

EMULSIONS,

FOAMS, AND

THIN FILMS

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Unity in Diversity in Interfacial Phenomena

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ABSTRACT

This chapter summarizes three decades of studies performed by our research group on monolayers, micelles, foams, emulsions and wetting phenomena, in which a commonality in the performance of surfactant systems was observed. Parameters such as chain-length compatibility, surfactant concentration, salinity, and molecular association were considered.

It was found that the effect of chain-length compatibility was particularly important to interfacial properties and technological applications. When mixed-surfactant systems have equal chain length, the average area per molecule is minimum, resulting in minimum interfacial tension, maximum surface viscosity, and maximum micellar stability. These results, in turn, influence technological processes,

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such as foaming, wetting, lubrication, enhanced oil recovery, and microemulsion stability.

It was observed that the concentration of sodium dodecyl sulfate (SDS) in aqueous solution strikingly influenced the dynamic interfacial properties of the system. The slow micellar relaxation time τ_2 , which is directly related to the micellar stability, was found to be maximum at 200 mM SDS concentration (i.e., 25 times cmc), corresponding to the least foaming, largest bubble size, longest wetting time of textile, largest emulsion droplet size, and the most rapid solubilization of oil.

The importance of the molecular ratio in interfacial properties was investigated for a variety of mixed-surfactant systems. At the 1:3 and 3:1 molar ratios, minima and maxima in various interfacial as well as bulk properties were observed. A possible hexagonal arrangement of molecules allows one type of molecules to occupy the corners of the hexagon and the second type of the molecules to occupy the centers. This arrangement results in the tightest possible packing at the surface and, hence, minimum area per molecule, maximum surface viscosity, lowest rate of drainage, and minimum surface tension. These surface properties, in turn, influence the performance of foams, emulsions, and monolayers.

One parameter that has been discovered to be crucially important in the successful implementation of the surfactant-polymer flooding process for enhanced oil recovery is the salinity of the aqueous phase. For a given oil-water-surfactant system at a given temperature and pressure, a specific salinity is required to produce an ultralow interfacial tension. Parameters, such as interfacial tension, viscosity of emulsions or pressure difference in porous media, surfactant retention, and overall oil-recovery efficiency exhibit maxima or minima at the optimal salinity, indicating that these processes are all interrelated for the oil displacement in porous media by the surfactant-polymer flooding process.

The last study showing a commonality in interfacial properties is the effect of tetraalkyl ammonium salt on foaming properties of SDS solutions. At low concentrations, the molecular interaction between SDS and tetraalkylammonium ions increases the molecular packing in the adsorbed film, resulting in lower surface tensions and higher surface viscosity. However, above a critical concentration (depending on the alkyl chain length of the tetraalkylammonium ion), the interfacial properties go in the reverse direction, indicating a disruption of the molecular packing at the interface and resulting in a higher surface tension and a lower surface viscosity.

The parameters investigated over the years clearly show the existence of the unity in diversity as illustrated by the interfacial phenomena studied for several surfactant systems. This commonality determines various surface properties, microstructures, and macroscopic properties of surfactant solutions, monolayers, foams, and emulsions, yielding “master diagrams” in support of this statement.

I. INTRODUCTION

During the past three decades, the Center for Surface Science and Engineering at the University of Florida has carried out considerable studies on monolayers, micelles, foams, emulsions, and wetting phenomena [1]. From various theoretical considerations, as well as experimental results, we have observed a commonality in the performance of surfactant systems considering parameters such as chain-length compatibility, surfactant concentration, salinity, or molecular association. In this chapter, we will discuss the commonality observed for several mixed-surfactant systems studied over the years to show the existence of a unity in diversity.

Figure 1 illustrates how molecular properties of surfactants are related to the performance in technological processes. The structure of surfactant molecules influences the properties of adsorbed films as well as micellar characteristics. Both of these, in turn, influence the performance of technological processes such as foaming, emulsification, solubilization, wetting, and lubrication.

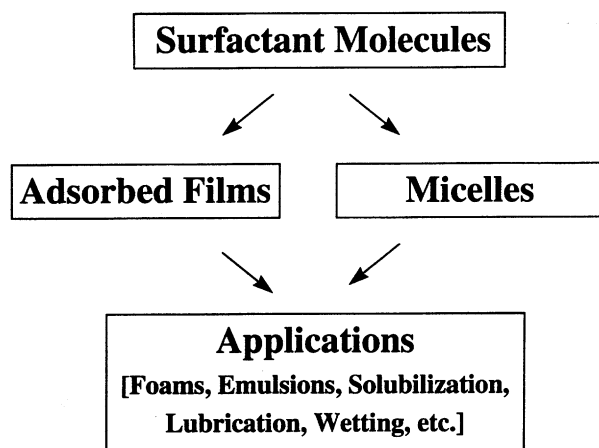


Figure 1 Correlation between molecular properties and macroscopic phenomena.

II. CHAIN-LENGTH COMPATIBILITY EFFECTS IN MIXED-SURFACTANT SYSTEMS

The chain-length compatibility is an important factor in systems involving interfacial films. As surface-active as well as other hydrocarbon molecules are aligned at interfaces, the properties of the interface are impacted, to a large extent, by the matching or mismatching of the alkyl chain lengths. The effect of chain-length compatibility is particularly important to interfacial properties and technologies such as surface tension, surface viscosity, foamability, lubrication, contact angle, bubble size, environmental remediation, enhanced oil recovery, water solubilization in microemulsions, and microemulsion stability [2]. Figure 2 shows schematically mixed-surfactant systems having equal or different chain lengths. It is evident that when the two chains are unequal, the excess hydrocarbon tails have more freedom to disrupt the molecular packing through conformational disorder and thermal motion. This causes a slight increase in the intermolecular distance and, hence, the average area per molecule. The greater the length of the excess segment, the greater the area per molecule.

An example of the influence of chain-length compatibility on interfacial properties for the mixed-surfactant system sodium dodecyl sulfate (SDS)/long-chain alcohols (C_nOH for $n = 8, 10, 12, 14$, and 16) is shown in Figure 3 [2,3]. It shows that the surface tension is minimum and the surface viscosity (in surface poise, SP) is maximum when both molecules have equal chain length (i.e., for SDS/ $C_{12}OH$ mixtures). The stability of micelles, as reflected by the slow micellar relaxation time, τ_2 , is maximum when both surfactants have the same chain length. It was shown recently [4] that any long-chain alcohol (C_nOH for $n = 8, 10, 12, 14$, and 16) will stabilize SDS micelles because of the introduction of ion-dipole interactions between the alcohol and SDS molecule, causing a tighter packing of the micelle. However, beyond a certain concentration of SDS (de-

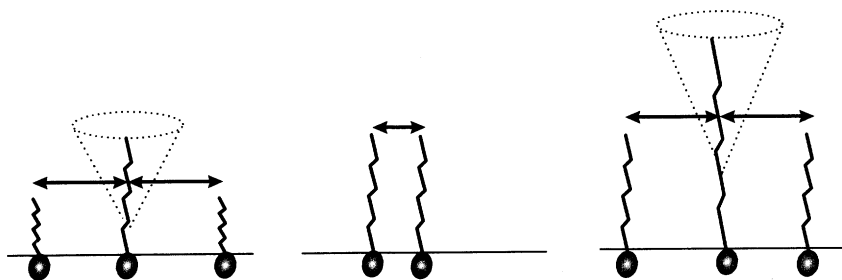


Figure 2 Effect of chain-length compatibility on molecular packing in mixed-surfactant systems.

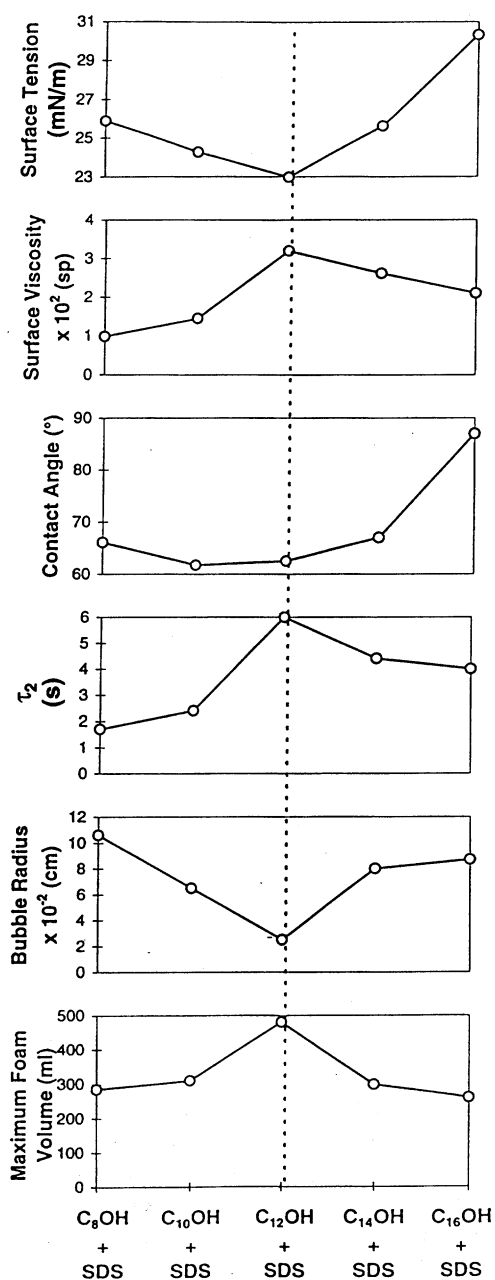


Figure 3 Effect of chain-length compatibility on interfacial properties of sodium dodecyl sulfate/long-chain alcohol (SDS/C_nOH) solutions.

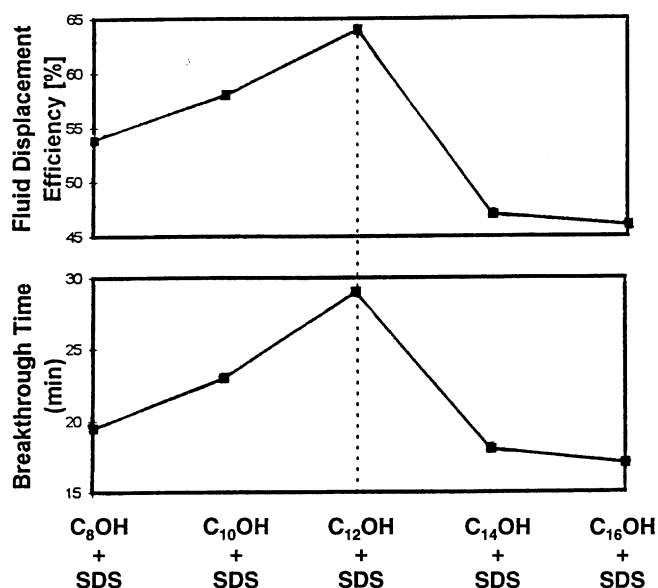


Figure 4 Chain-length-compatibility effect on fluid-displacement efficiency and breakthrough time for removal of residual trapped oil in porous media.

pending on the alcohol chain length), long-chain alcohols other than C₁₂OH start destabilizing micelles, due to mismatching of the chains resulting in a disruption of the molecular packing causing the micelles to destabilize and, hence, shorter micellar relaxation times are obtained. Figure 3 also shows that a minimum bubble radius was found for the SDS/C₁₂OH system, indicating that the lowest interfacial tension occurs when the chain lengths of the surfactant and the cosurfactant are equal. Because of the lowest interfacial tension, the foaming ability was maximum for the equal-chain-lengths system. Thus, these results show that the chain-length equality strikingly influences surface, micellar, and foam properties.

Previous research [3] has shown that the chain-length compatibility of mixed-surfactant systems also plays an important role in foaming systems, in particular for applications in enhanced oil recovery and environmental remediation of contaminated aquifer sites. Figure 4 shows the fluid displacement and breakthrough time in porous media (e.g., sand-pack). The time required for the gas to break through at the other end of the porous medium and the fluid-displacement efficiency show maxima when the chain lengths of the two components are equal. In the case of SDS/C_nOH systems, molecules interact with the ion–dipole association. A much stronger interaction is expected for ion–ion interactions.

Patist et al. [5] studied the effect of chain-length compatibility on interfacial properties for mixtures of sodium dodecyl sulfate and alkyltrimethylammonium bromides (C_n TAB for $n = 8, 10, 12, 14$, and 16). Figure 5 shows various surface properties as well as foam characteristics for the SDS/ C_n TAB system at a 20:1 molar ratio. When the chain lengths of two surfactants are equal, the surface tension and foam ability show minima, whereas the surface viscosity, the micelle stability, and the foam stability show maxima. Thus, for mixed anionic/cationic surfactant mixtures, the Coulombic interaction as well as the chain-length compatibility determine the molecular packing in micelles and at the air–water interface. In conclusion, the equality of chain length offers a common denominator for adsorbed films, micelles, and foams.

III. EFFECT OF SDS CONCENTRATION ON VARIOUS INTERFACIAL PHENOMENA

It is well known that the critical micelle concentration of SDS is approximately 8.3 mM [6]. Gradually increasing the SDS concentration up to 300 mM leads to some interesting changes in interfacial properties of SDS solutions, showing minima and maxima at a concentration of 200 mM. Oh and Shah [7] determined the slow micellar relaxation time, τ_2 (which is directly related to the lifetime or stability of the micelle), by the pressure-jump technique [8]. Figure 6 shows the slow micellar relaxation time τ_2 as a function of SDS concentration. A maximum micellar stability was found at 200 mM (5 s). The micellar stability influences many processes of interest, such as foaming, wetting, emulsification, and solubilization [9]. Figure 7 presents the various phenomena exhibiting minima and maxima at the liquid–gas interface. At 200 mM SDS, minimum foamability, maximum single-film stability, maximum single-bubble volume, and a minimum frequency of bubble generation were found. These phenomena were explained based on the monomer flux to the newly created interface. If the micelles in solution are very stable, they cannot provide a monomer fast enough to the interface and thus the interfacial tension remains higher. Therefore, lower foamability, larger single-bubble foam volumes, and a minimum frequency of bubble generation were found [10,11]. A maximum single-film stability was found at 200 mM (i.e., when the micelles are most stable) [12]. An important factor influencing single-film stability is the micellar structure inside the thin liquid film, which has been investigated by Wasan and co-workers [13,14]. The stratification of thin liquid films can be explained as a layer-by-layer thinning of ordered structures of micelles inside the film. It is proposed that this structural effect is influenced by the micellar effective volume fraction, their stability, interaction, and polydispersity. Therefore, very stable micelles contribute to the stability of the thin liquid film.

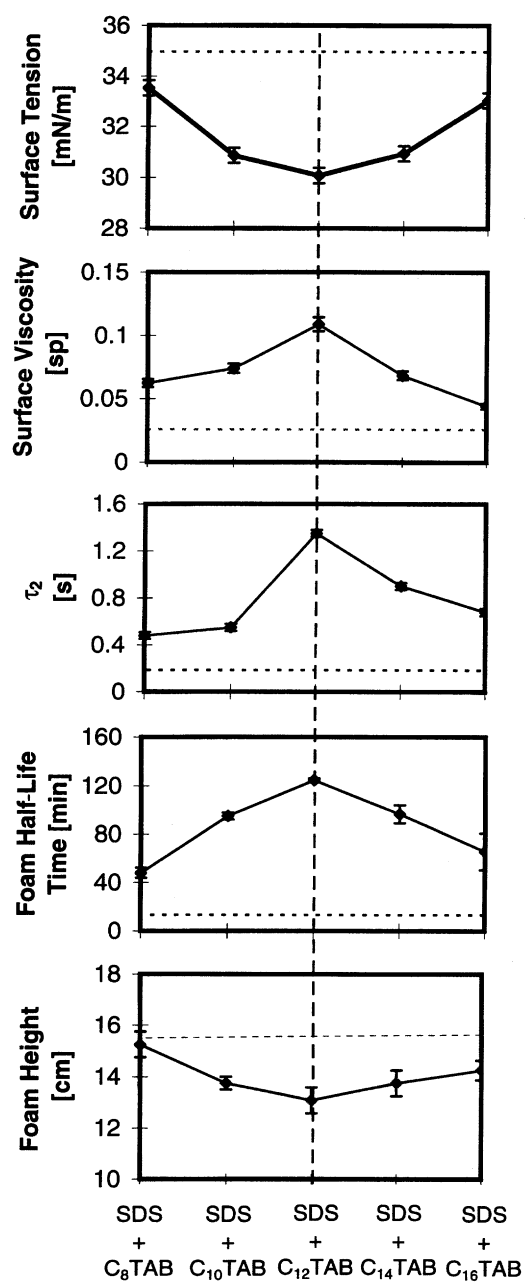


Figure 5 Chain-length-compatibility effect on interfacial properties of sodium dodecyl sulfate/alkyltrimethylammonium bromide (SDS/C_nTAB, 20:1) solutions. The horizontal dashed lines represent 100 mM pure SDS solutions.

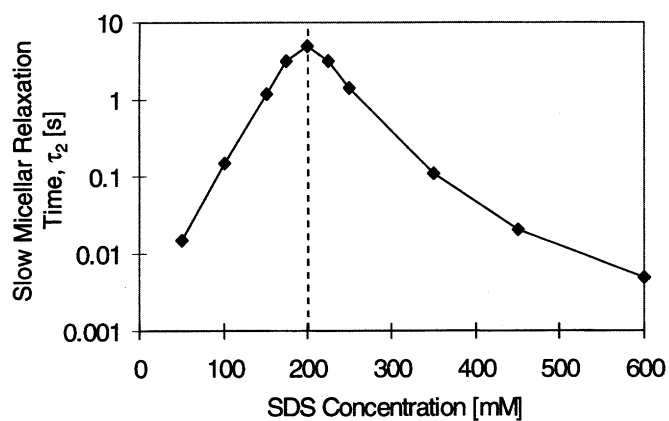


Figure 6 Slow micellar relaxation time τ_2 versus concentration of SDS at 25°C.

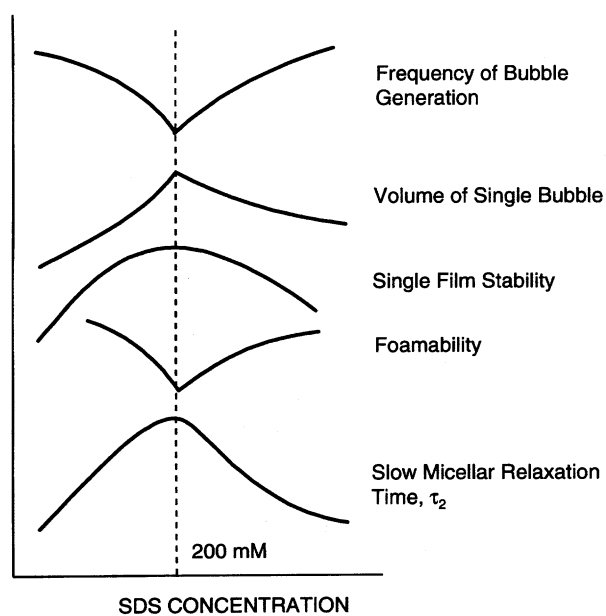


Figure 7 Liquid-gas phenomena exhibiting minima and maxima at 200 mM SDS concentration.

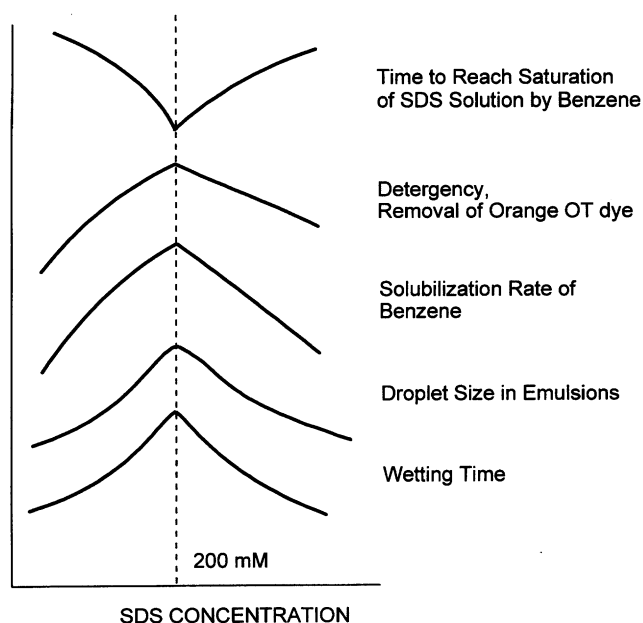


Figure 8 Liquid–liquid and solid–liquid phenomena exhibiting minima and maxima at 200 mM SDS concentration.

Very unstable micelles, however, provide monomers fast enough to the surface, resulting in lower interfacial tensions.

Interfacial phenomena occurring at the liquid–liquid and solid–liquid interfaces in SDS solutions at various concentrations are shown in Figure 8. The wetting time and droplet size in emulsions exhibit maxima at 200 mM. These phenomena can also be explained based on the monomer flux necessary to stabilize the newly created interface. Very stable micelles at 200 mM result in a high dynamic surface tension; hence, a larger droplet size and longer wetting time are obtained [15,16]. The solubilization rate of benzene in surfactant solutions as well as the detergency or removal of Orange OT dye from the fabric's surface also show maxima at 200 mM SDS concentration. The time required to reach saturation of the SDS solution upon the addition of benzene is minimum at 200 mM SDS concentration. This suggests that very stable micelles (i.e., tightly packed micelles) are more effective in solubilizing oil. This can be explained based on the interior of the micelles. The interior of rigid (i.e., tightly packed) micelles is more hydrophobic as compared to that of loosely packed micelles;

hence, the stronger hydrophobic core causes a more rapid solubilization of benzene and Orange OT dye into the micelles at 200 mM SDS concentration.

IV. INTERMICELLAR COULOMBIC REPULSION MODEL

In order to explain the maxima and minima in various phenomena occurring at 200 mM SDS solutions, the following Intermicellar Coulombic Repulsion Model (ICRM) was proposed. Knowing the aggregation number of SDS micelles and the total SDS concentration, one can calculate the number of micelles at a specific SDS concentration in the solution. By dividing the solution into identical cubes, equal to the number of micelles, one can equate the distance between the centers of the adjacent cubes as the average intermicellar distance. By this approach, we found that the intermicellar distance was 13, 10, and 7.86 nm respectively at 50 mM, 100 mM, and 200 mM SDS concentrations. This suggests that the adjacent micelles are one diameter apart at 200 mM concentration. The small gap of about 4 nm causes a Coulombic repulsion between SDS micelles and hence induces a rapid uptake of counterions to minimize the charge repulsion between adjacent micelles. This provides considerable stability to the micellar structure, resulting in a long relaxation time. Above 250 mM SDS concentration, a structural transition from spherical to cylindrical SDS micelles occurs. However, this structural transition is gradual, and in this concentration range (250–400 mM), the solution consists of a mixture of spherical and cylindrical micelles. Because the number of spherical micelles is less as compared to that at 200 mM concentration, as some of them have become cylindrical micelles, the distance between spherical micelles increases, which leads to shorter relaxation times. In a binary mixture, it is the most labile structure (i.e., spherical micelles), which responds more quickly to the change in pressure in the pressure-jump studies compared to cylindrical micelles [8]. The intermicellar distances obtained from this procedure at various SDS concentrations are shown in Figure 9.

In summary, SDS solutions exhibit maxima and minima for various properties at 200 mM concentration due to maximum stability of SDS micelles at this concentration. Most ionic surfactants may exhibit such a characteristic concentration at which the micellar stability is maximum due to a reduction in intermicellar distance.

V. SIGNIFICANCE OF THE 1:3 MOLECULAR RATIO IN MIXED-SURFACTANT SYSTEMS

Many mixed-surfactant systems exhibit unusual properties at the 1:3 or 3:1 molecular ratios. Shah [17] investigated interfacial properties, such as foamability,

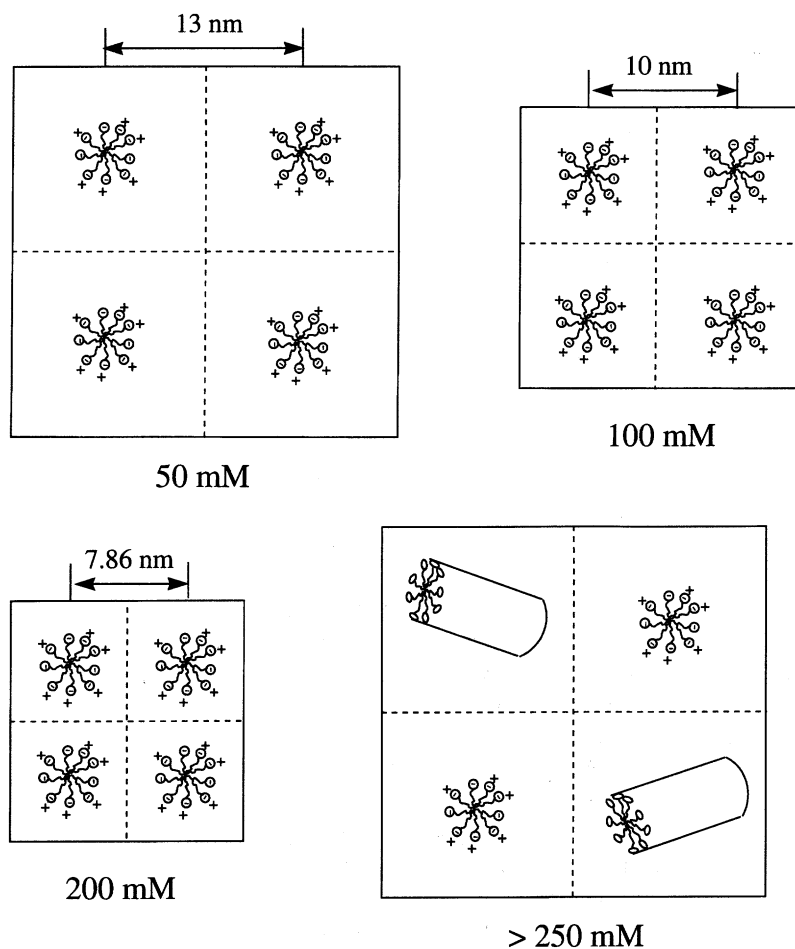


Figure 9 Schematic diagrams for micellar packing at 50, 100, 200, and 250 mM SDS concentration.

foam stability, and rate of evaporation of water for the system decanoic acid/decanol. Figure 10 shows the foam volume in various cylinders containing mixtures of decanoic acid/decanol after 16 h of foam generation by vigorous shaking. It is evident that cylinder 7, which contains a 1:3 molecular ratio of the decanoic acid/decanol mixture, exhibits maximum foam stability. From Figure 11, it appears that the maximum foam stability coincides with a minimum rate of drainage and maximum surface viscosity. Apparently, decanoic acid and decanol associate

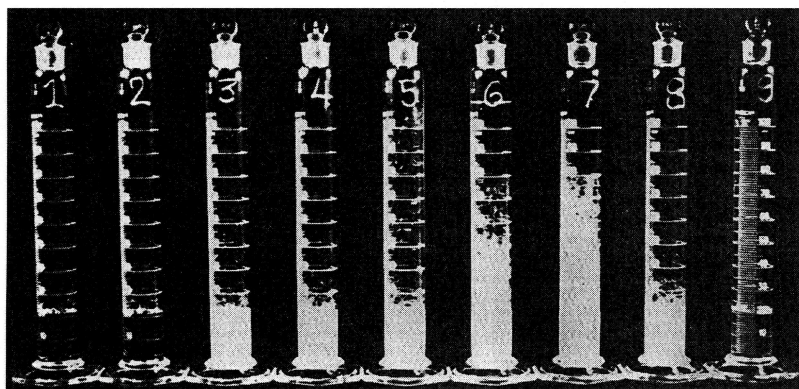


Figure 10 Foam volumes of decanoic acid/decanol mixtures, 16 h after foam generation. The mixture in cylinder 7 (1:3 ratio) shows the maximum foam stability.

at the 1:3 ratio, causing a tighter packing of molecules, resulting in an increase in surface viscosity, a decrease in drainage rate, and, therefore, an increase in foam stability, in agreement with the results reported by others [18–20].

Figure 12 shows the average area per molecule in mixed monolayers of stearic acid and stearyl alcohol [17]. The data indicate that the minimum area

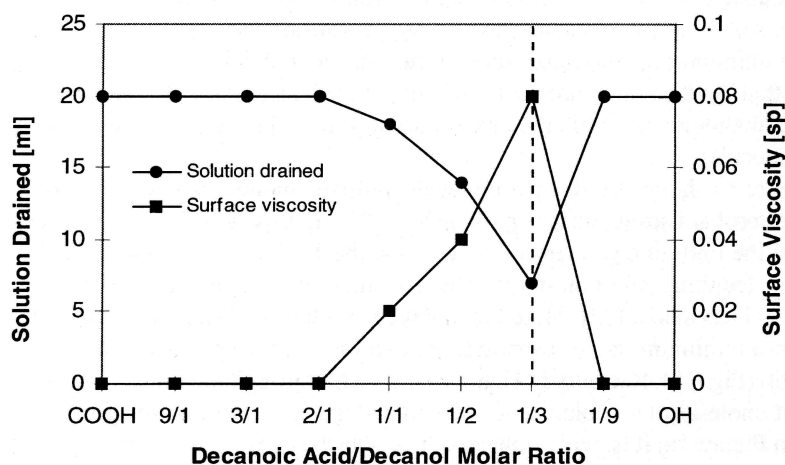


Figure 11 Relation between the amount of solution remaining under decanoic acid/decanol foams, 10 min after foam generation, and the surface viscosity.

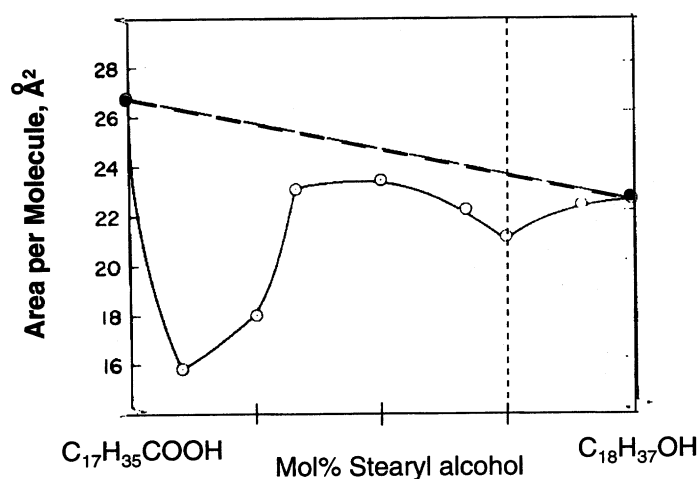


Figure 12 Average area per molecule in mixed monolayers of stearic acid and stearyl alcohol at a surface pressure of 10 mN/m. The vertical dashed line represents the 1:3 molar ratio.

per molecule occurs at the 1:3 and 9:1 molar ratios. In order to show that the minimum area per molecule at the 1:3 molar ratio is due to the tight packing of molecules, studies were carried out on the evaporation of water through these mixed monolayers. Figure 13 shows the evaporation rate of water through mixed monolayers of stearic acid and stearyl alcohol at various ratios [17]. It is evident that the minimum rate of evaporation occurs at the 1:3 molar ratio. This also suggests that the minimum area per molecule at the 9:1 molar ratio must be due to structural alterations within the mixed monolayers and not due to tight packing of the molecules.

Figure 14 shows the area per molecule in mixed monolayers of egg lecithin and cholesterol at various surface pressures [17,21]. It is evident that at all surface pressures, the optimum condensation occurs at the 1:3 and 3:1 molar ratios between egg lecithin and cholesterol. These results are in agreement with those reported by Dervichian [22]. Mixed monolayers of oleic acid and cholesterol [23] also show a minimum rate of evaporation at various surface pressures at the 1:3 molar ratio (Fig. 15). Recently [24], the heat transfer through the same monolayer system of cholesterol and oleic acid was studied using an infrared imaging camera. From Figure 16, it is evident that the heat-transfer process was most efficient through the mixed monolayer at the 1:3 molar ratio, due to the tight packing of molecules.

Booij [25] showed the importance of molecular association on mineral oil

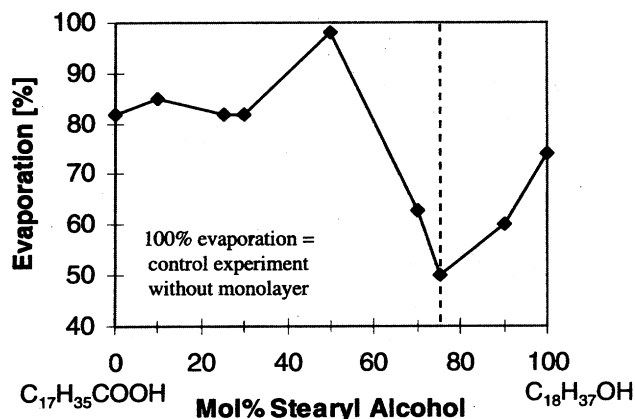


Figure 13 Rate of evaporation through mixed monolayers of stearic acid and stearyl alcohol. The vertical dashed line represents the 1:3 molar ratio.

extraction from emulsions stabilized by a mixture of sodium dodecyl sulfate and cetyl pyridinium chloride (Fig. 17). It is evident that at the 1:3 and 3:1 molar ratios, the maximum amount of oil is extracted from the emulsions, indicating that the 1:3 association also occurs at the oil–water interface. The same system was recently investigated for surface properties by Patist et al. [26] at low concentrations (total concentration: 1 mM). Figure 18 shows that again at the 1:3 and 3:1 molar ratios, minima and maxima are found due to tight packing of anionic and cationic surfactant molecules.

The observed minima and maxima in various properties of mixed-surfactant systems at the 1:3 or 3:1 ratio cannot be considered a coincidence. This must be due to a very fundamental mechanism, operating in mixed-surfactant systems. Figure 19 presents the proposed explanation for the molecular packing at the 1:3 and 3:1 molar ratios at the interface. This type of hexagonal arrangement allows one type of molecule to occupy the corners of the hexagon and the second type of molecule to occupy the centers. This arrangement results in the tightest possible packing at the surface and, hence, the minimum area per molecule, maximum surface viscosity, lowest rate of drainage, and minimum surface tension. These surface properties then, in turn, influence the performance of foams, emulsions, and monolayers.

VI. OPTIMAL SALINITY AND ENHANCED OIL RECOVERY

The efficient production of oil has been an important objective by the petroleum industry. Geological evolution has been kind to the industry insofar as producing

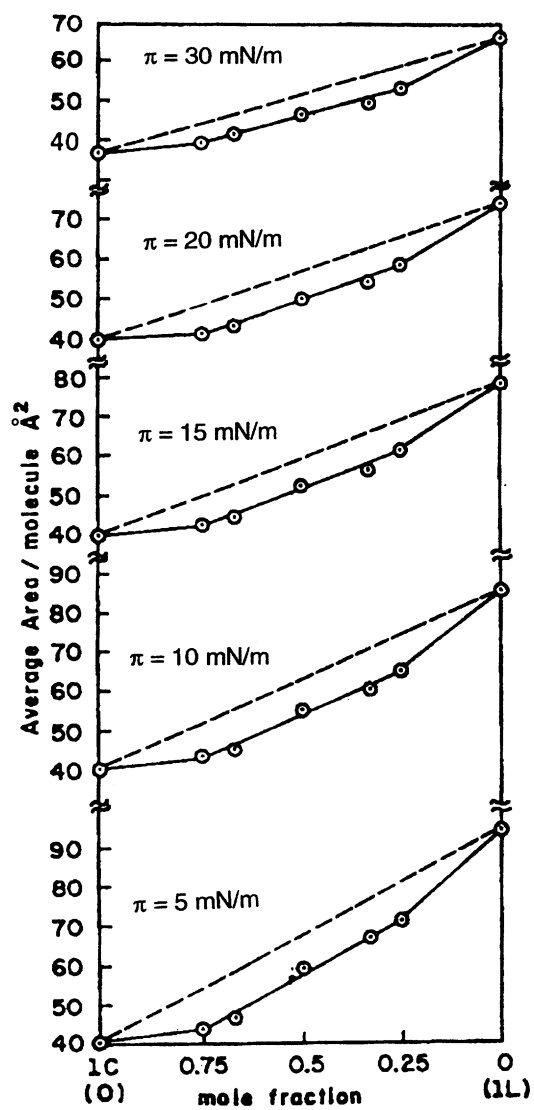


Figure 14 Average area per molecule in mixed monolayers of egg lecithin and cholesterol at various surface pressures.

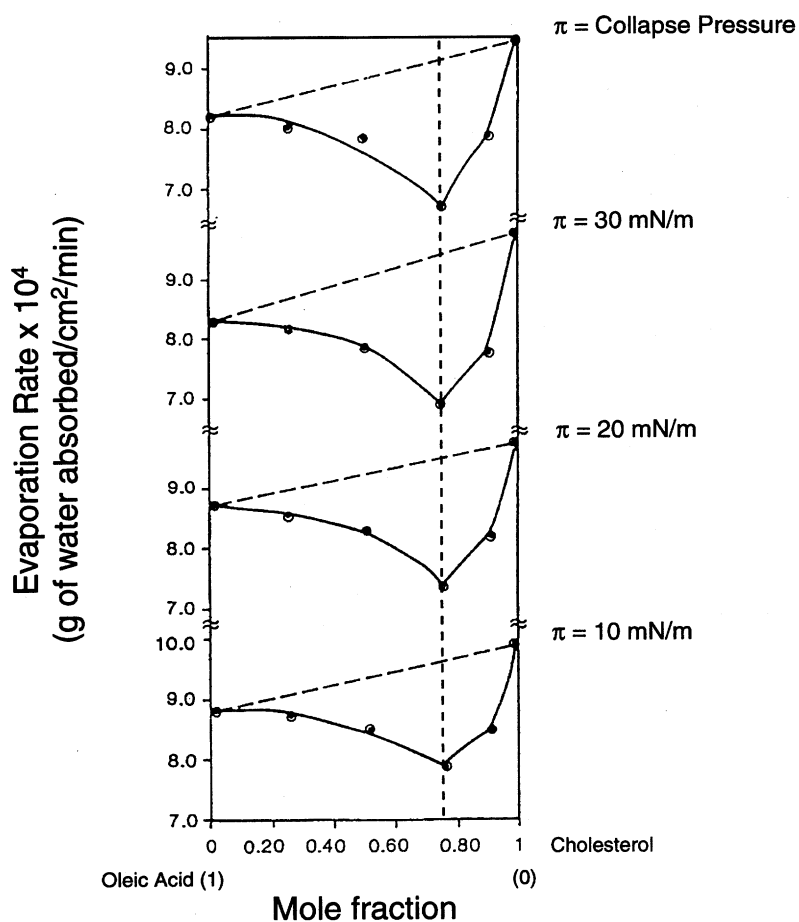


Figure 15 Rate of evaporation through mixed monolayers of oleic acid and cholesterol at various surface pressures. The vertical dashed line represents the 1:3 molar ratio.

high-pressure oil reserves in which primary and secondary oil-recovery methods can achieve close to 35% production efficiency. The remaining 65%, which is in the reservoir, has provided an engineering challenge. This area has been known as tertiary or enhanced oil recovery (EOR). Initial areas of research, brought about by the oil shortages of the 1970s, focused on the importance of reducing the interfacial tension (IFT) of the oil–water interface with the use of surfactants [6]. The petroleum industry seized this concept as a method to increase oil production through modified water-flushing strategies. Figure 20 shows a three-

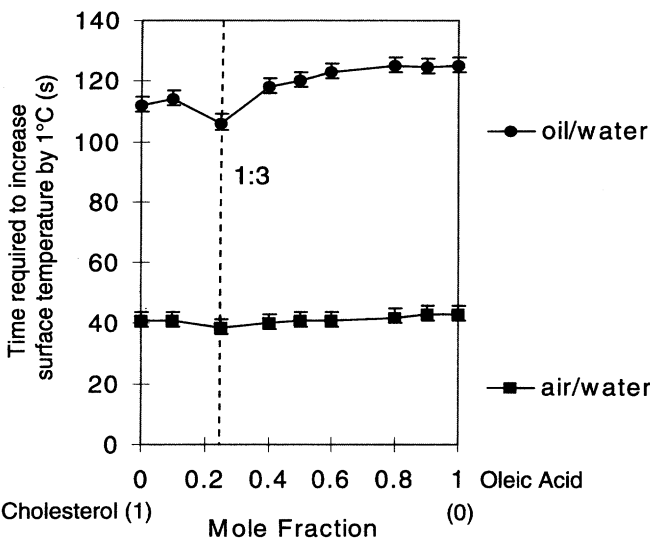


Figure 16 Time required for the surface temperature of water or oil (hexadecane) with mixed monolayers of oleic acid and cholesterol to increase by 1°C.

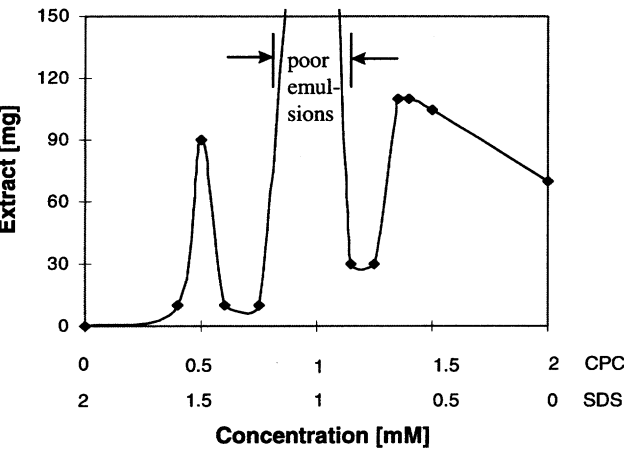


Figure 17 Extraction of mineral oil from sodium dodecyl sulfate/cetyl pyridinium chloride (SDS/CPC) mixtures.

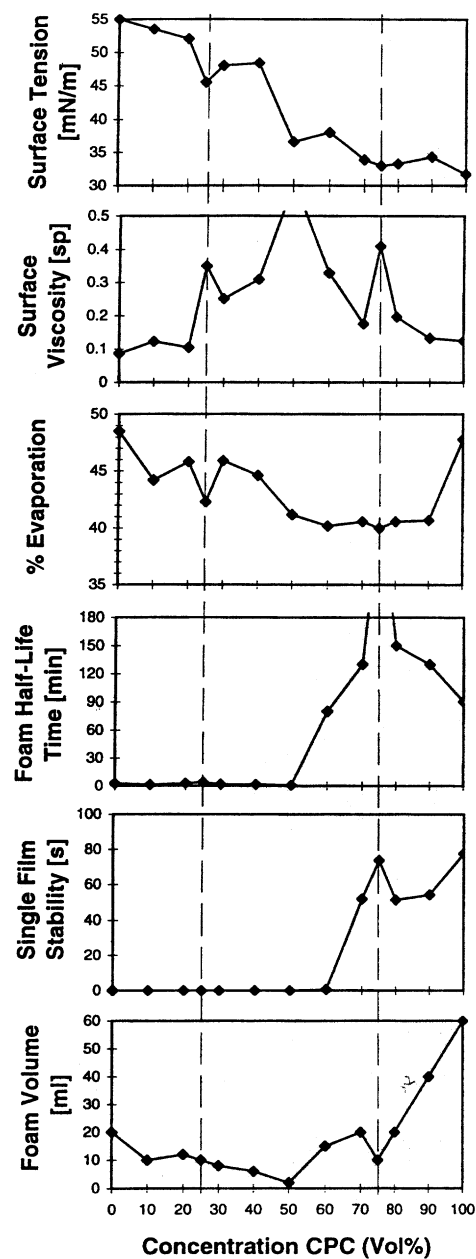


Figure 18 Effect of molar ratio on interfacial properties of sodium dodecyl sulfate/cetyl pyridinium chloride (SDS/CPC) mixtures. Total concentration: 1 mM. The vertical dashed lines represent the 1:3 and 3:1 molecular ratios.

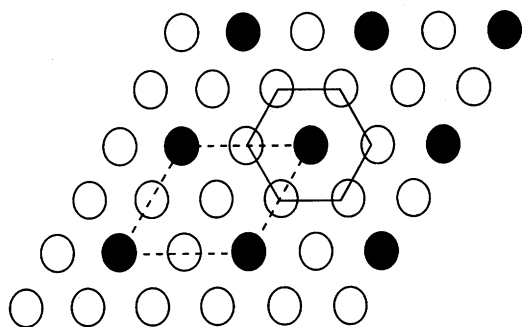


Figure 19 Proposed two-dimensional hexagonal arrangement of molecules at the 1:3 molar ratio in mixed-surfactant systems.

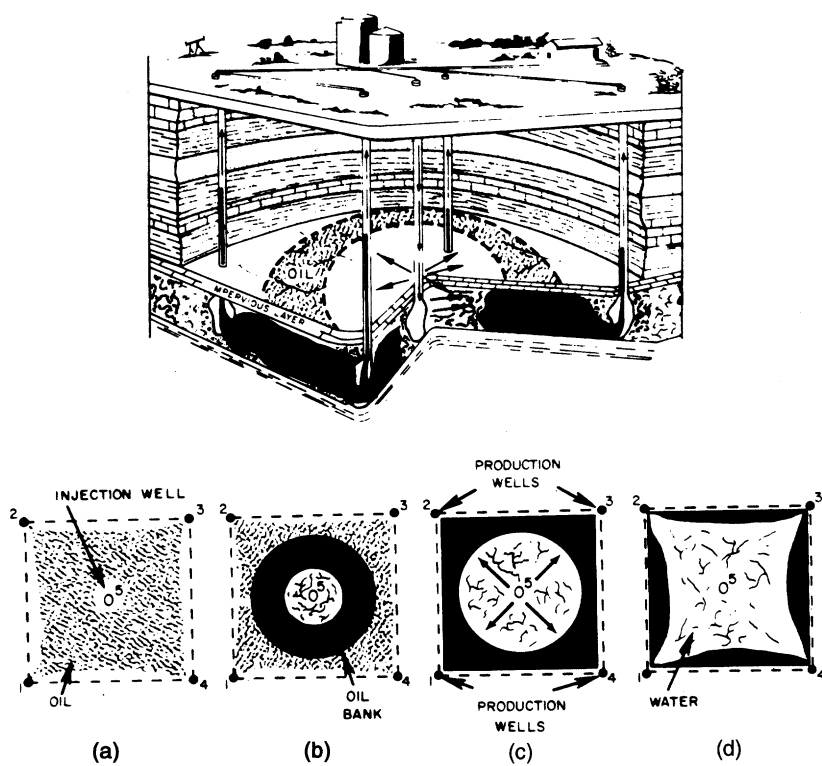


Figure 20 Schematic view of a petroleum reservoir (five-spot pattern) and the process of water or chemical flooding.

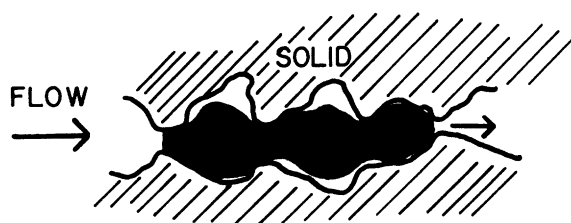


Figure 21 For the movement of oil through narrow necks of pores, an ultralow interfacial tension is required (≈ 0.001 mN/m).

dimensional view of a petroleum reservoir and the process of water or chemical flooding [27]. The objective of tertiary oil recovery is to reduce the interfacial tension at the oil–water interface (20–25 mN/m) to 10^{-3} – 10^{-5} mN/m and hence promote the mobilization of oil in porous media. Figure 21 shows that an ultralow interfacial tension is required for the mobilization of oil ganglia in porous media [28–30]. The attainment of such an ultralow interfacial tension requires the tailoring of a surfactant to produce ultralow interfacial tensions under the reservoir conditions of temperature, pressure, and salinity. Conceptually, a surfactant formulation is injected into the porous media in the petroleum reservoir, so that upon mixing with the reservoir brine and oil, the surfactant produces a middle-phase microemulsion *in situ*. This middle-phase microemulsion, in equilibrium with excess oil and excess brine, propagates through the petroleum reservoir [31,32]. The design of the process is such that the oil bank maintains an ultralow interfacial tension with the reservoir brine until it arrives at the production wells. One parameter that has been discovered to be crucially important in the successful implementation of the surfactant–polymer flooding process is the salinity of the aqueous phase [27]. Figure 22 shows the effect of optimal salinity on various interfacial properties and phenomena relevant to enhanced oil recovery. For a given oil/water/surfactant system at a given temperature and pressure, a specific salinity is required to produce an ultralow interfacial tension. It is evident that all these parameters exhibit a maximum or minimum at the optimal salinity, indicating that these processes are all interrelated for the oil displacement in porous media by the surfactant–polymer flooding process. It also appears that the optimal salinity value is a critical parameter for oil recovery in this process. The field of enhanced oil recovery has received a great deal of attention over the last three decades. The insight and information obtained during these years has not only increased oil production but has led to other applications of microemulsions as well [33].

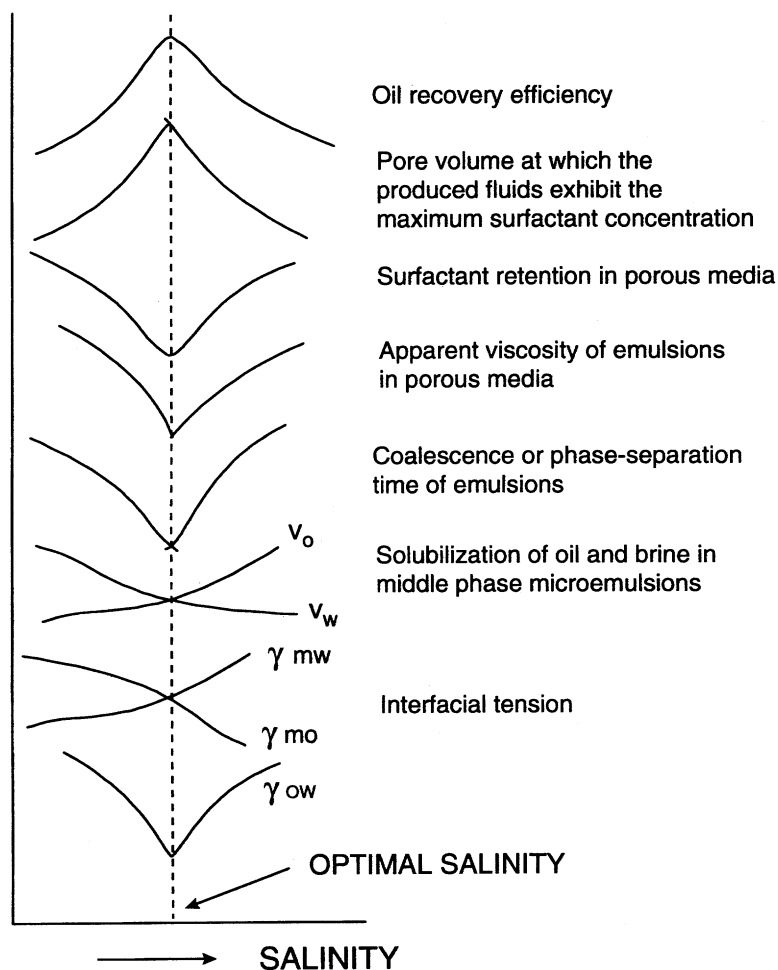


Figure 22 Effect of optimal salinity on various interfacial properties and phenomena relevant to EOR.

VII. EFFECT OF ORGANIC CATIONS ON FOAMING PROPERTIES OF SDS SOLUTIONS

It is well known that foaming properties can be greatly modified by the addition of organic materials [6,34,35]. It was shown recently that the influence of tetraalkylammonium salts on the SDS foam stability and foamability was a result of

the effect of these compounds on the molecular packing at the air–water interface and in micelles [35,36]. Figure 23 shows the effect of concentration of tetraethylammonium chloride (TC_2AC) on surface tension, surface viscosity, foam stability, foaming ability, and slow micellar relaxation time, τ_2 , in 150 mM SDS solutions. It is evident that the maxima and minima in various properties occur at a critical concentration of 5 mM of organic cations. Thus, it can be interpreted that at low concentrations of TC_2AC , the interaction between surfactant and TC_2A^+ ions increases and, hence, the surface tension decreases and surface viscosity increases, causing an increase in the foam stability as well as an increase in the slow relaxation time of micelles. However, above 5 mM of TC_2AC , all these properties go in the reverse direction, indicating that upon further penetration of TC_2A^+ ions, the SDS molecules increase the surface tension and foaming ability and decrease the surface viscosity, foam stability, and relaxation time τ_2 . The results were explained in terms of the molecular packing at interfaces and in micelles. At concentrations lower than 5 mM, the ion–ion interaction between the SDS headgroups and the tetraalkylammonium salt causes the surfactant molecules to pack closer, thereby lowering the surface tension. However, beyond 5 mM of TC_2AC , the antifoamer salt starts penetrating between the SDS molecular packing at the air–water interface, resulting in a larger area per molecule and, hence, a higher surface tension is obtained. The effect of tetraalkylammonium salts on the molecular packing at interfaces and in micelles is schematically shown in Figure 24.

VIII. SUMMARY

This chapter illustrates that for various interfacial phenomena, a commonality exists which determines various surface properties, microstructures, and macroscopic properties of surfactant solutions, monolayers, foams, and emulsions.

It was shown that chain-length compatibility was an important factor in systems involving interfacial films. For the mixed-surfactant system sodium dodecyl sulfate (SDS)/long-chain alcohols, it was shown that the surface tension was minimum and the surface viscosity was maximum when both molecules had the same chain length (i.e., for SDS/ C_{12}OH mixtures). The slow micellar relaxation time, τ_2 , of the mixed micelles exhibits a maximum value, due to the ion–dipole interactions between the SDS and the long-chain alcohol, resulting in very stable micelles. Because of the lowest interfacial tension, the foaming ability was maximum for the equal-chain-length system. Thus, these results show that the chain-length equality strikingly influences surface, micellar, and foam properties.

The second parameter discussed in this chapter was the effect of concentration of SDS on various interfacial phenomena. The slow micellar relaxation time, τ_2 , increased as a function of SDS concentration, showing a maximum at 200

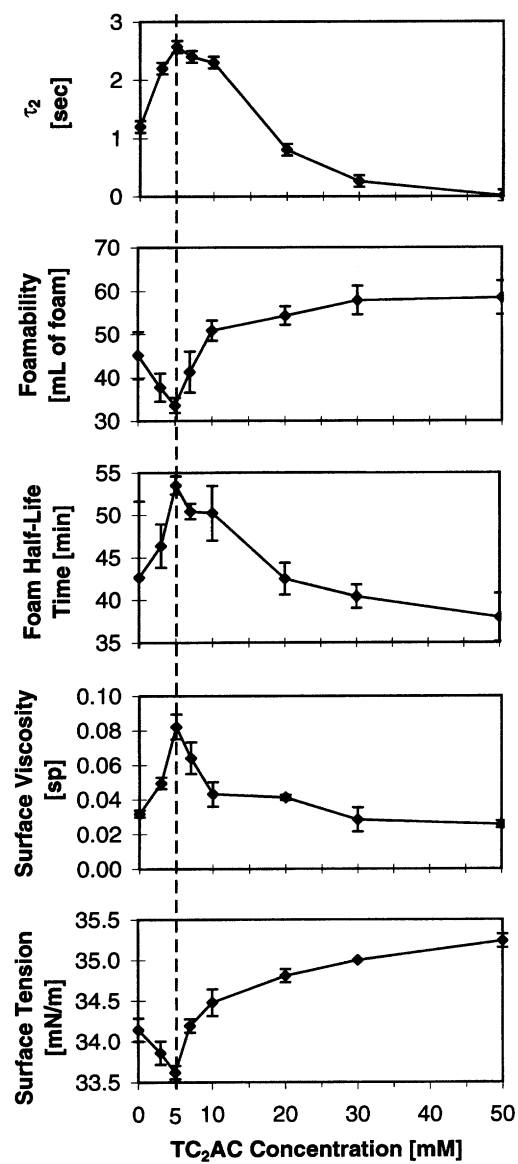


Figure 23 Effect of TC₂AC on foaming properties of 150 mM SDS solutions.

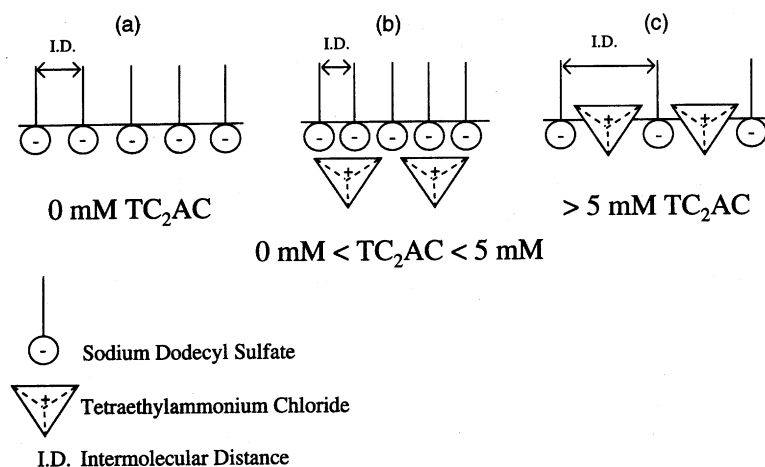


Figure 24 Schematic diagram showing the effect of tetraalkylammonium chlorides on the SDS molecular packing at interfaces [(a) pure SDS; (b) decrease in electrical repulsion due to adsorption of TC₂AC below the SDS monolayer results in a smaller area per molecule; (c) penetration of TC₂AC into the SDS monolayer increases the area per molecule].

mM (5 s). Beyond 200 mM of SDS, the stability decreased again. The micellar stability influenced many dynamic interfacial processes, such as foaming, wetting, emulsification, and solubilization. Very stable micelles were not able to break up fast enough to augment the flux of monomers necessary to stabilize the newly created interface. Hence, a higher interfacial tension was obtained. Therefore, at 200 mM, minimum foamability, maximum single-film stability, maximum single-bubble volume, and a minimum frequency of bubble generation were found. A similar process occurred at both the solid–liquid and liquid–liquid interface. Both the wetting time of fabrics and the droplet size in emulsions were maximum at 200 mM SDS solution.

The molecular ratio in mixed-surfactant system was an important factor that influenced many interfacial properties. Various binary systems, such as decanoic acid/decanol, stearic acid/stearyl alcohol, and SDS/cetyl pyridinium chloride (CPC), exhibited minima and maxima in interfacial properties at the 1:3 and 3:1 molecular ratios. The maximum foam stability, maximum surface viscosity, minimum surface tension, minimum rate of drainage, and minimum area per molecule were found. The observed minima and maxima were attributed to a hexagonal packing of molecules at the 1:3 and 3:1 molecular ratios at the interface. This type of hexagonal arrangement allowed one type of molecule to occupy the corners of the hexagon and the second type of molecule to occupy the centers.

This resulted in the tightest possible packing at the surface and, hence, the observed minima and maxima mentioned above.

One parameter that had been discovered to be crucially important in the successful implementation of the surfactant–polymer flooding process was the salinity of the aqueous phase. For a given oil/water/surfactant system at a given temperature and pressure, a specific salinity was required to produce an ultralow interfacial tension. At the optimal salinity, minimum interfacial tension, maximum oil recovery efficiency, minimum surfactant retention, and minimum viscosity of emulsions in porous media were observed. It was evident that all these processes are interrelated for the oil displacement in porous media by the surfactant–polymer flooding process.

The last parameter investigated in this chapter was the effect of tetraalkylammonium chloride on interfacial properties of SDS solutions. At low concentrations of tetraalkylammonium chloride, the micellar stability increased, due to shielding of the negative charges of the SDS headgroup. However, beyond a critical concentration (depending on the alkyl chain length of the tetraalkylammonium ion), the micellar stability decreased again, due to disruption of the molecular packing in the micelle. Similar results were found in interfacial properties. At the critical concentration (5 mM for tetraethylammonium chloride), minimum foamability, maximum foam stability, maximum surface viscosity, and minimum surface tension were observed. Thus, all the interfacial phenomena described above indicated a “common parameter” which influenced surface, micellar, and macroscopic properties of various surfactant systems.

ACKNOWLEDGMENTS

The authors wish to convey their sincere thanks to the National Science Foundation (Grant NSF-CPE 8005851), to the NFS–ERC Research Center for Particle Science and Technology (Grant EEC 94-02989), and to the ICI Corporation, Alcoa Foundation, and Dow Corning Company for their partial support of this research. D.O. Shah also expresses his indebtedness to his students and postdoctoral associates who contributed to this research.

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