

The importance of sub-angstrom distances in mixed surfactant systems for technological processes

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Abstract

The spacing between atoms and molecules at interfaces and within materials is extremely important in determining the properties of such interfaces and materials. In surfactant monolayers at the air–water interface, it has been shown that small changes in molecular packing lead to large changes in the interfacial properties. Changes in intermolecular distance as small as 0.04 Å have been attributed to the effect of mixing surfactants of different chain lengths. This paper discusses the effect of these sub-angstrom distance changes on foaming, micellar stability, melting points, bubble size, surface viscosity, lubrication, environmental remediation, enhanced oil recovery, and microemulsion stability that result from chain length compatibility. © 1997 Elsevier Science B.V.

Keywords: Chain length compatibility; Mixed surfactant systems; Surfactants in technological processes

1. Introduction

Surfactants are used in a wide variety of applications in which the chain length of the surfactant must be compatible with the chain lengths of other surfactants or hydrocarbons present in the system in order to maximize their performance. In general the chain length of the surfactants used in a given system must be the same to maximize lateral molecular interactions that stabilize surfactant-coated interfaces. When chain lengths are not the same, the resulting monolayer film is disrupted as shown in Fig. 1. It has been reported [1] that as the difference in chain lengths of mixed surfactants increases, the spacing between adjacent surfactant molecules increases. It was further shown that a

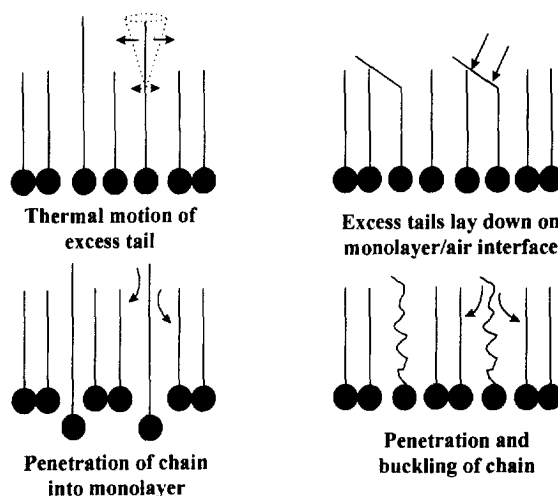


Fig. 1. Schematic diagrams showing possible mechanisms by which chain length compatibility affects molecular packing.

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difference in chain length of two methylene groups resulted in a change of between 0.04 and 0.10 Å in the intermolecular distance in surfactant monolayers. Although these changes are very small, they have a very large effect upon the properties of the interfaces [2]. Consequently, foaming, micellar stability, melting points, bubble size, surface viscosity, lubrication, environmental remediation, enhanced oil recovery, and microemulsion stability are all affected by chain length compatibility and the associated sub-angstrom changes in intermolecular packing.

2. Crystal melting points

Evidence of the chain length compatibility effect has been seen in the melting temperature of some crystals made from mixtures of surface active materials [1]. Increased order is possible in a solid composed of molecules of equal length. This order may result in stronger intermolecular interactions, and thus a higher melting point than one would expect in mixtures of surfactants with different chain lengths. In a similar manner, the effect of chain length incompatibility in decreasing the melting point of fatty acids was demonstrated by Shiao [1] using equimolar mixtures of fatty acids with differing chain lengths as illustrated in Fig. 2. The data presented in Fig. 2 show that as the chain lengths of the two fatty acids become increasingly different, the melting point of the mixture decreases from the pure compound melting point. It is important to note that the lowering of the melting point does not increase significantly for a difference in the chain length of more than two methylene groups.

3. Effect of chain length compatibility on retardation of evaporation of water

It is widely known that an oil film on the surface of water can reduce the evaporation rate. A monolayer of an alkanol on the surface of water also imposes a barrier to the evaporation of water. The transport of water molecules from the surface to the gas phase is influenced by intermolecular spac-

ing in the monolayer. Therefore, the packing density of the surfactants in the monolayer components influences this accessible area.

Monolayers of alkanols were created on a Langmuir trough, similar to the method used for the molecular area study [1]. The monolayer was compressed to a surface pressure of 30 mN m⁻¹. The evaporation rate was determined by covering a petri dish filled with desiccant, and placing this inverted dish 4 mm above the monolayer surface. The change in weight of the desiccant was measured after 10 min, with the increase attributed to water evaporated through the monolayer. This evaporation rate is corrected by determining the rate of absorption of the desiccant for water in the ambient air. A resistance to evaporation is calculated based upon its inverse relationship to the evaporation rate. As can be seen in Fig. 3, the resistance to evaporation falls for mixed monolayers, compared to monolayers of pure alkanols. This lower evaporation resistance is attributed to decreased molecular packing in the monolayer due to the chain length differences.

4. The effect of chain length compatibility on micellar stability

The association of many classes of surface active molecules into micellar aggregates is a well-known phenomenon. Micelles are often drawn as spherical aggregates of oriented surfactant molecules. However, micelles are in dynamic equilibrium with individual surfactant molecules that are constantly being exchanged into and out of micelles. Additionally, the micelles themselves are continuously disintegrating and reforming. The kinetics of this process has been evaluated by Aniansson et al. [3], and the relevance of micellar relaxation to technological processes for single surfactant systems such as sodium dodecyl sulfate (SDS) in water has been studied by Shah and co-workers [4–6].

The effect of alcohol chain length on the micellar relaxation time was recently determined by Patist et al. [7] as shown in Fig. 4. At a constant SDS concentration of 200 mM and 5 mM alcohol, the micellar stability reaches a maximum for C₁₂OH,

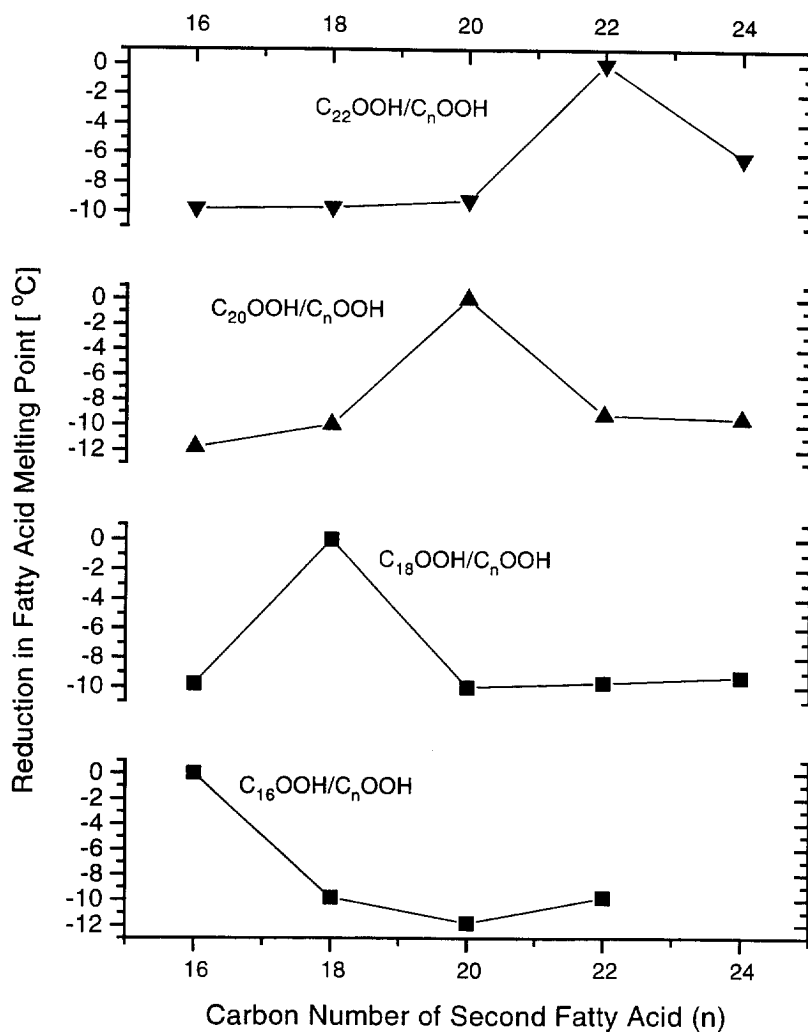


Fig. 2. The reduction in melting point for equimolar mixtures of fatty acids with different chain lengths.

where the alcohol chain lengths are equal to the surfactant (SDS) chain length (12 carbon atoms). The presence of shorter or longer chain alcohols decreases the stability, resulting in a lower relaxation time, τ_2 . The horizontal line in Fig. 4 corresponds to the maximum relaxation time (5 s) observed for pure SDS at 200 mM [6].

The stability associated with chain length compatibility is also expected to increase substantially for the addition of a cationic surfactant (C₁₂TAB) to a micellar SDS solution. In this case ion-ion interactions play an important role [8]. Fig. 5 shows the effect of 5 mM C₁₂TAB on the

micellar stability of a 100 mM SDS solution. The horizontal line in Fig. 5 corresponds to the relaxation time of pure SDS at 100 mM. Even for the addition of C_nTAB of non-equal chain lengths, τ_2 increases above the level for a pure SDS system. However, the maximum increase in micellar stability is observed for C₁₂TAB due to what is interpreted to be tighter packing of the micelles caused by ionic attraction between the head groups of the positively charged C₁₂TAB and the negatively charged SDS.

As discussed previously, micellar stability has a significant effect on many processes involving an

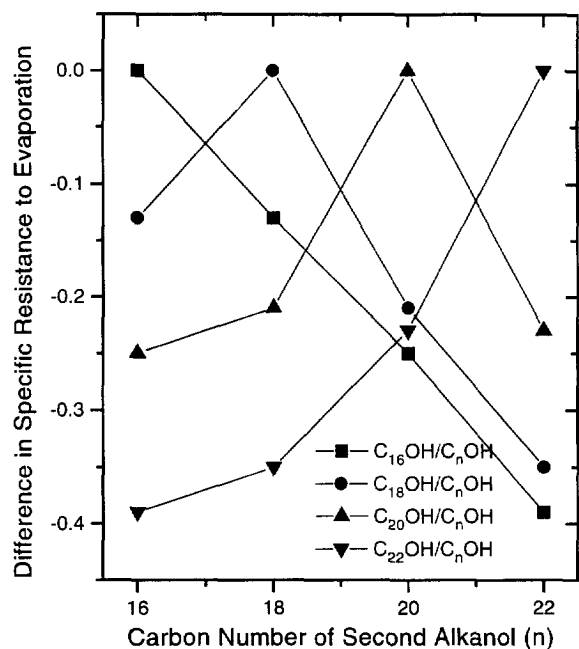


Fig. 3. The change in resistance to evaporation from a water surface, for mixtures of alkanols of different chain lengths.

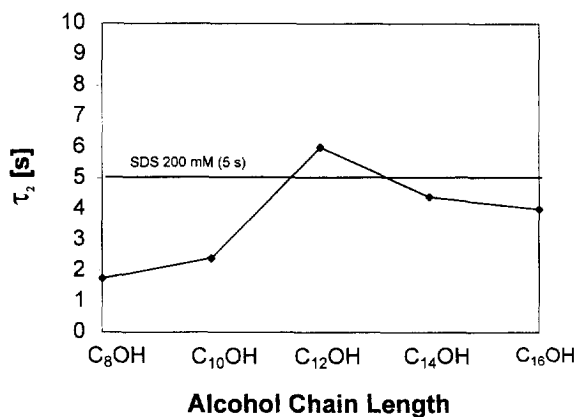


Fig. 4. The effect of alcohol chain length on the micellar relaxation time (τ_1) in SDS solutions (200 mM, 5 mM alcohol) at 25°C.

increase in interfacial area. Sharma [9] showed that the foam stability follows the same trend as the micellar stability. The maximum foam stability is obtained at the maximum micellar relaxation time. The foam stability of SDS + C_nTAB is shown in Fig. 6. At equal carbon chain length the foam

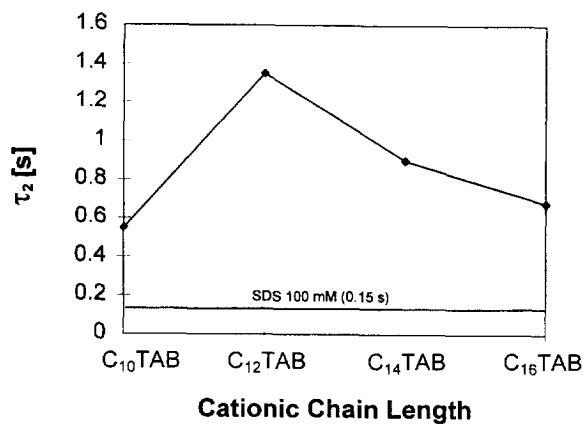


Fig. 5. The effect of 5 mM C_xTAB on the micellar relaxation time (τ_2) in 100 mM SDS solutions at 25°C.

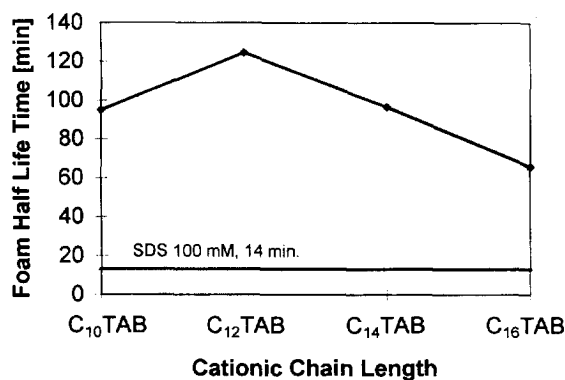


Fig. 6. The effect of 5 mM C_xTAB on the foam stability of 100 mM SDS solutions at 25°C.

stability appears to be maximum. From the data it can be concluded that the micellar stability increases by the addition of C₁₂ alcohol to a SDS solution. The addition of short chain alcohols destabilizes the micelles resulting in a lower relaxation time.

The addition of C₁₂TAB to 100 mM SDS solutions increases the stability of SDS micelles even when the chain lengths are not equal. This is likely due to the strong ion-ion interaction between the anionic sulfate head group and the cationic trimethyl-ammonium head group. However, the most stable micelles are again formed when the chain lengths of the adjacent molecules are the same.

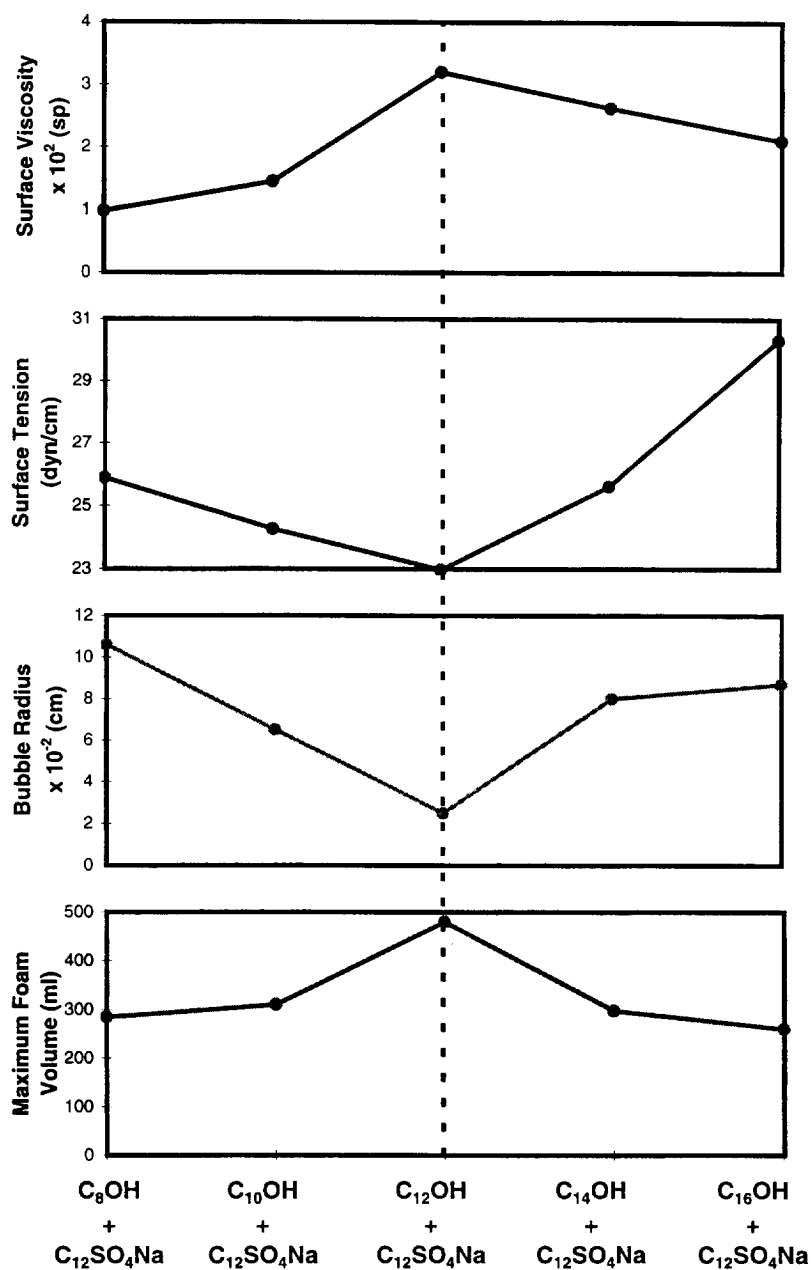


Fig. 7. Bubble size and other surface properties of mixed sodium dodecyl sulfate–long chain alcohol mixtures such as foaminess, surface tension and surface viscosity.

5. Effect of chain length compatibility on foaming and interfacial properties

The significance of chain length compatibility on properties which affect foam formation and

foam stability cannot be understated. These molecular interactions influence surface shear viscosity and surface tension of a given mixed surfactant system. In addition to these inherent surface properties, rate of film drainage and foam bubble radius

are also influenced by the effect of surfactant chain length compatibility. Ultimately, these microscopic properties contribute to macroscopic foaming characteristics such as foam stability and foaminess.

The effect of chain length compatibility on properties that relate to foaming such as surface viscosity, surface tension, bubble radius, and foaminess is illustrated in Fig. 7 for the sodium dodecyl sulfate-alkanol system. The data in Fig. 7 show that the $C_{12}OH + NaC_{12}SO_4$ combination of equal chain lengths leads to smaller bubbles and greater foam stability. The data also show that the surface tension is at a minimum, indicating a maximum in molecular packing at the air-water interface. Because the molecular packing is maximum, there is a corresponding maximum in the surface viscosity when the chain lengths are equal. As the chain length of the alkanol deviates from that of the SDS (12 carbons), the properties of the interface change dramatically, clearly illustrating the effect of chain length compatibility in foaming and related phenomena [10].

6. Lubrication

The effect of chain length compatibility on boundary lubrication has been studied by a variety of methods. Properties such as the coefficient of friction, scuff load, wear scar diameter, and dwell time have been measured in the laboratory using different surfaces and mixed surfactant systems. The theory behind boundary lubrication has been related to the surfactants' configuration at the surface of an adsorbed liquid film.

Intermolecular cohesion between two different surfactants, primarily due to van der Waal's forces between the surfactant methylene groups, strengthens adsorption with increasing surfactant chain length. In essence, increased adsorption of mixed surfactants on a substrate reduces friction between that substrate and another surface.

Fort [2] examined the reduction of polymer friction with the use of a turntable device that rotated in contact with a lever arm that was attached to a strain gauge. This apparatus enabled the calculation of coefficients of friction for surfac-

tant adsorbed on polymer surfaces. In terms of chain length compatibility, stearic acid ($CH_3-(CH_2)_{16}-COOH$) was dissolved in hexane, decane and hexadecane and coefficients of friction of these solutions on polyethylene terephthalate were recorded to be 0.24, 0.17 and 0.11, respectively. Thus, it was shown that the stearic acid-hexadecane system adsorbed with the greatest strength due to the highest intermolecular cohesive forces.

Askwith et al. [11] evaluated a number of parameters while examining the effects of chain length compatibility using mixed lubricants, including coefficient of friction, scar diameter and dwell time. For each paraffin oil, the additive with the chain length equal to that of the paraffin oil resulted in the greatest dwell time, which indicates high film stability. In addition, the dwell times for the chain length matched $C_{16}-C_{16}$ system yielded the overall greatest dwell times. Experiments using nonmatched oil/surfactant chain lengths yielded lower dwell times or decreased film stability.

More recent studies [12] have related monolayer properties to chain length compatibility and boundary lubrication. Both coefficient of friction and wear scar diameter experiments on aluminum surfaces yielded local minima for the hexadecane- C_{16} fatty acid system as shown in Fig. 8. The minima of coefficient of friction and wear scar diameter for the $C_{16}-C_{16}$ system correlate with previous findings. However, these systems were also tested on polymethyl methacrylate, and the coefficient of friction remained constant for all chain length combinations. This suggests that the chemical reaction of the carboxyl group with the metal surface is required to produce a stable monolayer of fatty acid and hexadecane on the substrate, a condition necessary for maximum reduction of friction.

7. Effect of chain length compatibility on oil removal from porous media

The removal of oil from porous media has been studied extensively during the last two decades both for enhanced oil recovery and environmental remediation. Because the removal of oil from porous media involves interfacial tension, which is

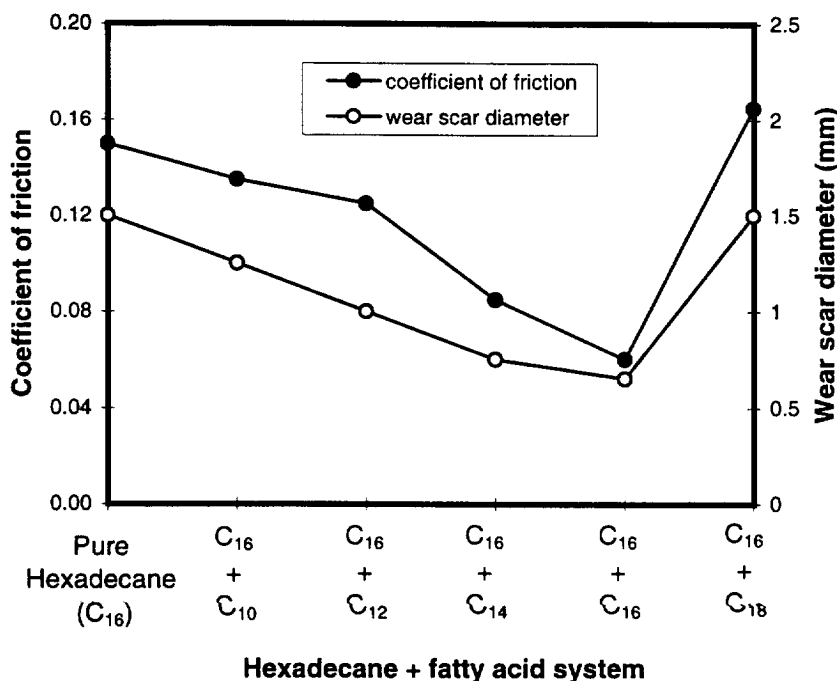


Fig. 8. Coefficient of friction and wear scan diameter of varying chain length hexadecane–fatty acid systems.

a function of interfacial molecular interactions, the effect of chain length compatibility is an important factor in oil removal as illustrated in Fig. 9. As presented in Fig. 9 the fluid displacement efficiency reaches a maximum when the chain lengths of the alcohol and surfactant are matched. In addition, there is a maximum in the breakthrough time when the chain lengths of the alcohol and surfactant are equal. As the chain lengths become mismatched by even two methylene groups, the breakthrough time and fluid displacement efficiency decrease by 10–35%, showing the important role of chain length compatibility in oil removal from porous media [10].

8. Effect of chain length compatibility on rust prevention

The chain length compatibility between additives (fatty acids) and solvents in rust prevention has been investigated by Ries et al. [13]. The compatibility was investigated using ASTM rust experiments. The results from the rust tests showed

that a C₁₆ acid added to *n*-hexadecane, at three concentrations of 0.4, 0.2, and 0.1%, is considerably superior when compared to the C₁₅ and C₁₇ acids. Fatty acids of varying chain length were then added to a pentadecane (C₁₅) solvent. Again, the combination of fatty acid and solvent of matching chain length (C_{15acid}–C_{15solvent}) provided the greatest protection against rust. The results showed that mixed films whose acid and hydrocarbon molecules have the same chain length may provide better protection. It is believed that such equal chain length film combinations are tightly packed and more difficult to displace.

In a separate study the scuffing loads for two-component systems were measured in a four-ball machine [14]. Interestingly, the plot of scuffing load vs. chain length of additive provided sharp peaks when the additive and solvent had the same number of carbon atoms. The authors attributed the equal chain length effect to the more favorable peptization of wear debris. Others have postulated that the maximum observed is due to a more effective protective film on the initial surfaces because of the chain length compatibility.

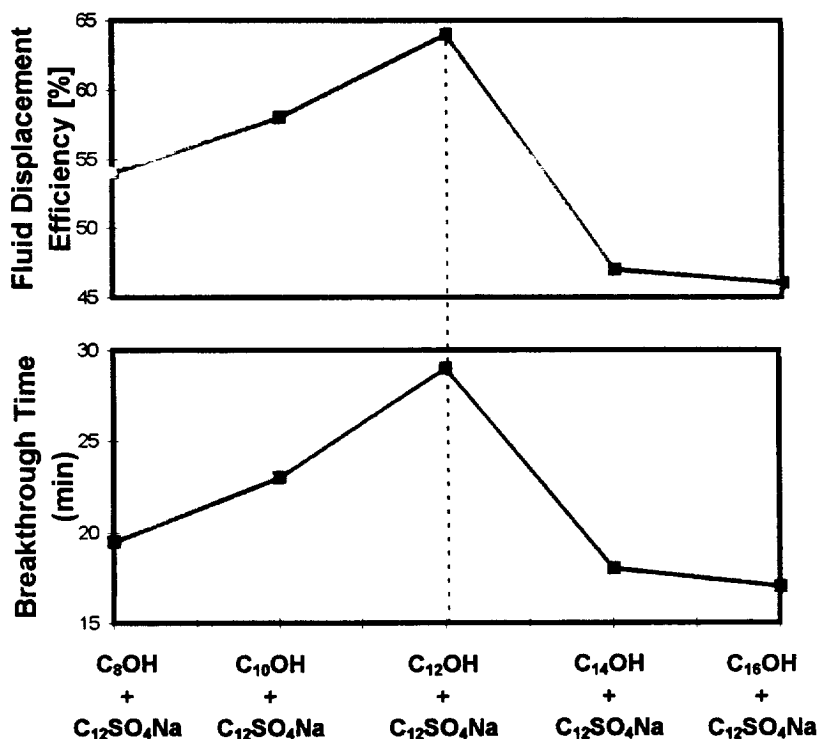


Fig. 9. Chain length (alcohol/SDS) effect on breakthrough time and fluid displacement efficiency for removal of residual trapped oil in porous media by in situ foaming.

9. Chain length compatibility in macro- and micro-emulsions

The effect of chain length compatibility in emulsion systems has been studied in systems involving surfactants, cosurfactants, and oils [15]. The effect of chain lengths is particularly important to microemulsion systems in which the interfacial tension must remain extremely low ($<10^{-3}$ dyn cm^{-1}) in order to maintain stability. In microemulsion systems, both a surfactant and a cosurfactant (usually an alcohol) are generally required. The effect of the alcohol chain length relative to the surfactant chain length and oil chain length has been shown to be very important. One of most revealing methods of observing this phenomenon is to measure the water solubilization capacity of a water-in-oil microemulsion as shown in Fig. 10. The data in Fig. 10 for butanol show that the quantity of water solubilized in the microemulsion prior to phase separation decreased as the oil chain length

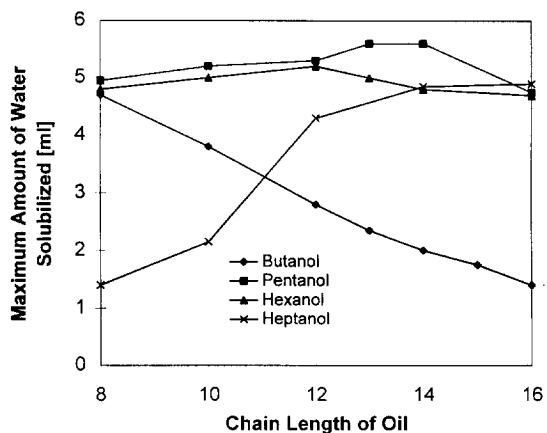


Fig. 10. Water solubilization capacity of water-in-oil microemulsions produced using 4 ml of the specified alcohol with 1 g of sodium stearate and 10 ml of the specified straight-chain hydrocarbon oil.

increased. As water is added to the system, the concentration of butanol in the aqueous phase increases as the chain length of oil increases. This causes desorption of the soap from the interface into the water + butanol phase.

In contrast, the data in Fig. 10 for heptanol show the opposite trend and this is attributed to the chain length of heptanol, resulting in partitioning behavior different from that of butanol. The longer heptanol chain allows for greater heptanol solubility in the oil phase and negligible solubility in water. As the oil chain length increases, the solubility of the heptanol in the oil phase decreases, forcing more heptanol to the interfacial region, thereby allowing an increase in the total area of the oil–water interface. Alcohol molecules with intermediate chain lengths such as pentanol and hexanol do not show the same partitioning behavior as butanol and heptanol as shown in Fig. 10.

As the quantity of butanol, pentanol, and hexanol is doubled, the quantity of water solubilized increases as shown in Fig. 11. However, for pentanol and hexanol it is also apparent that there is a distinct oil chain length that corresponds to the maximum water solubilization. For pentanol and hexanol the maximum solubilization occurs with oil chain lengths of 13 and 12, respectively, or when the sum of the oil chain length and the alcohol chain length equals the surfactant chain

length (18 for stearate). In other words the maximum water solubilization occurs when $la + lo = ls$ (la is the length of the hydrocarbon chain in the alcohol, lo is the length of the hydrocarbon chain in the oil, and ls is the length of the hydrocarbon chain in the soap). It is believed that the maximization in solubilization observed at $la + lo = ls$ is due to either the maximum cohesive interaction between hydrocarbon chains or the minimum disruption in the interfacial region as shown in Fig. 12.

The effect of changing the chain length has a very pronounced effect upon the interfacial properties of microemulsions. Even changing the oil chain length by one atom has a dramatic effect on the dielectric constant of a microemulsion as illustrated in Fig. 13. As shown in Fig. 13, increasing the oil chain length from 11 to 12 carbon atoms in microemulsions results in a near doubling of the dielectric constant at 0.5 MHz.

Other research on the effect of chain length compatibility in emulsion systems has been evaluated and compared by Bansal et al. [15]. The chain length compatibility approach used by Bansal et al. has been used to interpret the solubilization behavior of some water-in-oil microemulsions composed of cationic surfactants, water, and aromatic solvents [16,17], and of the same systems in the presence of alcohols or carboxylic acids as cosurfactant [18,19]. The BSO equation ($lo + la = ls$) was re-examined by Li et al. [20], who showed that this equation is valid for anionic surfactants (sulfates and carboxylates). However, it did not hold for mixtures of cetyltrimethylammonium bromide (CTAB)/(C₃–C₁₂) *n*-aliphatic alcohols/*n*-octane/water. The authors attributed this discrepancy to the repulsion of the cationic head-group of the surfactant and the electropositive hydrogen of the hydroxyl group of the alcohol. Another exception to the BSO equation is sodium dioctylsulfosuccinate (Aerosol OT) which has proven to be more efficient than expected. This was ascribed to its double-chain configuration [21].

Garti et al. [22] have investigated the validity of the BSO equation for nonionic microemulsions in several systems based on the following components: ethoxylated alcohols/C₁₀–C₁₆ *n*-alkanes/C₂–C₁₂ *n*-aliphatic alcohols/water. They have

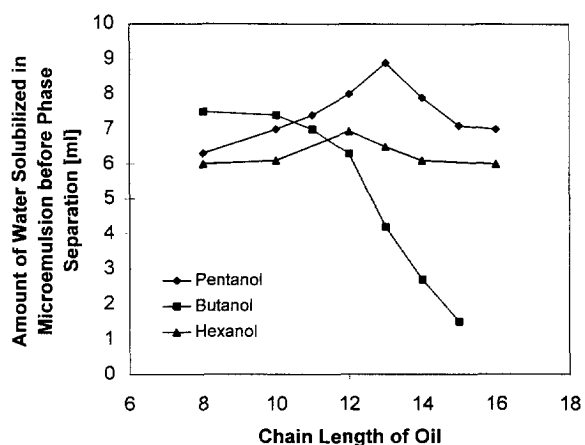


Fig. 11. Water solubilization capacity of water-in-oil microemulsions produced using 8 ml of the specified alcohol with 1 g of sodium stearate and 10 ml of the specified straight-chain hydrocarbon oil.

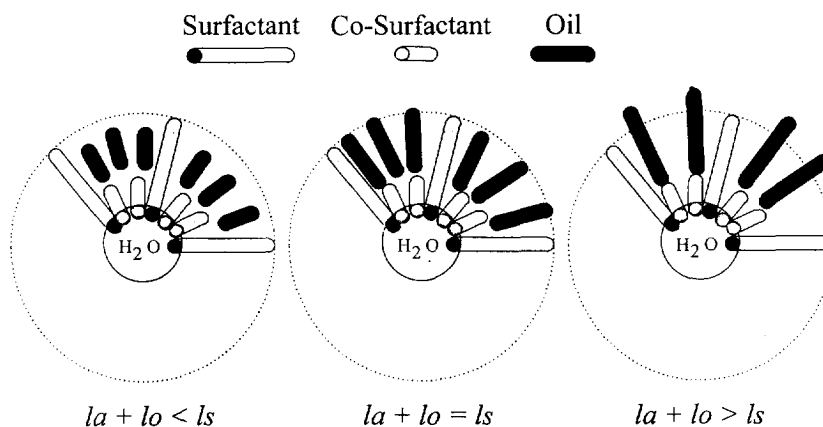


Fig. 12. Schematic diagram showing the effect of surfactant, oil, and cosurfactant (alcohol) chain lengths at the water–oil interface.

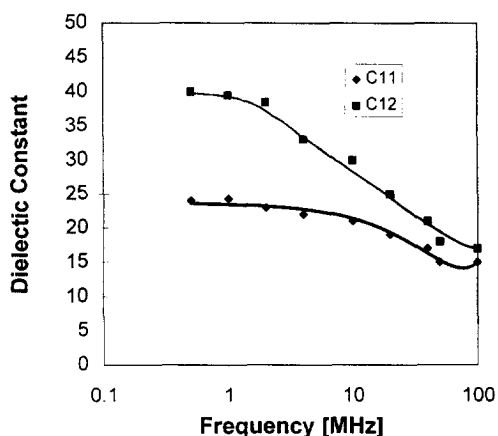


Fig. 13. Effect of increasing the oil chain length on the dielectric constant of microemulsions at various frequencies.

described water solubilization only in monophasic areas of the phase diagrams. Although phase diagrams of quaternary systems are generally based on constant ratios of surfactant-to-water or cosurfactant-to-surfactant [23], their representation [22], is also quite common, particularly among solubilization researchers [24–26]. In their phase diagrams, the alcohol has been considered as a cosolvent [27], rather than a cosurfactant. Garti et al. [22] have shown for the first time that the BSO equation and the concept of chain length compatibility [15,28] can predict, within some limits, conditions for maximum water solubilization in the presence of nonionic surfactant. Limitations on their predictive capacity are

enforced by, for example, requirements that the cosurfactant (alcohol) is not too soluble in either water or oil. The appearance of a maximum in water solubilization as a function of the chain length of either the alcohol or the oil is consistent with the concept of competition between the spontaneous curvature of the interface and its critical radius as outlined by Leung and Shah [29,30].

John and Rakshit [31] have studied the phase behavior and properties of a microemulsion system containing alkanol as cosurfactant, where alkanol indicates various mixtures of two short chain alcohols (propanol and hexanol). They have shown that the area of the single-phase microemulsion region in the ternary phase diagram increased considerably in the systems containing mixed alkanols as cosurfactants compared with pure alkanol systems. Temperature increase induces a Winsor transition in the order II→III→I in the mixed systems, which was opposite to the trend observed in the pure propanol system. The conductivity studies in the propanol–hexanol system revealed that the mixtures of two alkanols behave somewhat like alcohols of carbon chain lengths (C_4 or C_5) that are between those of the two components.

Panitz et al. [32] have used the pulsed field gradient NMR method to determine self-diffusion coefficients of surfactant molecules, solubilized hydrocarbons, and D_2O solvent in ternary *N*-alkyl-*N*, *N*-dimethylamine oxide/alkane/ D_2O surfactant systems. They have shown that in the micellar phase, diffusion is governed by hydrodynamic

transport of the micelles, supplemented by an exchange of solubilized hydrocarbon upon micellar collisions. They have tested this model by varying both the surfactant chain length and the size of the hydrocarbon molecules. Mobilities of the surfactant in the gel phase are low and they have been determined only for the surfactant with the shortest chain length (C_{12} -DMAO). They have found that exchange of hydrocarbon between micellar entities in the gel occurs by a hopping process in which the associated rate decreases with the surfactant chain length.

10. Conclusions

Chain length compatibility has an important effect upon fundamental interfacial properties and processes. The effect of chain length compatibility can be explained using experimental results as well as by using theoretical calculations that are based to some extent upon experimental observations. All of the resulting information from experimental and theoretical calculations shows that as the chain length of adjacent hydrocarbon chains is matched, the resulting hydrocarbon layer has more order, tighter packing, and greater stability. The increased packing and order that results from chain length matching leads to a maximization in the surface viscosity, micellar lifetime, and maximum foamability as illustrated in Fig. 14. As a consequence of this packing there is also a corresponding minimum in the surface tension, contact angle, and bubble radius. In microemulsion systems, it has been shown that for some systems the chain length compatibility is important to the stability of microemulsions with the maximum stability occurring when the sum of the alcohol and oil chain lengths equals the surfactant chain length ($l_o + l_a = l_s$). Finally, on a practical note it has been shown that chain length compatibility has an important direct influence in technologies such as detergency, solubilization, foaming, wetting, lubrication, evaporation control, corrosion, oil recovery, envi-

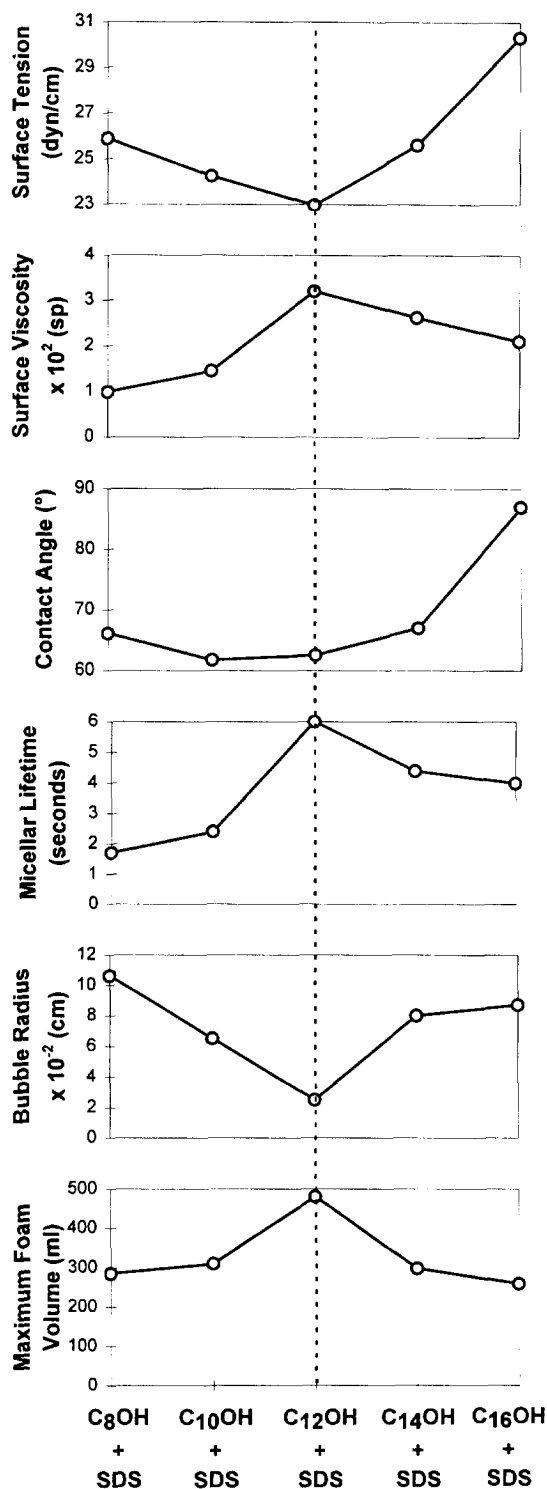


Fig. 14. Effect of chain length compatibility on interface-related properties for the dodecyl sulfate-alkanol systems shown.

ronmental remediation, and microemulsion stabilization, in addition to many other technologies that utilize surfactants.

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