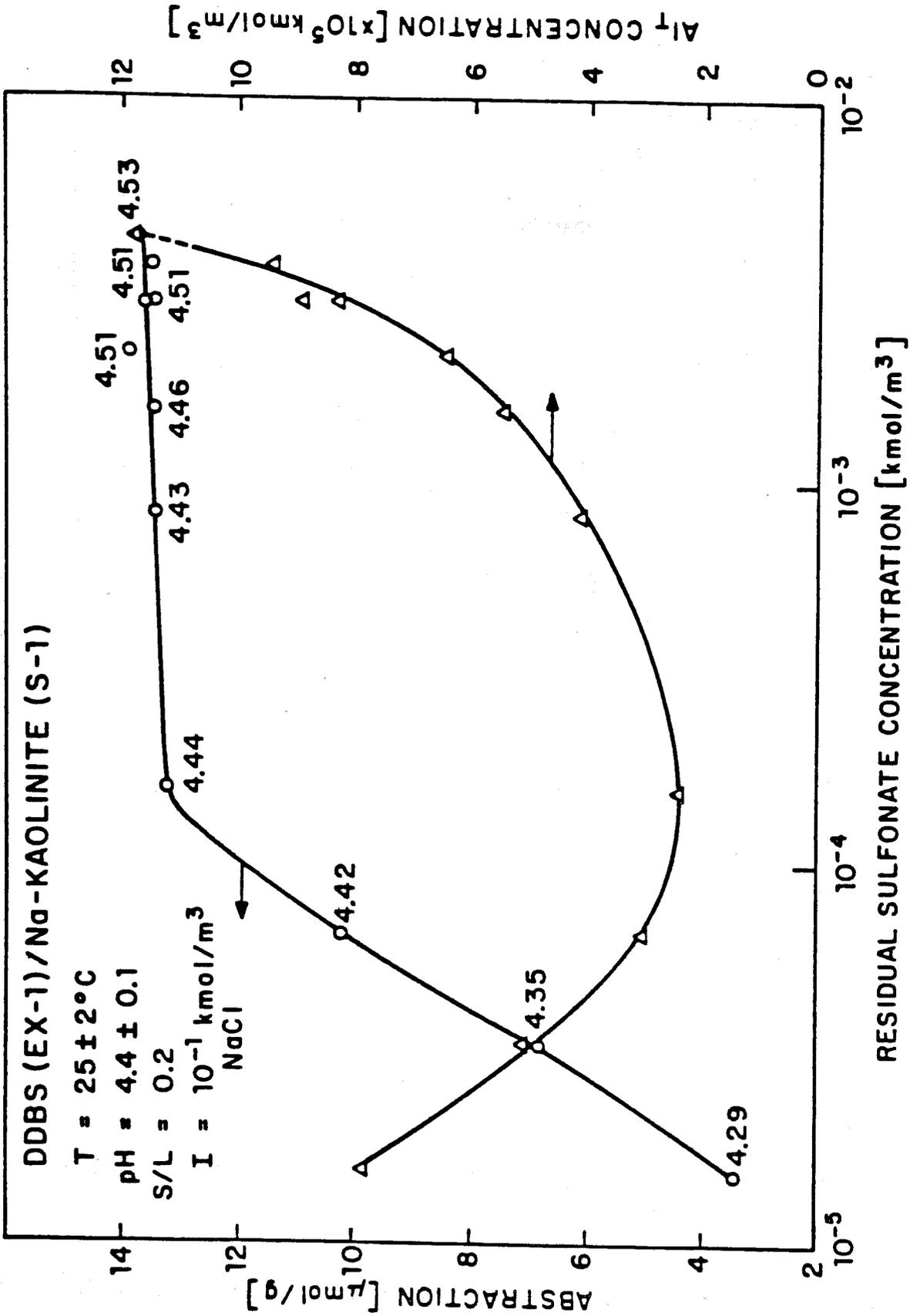


Figure 9: Abstraction isotherm and measured total aluminum concentrations for DBBS (EX-1) [Sodium dodecylbenzenesulfonate] on Na-kaolinite in 10^{-1} kmol/m^3 NaCl at 25 degrees C. pH values are given for each abstraction point.

hindered and micellar limited plateau regions obtained (e.g. alumina, magnesite). Gypsum, calcite, and kaolinite, on the other hand, represent systems with different degrees of dissolution and hence, sulfonate precipitation. Most importantly, some recent studies have also suggested that dissolution of mineral in the presence of surfactant is significantly modified and possibly even prevented, perhaps due to the masking of the surface by adsorbed surfactant. It is clear that a detailed knowledge of dissolution characteristics, especially in the presence of surfactant, is needed to fully understand the abstraction behavior of reservoir rock system.

The significance of the presence of minerals of relatively high solubility, such as gypsum, in reservoir systems is illustrated in Figure 10. It was shown that even when present as a minor component, gypsum has a predominating effect on sulfonate depletion behavior. Similar results were obtained with the Na-kaolinite-gypsum system.

The effect of gypsum is more marked in gypsum-SiO₂ mixtures (Fig. 11). Silica does not adsorb sulfonate in the absence of gypsum. However, in the presence of as little as 4.8% gypsum, the abstraction curve for the silica-gypsum system is similar to that obtained for gypsum alone, showing that surfactant depletion is again due to the precipitation of Ca(DBS)₂.

The role of mineralogy becomes increasingly more complex when more than one soluble mineral is present, as in the case of

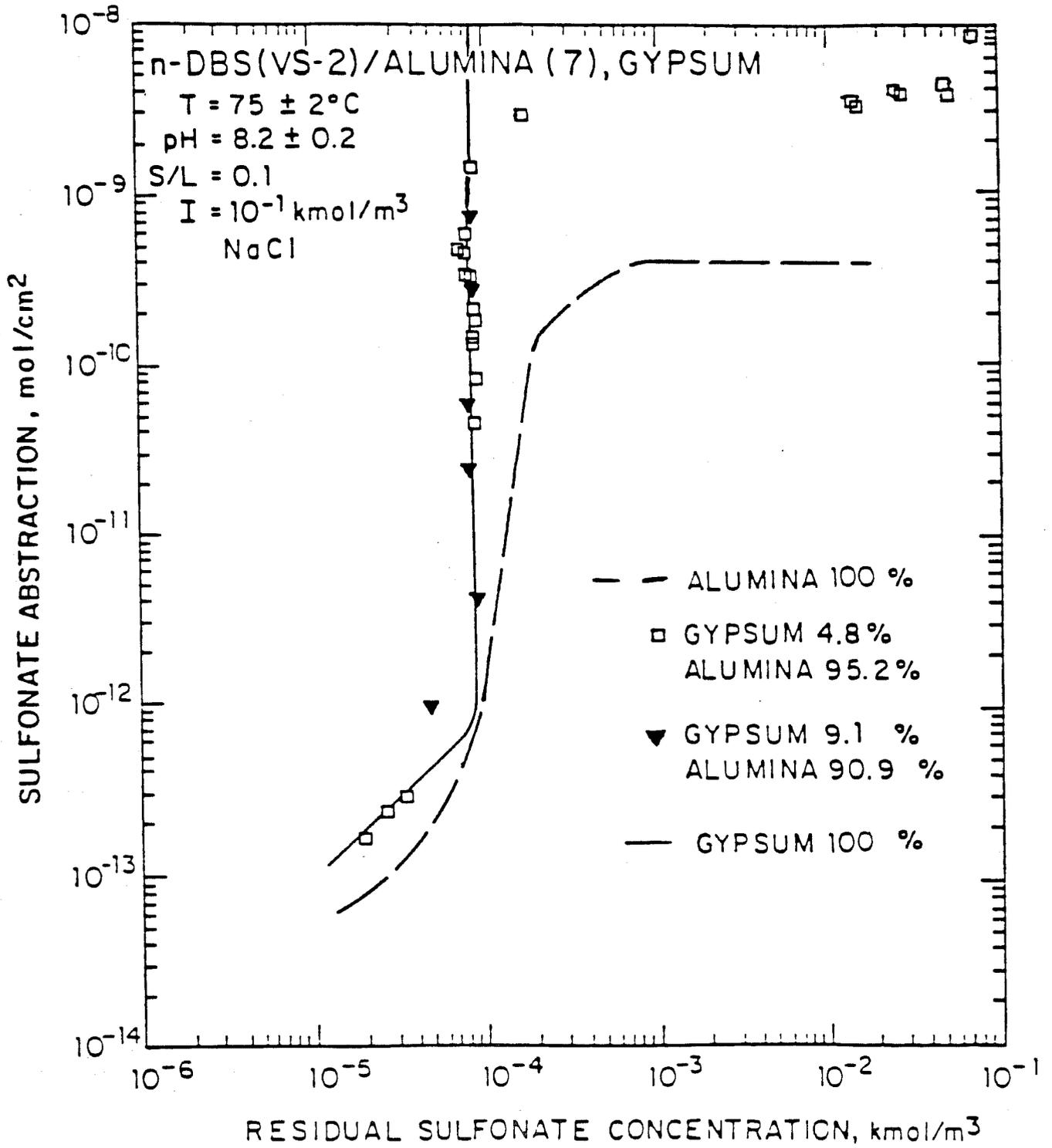


Figure 10: Abstraction of n-DBS (Sodium n-decylbenzenesulfonate) on alumina in the presence of gypsum at 75 degrees C and in 10⁻¹ kmol/m³ NaCl.

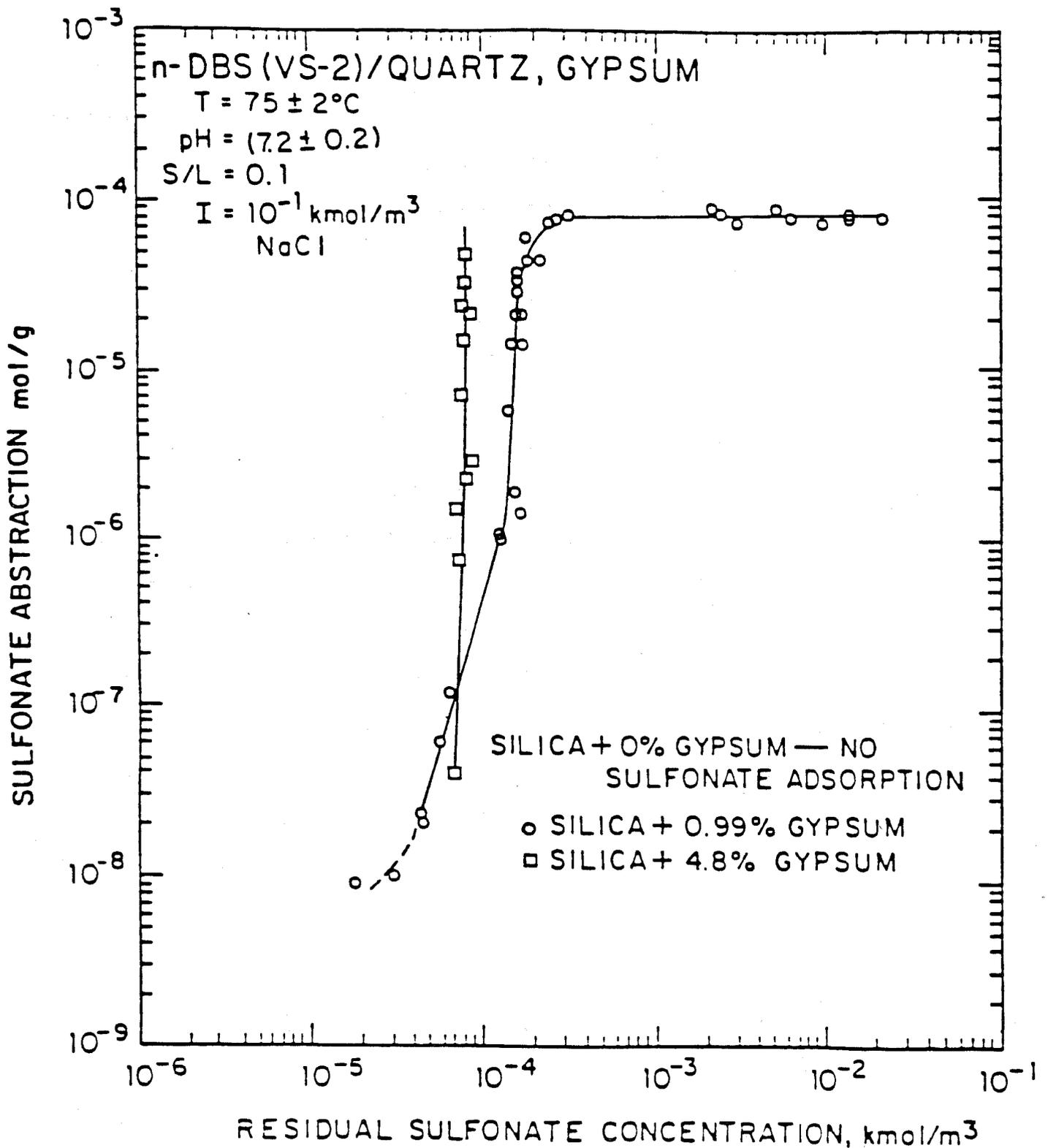


Figure 11: Abstraction of n-DBS (Sodium n-decylbenzene-sulfonate) on silica in the presence of gypsum at 75 degrees C and in 10⁻¹ kmol/m³ NaCl.

the magnesite-gypsum system, which behaves differently from gypsum-silica, gypsum-kaolinite, and gypsum-alumina mixtures. This is depicted in Figure 12. Precipitation at various levels of gypsum occurs in this case at higher sulfonate concentrations than in the case of gypsum alone, or its mixtures with Na-kaolinite or silica. This is found to be due to lower calcium levels in gypsum suspensions containing magnesite. On the other hand, magnesium in solution is correspondingly higher in gypsum-magnesite mixtures than in suspensions containing only magnesite. Increased magnesium is thought to be due to the solution equilibria involving carbonate depletion for forming calcite and/or dolomite as a new solid phase; calcite and/or dolomite in turn controls the calcium level in solution and, hence, the total sulfonate depletion in the system. Evidently, in addition to interactions with surfactant species, inorganics released by one mineral can interact with those from another so that the total sulfonate depletion becomes more and more complex in a heterogeneous rock environment. Clearly more detailed knowledge of behavior in such systems is required.

The above studies have established that the nature and type of minerals present in reservoir systems will indeed play a governing role in determining the extent of depletion of surfactants like alkylbenzenesulfonates. The depletion behavior can be extremely complex so that a full understanding can be achieved only with a detailed knowledge of mineral characteristics (electrical properties, dissolution, morphology,

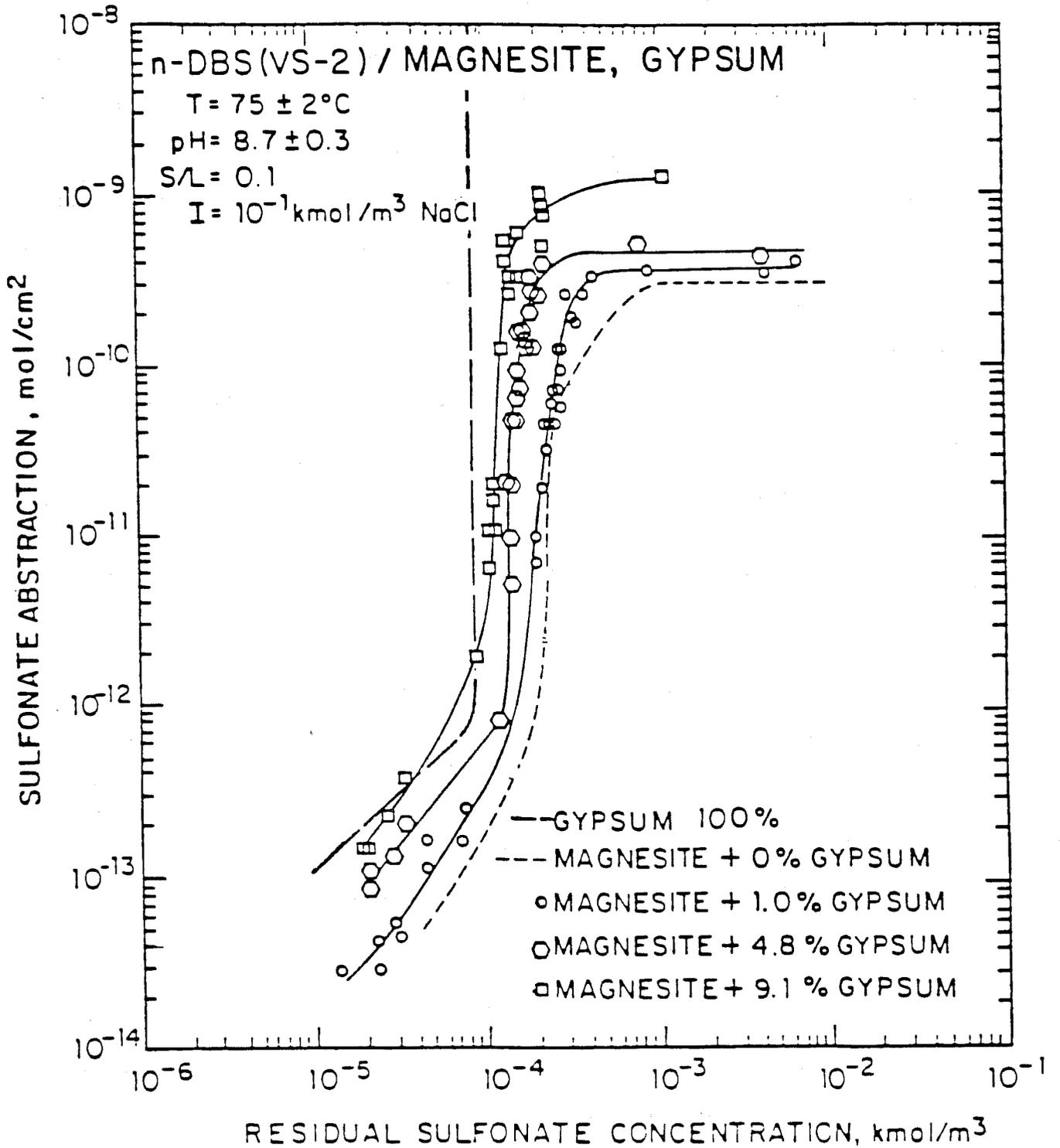


Figure 12: Abstraction of n-DBS (Sodium n-decylbenzene-sulfonate) on magnesite in the presence of gypsum at 75 degrees C and in 10⁻¹ kmol/m³ NaCl.

etc.), both individually, as well as in mixed mineral-surfactant systems. There is a great need for systematic research to generate such information.

3. ROLE OF SURFACTANT STRUCTURE

An ideal surfactant for enhanced oil recovery in micellar flooding must have high salt tolerance (for mono and multivalent ions), good thermal stability, and should produce low interfacial tension. Many structural modifications have been suggested only recently; therefore little information on the adsorption behavior of such surfactants is available. Some of the commercially available modified surfactants studied in this project in this regard are:

- 1) Xylene sulfonates (Exxon)
- 2) Linear and branched chain alkylarylsulfonates
(Cities Service, Pfaltz & Bauer, etc.)
- 3) Alkyl diphenoxydisulfonates (Dow)
- 4) Ethoxylated alkyl- and alkylarylsulfonates/sulfates
(Diamond Shamrock, Rohm & Haas)
- 5) Dialkylarylsulfonates (Pilot Chemicals, etc.)

Each structural modification of the surfactant can indeed affect the various interactions that govern the adsorption process and it is the cumulative effect of all these modifications that will determine the overall adsorption behavior

of a surfactant.

3.1 Structural Modification of Hydrophobe: Modified Alkylbenzenesulfonates

Comparative adsorption studies on alumina using a series of sulfonates with systematic structural variations have shown that the magnitude and shape of the adsorption isotherms can be significantly different. An increase in adsorption resulted from an increase in the alkyl chain length of n-alkylbenzenesulfonates (see Fig. 13). Incorporation of an aromatic group effectively increased the chain length by 3 to 4 CH₂ groups. These results are indicative of the greater hydrophobicity and stronger hemimicellization of the larger hydrocarbon chain.

Branching of the alkyl chain of hexadecylbenzenesulfonate was found to decrease the ability of the surfactant to adsorb. 8-phenyl-C₁₆SO₃Na adsorbed less than 2-phenyl-C₁₆SO₃Na, and the former surfactant functioned (lower adsorption) only about as effectively as n-tridecylbenzenesulfonate. A decrease in adsorption was also observed when there were short alkyl chain substitutions on the aromatic ring of alkylbenzenesulfonates (Figure 14). These results suggest that the lower adsorption of these surfactants is the result of a decrease in their ability to pack as two-dimensional aggregates at the solid-liquid interface due to the bulky character of their hydrocarbon moiety.

The effect of the bulky character of the hydrocarbon moiety

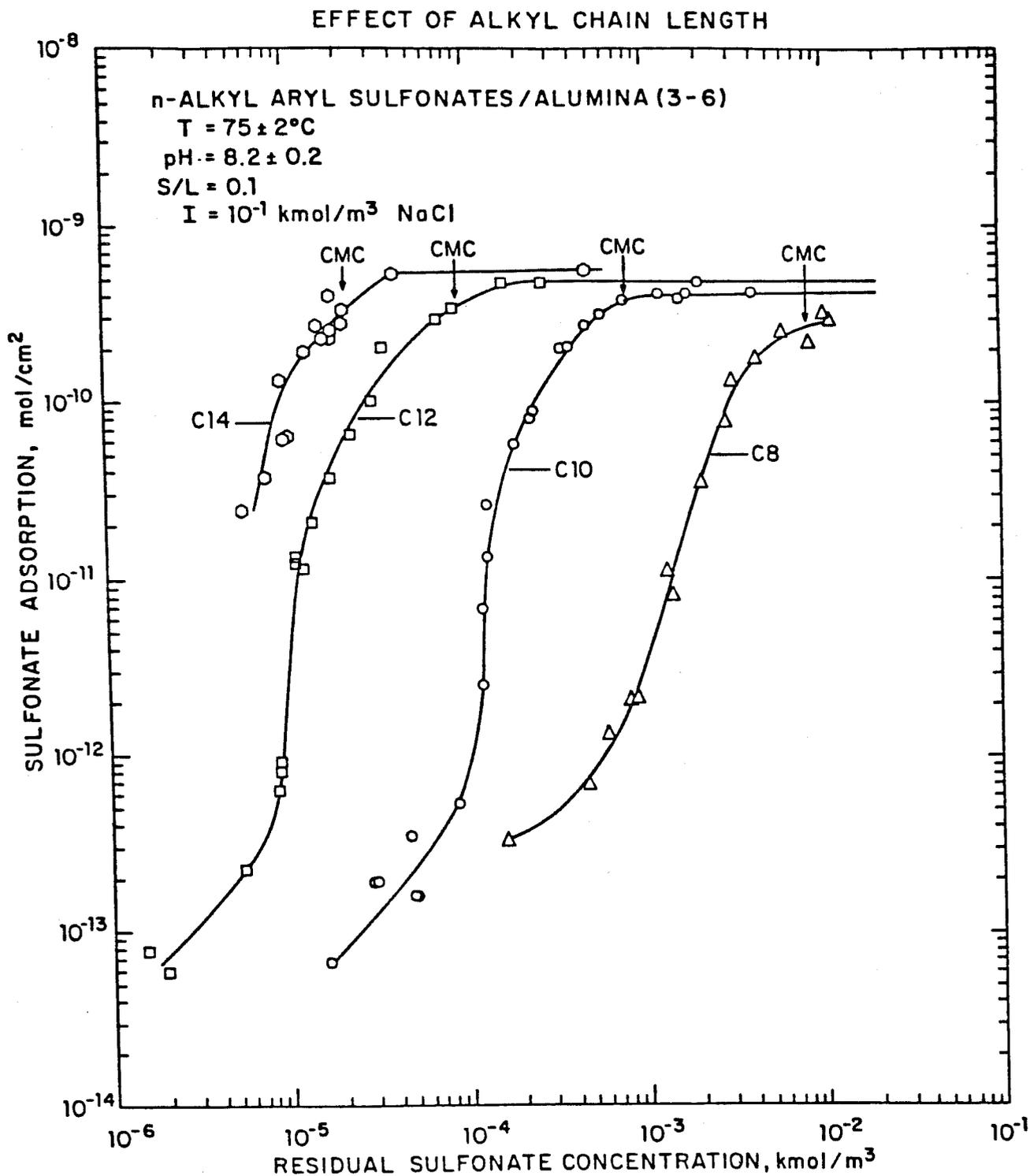


Figure 13: Effect of chain length on adsorption of alkylaryl sulfonates on alumina at 75 degrees C and in 10⁻¹ kmol/m³ NaCl.

STRUCTURAL COMPARISON:

n-ALKYL ARYL SULFONATES vs ALKYL ARYL XYLENE SULFONATES (DEOILED)

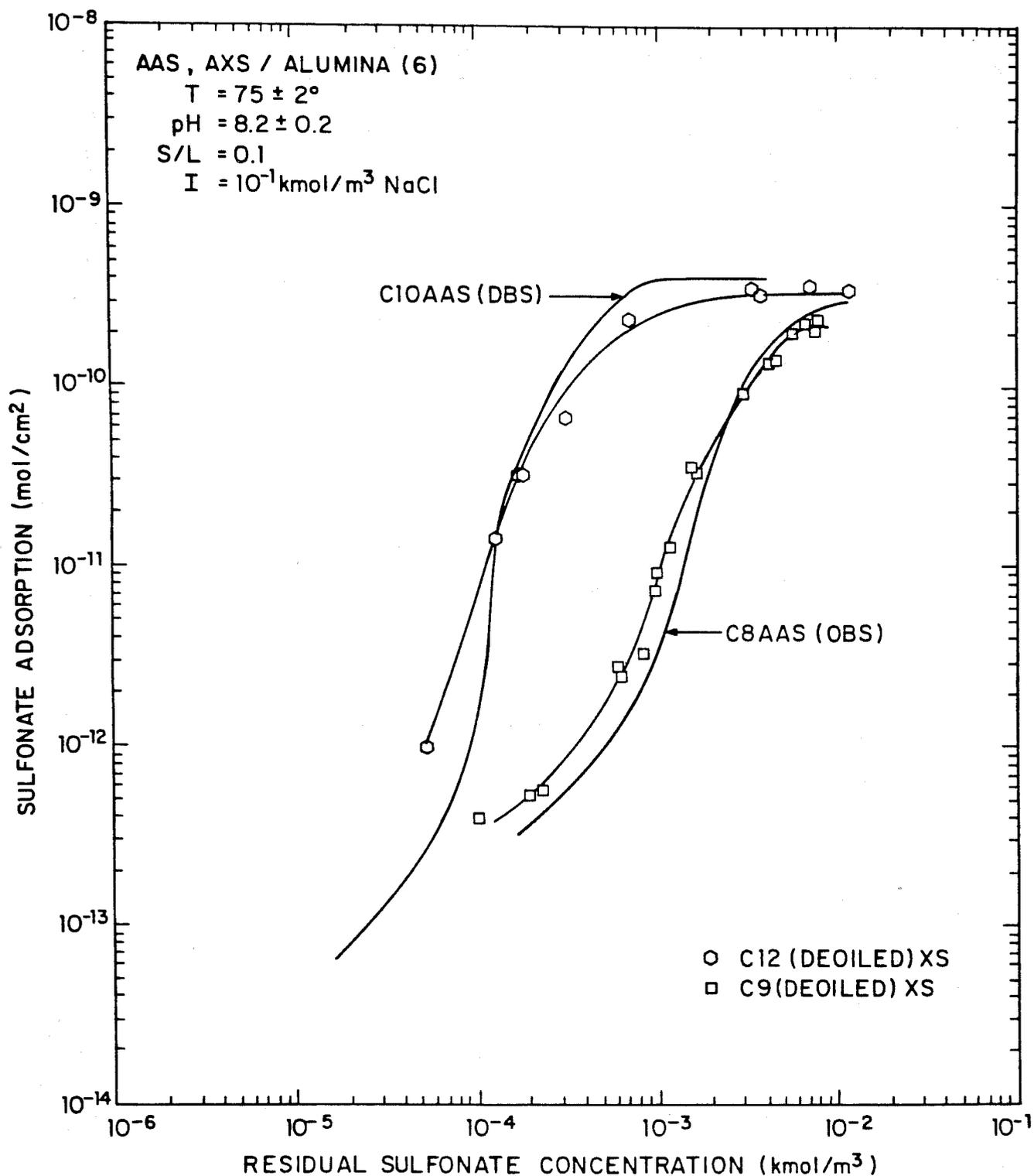


Figure 14: Adsorption of xylene sulfonates on alumina at 75 degrees C and in 10⁻¹ kmol/m³ NaCl.

is more clearly shown in Figure 15 for the adsorption of didecyl diphenoxy disulfonates. The shape of the isotherm indicates the absence of hemimicellar interactions, possibly resulting from the bulkiness introduced through the ether linkage connecting the two alkylbenzenesulfonates. It is clear that modifications in the hydrocarbon moiety of surfactants leads to considerable differences in adsorption behavior. However, there is insufficient information on the role of such structural changes, particularly in terms of the adsorption behavior of surfactants which have potential in micellar flooding processes (i.e. surfactants capable of producing low oil-water interfacial tension). Attention has to be focussed in the future on developing a fundamental understanding of the role of surfactant structure in adsorption.

3.2 Ethoxylated Alkylarylsulfonates and sulfates

While, in general, the low interfacial tensions required in EOR can be achieved by altering the hydrophobic nature of the surfactant by varying chain length and branching, the required salt tolerance and oil compatibility are brought about by adding cosurfactants (alcohols). Ethoxylated surfactants are particularly attractive in that the IFT behavior, salt tolerance and oil compatibility could be optimized for a particular type of surfactant by adjusting the hydrophilic-lipophilic balance through the degree of ethoxylation.

Adsorption isotherms were obtained for Triton X-200 on

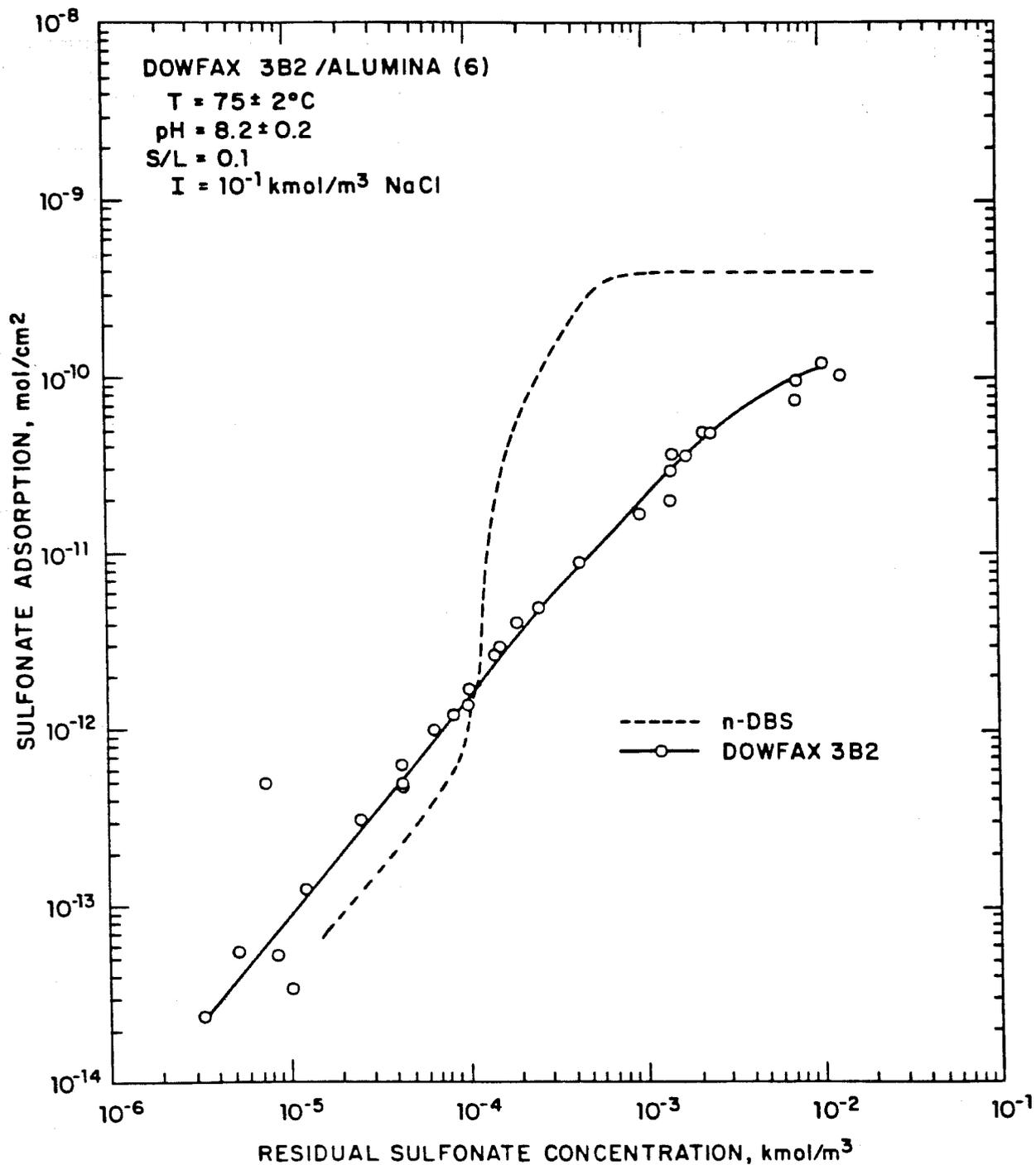


Figure 15: Adsorption of n-DBS (Sodium n-decylbenzenesulfonate) and DOWFAX 3B2 (Sodium alkyldiphenoxydisulfonate) on alumina at 75 degrees C and in 10⁻¹ kmol/m³ NaCl.

different insoluble and semisoluble reservoir minerals and the results are given in Figure 16. Unlike sodium n-decylbenzenesulfonate adsorption on these minerals (Figure 6), the adsorption isotherms are "S" shaped, showing the electrostatic, hemimicellar and micellar regions (absence of precipitation). Similar results were also obtained with two other commercially available surfactants having 2.5 and 3.5 ethoxylation numbers.

The role of dissolved mineral species on the adsorption of Triton X-200 on Na-kaolinite, Al_2O_3 , magnesite, and calcite was studied using mineral mixtures containing gypsum. A typical adsorption isotherm result for Triton X-200 on Na-kaolinite in the presence of 25% gypsum is given in Figure 17, along with those obtained previously using n-DBS for this mineral mixture. The adsorption isotherm obtained for Triton X-200 in the presence of gypsum does not have the vertical region that was obtained with sodium n-decylbenzenesulfonate. It is to be noted that the sharp rise in adsorption in the sodium n-decylbenzenesulfonate system is the result of precipitation of calcium disulfonate. The present result suggests that similar precipitation does not occur when Triton X-200 is used as the surfactant.

The tolerance of Triton X-200 solutions to NaCl and $CaCl_2$ solutions at 75 degrees was confirmed from precipitation tests. These tests showed that precipitation of 10^{-2} kmol/m³ surfactant solutions occurs only above 14% NaCl and 7.4% $CaCl_2$ (compared to

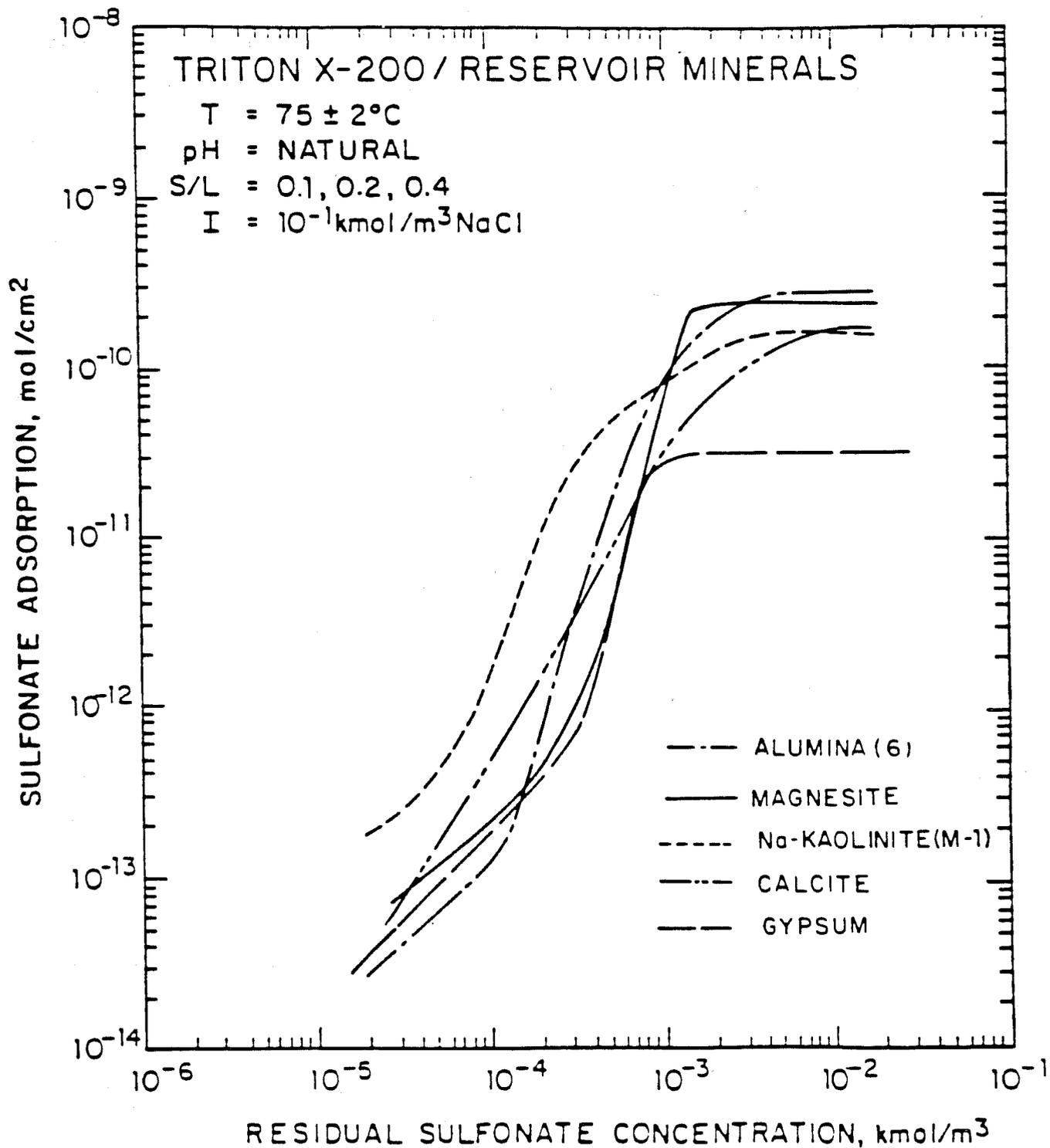


Figure 16: Adsorption of Triton X-200 on selected reservoir minerals at 75 degrees C in 10⁻¹ kmol/m³ NaCl.

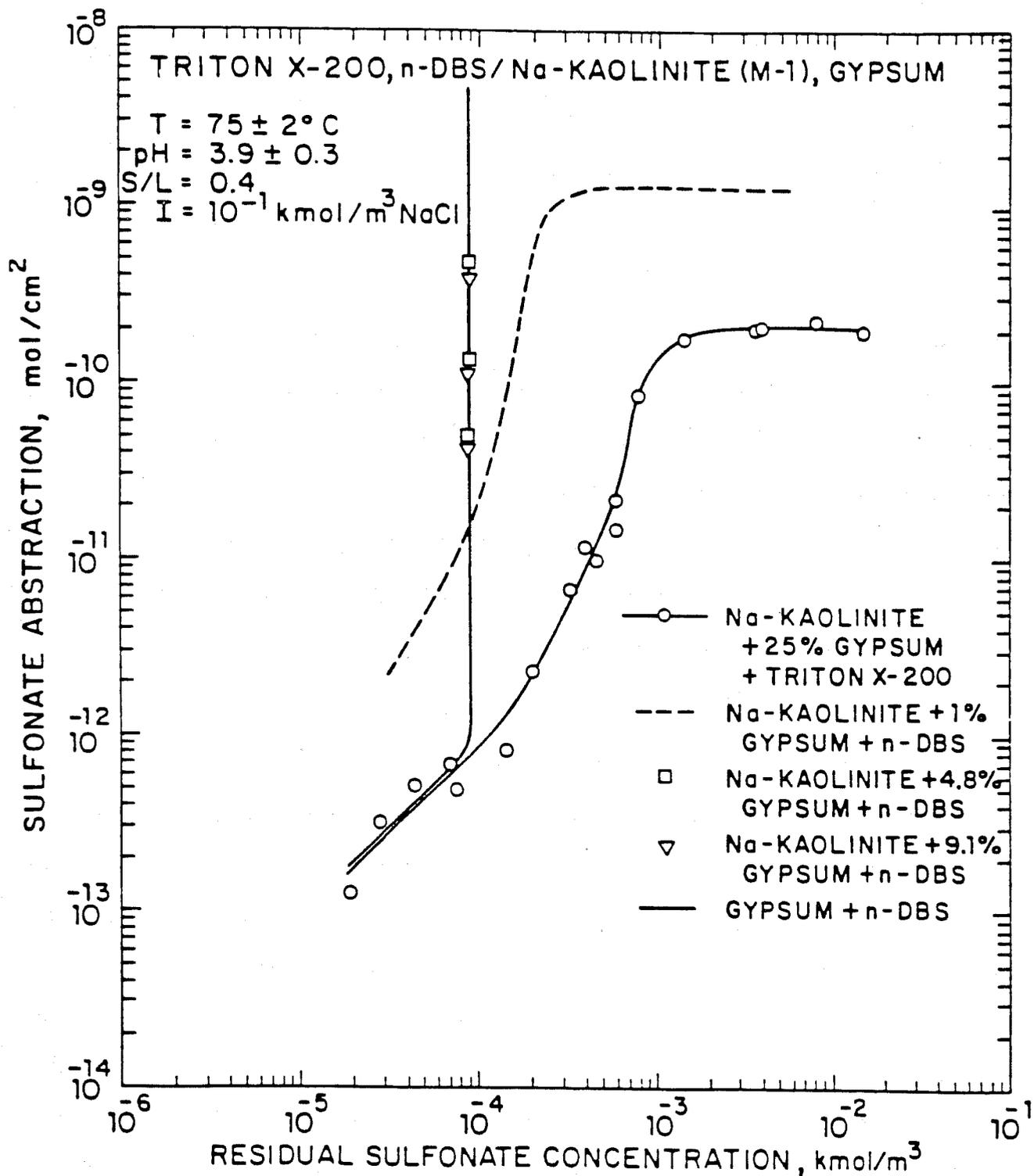


Figure 17: Adsorption of Triton X-200 and n-DBS (Sodium n-Decylbenzenesulfonate) on Na-kaolinite in the presence of different amounts of gypsum at 75 degrees C in $10^{-1} \text{ kmol/m}^3 \text{ NaCl}$.

0.6% NaCl and 0.002% CaCl₂ for NaDDBS). Thus, Triton X-200 is not expected to precipitate under medium reservoir salinity conditions (5% NaCl and 2000 ppm Ca(0.2%)).

The above studies clearly show the superior salt tolerance of ethoxylated sulfonates compared to n-alkylbenzenesulfonates. Currently, the emphasis is on understanding the role of ethoxylation in determining the adsorption behavior and high salt tolerance of this class of surfactants. A major problem encountered in these studies is obtaining samples of pure surfactants with a narrow distribution of ethoxylation numbers. Work is in progress to synthesize such pure surfactants, which would be essential in understanding the role of ethoxylation on the surfactant depletion behavior.

It should be noted that even in the absence of precipitation, as when ethoxylated sulfonates are used, dissolved mineral species can cause significant effects on the adsorption of minerals through activation or depression of mineral surface with respect to adsorption. In particular, in heterogeneous mineral systems containing sparingly soluble minerals, the adsorption behavior of minerals like Na-kaolinite can be significantly different from that expected on the basis of single mineral tests. Adsorption studies were therefore conducted on Al₂O₃ and Na-kaolinite using 10⁻² kmol/m³ Na₂SO₄ and 10⁻² kmol/m³ CaCl₂ to isolate the effects of the bivalent ions of gypsum [10⁻²

kmol/m³ is the solubility of gypsum]. Typical results obtained with Na-kaolinite are given in Figure 18. It is seen from this figure that the effect of Ca²⁺ is to enhance adsorption of Triton X-200, while the effect of SO₄²⁻ is to depress its adsorption. Comparison of these curves with those obtained for calcium and sulfate together, shows that in both systems, the effect of addition of calcium alone and that of calcium and sulfate together appears to be the same. This suggests that the enhancing effect of Ca²⁺ predominates over the depressing effect of SO₄²⁻. A thorough understanding of such activation/depression phenomena requires a detailed study of these systems under carefully controlled conditions.

4. SOLUTION CHEMISTRY OF SURFACTANTS

As the earlier results clearly show, the overall depletion of surfactant depends to a large extent upon surfactant interactions in bulk solution, such as precipitation and surfactant association (micellization). Detailed investigations were carried out on selected systems in order to understand the role of solution chemistry of surfactants.

4.1. Precipitation-Redissolution

In the presence of multivalent cations, significant surfactant precipitation can occur. Precipitation studies using alkyl sulfonates and alkylbenzenesulfonates with multivalent ions

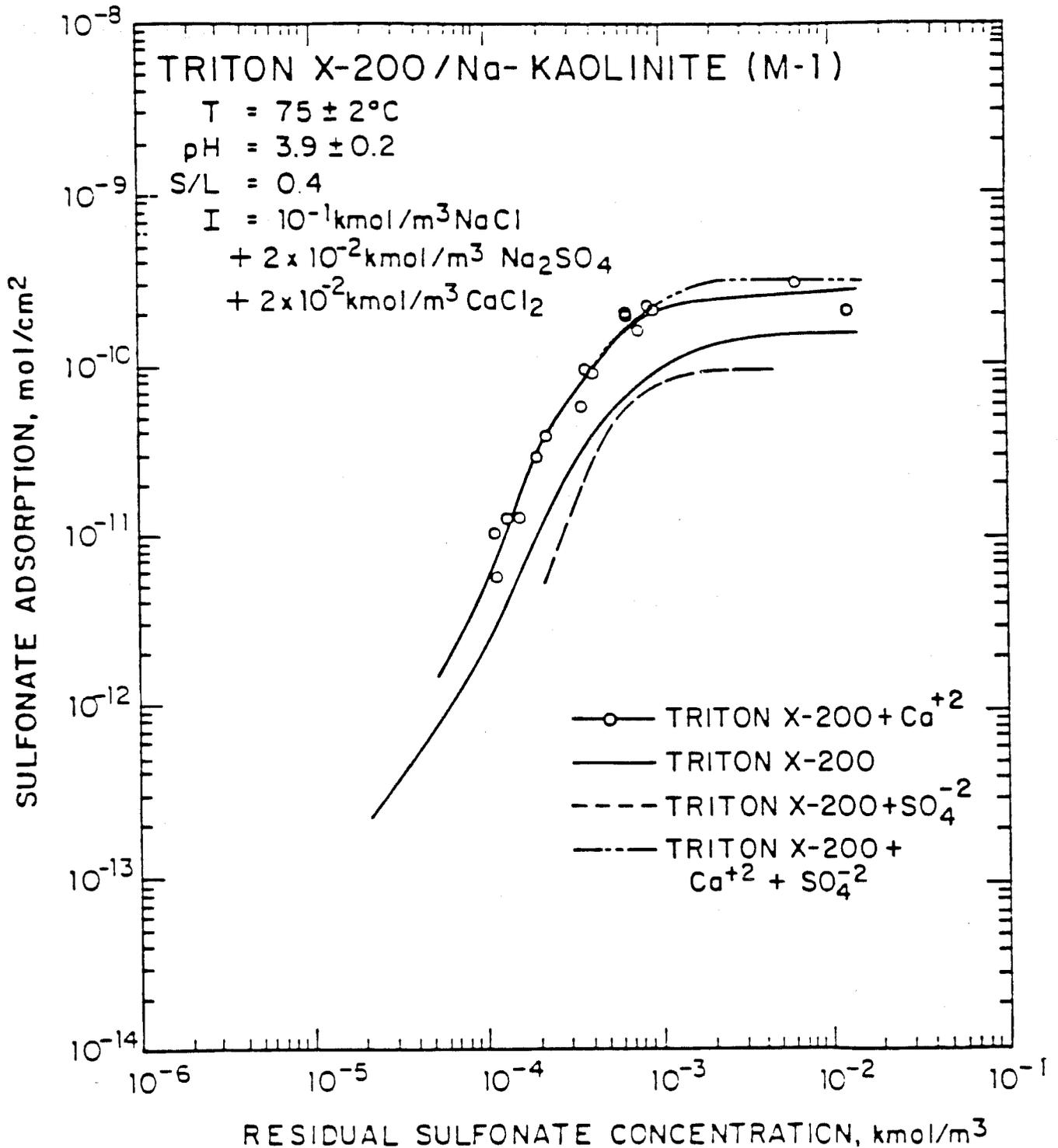


Figure 18: Adsorption of Triton X-200 on Na-kaolinite in the presence of $10^{-2} \text{ kmol/m}^3 \text{ CaCl}_2$, $10^{-2} \text{ kmol/m}^3 \text{ Na}_2\text{SO}_4$ at 75 degrees C in $10^{-1} \text{ kmol/m}^3 \text{ NaCl}$.

showed precipitates of these sulfonates to redissolve upon increasing the sulfonate concentration to the CMC, and then to reprecipitate at even higher concentrations. This precipitation - redissolution - reprecipitation behavior (PRR) is illustrated in Figure 19(a) for the sodium dodecylsulfonate (NaDDS)/CaCl₂/NaCl and 19 (b) (NaDBS)/CaCl₂/NaCl system. Chemical analysis of the bulk solution showed that the sulfonate precipitate existing in the precipitation-redissolution region was calcium disulfonate. Measurable redissolution of precipitates was found to occur only in the presence of micelles. In addition to the chemical analysis of the bulk solution, morphological and chemical analysis of the precipitate was also made using SEM/EDXRF technique. These studies supported the results of our bulk solution analysis. Depending on the the Na/Ca ratio, the precipitates in the reprecipitation region can be sodium sulfonate or a mixture of sodium and calcium sulfonates.

Studies of the precipitation - redissolution behavior of CaCl₂/Na-alkylsulfonates as a function of chain length of the sulfonates, showed that C₁₈ sulfonate, which did not form micelles, could not solubilize its calcium sulfonate precipitate. This observation supports our theory that redissolution is caused by micelles. Most interestingly, the solubilization patterns of Ca(C₁₆S₃)₂ and Ca(C₁₀S₃)₂ in C₁₀ micelles were identical, indicating that the solubilization power

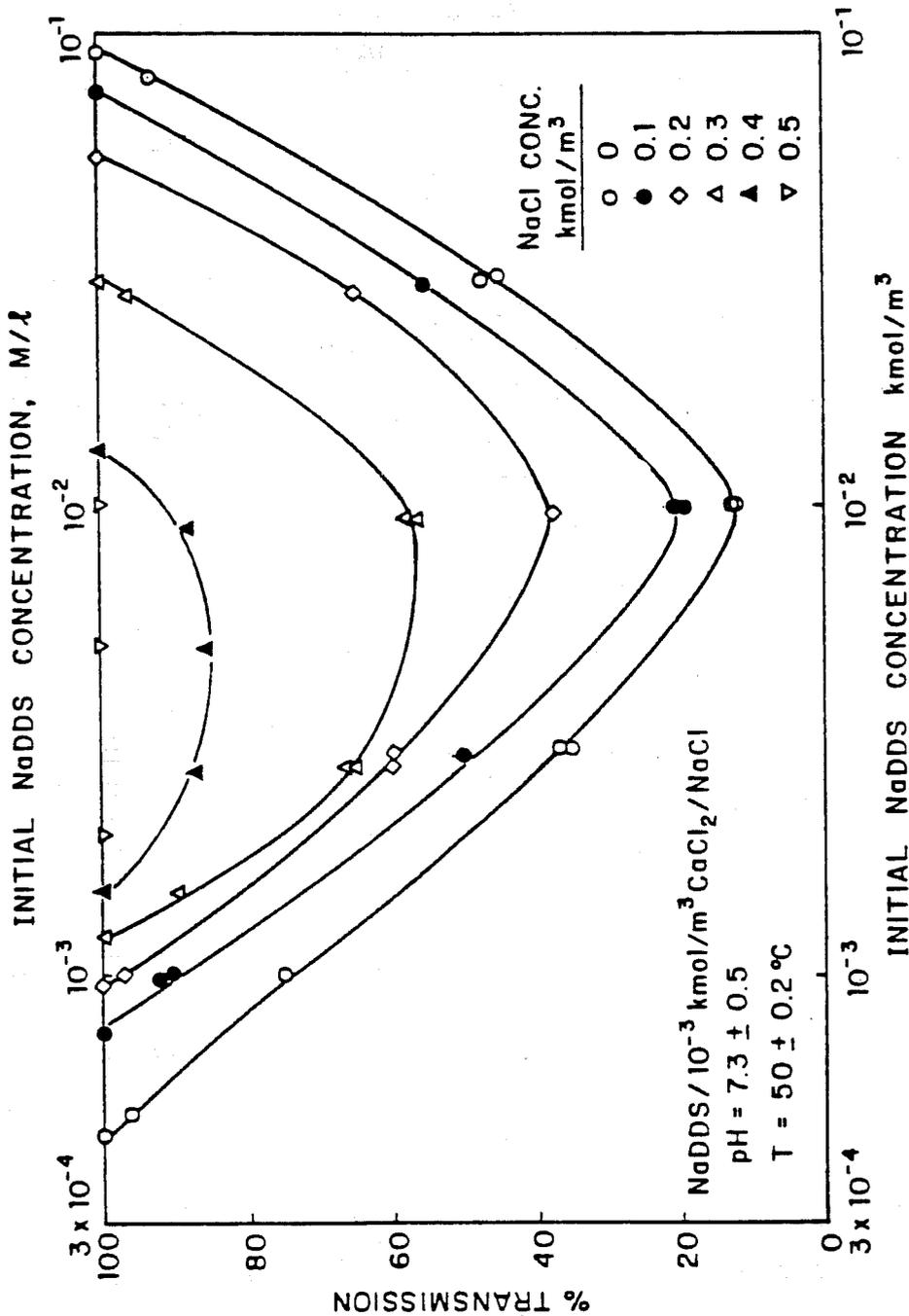


Figure 19A: Light transmission of NaDDS (Sodium dodecyl-sulfonate)/CaCl₂/NaCl solutions as a function of NaCl concentration.

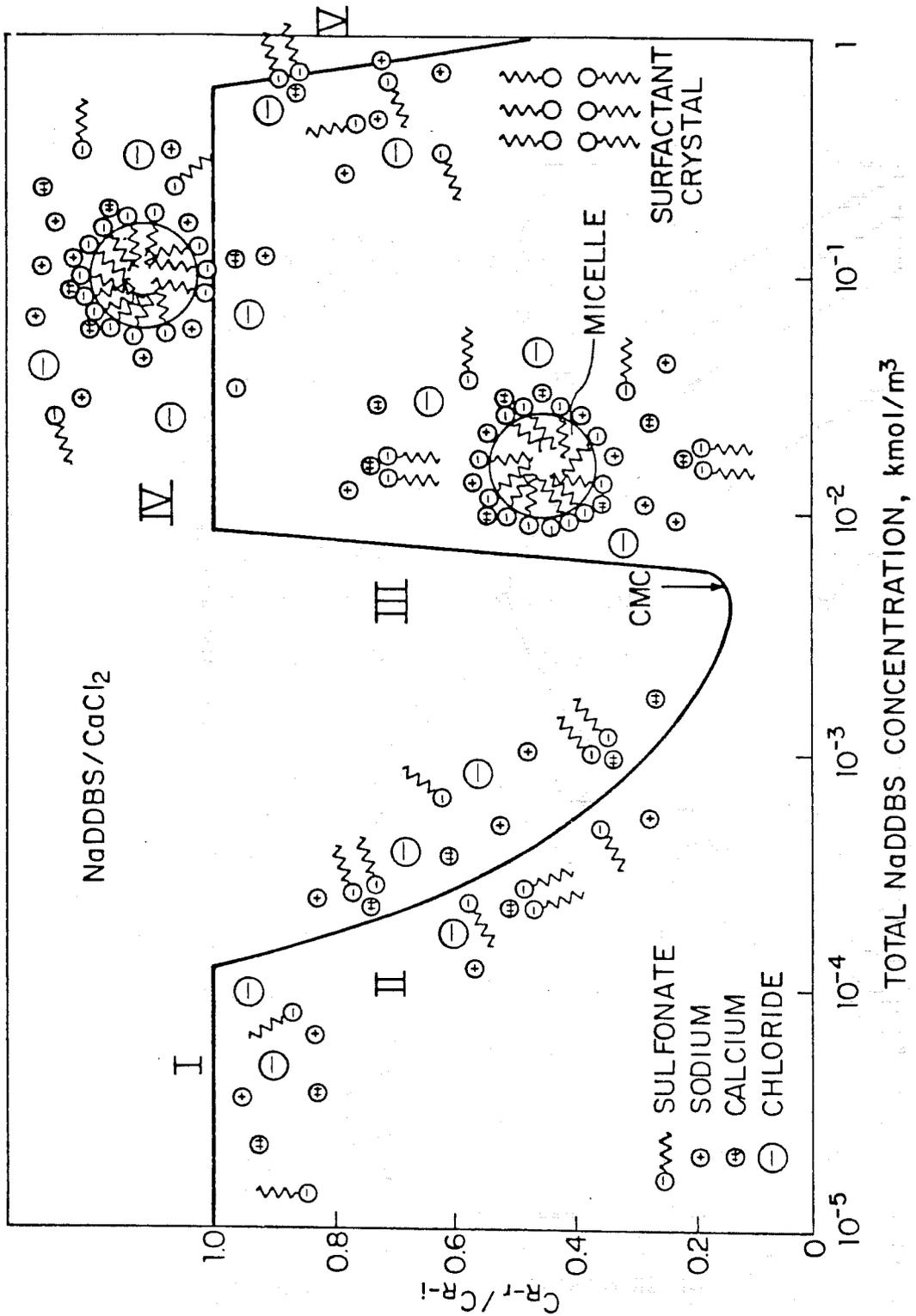


Figure 19B: Schematic diagram of the mechanism of precipitation-redissolution-reprecipitation process.

of the micelle is independent of chain length of the precipitate. This leads to the conclusion that the surface of the micelle rather than the interior plays a major role in the solubilization process. Examination of the results obtained for $\text{CaCl}_2/\text{NaDDS}$, and $\text{CaCl}_2/\text{NaDDBS}$ systems showed that precipitation regions can be characterized by a solubility product and the redissolution region by a term which we have called the solubilization constant. A model has been developed to predict the precipitation behavior and the composition of the system (see Figure 20). The molecular mechanism for the redissolution phenomenon, proposed on the basis of all the results that we have obtained for the $\text{CaCl}_2/\text{sulfonate}$ systems, involves the uptake of Ca^{+2} by the micelle, followed by redissolution of the precipitate to replenish the system with Ca^{+2} , and then the formation of additional micelles by the released sulfonate.

The marked differences in the solubilization powers of sodium dodecylbenzenesulfonate and sodium dodecylsulfonate for their calcium salts were correlated with their charge characteristics and counter ion bindings of their micelles, and the capability of micelles to adsorb calcium ions. (P. Somasundaran, et al. SPE Dec.1984, p 667-676.)

The thermodynamic model involving the adsorption of Ca^{+2} on micelles involves a series of molecular processes for the precipitation-redissolution phenomena. The results obtained for the dependence of precipitation - redissolution on temperature

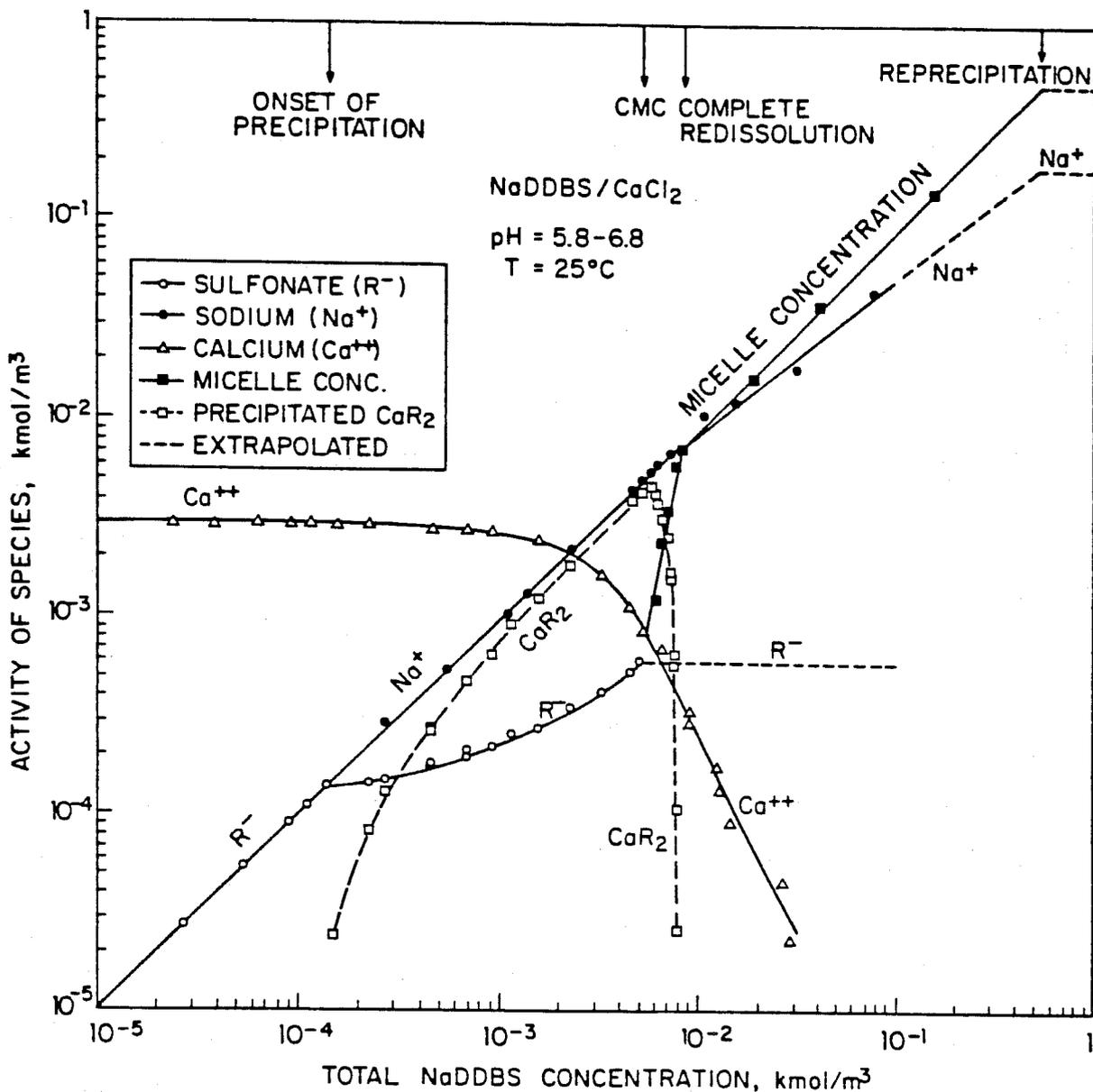


Figure 20: Experimentally obtained variations in the activities of different species in NaDDBS(Sodium dodecylbenzenesulfonate)/CaCl₂ system as a function of sulfonate concentration.

was used to test the above model, and the model was found to be in agreement with the experimental results.

Studies extended to trivalent ion systems such as AlCl_3 , showed that precipitation-redissolution-reprecipitation (PRR) behavior is similar to that of the CaCl_2 system, but with a marked pH dependence as shown in Figure 21. It is evident from the figure that in the pH range 1-3, the DDS/Al ratio in the precipitate is 3, confirming that the precipitate is $\text{Al}(\text{DDS})_3$. A marked decrease in the ratio is observed beyond this pH. This sharp decrease in DDS/Al ratio above pH 3 can be due to the formation of $\text{Al}(\text{OH})\text{R}_2$ or $\text{Al}(\text{OH})_2\text{R}$, or due to adsorption of sulfonate on precipitated $\text{Al}(\text{OH})_3$ (beyond pH 4.6).

Exploratory work on the effect of oils and alcohols, both of which are relevant to micellar flooding, on precipitation - redissolution was tested under selected conditions. Alcohol was found to decrease the precipitation and even eliminate it at higher levels (The solubilization power of micelle itself was found to decrease in the presence of oils and alcohols). The effect of n-dodecane on calcium-dodecylbenzene sulfonate precipitation - redissolution is apparently only to shift the point of onset of precipitate redissolution to lower sulfonate concentrations. Comparison of precipitate dissolution in both the presence and absence of oil, as indicated by the solubilization constant of the micelle, K_s , results in K_s values

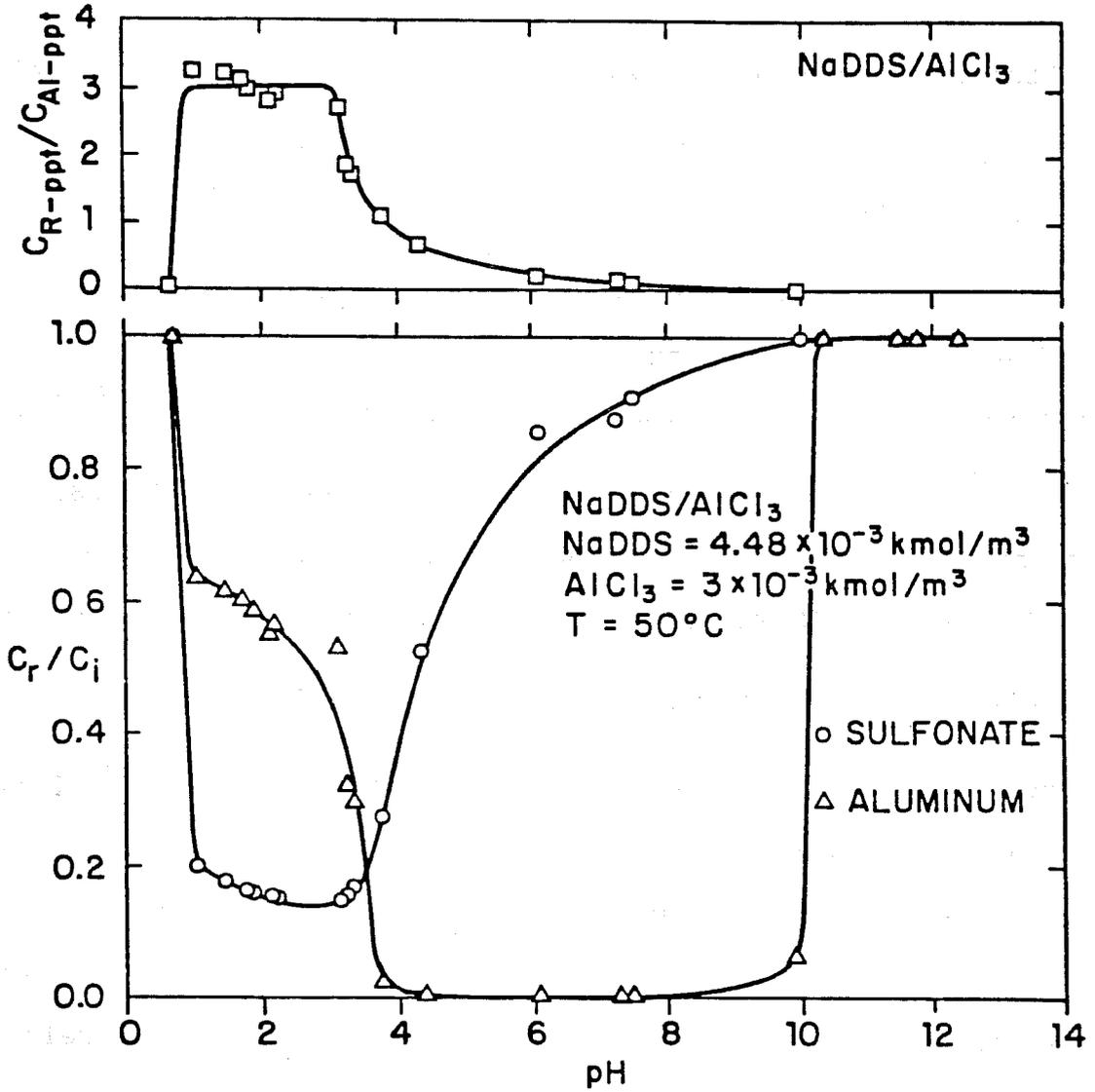


Figure 21: pH dependence of NaDDS (Sodium dodecylsulfonate) and Aluminum precipitation at $3 \times 10^{-3} \text{ kmol/m}^3$ $AlCl_3$ and $4.48 \times 10^{-3} \text{ kmol/m}^3$ NaDDS.

of 0.2 and 0.35 for the solubilization in the presence and absence of oil, respectively. The lower solubilization power in the presence of oil suggests competition of oil molecules with the precipitate for the micelles.

This aspect of study is in its preliminary stage and its relevance to micellar flooding systems needs clear understanding and is therefore being investigated in detail.

4.2. Pre-micellar Associative Interactions of Surfactants

In addition to micellization and precipitation, surfactant species of hydrolyzable surfactants like amines and fatty acids, can undergo various associative interactions in aqueous solutions that give rise to dimers, acid-soaps, etc.

Associative complexes can be expected to be highly surface active and as such can have a predominating role in the overall adsorption behavior of the surfactant. Estimates of the surface activities of complexes such as dimers and acid-soap show that the surface concentrations of these complexes can be comparable to that of monomers even when the concentration of such complexes in solution is six to eight orders of magnitude lower than that of the monomers.

A thermodynamic model of the surface tension behavior of surfactant solutions, incorporating the formation of such association complexes as a function of pH and total concentration, has been developed. (Somasundaran p. and

Ananthapadmanabhan, K. P. Solution Chemistry Of Surfactants, Vol.2,ed. Mittal, K. L.,pub. Plenum Press,N.Y.,1979). From the model, formation constants of association complexes under selected conditions could be obtained, and these values in turn could be used to evaluate the species distribution diagrams for the surfactants concerned. Typical results obtained for oleic acid are shown in Figure 22. Such association complexes can adsorb on the surface of the minerals and change the wettability of the minerals. It was found that maximum nonwettability (hydrophobicity) was obtained under pH conditions that correspond to the maximum concentration of the acid-soap species of oleic acid.

These results clearly suggest that a knowledge of such surfactant solution chemistry is also essential in developing mechanisms of adsorption behavior of surfactants.

5. ADSORPTION IN THE PRESENCE OF OILS AND ALCOHOLS.

Oils and alcohols are invariably present in micellar flooding systems, and their presence can increase or decrease the surfactant adsorption/precipitation. We have investigated the effect of oil (dodecane) on the adsorption of DBS and DDBS on alumina. The effect of the addition of dodecane on the adsorption of DBS on Al_2O_3 is given in Figure 23. The significant enhancement in adsorption observed in the electrostatic region was attributed to a reduction in the repulsive lateral interactions between the adsorbed sulfonate. Supporting oil

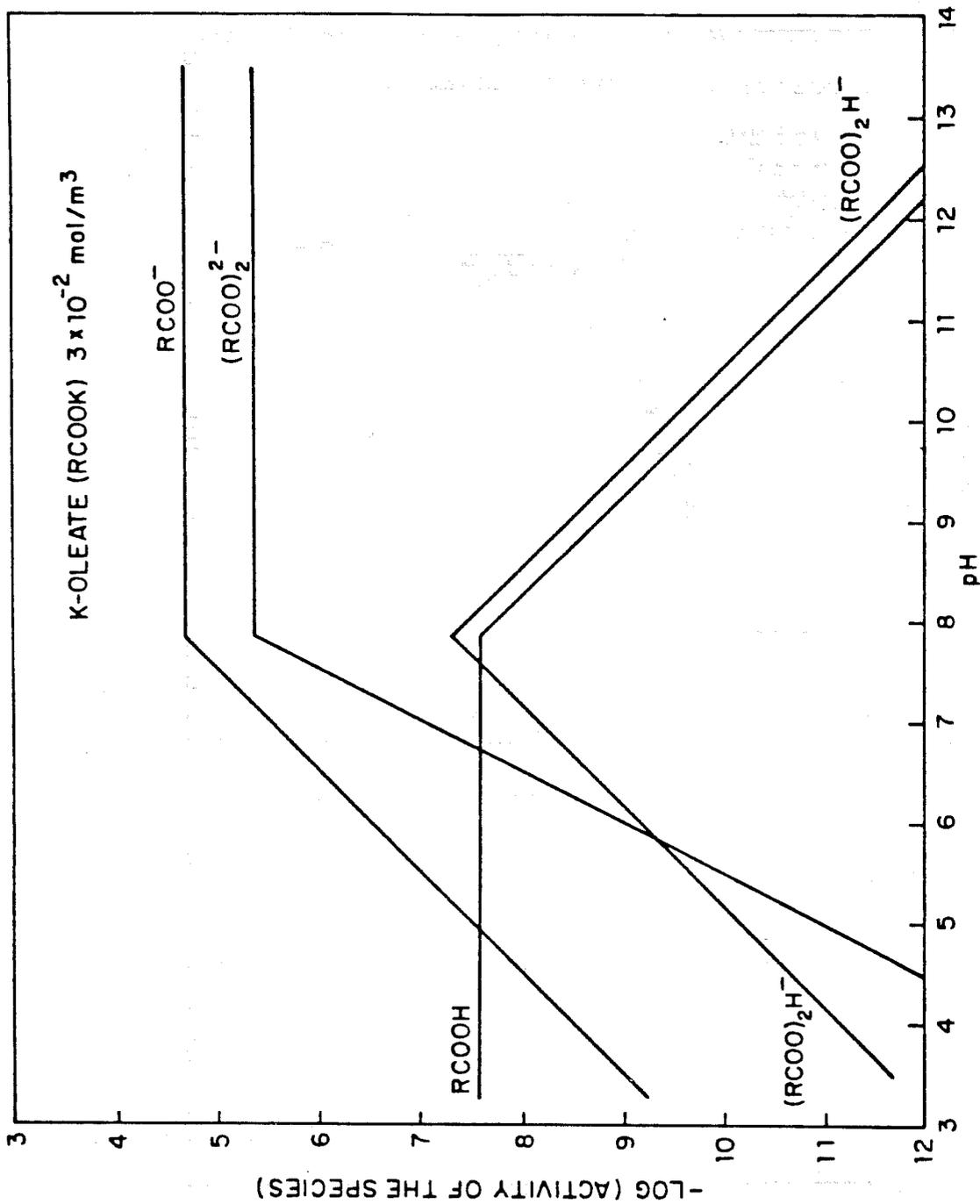


Figure 22: Species distribution diagram of potassium oleate solutions as a function of pH at $C_T = 3 \times 10^{-5}$ kmol/m³. The constants used in computing this diagram are $pK_S = 7.6$, $pK_a = 4.95$, $pK_D = -4.0$, and $pK_{AD} = -4.95$.

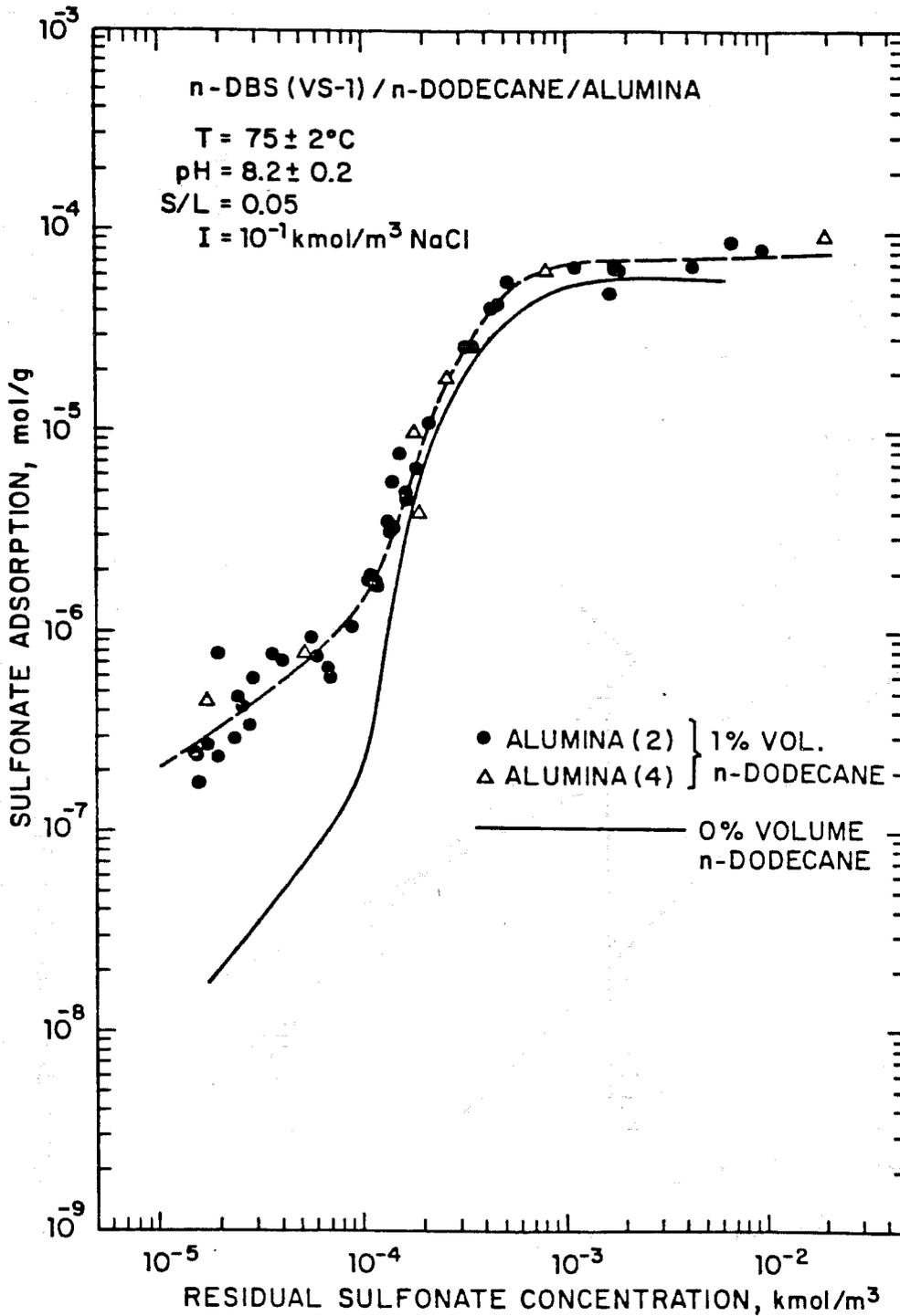


Figure 23: Effect on n-dodecane on the adsorption of n-DBS (Sodium n-decylbenzenesulfonate) on alumina at 75 degrees C in 10⁻¹ kmol/m³ NaCl.

extraction experiments showed considerable uptake of oil, but only in the presence of sulfonate, suggesting that the driving force for the dodecane adsorption is the lateral interaction between dodecane and the alkyl chain of the surfactant. Apparently, at sulfonate concentrations beyond the electrostatic region, the self aggregation tendency of the surfactant itself (hemimicellization) is strong enough to minimize the effect of the dodecane at the 1% level of addition. Adsorption studies of n-dodecane showed that multilayer coating of the oil is found to take place on alumina even at low sulfonate concentration. This is further supported by the fact that adsorption continues to increase with increase in percentage of oil in the bulk. Examination of the solids after adsorption tests showed their aggregation into larger spherical particles, with the size of the aggregate increasing with oil concentration. Such aggregation of particles in the presence of oil may be deleterious for enhanced oil recovery as such aggregates can block the micropores and thus prevent the micellar fluid from entering such pores.

Addition of alcohols was also found to have a measurable effect on adsorption, with the degree of effect dependent on the chain length of the alcohol (see Figure 24). Addition of 1% propanol was found to decrease the adsorption in the electrostatic region. Higher levels of addition reduced sulfonate adsorption considerably, even beyond the electrostatic region. The effect of short chain, completely miscible alcohols is considered to be due to an increase in the solvent power of

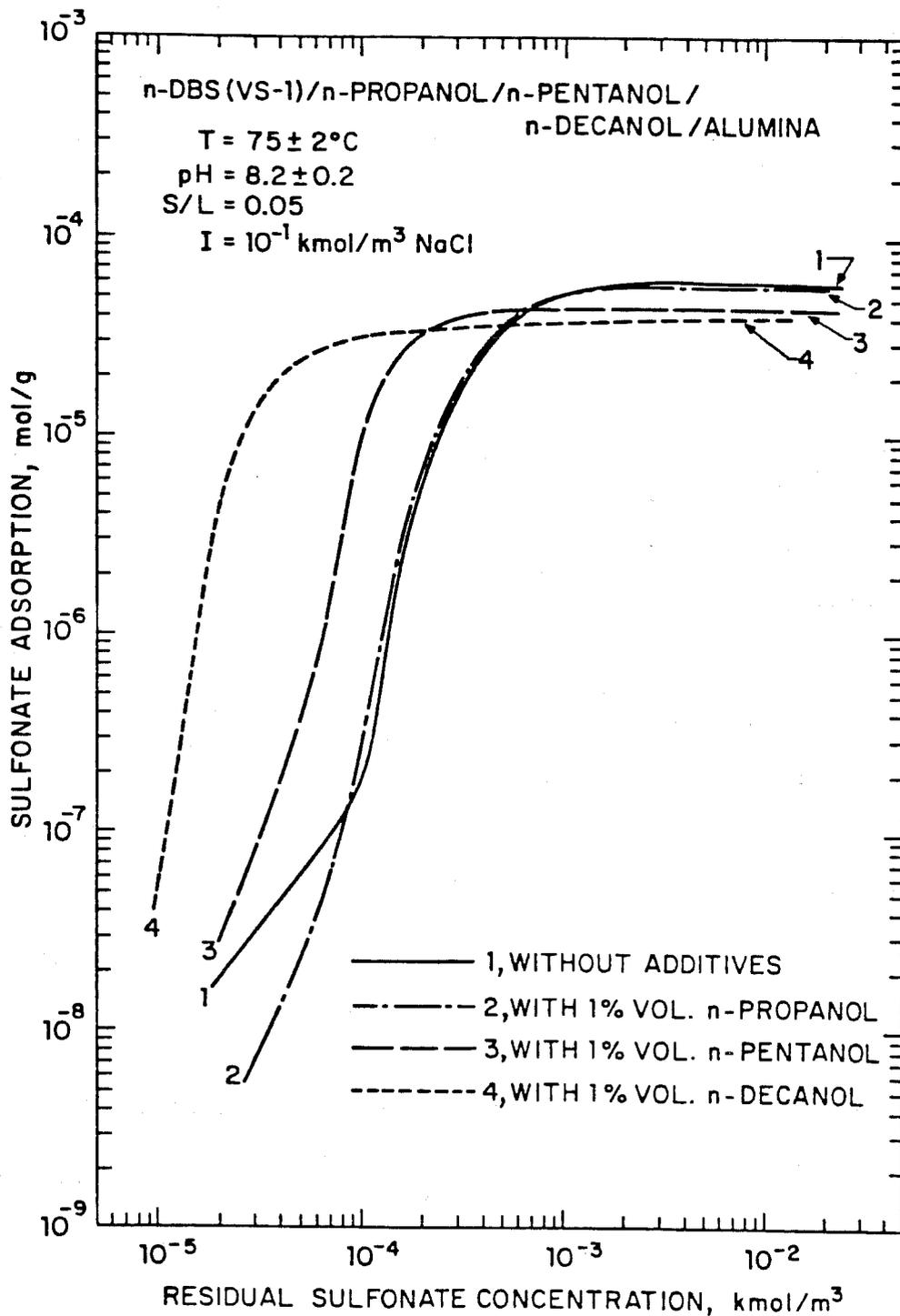


Figure 24: Effect of alcohols on the adsorption of n-DBS (Sodium n-decylbenzenesulfonate) on alumina at 75 degrees C in 10⁻¹ kmol/m³ NaCl.

the medium, which results in the observed decrease in adsorption. Medium and long chain alcohols such as pentanol and decanol which have low aqueous solubility compared to propanol cannot be expected to increase the solubility of ionic surfactants markedly. More importantly, co-adsorption of these molecules at the solid-liquid interface can be expected to enhance hemimicellization, which results in an increase in sulfonate adsorption in the pre-micellar region as seen in Figure 23. This adsorption enhancement can, however, be expected only under submonolayer conditions. Under conditions of saturation and near saturation adsorption, co-adsorption of alcohol should be expected to lead to a competition of alcohol with sulfonate species for adsorption sites. The decrease in the plateau adsorption seen especially with decanol supports this hypothesis of co-adsorption. In order to develop a quantitative model for surfactant adsorption in these systems, detailed studies involving simultaneous determination of adsorption of both the surfactant and the alcohol at various levels of alcohol addition were conducted (using ^{14}C -labelled alcohol and HPLC technique).

The solubility of decanol under our experimental conditions is $2 \times 10^{-4} \text{ kmol/m}^3$. The uptake of decanol and sulfonate below the solubility level of decanol ($6.7 \times 10^{-5} \text{ kmol/m}^3$) on Al_2O_3 is given in Figure 25. Clearly, decanol at this very low concentration has a less pronounced effect on sulfonate adsorption. The most noticeable effect is the decrease in the

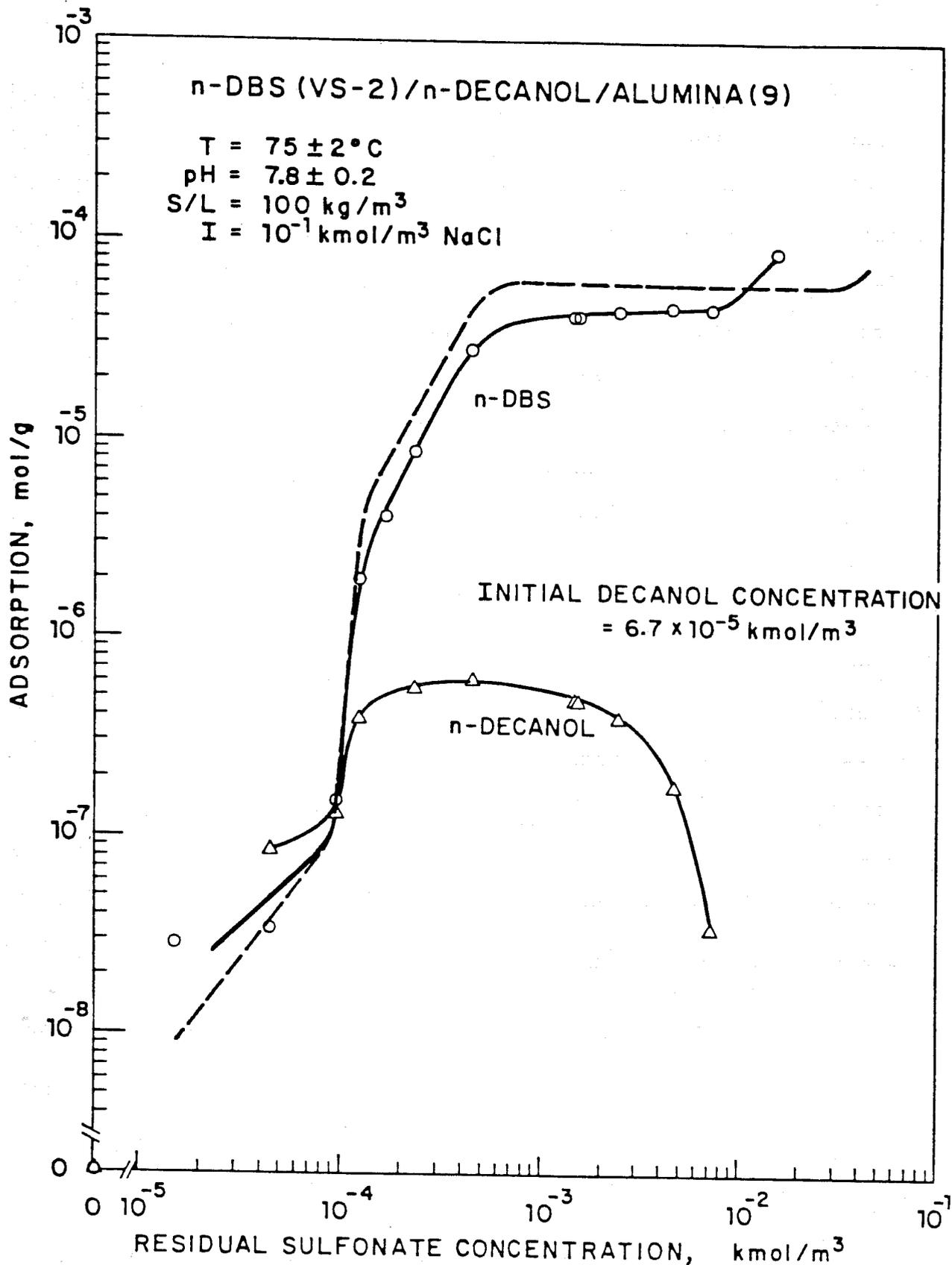


Figure 25: The uptake of decanol and n-DBS (Sodium n-Decylbenzenesulfonate) on alumina at 75 degrees C in 10⁻¹ kmol/m³ NaCl.

plateau adsorption from 6.2×10^{-5} mol/g to 4.8×10^{-5} mol/g. The decanol adsorption curve exhibits a maximum at approximately the same residual sulfonate concentration where sulfonate adsorption reaches a plateau. A similar observation was made for the n-DBS/dodecane system. The decrease in decanol abstraction above 6×10^{-4} kmol/m³ can be attributed to micellar solubilization. It is interesting to note that the decanol adsorption varied from zero in the absence of surfactant to about 90% at the maximum. This clearly shows the synergism involved between sulfonate and alcohol at the solid - liquid interface. The partitioning coefficient of alcohol in the micellar phase to alcohol in the aqueous phase was determined by Gettin's method and the value of K was found to be 1900 m³/kmol, indicating that decanol is strongly solubilized by micelles.

6. POLYMER SURFACTANT INTERACTIONS

Interactions between polymer and surfactant can be of significance in enhanced oil recovery processes. The extent of interactions between charged and uncharged polyacrylamide and sodium dodecylsulfonate or dodecylamine hydrochloride, on polymer solution properties such as surface tension, relative viscosity, conductivity, and precipitation behavior, was studied. Significant bulk interaction was found to occur between nonionic polyacrylamide and anionic dodecylsulfonate (see Figure 26). Similar results were obtained with cationic dodecylamine hydrochloride and anionic polyacrylamide systems. In the case of

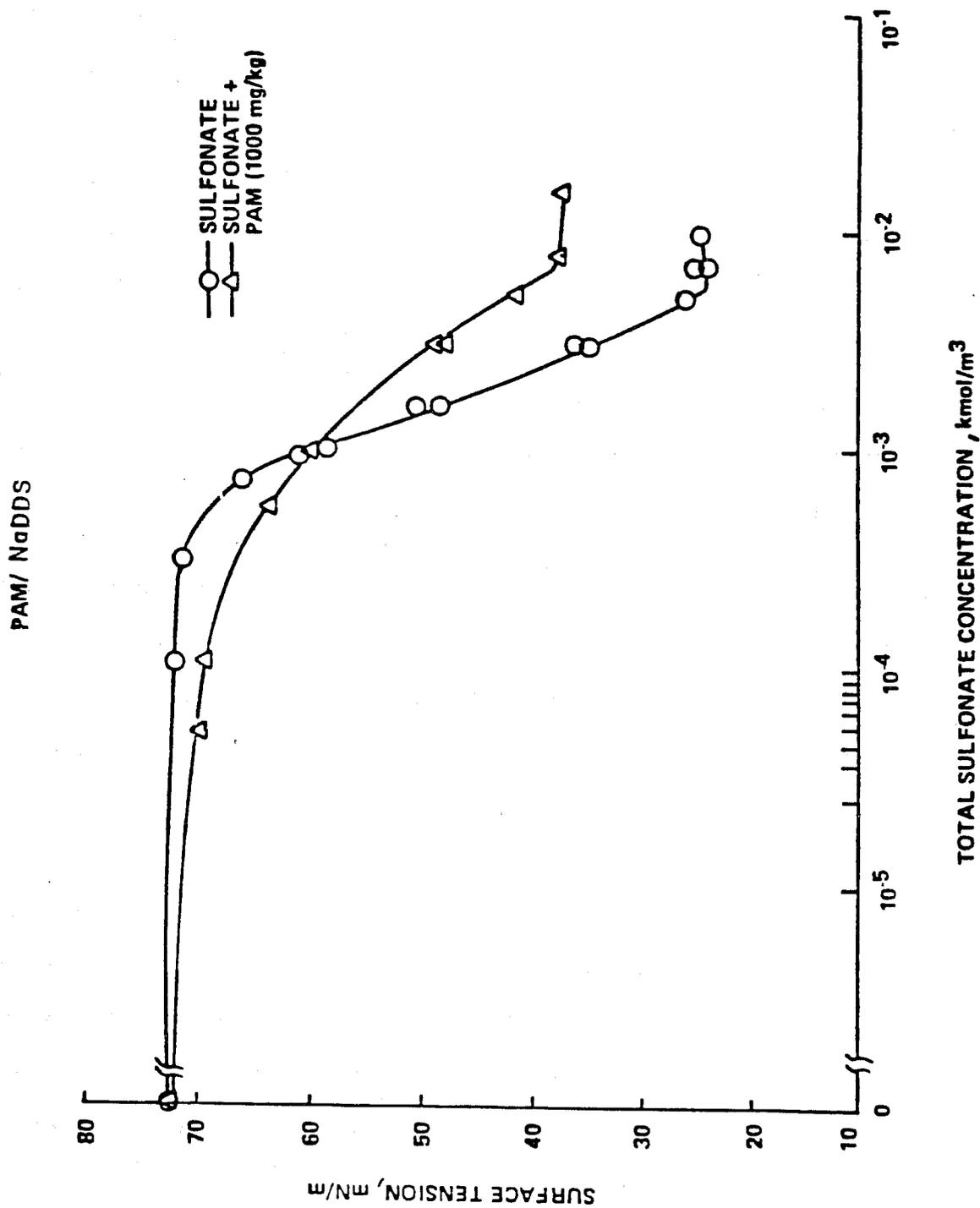


Figure 26: Effect of addition of PAM (nonionic polyacrylamide) on the surface tension of dodecylsulfonate.

oppositely charged polymer and surfactant systems, bulk complexation takes place to a significant extent. Also, depending upon the ionic nature of the polymer and the surfactant, they can precipitate and in some cases the precipitate thus formed can redissolve upon increasing the surfactant concentration (see Figure 27). Redissolution of the precipitate is suggested to occur through micellar solubilization or through complexations. Redissolution of the precipitate was found to occur in the anionic polyacrylamide-dodecylamine system. Redissolution was not found to occur in the system dodecylsulfonate/cationic polyacrylamide.

It is to be noted that the type of modification observed in bulk properties can also result in major changes in the adsorption of different species at various interfaces, and thereby affect processes such as wetting. This is illustrated in Figures 28 and 29. The hydrophobic quartz surface with adsorbed dodecylamine can be converted to a hydrophilic one by the addition of a cationic polymer (acrylamide-methylacrylamidopropyltrimethylammonium chloride co-polymer) without any change in the adsorption of the amine itself (see insert). Electrokinetic measurements indicated that as long as polymer is adsorbed, irrespective of amine adsorption and potential of the bare quartz particle, the measured zeta potential was characteristic of a surface masked entirely by the polymer. Based on the above results a molecular model depicted in Figure 29a is proposed for the polymer surfactant layer of the

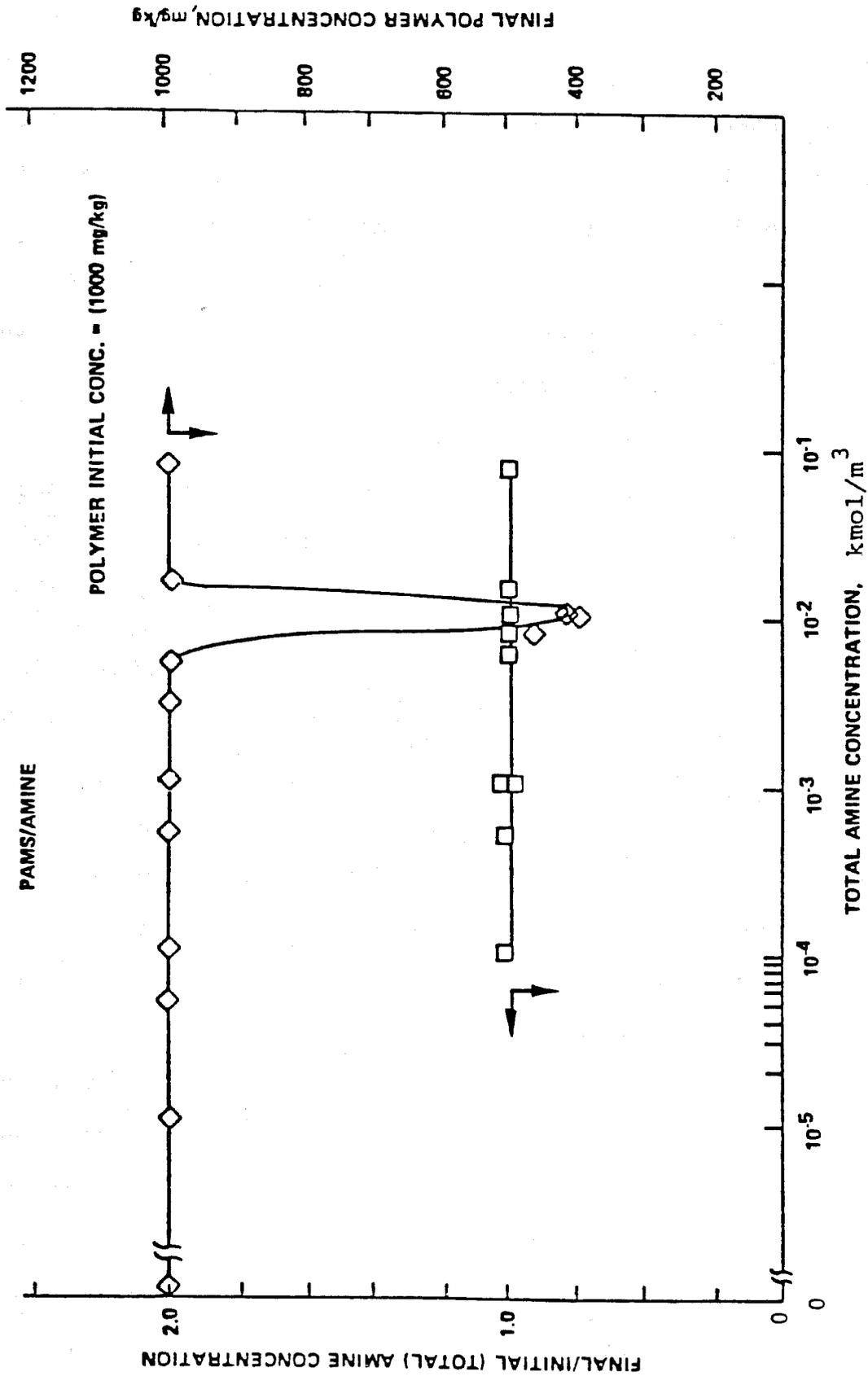


Figure 27: Effect of dodecylamine concentration on the precipitation behavior of PAMS (anionic polyacrylamide) and dodecylamine mixture.

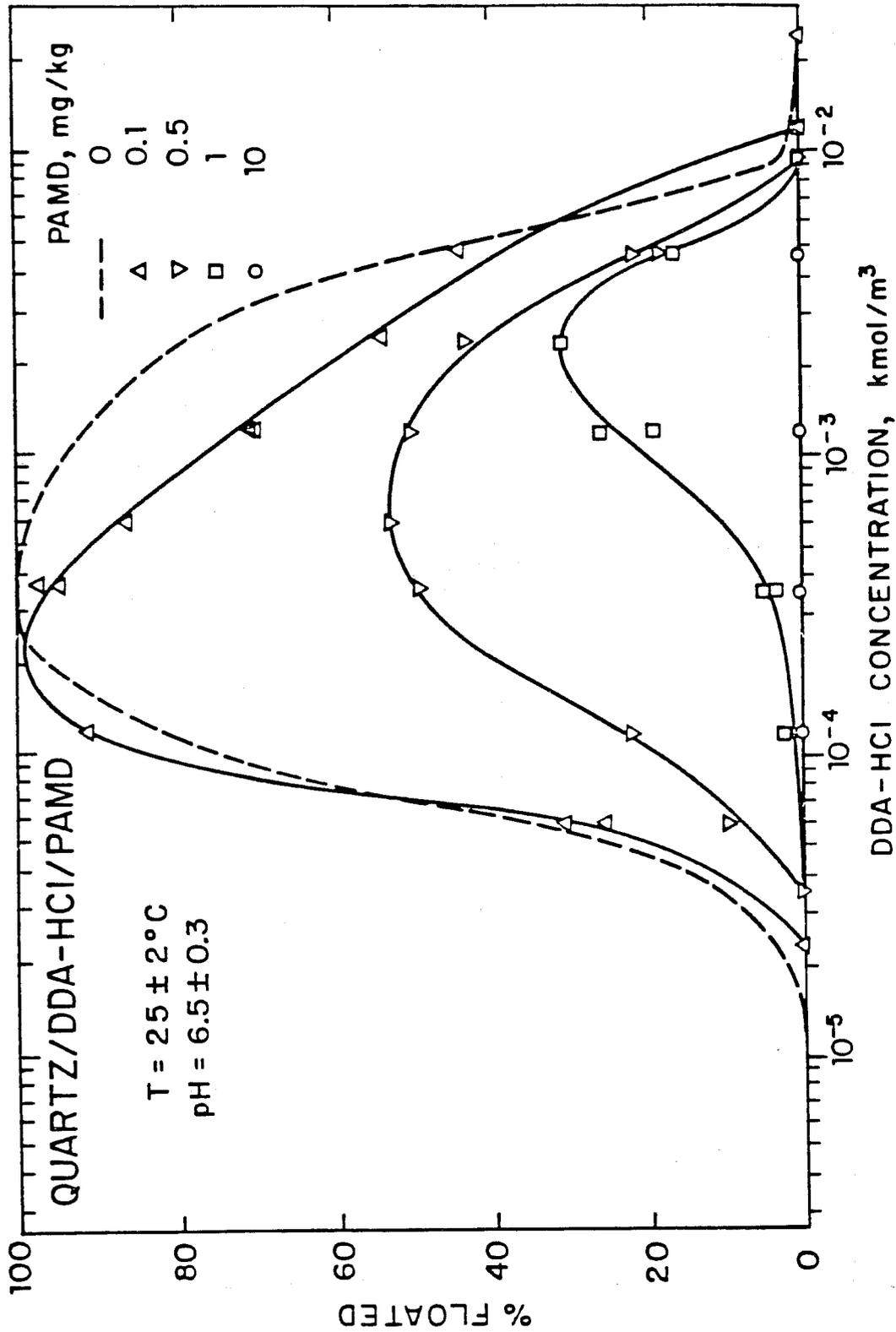
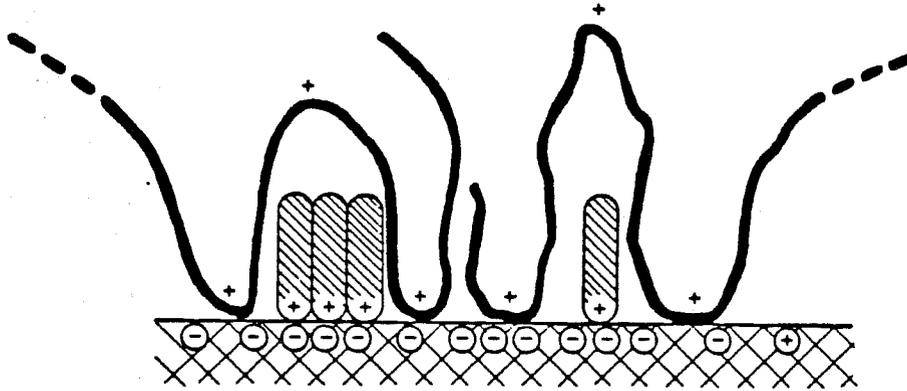
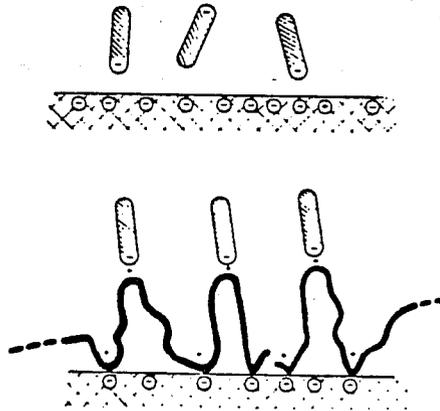


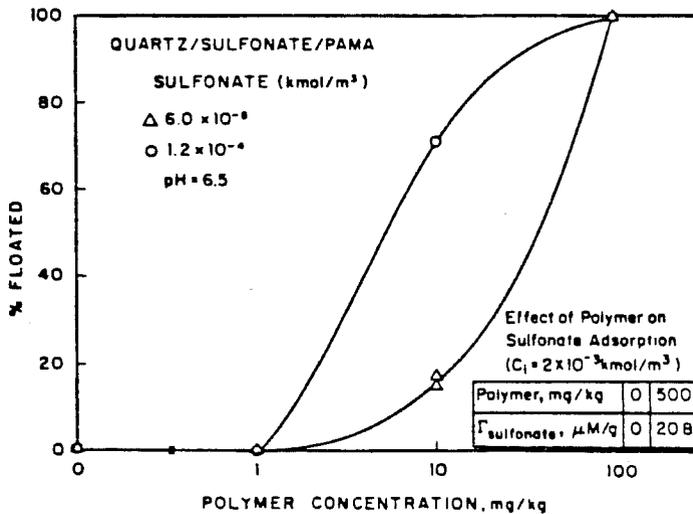
Figure 28: Effect of cationic polymer, PAMD, on the wettability of quartz as measured by its flotation in DDA-HCl solutions.



A. Schematic representation of cationic polymer-dodecylamine layer on quartz.



B. Schematic representation of the activation of quartz for sulfonate adsorption by cationic polymer.



C. Flotation and adsorption activation of quartz/dodecylsulfonate system using cationic polymer.

Figure 29

quartz particle to account for the hydrophilic characteristics. On the basis of the above model, adsorption of anionic dodecylsulfonate was found to be activated by the cationic polymer, resulting in a hydrophobic surface (Figure 29b and 29c).

Thus, it is seen that the nature of polymer/ surfactant interactions at the solid-liquid interface can markedly affect surfactant adsorption and influence wettability of the reservoir rock, both of which are important in determining the overall efficiency of micellar flooding processes.

7. SUMMARY AND SUGGESTIONS FOR FUTURE RESEARCH

Our studies with mineral-surfactant systems have shown that adsorption and precipitation are the major causes for the loss of surfactants, and in order to understand the complex phenomena of surfactant loss in micellar flooding systems we have directed our efforts to identify the roles of the major system parameters such as mineralogy, surfactant structure, and the levels of other components (inorganics, organics, oils, alcohols, and polymers).

Investigations using simpler systems have clearly shown that mineralogy of the rock plays an important role. Many other sub-processes leading to surfactant loss that could occur in a flooding system are controlled to a significant extent by the complex mineralogy of the reservoir rock, which contains oxides, silicates and salt-type minerals (minerals with high solubility). For example, in the presence of salt-type minerals, surfactant loss is mainly in the form of precipitation. Such precipitation has to be minimized in order to improve the economic feasibility of the process. The use of complexing agents or sacrificial agents represent possible solutions, although sufficient studies have not been carried out in this regard so far. Adsorption studies with mixed mineral systems using gypsum (salt-type mineral) as one of the components in the mixture, have shown that surface conversion and possible formation of other minerals can take place under certain conditions. The role of mineralogy becomes increasingly complex

in reservoir environments which can contain numerous salt type minerals, including gypsum, calcite and magnesite. Future research must be aimed at understanding the complex role of these salt type minerals.

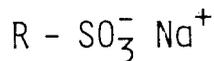
Solution chemistry studies have shown that dissolved inorganics from salt type and other minerals present in the reservoir rock are responsible for surfactant loss by precipitation, and that such losses can be prevented by employing structurally modified surfactants. Studies with ethoxylated surfactants have shown that this modification may have the required salt tolerance characteristics so that precipitation loss can be minimized. The precise role of ethoxylation in inhibiting precipitation, as well as its role in adsorption phenomena has not yet been thoroughly investigated. Commercially available ethoxylated surfactants contain unsulfonated nonionic and isomeric impurities. Efforts should be directed towards synthesis and purification of isomerically pure ethoxylated sulfonates to make it possible to elucidate the mechanisms involving these surfactants.

In addition to interactions of surfactants involving inorganics (mono and multivalent ions), interactions between surfactants (dimerization, micellization), and between surfactant and oil/alcohols/polymers take place in bulk as well as in the adsorbed layer. This may result in significant changes in adsorption, precipitation, rock wettability etc. Marked

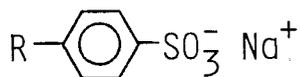
synergistic effects have been observed involving adsorption of surfactants in the presence of oils and alcohols. In addition, interactions involving polymers and surfactants have been shown to drastically alter rock wettability. Both surfactant adsorption and wettability are important for the overall efficiency of micellar flooding processes. However, sufficient data are not available to fully analyze these effects. Detailed investigations on such interactions with relevant mineral systems need to be carried out with the aim of developing the required basic information.

APPENDIX I

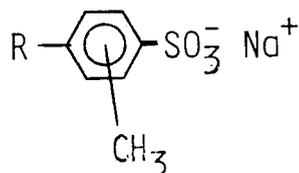
CHEMICAL STRUCTURE OF SURFACTANTS



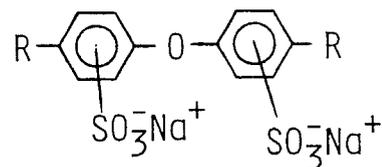
ALKYLSULFONATES



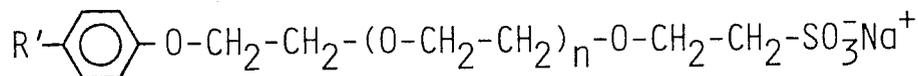
ALKYLARYLSULFONATES



XYLENESULFONATES



DOWFAX 3B2



ALKYLARYLETHOXYLATED SULFONATE

n = 0.5: TRITON X-202

n = 1.0: TRITON X-200

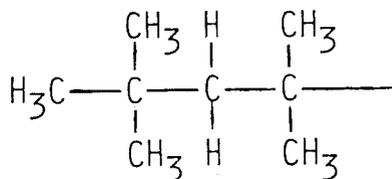
n = 1.5: ALIPAL SE463

R: $\text{CH}_3 - \text{CH}_2 -$ OCTYL

$\text{CH}_3 - \text{CH}_2 -$ DECYL

$\text{CH}_3 - \text{CH}_2 -$ DODECYL

R':



TERTIARY OCTYL