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Adsorption of surfactants on minerals for wettability control in improved oil recovery processes

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Abstract

Chemical-flooding schemes for recovering residual oil have been in general less than satisfactory due to loss of chemicals by adsorption on reservoir rocks, precipitation, and resultant changes in rock wettability. Adsorption and wettability changes are determined mainly by the chemical structure and mix of the surfactants, surface properties of the rock, composition of the oil and reservoir fluids, nature of the polymers added and solution conditions such as salinity, pH and temperature. The mineralogical composition of reservoir rocks plays an important role in determining interactions between reservoir minerals and externally added reagents (surfactants/polymers) and their effects on solid–liquid interfacial properties such as surface charge and wettability. Some of the reservoir minerals can be sparingly soluble causing precipitation and changes in wettabilty as well as drastic depletion of surfactants/polymers.

Most importantly, the effect of surfactants on wettability depends not only how much is adsorbed but also on how they adsorb. A water wetted rock surface that is beneficial for displacement of oil can be obtained by manipulating the orientation of the adsorbed layers. New surfactants capable of tolerating harsh conditions created by extremes of pH, temperature or inorganics and capable of interacting favorably with inorganics and polymers are promising for enhanced oil recovery. In this regard, such surfactants as sugar based ones and pyrrolidones are attracting attention, as they are also biodegradable. In many cases, mixed surfactants perform much better than single surfactants due to synergetic effects and ability to alleviate precipitation. Also, addition of inorganics such as silicates, phosphates and carbonates and polymers such as lignins can be used to control the adsorption and the wettability. In this paper, use of specialty surfactants and their mixtures is discussed along with the mechanisms involved.
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1. Introduction

A large amount of oil is still trapped in reservoirs after the traditional oil production and a number of techniques have been proposed for recovering such residual oil.

Surfactant flooding is one of the enhanced oil recovery processes considered most promising but it is often uneconomical due to loss of chemicals by adsorption on reservoir rocks and precipitation and resultant changes in rock wettability. In addition, soluble minerals, which occur in many reservoirs, can cause further changes in interaction of surfactants with rocks and their wettability. Adsorption and wettability are also affected by the presence of other inorganic, organic or polymeric additives. Sacrificial agents

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such as silicates, carbonates and lignins have been suggested to reduce adsorption and control wettability. Availability of modern equipment such as atomic force microscopy, analytical ultracentrifuge, fluorescence and electron spin resonance spectrophotometers has made it possible to monitor such nanostructure of interfacial layers, and to correlate the nanostructure with interfacial performance and thereby identify the optimum conditions.

In this paper, our work on the adsorption of surfactants on minerals and its effect on mineral wettability is discussed along with the role of dissolved mineral species in the system following a discussion of the methods to measure the wettability of minerals in various forms.

2. Techniques for monitoring wettability

Various experimental techniques have been developed to measure the wettability of surface. These techniques include contact angle measurement, two phase separation, bubble pickup, microflotation, and vacuum flotation, and are based on the fact that water wetting process is essentially an oil displacement phenomenon on the solid surface. In this process the degree of wetting (or wettability) is governed by the surface free energy of the substrate and the wetting solution. The surface that has a higher surface free energy tends to be replaced by a liquid that has a lower surface free energy, thus reducing the total free energy of the system.

Wetting has been described in terms of spreading coefficient. For a liquid spreading on solid in the air, the spreading coefficient, σ^{LSG}, is defined as

$$\sigma^{LSG} = \gamma^{SG} - \gamma^{SL} - \gamma^{LG}$$

where γ^{SG}, γ^{SL}, and γ^{LG} are solid/gas, solid/liquid and liquid/gas interface tensions. When σ^{LSG} is positive, spreading of the liquid occurs spontaneously. Since it is very difficult to determine γ^{SG} directly, Young's equation is employed by considering the equilibrium between force vectors at the S/L/G contact:

$$\gamma^{SG} = \gamma^{SL} + \gamma^{LG}\cos\theta$$

where θ is angle of contact that the liquid/gas interface subtends with the solid/liquid interface (Fig. 1).

From Fig. 1, it can be seen that contact angle, θ, is a direct measure of the surface wettability. A contact angle of 0° indicates total hydrophilicity (zero hydrophobicity or complete water wettability), whereas an angle of 180° means the surface is totally hydrophobic (no hydrophilicity or complete oil wettability). It is to be noted that minimum contact angle to avoid oil wettability will vary depending on the mineral and even its history. The
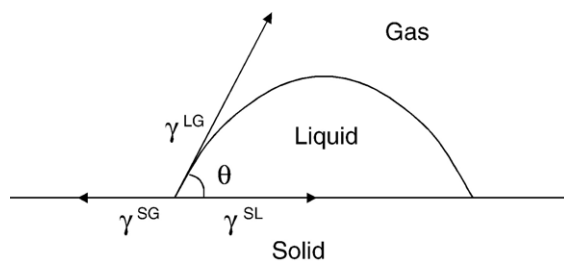

Fig. 1. Interfacial tensions and contact angle.

wettability threshold for hematite or even silica that is aged in water and hence hydrated will be higher than 10°, while that for pyrite or galena can be 1° or less. Furthermore these angles will also depend markedly on the porous nature of the mineral due to possible presence of air micro- and nano-bubbles in the crevices.

Techniques to measure contact angle include direct measurement based on projected or photographed images as well as indirect evaluations in which the angle is calculated from measured dimensions or measured mass of sessile drops (Fig. 2).

For contact angle measurements, the solid surface needs to be polished and stored free from contamination. Due to surface roughness, contamination, nonequilibrium adsorption, and mineralogical heterogeneity, the measured data could have considerable variation. The requirement of polished surfaces for contact angle measurements often limits its practical application since rock sample surfaces are invariably rough. Many different techniques have been developed for measuring the wettability of particulate minerals, each technique with its advantages and limitations (Somasundaran and Ananthapadmanabhan, 1985). Choice of the techniques depends on the mineral size and shape and the phenomenon that is being studied.

2.1. Two-phase separation

The wettability of particle can be easily determined by mixing toluene with mineral–water system in a separatory funnel. The mineral–water–toluene system is shaken for desired time interval and then allowed to separate. The two phases (aqueous and toluene) are allowed to flow out of the funnel separately and weight of the mineral particle in these phases and interface measured. The wettability is calculated as the percentage of solid that is in aqueous phase.

2.2. Induction time

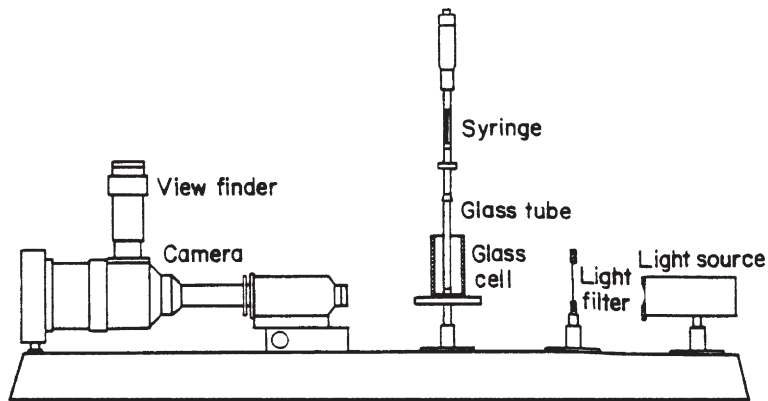During the course of the attachment of a bubble to a particle, the liquid film separating the bubble and the

Fig. 2. Schematic diagram of contact angle setup.

solid thins and finally ruptures. In most cases the time period between the contact of the bubble with the particle and its adhesion is called the induction time. The time taken for the process of drainage of the liquid film contributes towards induction time. A technique to determine induction time has been developed based on a captive bubble contacting a submerged bed of solid particles. The frequency of vibration is varied and the time period corresponding to the frequency at which the attachment just occurs is taken as the induction period (Yoon and Yordan, 1991).

2.3. Bubble pickup

In this technique a single bubble created at the end of a capillary by applying pressure to a rubber bulb is contacted with a suspension of particles and the amount of minerals collected on the bubble is estimated. A steady-state concentration of particles on the bubble surface can be obtained by introducing shear force into the system by stirring. An alternative procedure is to produce the bubble at the end of a capillary and letting the bubble contact the mineral bed, rather than a suspension of the particles (Fig. 3).

2.4. Centrifugal immersion

This technique is based on the force required to detach particles from the liquid/air or the liquid/liquid interface. To determine the centrifugal force required to wet and immerse the particles, fine particles are gently placed on the surface of water or at the interface in a centrifuge tube and subjected to a given centrifugal force for a constant time. Float and sink fractions are separated and weighed. The weight data as a function of speed of rotation of the centrifuge is used for constructing the partition curves (Ramesh and Somasundaran, 1990).

2.5. Microflotation

Microflotation using a modified Hallimond tube, shown in Fig. 4, can be used to measure the wettability of relatively coarse particles. The cell consists a glass well with a frit with uniform pore size at the bottom, and a bent glass tube with a vertical stem just above the bent. A Teflon-coated magnetic stirring bar inside the tube is used to keep the particles in suspension. In Hallimond tube, hydrophobic particles attach themselves to the rising air bubbles and levitate to the top of the cell. The floated product falls into the vertical stem or stay attached to the top part of the cell from where it is separated and weighed.

2.6. Film flotation

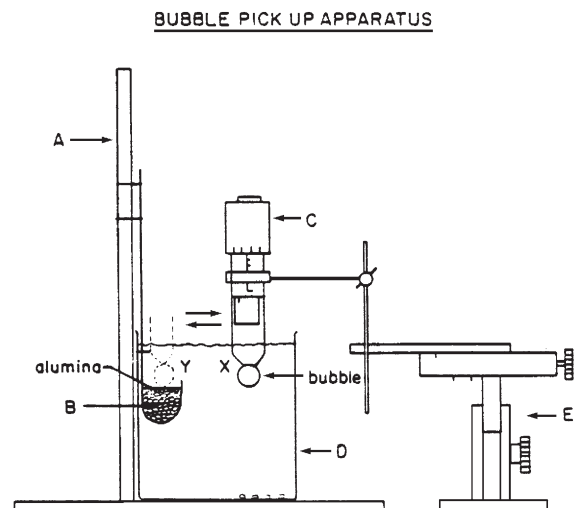In this technique, a monolayer of particles is placed onto the surface of a liquid of given surface tension,

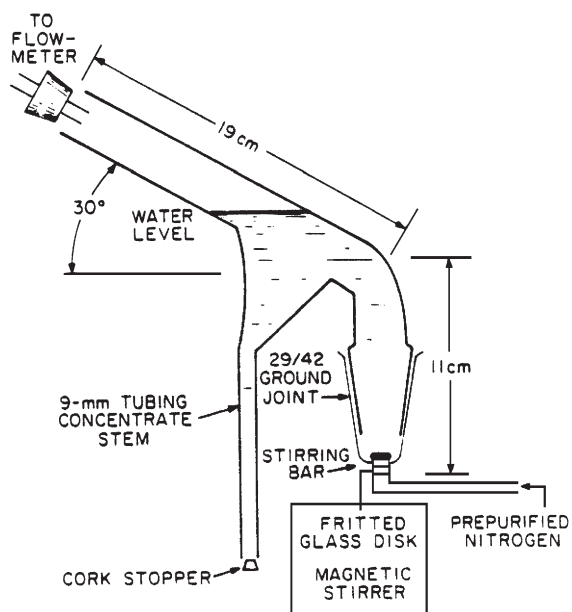Fig. 3. Schematic diagram of a bubble pickup setup.

Fig. 4. Hallimond Tube Setup.

usually a water–methanol mixture. In this procedure, the particles are partitioned into hydrophilic and hydrophobic fractions, which are then filtered, dried, and weighed. The weight percent of the hydrophilic fraction is plotted as a function of solution surface tension and a wetting tension distribution diagram is obtained for the wettability of the particles (Fuerstenau et al., 1998). However, in this method wettability data is for water-advancing contact angle. Also, the interference from the ethanol should be noted.

2.7. Levitation

The technique uses a modified Buchner funnel with a coarse sintered glass frit and an annular ring for collecting the levitated product (Fig. 5). A slurry of particles in solution is first transferred to the funnel and the excess solution is drawn out through the frit using a peristaltic pump. The flow is then reversed immediately after air bubbles are seen breaking through the frit. Hydrophobic particles, carried upwards from the air–water interface, are separated from the hydrophilic ones, and a wettability index is obtained based on weight percent float in the test (Li et al., 1993).

In addition to the techniques discussed above, there are many other wettability measurement methods used in the oil industry (Anderson, 1986; Dubey and Waxman, 1991; Spinler and Baldwin, 2000). All these techniques have their advantages and limitations. Before interpreting the wettability data obtained, it is important to examine the relevance of each method used.

3. Surfactant adsorption and wettability

Surfactant molecules contain both hydrophilic and hydrophobic moieties. They can adsorb to a significant extent even at very low concentrations. They can also form aggregates in solutions and at the solid/liquid interface by hydrophobic interactions above a concentration. Such adsorption of surfactants on solid can lead to changes in a variety of interfacial phenomena such as wetting behavior (oil displacement, flotation, detergency) and colloid stability (dispersion, flocculation). There are a number of mechanisms for adsorption such as electrostatic attraction/repulsion, ion-exchange, chemisorption, chain–chain interactions, hydrogen bonding and hydrophobic bonding. The nature of the surfactants, minerals and solution conditions as well as the mineralogical composition of reservoir rocks play a governing role in determining the interactions between the reservoir minerals and externally added reagents (surfactants/polymers) and their effect on solid–liquid interfacial properties such as surface charge and wettability.

The wettability of the minerals and hence the oil displacement is determined by adsorption of surfactants on the minerals and the orientation the surfactant assumes. Adsorption of surfactants on solid itself has been studied extensively (Somasundaran and Fuerstenau, 1966, 1972a; Scamehorn et al., 1982). The adsorption isotherms of long chain ionic surfactants on minerals are illustrated in Fig. 6. The S–F isotherm, in this figure, originally proposed by Somasundaran and Fuerstenau usually exhibits four characteristic regions (Chander et al., 1986).

Adsorption in various regions was explained by Somasundaran and Fuerstenau by considering electrostatic, hydrophobic and micellar interactions in the system: in Region I, the surfactant adsorbs mainly by electrostatic interactions between the surfactant headgroup and the charged sites on the mineral surface. In
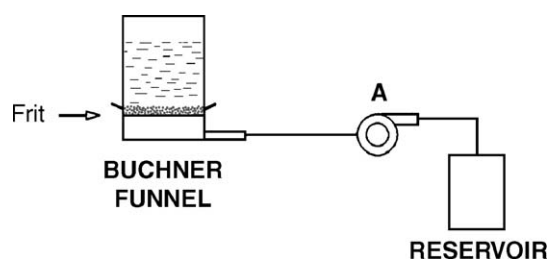

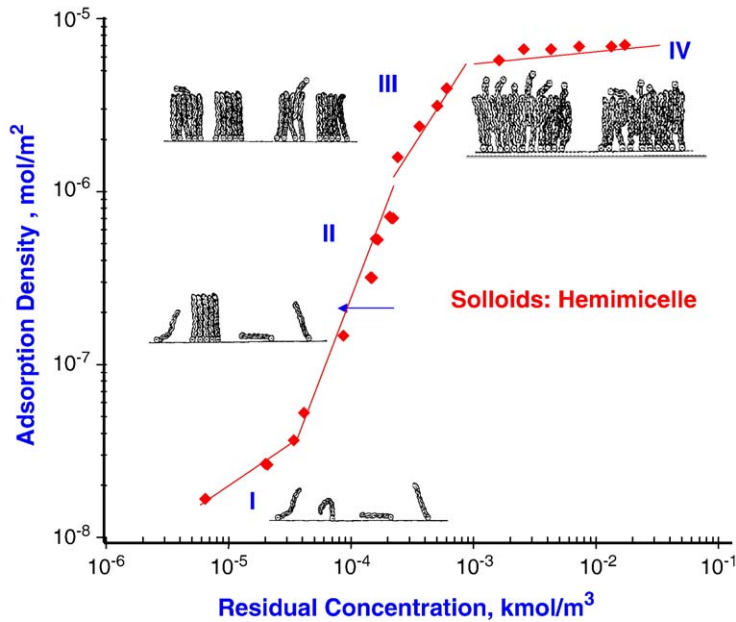Fig. 5. Schematic Diagram of Levitation device.

Fig. 6. Schematic representation of the growth of aggregates for various regions of the adsorption isotherm.

region II, there is a marked increase in the adsorption resulting from the interaction of the hydrophobic chains of ongoing surfactants with those previous adsorbed surfactants. This aggregation of hydrophobic groups, occur at concentrations far below the critical micelle concentration of the surfactant with the microstructures formed called solloids (*s*urface *colloids*, also termed hemimicelles in some cases) (Somasundaran and Kunjappu, 1989). In this region adsorption is due to electrostatic attraction between the surface sites and the

oppositely charged surfactant species and hydrophobic interactions between the hydrocarbon chains. At the end of the region II, the surface is electrically neutralized and further adsorption in region III takes place due to chain–chain hydrophobic interactions alone, countered by electrostatic repulsion that builds up as the surface begin to acquire the same charge as the adsorbing surfactant ions. Above the cmc of the surfactant in Region IV, monomer activity is essentially constant and under these conditions adsorption also remains constant.
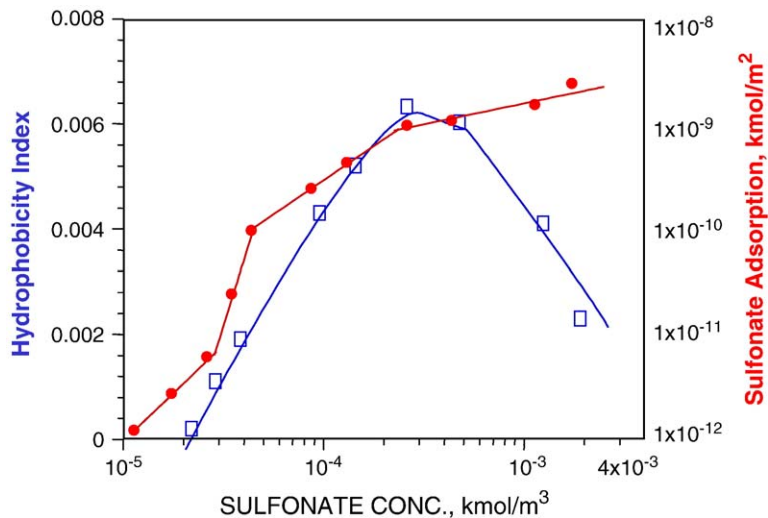

Fig. 7. Adsorption of *n*-dodecylbenzensulfonate and its effect on the hydrophobicity of lumina: (●) adsorption density, (□) hydrophobicity.
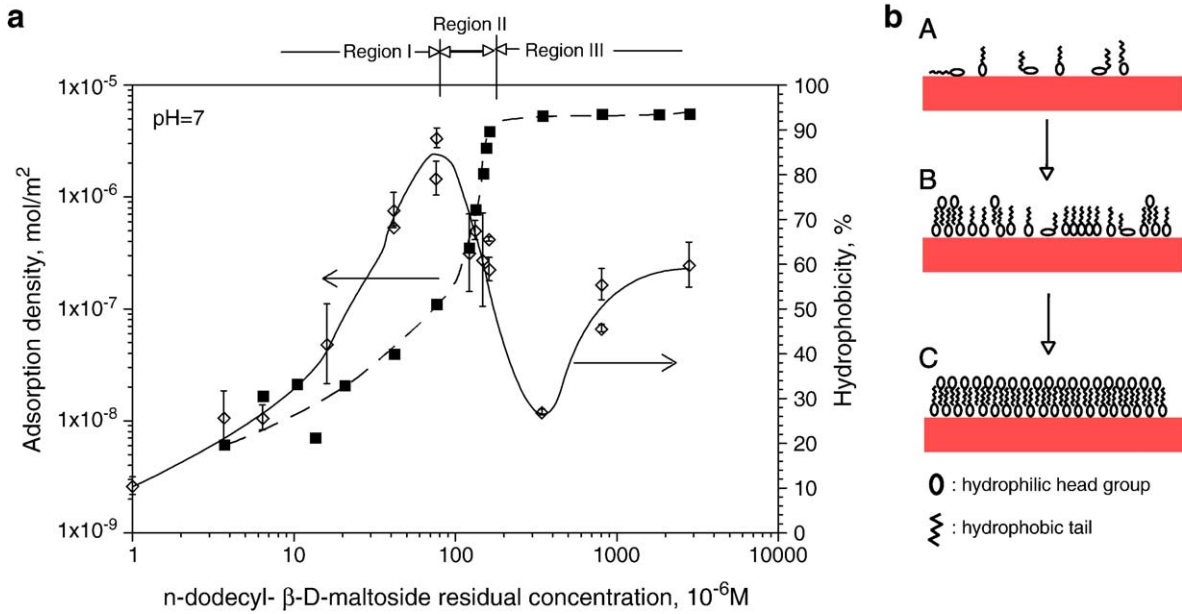
Fig. 8. (a) Adsorption of *n*-dodecyl-*β*-D-maltoside and its effect on the hydrophobicity of alumina particles. (b) Orientation model for the conformation of surfactant at the surfaces. A, B, C indicate the successive stages of adsorption.

Wettability of a solid surface is altered markedly by the adsorption of surfactants and this is clearly illustrated in Fig. 7 where the effect of anionic *n*-dodecylbenzensulfonate adsorption on the wettability of the alumina is shown along with the adsorption isotherm. In the Region I the surface is water wetted and in the Region II it is oil wetted while in regions III and IV it begins to become less oil wetted. In the absence of the surfactant the alumina exhibits complete hydrophilicity. With the surfactants aggregating on alumina, the surface becomes hydrophobic due to the surfactant orienting their hydrophobic tails towards the bulk solution. The hydrophobicity reaches a maximum at the end of region II where the surface charge is neutralized completely and then drops. The drop in hydrophobicity is attributed to adsorption with some of
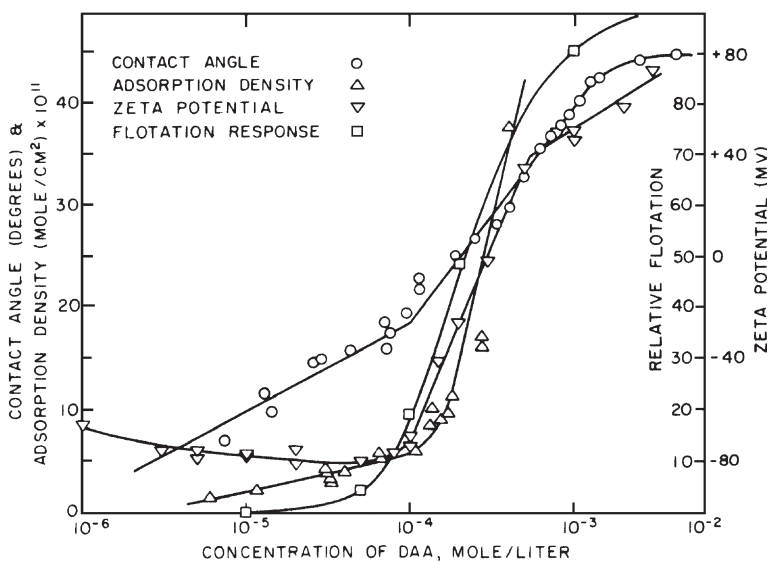

Fig. 9. Correlation of adsorption, contact angle, flotation response and zeta potential for quartz as a function of dodecylammonium acetate concentration at pH 6 to 7, 20 to 25 °C.
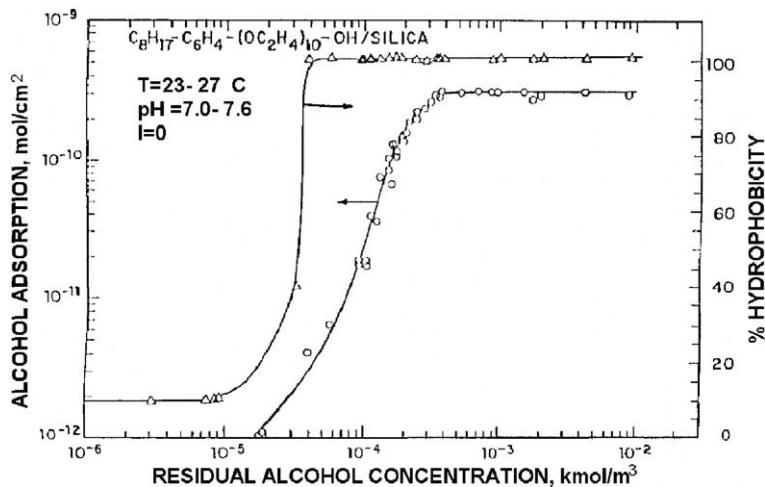
Fig. 10. Changes in the hydrophobicity of silica particles with adsorption of $C_8\Phi EO_{10}$.

the hydrophilic groups oriented towards the aqueous phase. The lower hydrophobicity in the plateau region is possibly caused by the bilayer adsorption, since that can render the surface hydrophilic. Similar results have been reported for nonionic *n*-dodecyl-β-D-maltoside adsorption on alumina and its effect on alumina wettability (Fig. 8a) (Zhang et al., 1997). An orientation scheme is proposed in Fig. 8b for the adsorption of *n*-dodecyl-β-D-maltoside on the alumina. The effect of surfactant orientation on the wettability of alumina is to be noted.

Various interfacial properties of the minerals have been investigated for the quartz/dodecylamine system further illustrating the role of adsorption and conformation of surfactants at interfaces. Effect of adsorption on zeta-potential, contact angle and wettability is shown in Fig. 9 for the cationic surfactant, dodecylammonium acetate (DAA), on quartz (Fuerstenau et al., 1997). For DAA and quartz at neutral pH, increase in adsorption due to association of surfactants adsorbed at the solid–liquid interface into solloids (hemimicelles) occurs at about 10^{-4} M DAA. This marked increase in adsorption density is accompanied by concomitant sharp changes in zeta-potential, contact angle and flotation recovery, again suggesting that wettability depends on the adsorption of surfactant at the solid–liquid interface.

As indicated earlier, the wettability of minerals is affected not only by the amount of surfactant adsorbed, but also by the structure of the adsorbed surfactants. The effect of two alkylphenol ethoxylated surfactant adsorption on the wettability of silica is illustrated in Figs. 10 and 11 (Somasundaran et al., 1991). In these figures, while in the absence of the surfactant the silica surface exhibits complete hydrophilicity, with increase in adsorption of both $C_8\Phi EO_{10}$ and $C_8\Phi EO_{40}$ on silica, the surface
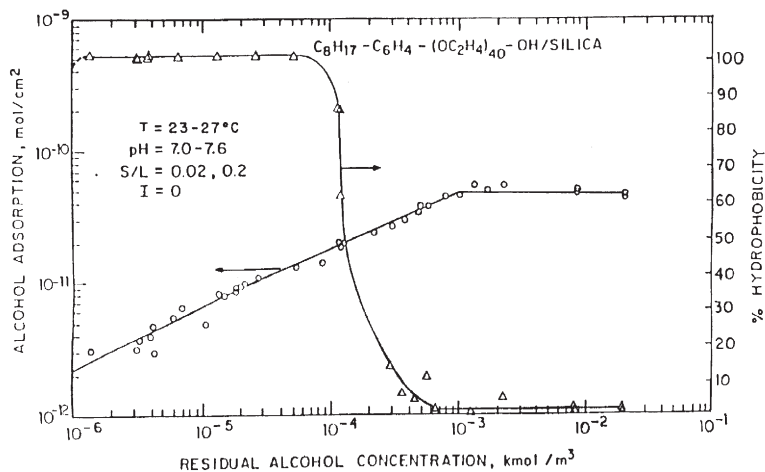

Fig. 11. Changes in the hydrophobicity of silica particles with adsorption of $C_8\Phi O_{40}$.
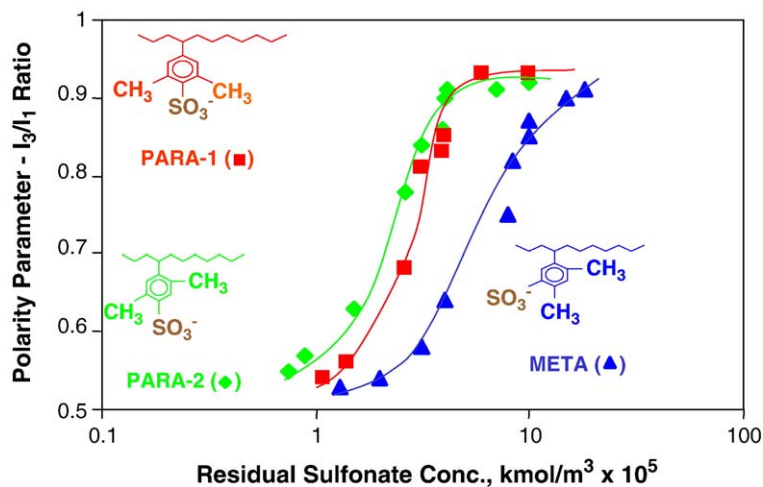
Fig. 12. Adsorption of alkylxylenesulfonates on alumina.

becomes hydrophobic. Whereas silica particles in $C_8\Phi EO_{10}$ solution remain hydrophobic as adsorption is increased, the $C_8\Phi EO_{40}$ surfactant makes the particles hydrophilic above a certain adsorption level. Interestingly, at saturation adsorption of $C_8\Phi EO_{40}$ the hydrophilicity of the silica particles is totally restored.

The change in hydrophobicity of particles is proposed to be the result of the corresponding changes in the orientation of the hydrocarbon chains at the interface. In the low concentration region, the hydrocarbon chains lie flat on the silica surface and render the silica hydrophobic. As adsorption increases, the flat hydrocarbon chains will tend to be squeezed out. In the case of $C_8\Phi EO_{40}$ adsorption, the effective surface area covered by the hydrocarbon chains is reduced, causing a decrease in hydrophobicity. At the maximum plateau adsorption, all the hydrocarbon chains are considered to be perpendicular to the solid surface, resulting in reduced coverage and low hydrophobicity. In the case of $C_8\Phi EO_{10}$, hydrophobicity increases with the adsorption density and remains constant in the plateau region. This is due to the high density of the hydrocarbon chains at the interface. At the plateau adsorption, the number of hydrocarbon chains with E_{10} is four times that of E_{40}.

It is interesting to note that changes in structure, which could appear to be minor, can cause marked differences in adsorption and hydrophobicity. For example, changes in the positions of the sulfonate and the methyl groups on the aromatic rings of alkylxylene sulfonate were found to produce an order of magnitude effect on the adsorption at the solid/liquid interface and hence hydrophobility of the solid (Fig. 12) (Sivakumar and Somasundaran, 1994). The polarity parameter I_3/I_1 from fluorescence spectroscopy represents the micro-

polarity of surfactant aggregates at solid–liquid interface. Typically this value is 0.55–0.6 in polar solvents such as water and 1–1.7 in nonpolar solvents such as hydrocarbons. In Fig. 12, the polarity parameter changes from ∼0.55 (hydrophilic) to ∼0.9 (hydrophobic) as a function of surfactant adsorption, indicating solid surface changes from hydrophilic to hydrophobic.

In addition to surfactants, the presence of the other chemicals such as polymers can also affect markedly the wettability of the minerals. This is illustrated by the fact that an essentially oil wetted quartz surface with adsorbed dodecylamine can be converted to a water wetted one by the addition of a cationic polymer (acrylamide-methacrylamidopropyltrimethyl-ammonium chloride copolymer) without any change in the adsorption of the amine itself. A conformational scheme was proposed with the polymer masking the surfactant layer on the quartz particle to account for the water wettability (Fig. 13) (Cleverdon and Somasundaran, 1985). By a similar approach, adsorption of anionic dodecylsulfonate on negatively charged silica can be activated by a
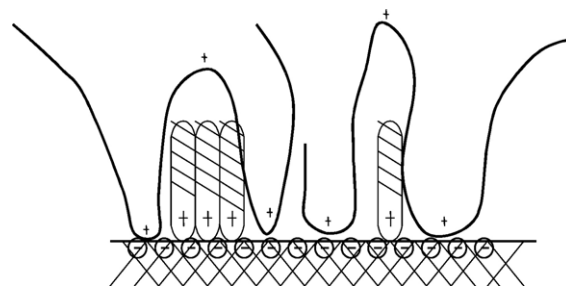

Fig. 13. Schematic representation of cationic polymer-dodecylamine layer on quartz.

cationic polymer, resulting in an oil-wetted surface. The nature of the polymer-surfactant interactions at the solid–liquid interface can thus affect the wettability of reservoir rocks and thereby the over all efficiency of surfactant flooding processes.

In this regard, hybrid polymers have been developed with characteristics of both the polymers and the surfactants (Deo et al., 2003). Hydrophobically modified polymers interact with different surfactants to form mixed aggregates with potential oil solubilization properties. At oil/water interface, they can spread out the hydrophobic and hydrophilic groups appropriately into oil and water phases respectively and potentially be efficient in lowering interfacial tension. These types of polymers are likely to find applications in improved oil recovery as more optimized structures and schemes are formulated.

From the above discussion, it is clear that wettability of minerals can be modified by the surfactant adsorption, which in turn is dependent on the structure of surfactants as well as surfactant/polymer interactions.

4. Effect of dissolved mineral species

In surfactant enhanced oil recovery process, water chemistry plays a profound role in the adsorption/ wetting process by affecting the surfactant-solution equilibria, the mineral-solution equilibria and consequently the interactions between the surfactants and the mineral particles. Relevant interactions in the reservoir rock — flooding solution system include dissolution of solids followed by hydrolysis, complexation and precipitation of the dissolved species, and the interactions between dissolved mineral species with surfactant in the bulk in various forms. The dissolved species, including those introduced from the dissolution of all the minerals present in the rock and those from the water source are the major elements that affect the water chemistry. In systems containing soluble or sparingly soluble minerals such as carbonates, gypsum and clay minerals where the extent of dissolution is measurably higher than that in most oxide systems, the effect of dissolved mineral species can be drastic. In addition, the presence of oil in such systems will further complicate various interactions. Clearly, understanding of the mineral–surfactant–solution–oil chemical equilibrium under different physicochemical conditions is critical for developing efficient reagent and processing schemes for oil recovery. Surfactants, particularly hydrolysable types, exist in many forms in solutions. Their forms can have marked effect on their surfactant activity. For example, a common surfactant, oleic acid, will undergo dissociation to form ions (Ol^-) at high pH values and exist as neutral molecules (HOl) at low pH value. In the intermediate region, the ionic and the neutral molecular species can associate to form ion-molecule complexes (($Ol)_2H^-$). As the surfactant concentration is increased, micellization or precipitation of the surfactant can occur in the solution. In addition, surfactant species can associate to form other aggregates such as the dimer (Ol_2^{2-}) in premicellar solutions. Long chain fatty acids such as oleic acid have very limited solubility, which is a sensitive function of pH. The species distribution of oleic
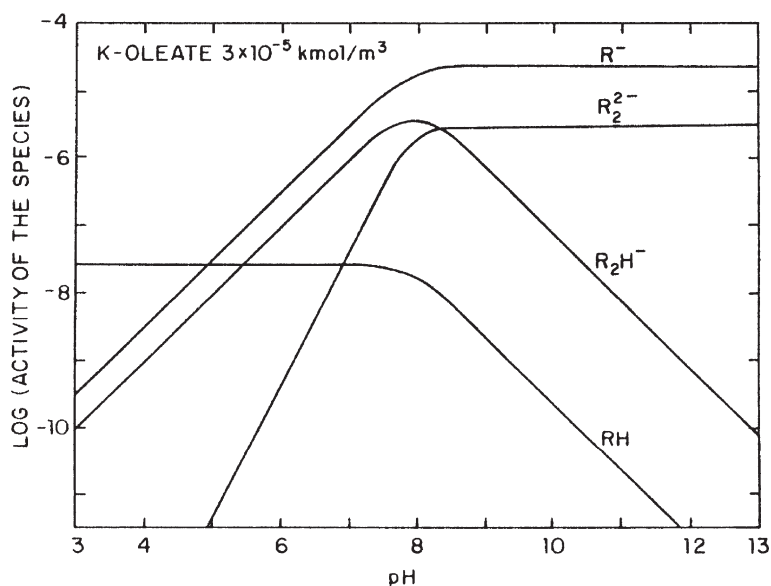

Fig. 14. Oleate species distribution as a function of pH. (Total oleate concentration $= 3 \times 10^{-5}$ M).
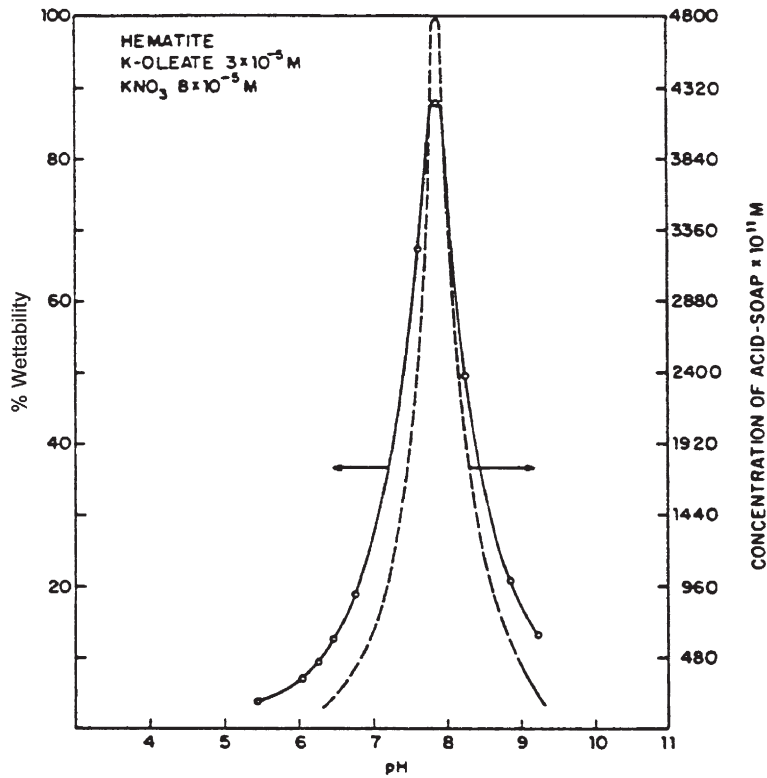
Fig. 15. Correlation of hematite wettability with the acid-soap concentration.

acid based on the above equilibria at a given concentration is shown in Fig. 14 as a function of pH (Ananthapadmanabhan and Somasundaran, 1988). It can be seen from this figure that:

1) The pH of the precipitation of oleic acid at the given concentration is 7.45.
2) The activities of oleic monomer and dimer remain almost constant above the precipitation pH and decrease sharply below it.
3) The activity of the acid-soap $(Ol)_2H^-$ exhibits a maximum in the neutral pH range.

The surface activities of the various surfactant species can be markedly different from each other. It has been estimated that the surface activity of the acid-soap $(Ol)_2H^-$ is five orders of magnitude higher than that of the neutral molecule (HOl) and about seven orders of magnitude higher than that of the oleate monomer Ol^- (Ananthapadmanabhan, 1980). Their effect on the surface wettability is to be noted. For example, in the hematite–oleate system, the pH of sharp maximum in hydrophobicity, as measured by the flotation, corresponds to the pH of maximum acid-soap formation (Fig. 15) (Ananthapadmanabhan and Soma-

sundaran, 1979). Similar effects have been proposed to be responsible for the dependence of the hydrophobicity of silica in amine solutions on pH (Somasundaran,
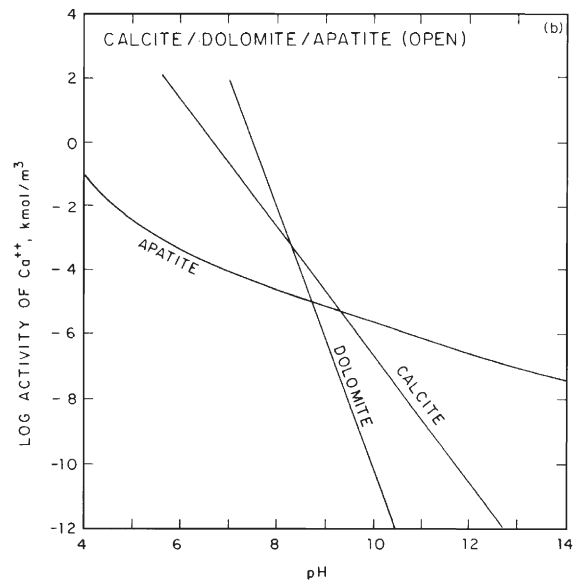

Fig. 16. Stability relation in calcite–apatite–dolomite system open to atmospheric carbon dioxide at 25 °C.

1976). Solution conditions such as temperature also have been shown to affect adsorption as well as hydrophobicity of the minerals (Somasundaran and Fuerstenau, 1966, 1972b; Kulkarni and Somasundaran, 1977)

When minerals are contacted with water, they undergo dissolution, the extent of which is dependent on the type and concentration of chemicals in solution. The dissolved mineral species can undergo further reactions such as complexation and precipitation. Complex equilibria involving all such reactions can be expected to determine the interfacial properties of the minerals and their wettability. In the case of sparing soluble minerals such as carbonates and phosphates, the dissolved species have a marked effect on their inter-facial properties. For example, depending on the solution conditions, the surface of apatite can be converted to calcite and vice versa through surface reactions or bulk precipitation of the more stable phase. The stoichiometry of the equilibrium governing the conversion of apatite to calcite can be written as (Amankonah et al., 1985a):

$$Ca_{10}(PO_4)_6(OH)_2(S) + 10CO_3^{2-}$$
$$= 10CaCO_3(S) + 6PO_4^{2-} + 2OH^-$$
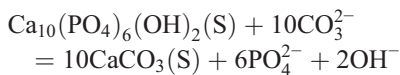
It can be seen from this equation that, depending on the pH of the solution, apatite can be converted to calcite if the total carbonate in solution exceeds a certain value. This surface conversion due to the reaction of the dissol-ved species with the mineral surface can be predicted using stability diagrams for heterogeneous mineral systems (Ananthapadmanabhan and Somasundaran, 1984; Somasundaran et al., 1985). This is illustrated in Fig. 16 for the calcite–apatite–dolomite system under open conditions (open to atmospheric CO_2). The activity of Ca^{2+} in equilibrium with various solid phases shows that the singular point for calcite and apatite is pH 9.3. Above this pH apatite is less stable than calcite and hence conversion of apatite to calcite can be expected in the calcite–apatite system. Similarly, apatite is more stable than calcite below pH 9.3. For calcite–dolomite and apatite–dolomite systems the singular points occur at pH 8.2 and 8.8, respectively. It is to be noted that Ca^{2+} in equilibrium with calcite in an open system is signifi-cantly different from that in a closed system. This surface conversion in calcite–apatite system in water has been experimentally confirmed by zeta potential and ESCA (Electron Spectroscopy for Chemical Analysis) mea-surements (Amankonah et al., 1985b).

The dissolved mineral species, especially multivalent cations, can interact with surfactant species and result in precipitation of the surfactants. In reservoirs, the presence of even small amount of minerals with relatively high solubility can drastically affect the surfactant adsorption. For example, when gypsum is present as a minor component in the reservoir, it has an overwhelming effect on the sulfonate depletion from solutions as illustrated in Fig. 17. Surfactant loss in the presence of gypsum is
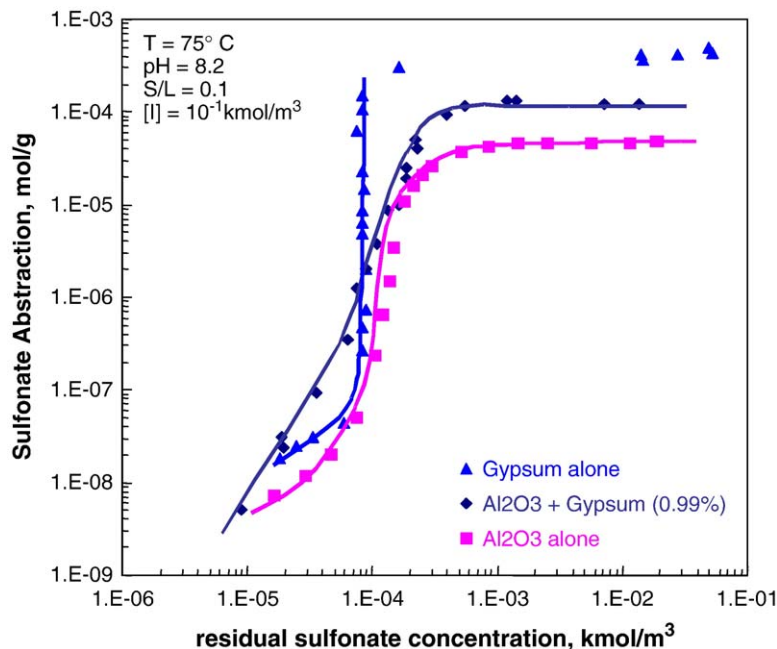

Fig. 17. *n*-decyl benzenesulfonate abstraction by alumina–gypsum mineral mixture.

characterized by a sharp rise in the abstraction (adsorption +precipitation) isotherm. The presence of about 1% gypsum in mineral systems has a predominating effect on the surfactant depletion (Somasundaran et al., 1983). The mineral heterogeneity, which exists in almost all natural systems, could have a profound effect on various interfacial characteristics such as adsorption and wetting (Kulkarni and Somasundaran, 1976).

Furthermore, precipitation of the surfactant in the presence of dissolved mineral species is also considered to contribute to the maximum often observed on the surfactant adsorption isotherms. In most cases adsorption is calculated from the difference between initial and final surfactant concentrations. Since any precipitation in the system can contribute to the observed difference in concentrations, the term "abstraction" is used instead of "adsorption" for systems that have precipitation phenomena. The abstraction and stepwise deabstraction isotherms of dodecylbenzenesulfonate on Na-kaolinite at different pH are shown in Fig. 18 (Somasundaran and Hanna, 1985).

The system clearly showed a maximum and more importantly, significant hysteresis effects. Deabstraction isotherms (by dilution) exhibit a maximum around the same concentration where the abstraction maximum was observed. The significant difference observed in the pH dependence of abstraction can be correlated well with the concentration of dissolved aluminum species in this pH range, suggesting the important role of released aluminum species in governing sulfonate abstraction. The abstraction maximum is caused by the surface precipitation of surfactant/multivalent ion complexes at sulfonate concentrations below the CMC, and their redissolution is caused by micellar solubilization above the CMC and redispersion of the coagulated colloids due to the development of charge from the adsorption of the ionic surfactants. The presence of hysteresis, on the other hand, is caused by the bulk precipitation, as opposed to surface precipitation, upon dilution (Ananthapadmanabhan and Somasundaran, 1983; Somasundaran et al., 1984).

5. Effects of organics

Oil and other organics are invariably present in enhanced oil recovery systems and this will affect the adsorption of surfactants on solids and resultant mineral wettability. Oil can also form emulsion with surfactants.
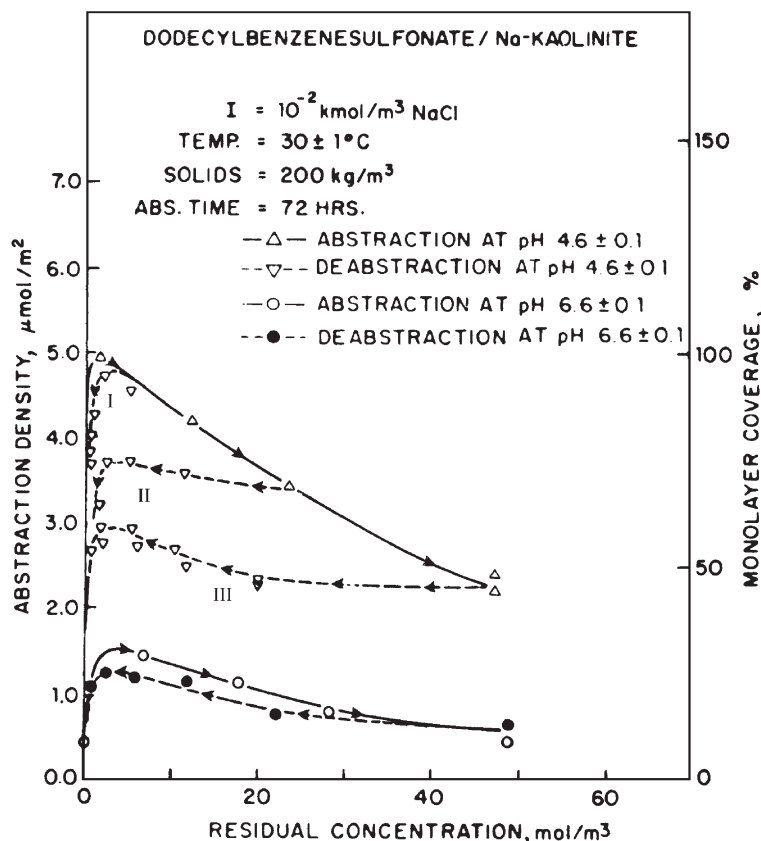

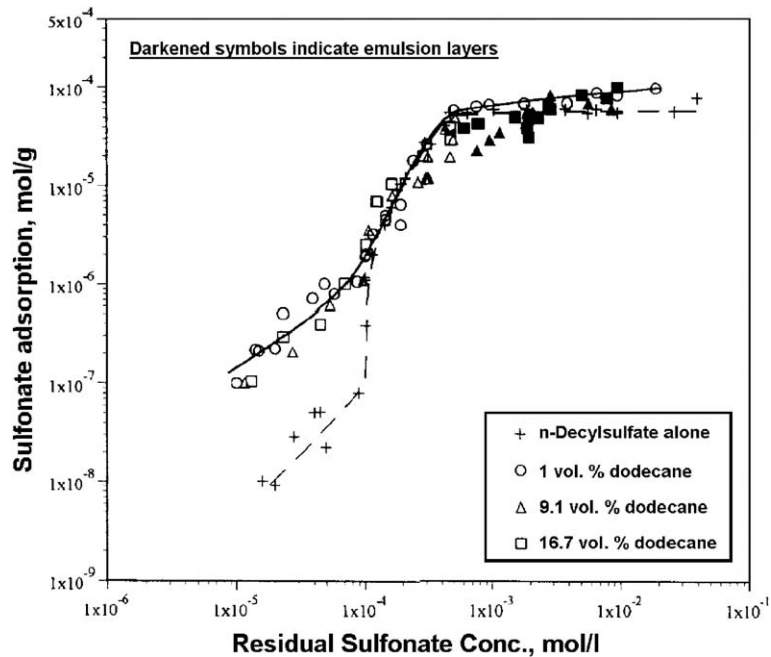Fig. 18. Abstraction/deabstraction of DDBS/NA-kaolinite system.

Fig. 19. Adsorption behavior of *n*-DBS on alumina in the presence of varying dodecane levels.

For example, the effect of dodecane on the adsorption of *n*-decyl benzenesulfonate (DBS) on alumina is shown in Fig. 19. Adsorption of DBS alone is typical of ionic surfactant adsorption on oxide minerals with four well-defined regions (Fig. 6). In the presence of dodecane, the adsorption density at the onset of hemimicellization is more than one order of magnitude higher. Here the coadsorbed dodecane enhances the sulfonate aggregation
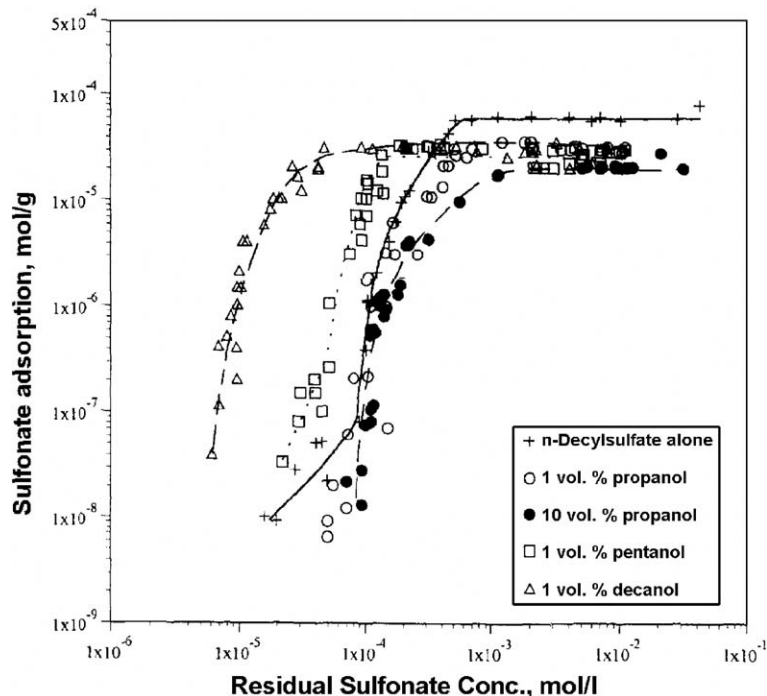

Fig. 20. Adsorption behavior of *n*-DBS on alumina in the presence of alcohols of chain length varying from propanol to decanol.

at the interface and this results in increased surfactant adsorption. Once sulfonate forms solloids and bilayers at the solid–liquid interface the oil will be solubilized into these aggregates and its effect on adsorption is reduced. Also the oil will preferentially solubilize into micelles at higher sulfonate concentrations and this results in minimal effects on the adsorption.

The results obtained for the effect of alcohols of varying chain length on the adsorption of *n*-DBS are given in Fig. 20. Propanol was found to decrease the adsorption measurably at low concentrations, whereas pentanol and decanol increase adsorption at lower concentrations. However, all alcohols reduce the plateau adsorption. These results clearly show the important role that alcohol and hydrocarbon additives play in surfactant adsorption. While small additive molecules will increase the solvent power for the surfactant and thus reduce adsorption, larger molecules will co-aggregate with the surfactant and lower the free energy of micellization and hemimicellization and thus enhance the adsorption (Fu et al., 1996).

6. Effects of inorganics

Brine exists in many reservoirs and the presence of such electrolytes could have a significant effect on the surfactant adsorption. Mahogany petroleum sulfonate has been reported to exhibit an adsorption maximum due to the presence of compounds such as hydrocarbons, alcohols, inorganics and polymers. This adsorption maximum has been shown to be sensitive to the concentration and type of salt in the solution. (Fig. 21) (Somasundaran et al., 1977; Hanna and Somasundaran, 1979). Interestingly, while a maximum in adsorption is obtained in 0.005 M Na_2SO_4 and 0.01 M NaCl, such maximum is seen in solution containing low NaCl. Water structure making and breaking properties of the inorganics have been shown to have drastic effects on surfactant adsorption.

It is to be noted that the presence of a maximum has important practical implications, since oil displacement with surfactant solutions at concentrations far above the maximum, could be conducted with very little surfactant loss by adsorption. The most probable cause for the adsorption maximum is the impure multicomponent nature of the surfactant and the precipitation of surfactant/multivalent salts below CMC and their redissolution above it, as mentioned earlier.

7. Summary

Wettability of reservoir minerals plays an important role in enhanced oil recovery. It has been shown that mineral wettability is affected by many factors including
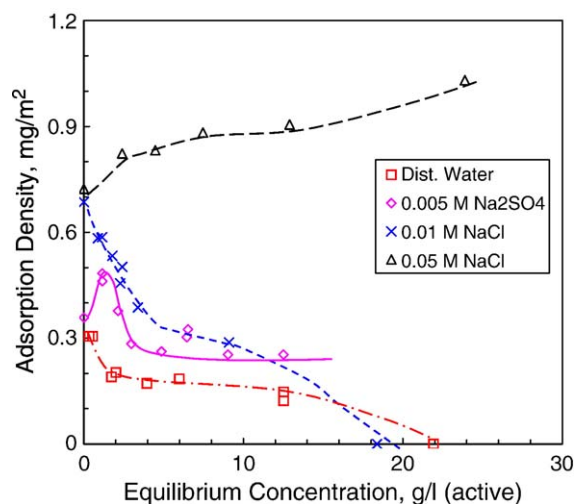

Fig. 21. Effect of sodium chloride and sodium sulfate on the adsorption of Mahogany sulfate AA on Berea sandstone.

surfactant/polymer adsorption and conformation, mineralogical composition, and solution conditions such as pH and salinity. Presence of various dissolved minerals species, precipitates from surfactant and mineral species, organic compounds and inorganic electrolytes can modify the wettability drastically. A full understanding of all the complex interactions involved could lead to new approaches and insights that are needed in improved oil production.

Acknowledgements

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