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Chain length compatibility effects in mixed surfactant systems for technological applications

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Abstract

Chain length compatibility is an important factor in systems involving interfacial films. As surface active molecules as well as other hydrocarbon molecules are aligned at interfaces, the properties of the interface are impacted to a large extent upon the matching or mismatching of the alkyl chain lengths. The effects of chain length compatibility are particularly important to interfacial properties and technologies such as: surface tension, surface viscosity, micellar stability, foamability, lubrication, contact angle, bubble size, environmental remediation, corrosion, enhanced oil recovery, microemulsion water solubilization and microemulsion stability. In this article the authors discuss the importance of chain length compatibility on these interfacial properties and related technologies from a practical and fundamental viewpoint. © 1998 Elsevier Science B.V.

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

Contents

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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. If chain length mismatching is present in a surfactant film, the excess hydrocarbon tails have more freedom to disrupt the molecular packing through conformational disorder, increased tail motion, or other factors as shown in Fig. 1. This disruption in the molecular packing leads to lower interaction energies and hence, lower film stability relative to comparable scenarios in which the chain

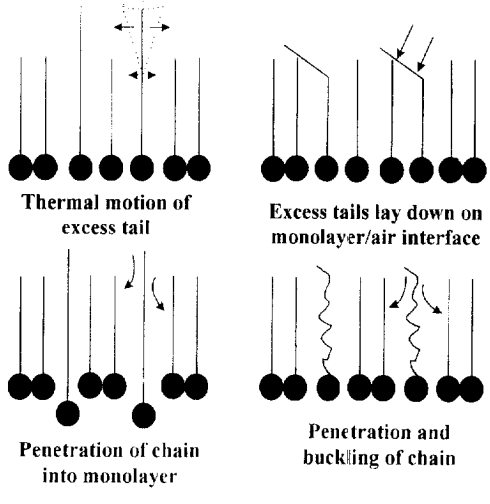

Fig. 1. Schematic diagram showing different ways in which chain length compatibility can influence molecular packing.

lengths are compatible. The chain length compatibility affects many film properties such as surface tension, surface viscosity, contact angle, micellar lifetime, bubble radius and foamability. In other systems such as microemulsions, the chain length of surfactant must be equal to the sum of the cosurfactant chain length and the hydrocarbon chain length in order to minimize disruption in the interfacial region. In all systems involving surfactants with different chain lengths, the effects of chain length compatibility are very important. In this study the effect of chain length compatibility will be examined for properties and technologies such as: surface tension, surface viscosity, micellar stability, foamability, lubrication, contact angle, bubble size, environmental remediation, corrosion, enhanced oil recovery, microemulsion water solubilization and microemulsion stability.

2. Effect of chain length compatibility on 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.

The effect of hydrocarbon chain length on the melting points of organic compounds has been well established. As the chain length increases, the melting point increases as shown in Fig. 2. In a similar manner, the effect of chain length compatibility in decreasing the melting point of fatty acids was performed by Shiao [1] using equimolar mixtures of fatty acids with differing chain lengths as illustrated in Fig. 3. The data presented in Fig. 3 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. Ideally, one would expect an additivity rule melting temperatures of mixtures of these materials. This appears to be true for alkanes and alkanols, but not for the fatty acids. Instead, the melting temperature of these mixtures is lower than this ideal value and even lower than either pure component, as can be seen in Fig. 3 for mixtures of C_{16} through C_{22} fatty acids. This chain length compatibility in fatty acids but not alkanes and alkanols can be attributed to the influence of the head groups. Chain length compatibility depends on order, but the alkanes have no head group, so the solid may be considered disordered. The alkanols have a small head group, but its influence is not strong enough to order the solid. The fatty acids, on the other hand, have the strongest head group interaction and this is apparently enough to cause ordering in the solid. It may be that layers of fatty acid are formed on crystallization, so that the hydrocarbon tails are much more ordered than in the alkanes or alkanols. This increased order apparently leads to the higher melting point of the fatty acids, as well as the excess reduction in melting point for crystals of mixed fatty acids.

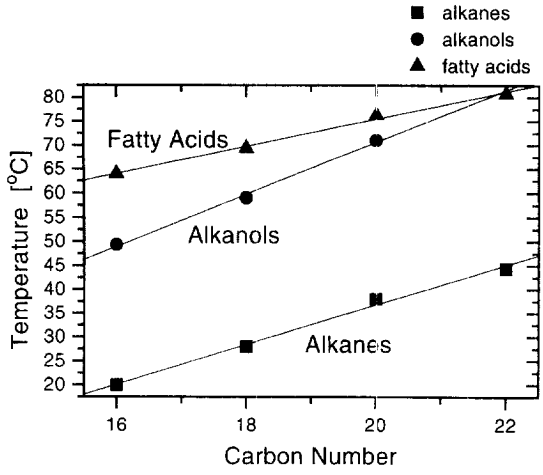

Fig. 2. Melting point of pure alkanes, alkanols and fatty acids.

3. Effect of chain length compatibility on contact angle and wettability

A chain length compatibility effect can be seen in the contact angle, spreading coefficient and the surface tension of sodium alkyl sulfate/alkanol mixtures. Wettability can be affected by chain length compatibility also, as it is related to contact angle.

Contact angle measurements of surfactant solutions of alkyl sulfate/alkanol mixtures were made on teflon surfaces [1]. Results from this comparison are presented in Fig. 4 along with surface tension measurements performed using a Wilhelmy Plate apparatus and the spreading coefficient that was calculated using Eq. (1) [2].

$$S_{L/S} = \gamma_{LA}(\cos\theta - 1) \tag{1}$$

Where $S_{L/S}$ is the spreading coefficient of the liquid on the solid substrate, γ_{LA} is the surface tension at the liquid/air interface and cos θ is the liquid contact angle on the solid substrate. Measurements were taken with sodium alkyl sulfate solutions mixed with alkanols at a 10:1 molar ratio. Concentrations of 25, 5 and 2 mM surfactant were used for $C_{10}SO_4$, $C_{12}SO_4$ and $C_{14}SO_4$, respectively. Alkanols ranging from C_8OH to $C_{16}OH$ were also used.

For the three sodium alkyl sulfates mixed with various alkanols, several trends appear in the data. The spreading coefficient is maximum, the contact angle is minimum and the surface tension is minimum when the chain length of the surfactant is equal to that of the alkanol (see Fig. 4). There are a few slight exceptions to this in the contact angle measurements, where the minimum for $C_{12}SO_4$ occurs when mixed with $C_{10}OH$ and for $C_{14}SO_4$ the minimum occurs with $C_{12}OH$. The minimum in surface tension can be explained by the closer packing of

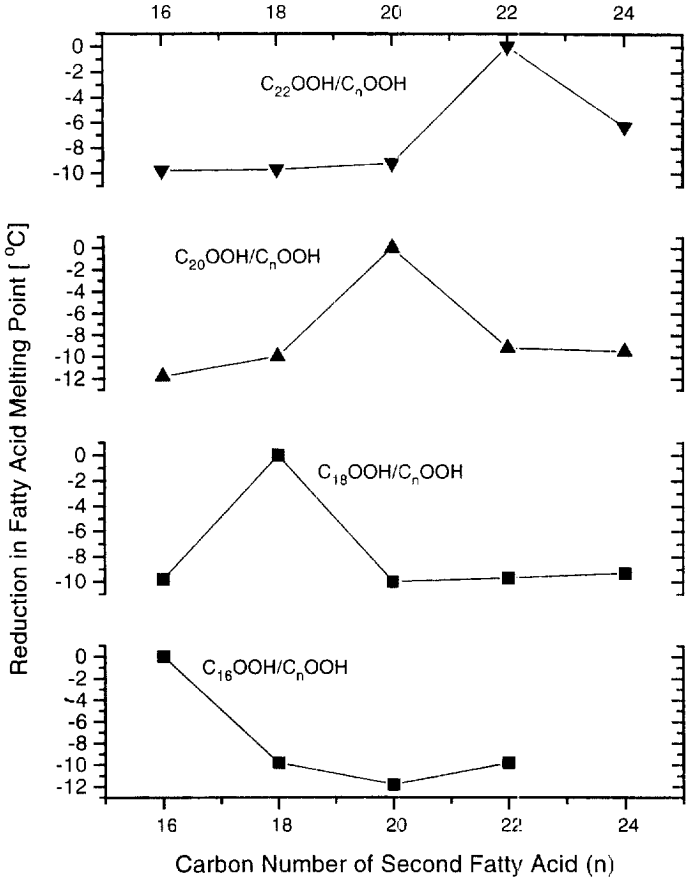

Fig. 3. The reduction in melting point for equimolar mixtures of fatty acids with different chain lengths.

the monolayer expected for matched surfactant/alkanol pairs. The same can account for the minimum in the contact angle, allowing for better spreading when the surface has a tighter surfactant/alkanol packing.

4. Effect of chain length compatibility on mixed monolayer properties

4.1. Effect of chain length compatibility on evaporation retardation

It is widely known that an oil film on the surface of a body 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 the accessible area of the gas

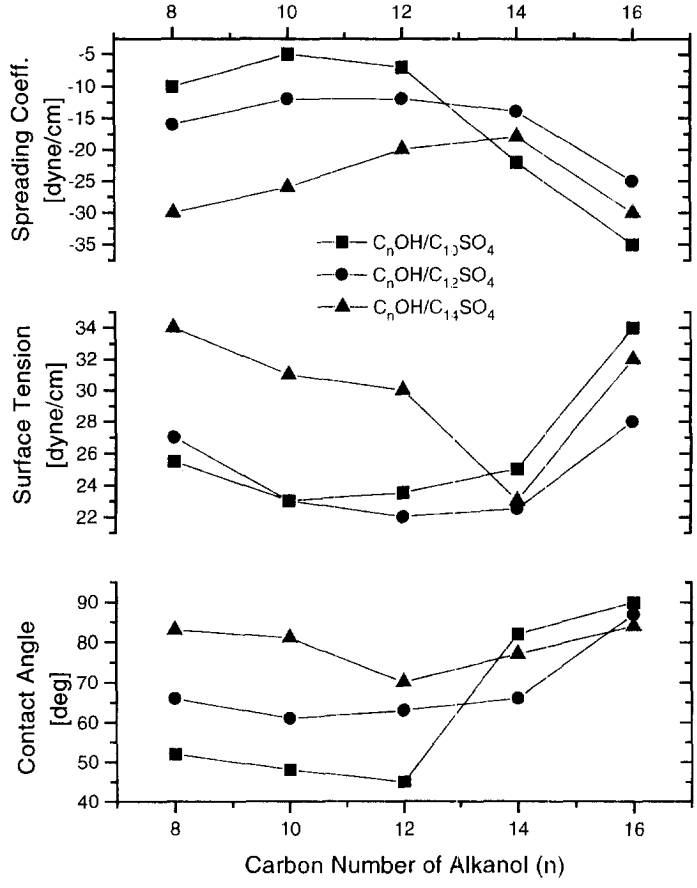

Fig. 4. Spreading coefficient, surface tension and contact angle for mixtures of alkanols and sodium alkyl sulfates of different chain lengths.

through the monolayer. The packing density of the monolayer components influences this accessible area.

It has been observed that mixed monolayers of alkanols with different chain lengths have a greater surface area per molecule than monolayers of either pure alkanol. This increase in area becomes larger as the difference in the chain length of the alkanols increases. This phenomenon has been termed the 'chain length compatibility effect' and has been attributed to repulsion due to the motion of the hydrocarbon tail ends of the longer alkanol.

Monolayers of alkanols were created on a Langmuir trough [1], similar to the method used for the molecular area study, which will be discussed in the next section. The monolayer was compressed to a surface pressure of 30 mN/m. 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

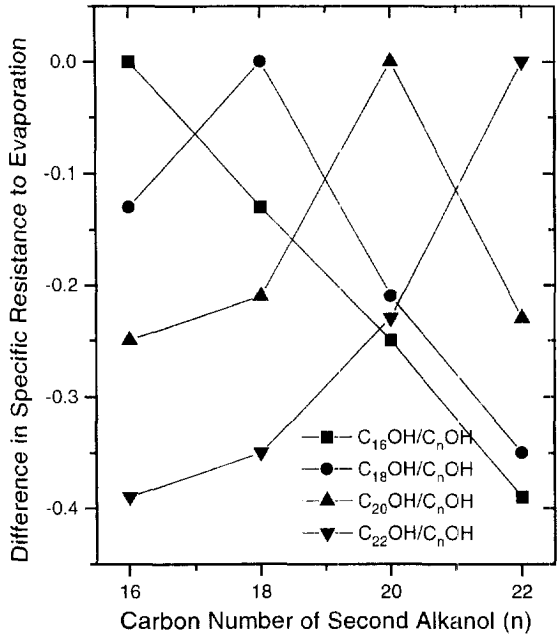

Fig. 5. The change in resistance to evaporation from a water surface, for mixtures of alkanols of different chain lengths.

of the desiccant was measured after 10 min, with the increase attributed to evaporated water 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. 5, 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 incompatibility.

4.2. Effect of chain length compatibility on molecular area

Evidence for the effect of mixed monolayers on molecular area was provided by Shiao [1] using a Langmuir trough. The alkanols, which are insoluble in water, were dissolved in a chloroform/methanol/*n*-hexane solvent and spread onto the water surface with a microsyringe. Surface pressure, as measured with a Wilhelmy plate, was monitored as the alkanol monolayer was compressed by a sliding barrier. The area/molecule was calculated from the trough area and the moles of alkanol added. During monolayer compression, surface pressure is zero at larger molecular areas down to ≈ 23 Å^2/molecule. Below this molecular area the surface pressure increases monotonically to an inflection point at ≈ 15 mN/m, where there is a

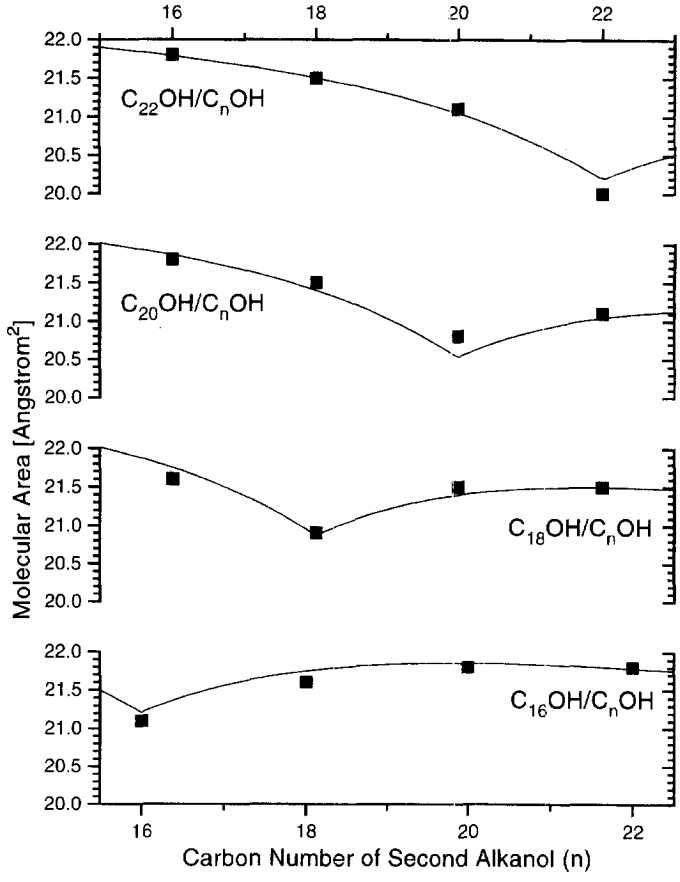

Fig. 6. Molecular areas for mixed monolayers of C_{16}–C_{22} alkanols.

sudden increase in the slope of the surface pressure vs. area curve. This change is attributed to the formation of a 'condensed' phase in the monolayer. Surface pressure increases along this steeper slope until the collapse of the monolayer. This slope, extrapolated back to zero surface pressure, results in the reported value of molecular area. [1].

For mixed alkanols at an air/water interface, the molecular area is larger than for either pure alkanol. This increase is attributed to the motion of the excess length of the tail of the longer alkanol. Molecular area for mixtures of $C_{16}OH$ through $C_{22}OH$ are presented in Fig. 6.

5. 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 which implies that micelles are static structures. 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. Aniansson [3] developed a theoretical model about the kinetics of micellization. There are two relaxation processes; the first one is the fast relaxation process with relaxation time τ_1 (generally on the order of microseconds), which is associated with the fast exchange of monomers between micelles and the surrounding bulk phase. The second relaxation time τ_2 (generally on the order of milliseconds to minutes) is attributed to the micelle formation and dissolution process. Interestingly, the two relaxation times can be used to calculate two important parameters of a micellar solution, namely the 'residence time' of a surfactant in a micelle and the 'average lifetime' or stability of micelles. The micellar stability influences many processes of interest such as foaming, wetting, solubilization and emulsification.

Various techniques such as stopped-flow, temperature jump, pressure jump and ultrasonic absorption have provided insight into the dynamic aspects and micellization kinetics of surfactant solutions [4–9]. The jump techniques have proven most useful when the relaxation of a physical parameter is observed as the system goes from one thermodynamic state into another. For sodium dodecyl sulfate (SDS) it has been shown that a maximum in micellar relaxation time (at 200 mM) correlates to reduced foamability, longer fabric wetting time, a maximum in gas bubble size and emulsion droplet size and a maximum in oil and hydrophobic solids (dye) solubilization rates in micellar solutions [10].

The molecular mechanism for change in relaxation time as a function of concentration and the occurrence of a maximum was proposed by Oh et al. [11,12].

Leung and Shah [13] have shown that the micellar stability of 100 mM SDS solution decreases by the addition of short chain alcohols (C_1OH–C_4OH). Short chain alcohols are believed to destabilize the micelles, lowering the micellar stability by decreasing the nucleus size or decreasing the activation energy of the micelle nuclei formation.

The effect of long chain alcohols (C_8OH–$C_{16}OH$) on the micellar relaxation time was investigated by Patist and Shah [14]. Fig. 7 shows that at a constant SDS concentration of 200 mM and 5 mol.% alcohol the micellar stability reaches a maximum for $C_{12}OH$, 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 dotted line in Fig. 7 corresponds to the maximum relaxation time (5 s) observed for pure SDS at 200 mM [10].

The effect of adding $C_{12}OH$ to solutions with lower SDS concentrations is shown in Fig. 8. At a concentration of 25 mM or approximately three times the CMC ($\approx$ 8 mM), the stabilizing effect of compatible chain length alcohol ($C_{12}OH$) is much more pronounced than it is at higher concentrations. This indicates that the micellar stability of relatively low concentration SDS solutions can be greatly enhanced by adding $C_{12}OH$.

However, at 200 mM the enhanced micellar stability resulting from the $C_{12}OH$ addition is very small indicating that the contribution of $C_{12}OH$ to already stable

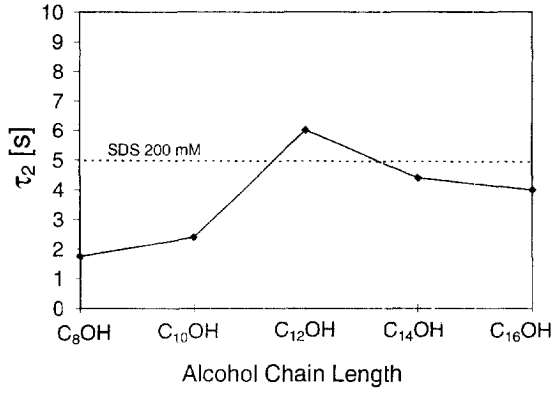

Fig. 7. The effect of alcohol chain length on the micellar relaxation time (τ_2) in SDS solutions (200 mM SDS, 5 mol.% alcohol) at 25°C.

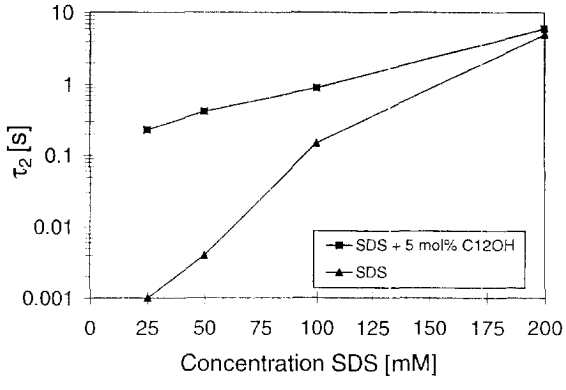

Fig. 8. The effect of 5 mol.% $C_{12}OH$ on the micellar relaxation time (T_2) of SDS solutions at 25°C.

micelles is not significant. The stabilizing effect of alcohol may be due to shielding of the negative charges of SDS with hydroxyl groups of alcohol molecules and a possible stabilizing effect of ion–dipole interactions between sulfate and hydroxyl groups.

The stability associated with chain length compatibility is also expected for the addition of a cationic surfactant (C_nTAB) to a micellar SDS solution. In this case ion–ion interactions play an important role [15]. Fig. 9 shows the effect of 5 mM C_nTAB on the micellar stability of a 100 mM SDS solution. The horizontal dotted line 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. However, the maximum increase in micellar stability is observed for $C_{12}TAB$ due to what is interpreted to be tighter packing of the micelles.

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

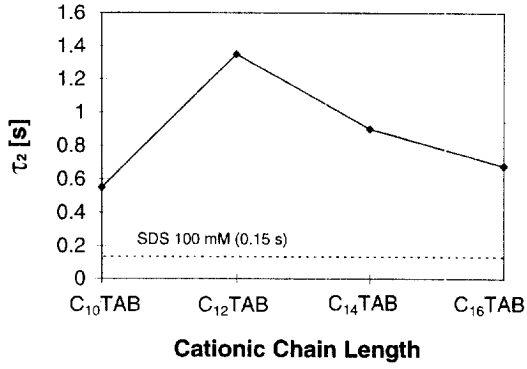

Fig. 9. The effect of 5 mM C_nTAB on the micellar relaxation time (τ_2) in 100-mM SDS solutions at 25°C.

processes involving an increase in interfacial area. Sharma [16] showed that the foam stability follows the same trend as the micellar stability. The maximum foam stability is obtained at maximum micellar relaxation time. The foam stability of SDS + C_nTAB is shown in Fig. 10. At equal carbon chain lengths the foam stability appears to be maximum.

From the data it can be concluded that the micellar stability increases by the addition of C_{12} alcohol to a SDS solution. The addition of short chain alcohols destabilizes the micelles resulting in a lower relaxation time.

The addition of $C_{12}TAB$ to 100-mM SDS solutions increases the stability of SDS micelles even when the chain lengths are not equal. This is 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 length of the adjacent molecules are the same [15].

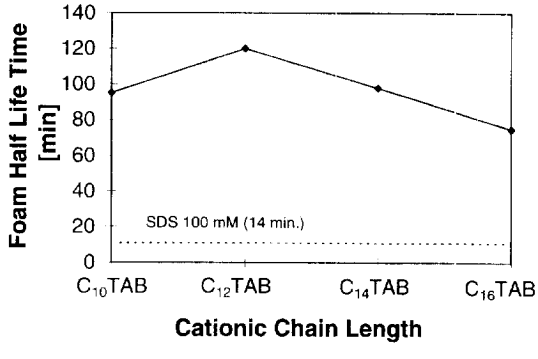

Fig. 10. The effect of 5 mM C_nTAB on the foam stability of 100-mM SDS solutions at 25°C.

6. Effect of chain length compatibility on foaming

The significance of chain length compatibility on properties which affect foam formation and foam stability cannot be understated. Previous studies have shown that the hydrocarbon chain length of additives has a profound effect upon the molecular interactions that occur at the gas/liquid interface. 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.

Shah et al. [17] have examined the effect of mixed surfactant systems on surface shear viscosity and area/molecule and their correlation to foam stability. By means of a modified deep channel viscous traction viscometer, surface shear viscosities of monolayers were measured. Foam stability was determined from agitating identical solutions inside a graduated cylinder as well as with a foam meter, which also served to measure the rate of drainage of each increment of liquid as the foam collapsed. It was found that single surfactant systems such as aqueous solutions of sodium dodecyl sulfate produce unstable foams with very high rates of drainage. This phenomenon corresponds to a system with a low surface shear viscosity. However, when an additional surfactant was introduced to the system, the rate of drainage and thus, foam stability became a function of surface shear viscosity. Mixed surfactant systems of equal carbon chain length fatty acid–fatty alcohol were tested. Maximum surface shear viscosity, maximum foam stability and minimum rate of drainage were observed for an octanoic acid–octanol (C_8) system and a decanoic acid–decanol (C_{10}) system with molar ratios of 9:1 and 1:3, respectively. This suggests that, at these given ratios, the interaction between surfactant molecules is greatest.

Further studies on foam stability and chain length compatibility have been applied to fluid displacement and chemical flooding [16–18]. In these studies analyzed properties, such as bubble size, surface viscosity and foaminess as well as those properties which pertain to foams in porous media such as breakthrough time and effective air mobility were examined. Mixed surfactant solutions of sodium dodecyl sulfate (SDS, $NaC_{12}SO_4$) and various long chain alcohols (C_8–C_{16}) were used to study the effect of chain length compatibility on these properties. Bubble size was measured by means of a rectangular plexiglass cell which contained some surfactant solution. The cell was initially shaken for a standard amount of time, then it was set to rest and photomicrographs of the foam bubbles were taken. An average bubble size was determined from the frequency of similar-sized bubbles in the cell. As depicted in Fig. 11, the C_{12} alcohol–C_{12} sulfate system clearly yielded the smallest average bubble size. Small bubbles, as opposed to larger ones, greatly enhance foam stability because of the increased surface area of the overall foam film within the foam itself. During the course of foam collapse, bubbles rupture and the liquid contained in the films around each bubble flows down onto other existing bubbles. The small bubbles reduce the rate of drainage

because their collapse results in smaller flows of liquid than result from the collapse of larger bubbles.

The observation that $C_{12}OH + NaC_{12}SO_4$ leads to smaller bubbles and greater foam stability illustrates the significance of chain length compatibility. When the chain lengths are the same, the intermolecular interaction is the strongest, corresponding to the tightest packing at the surface and hence, a maximum surface viscosity as illustrated by the data presented in Fig. 12 for the C_{12}–C_{12} system. In addition to surface shear viscosity, bubble radius, surface tension and foaminess are plotted in Fig. 12. Foaminess or foaming ability is a measure of the maximum foam produced at steady-state conditions for a given air pressure and time interval of aeration. Like foam stability and surface viscosity, tight molecular packing of surfactants, which is characteristically enhanced by the optimal condition of equal hydrocarbon chain length, maximizes these properties.

Other evidence for chain length compatibility in foaming using mixtures of anionic and non-ionic surfactants is presented by Schick and Fowkes [19]. They have investigated the structural relationship of effective combinations of additive and detergents by studying their mixed micelles. They have shown that the additives which lower the critical micelle concentration are the most effective for enhancing foam stability. The optimum combinations of detergent and additives are those which have an unbranched paraffin chain equal in length to the detergent. The shorter chain additives have larger cross-sectional areas, so more energy is required to maintain these molecules in the palisade layer and consequently some are squeezed into the interior of the micelles. On the other hand, if the additives have hydrocarbon chains longer than the detergent, they cannot fit into the palisade layer and tend to be solubilized into the interior.

7. 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 [20] 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 gage. This apparatus enabled the calculation of coefficients of friction for surfactant 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

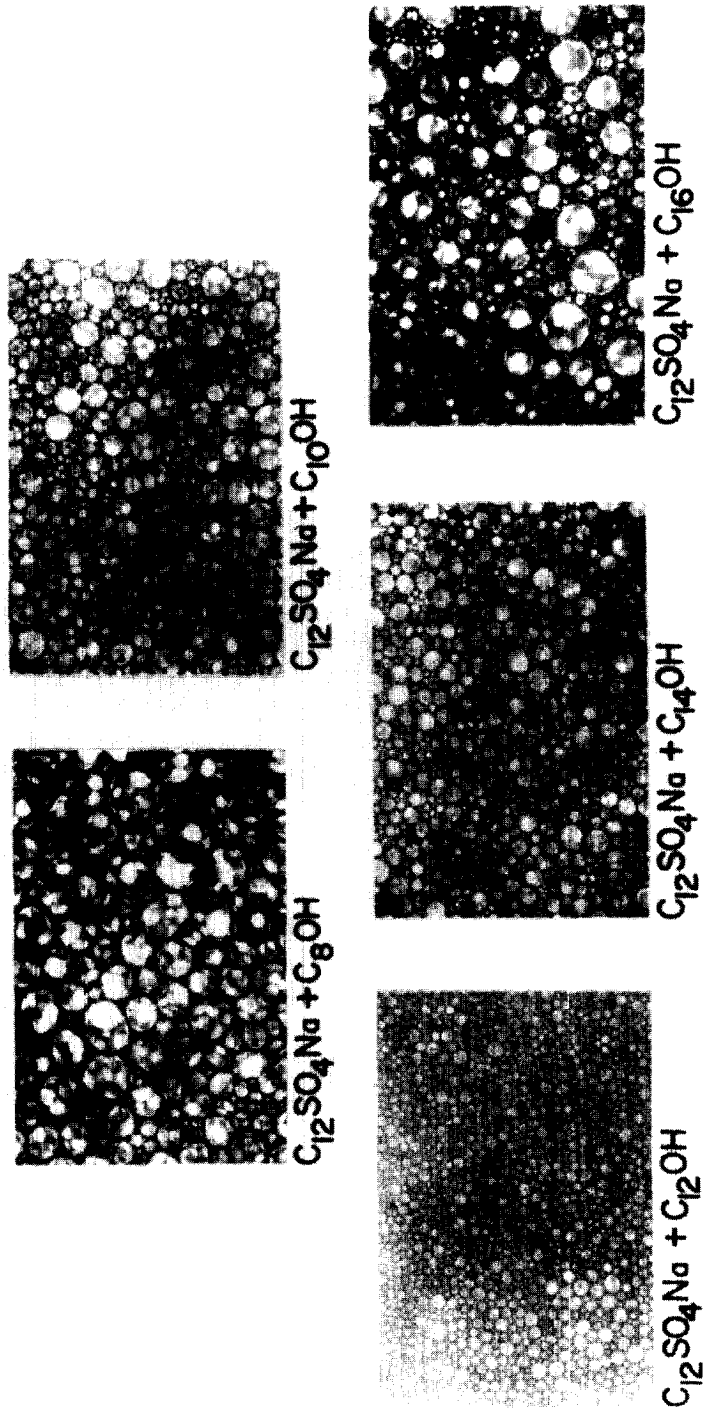

Fig. 11. Photomicrographs of foams containing sodium dodecylsulfate (5 mM) and various long chain alcohols (0.5 mM) at 15 min after initial foam production.

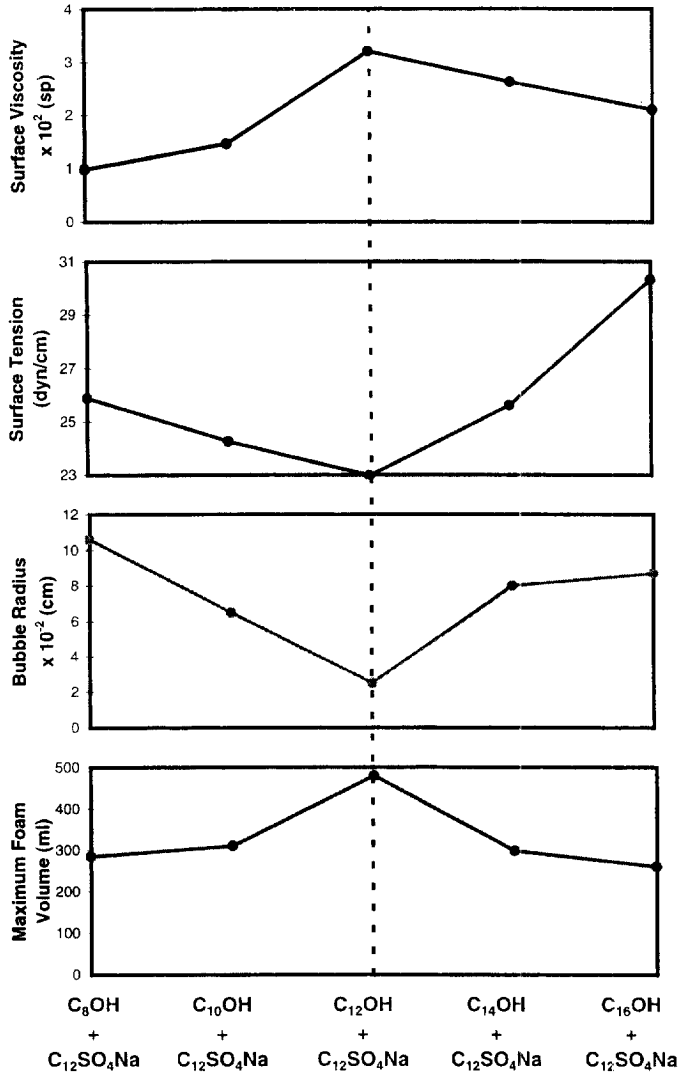

Fig. 12. Bubble size and other surface properties of mixed sodium dodecyl sulfate long chain alcohol mixtures such as surface viscosity, surface tension and foaminess.

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. [21] 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. Dwell time or the time needed to reach a given

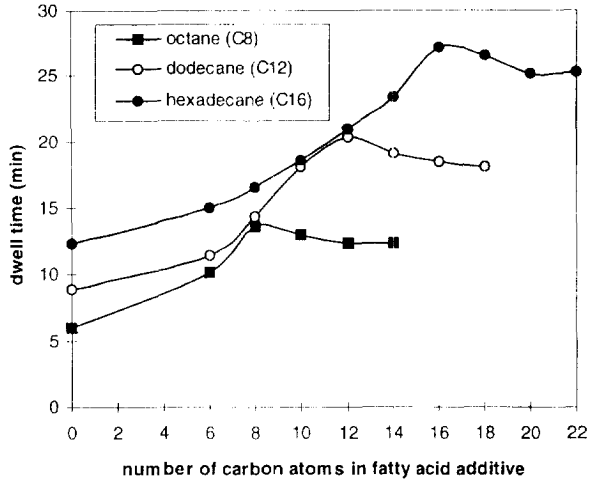

Fig. 13. Dwell times for paraffin–fatty acid chain length combinations.

coefficient of friction was determined with a disk and rider machine which is similar to the turntable apparatus, in that lubricant solution is used on a rotating disk. However, this method used a variable rider load that was lowered onto the disk and the variation of friction vs. time was observed. In short, high dwell times refer to well lubricated systems that have a high degree of additive interaction with the original lubricating molecule. It is the molecular interaction of the additive which prevents a well lubricated system from attaining a high coefficient of friction. Fig. 13 displays the dwell time plots for octane, dodecane and hexadecane vs. carbon chain length of the fatty acid additive. For each paraffin oil, the additive with the chain length equal to that of the paraffin oil resulted in the greatest dwell time. In addition, the dwell times for the C_{16}–C_{16} system yielded the overall greatest dwell times, corresponding to a greater chain length available for additive interaction, as well showing that the most compatible lubrication system is not necessarily the system with the greatest total hydrocarbon chain length.

More recent studies [22] have related monolayer properties to chain length compatibility and boundary lubrication. Both the coefficient of friction and wear scar diameter experiments on alumina surfaces yielded local minima for the hexadecane–C_{16} fatty acid system as shown in Fig. 14. The minima of the 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.

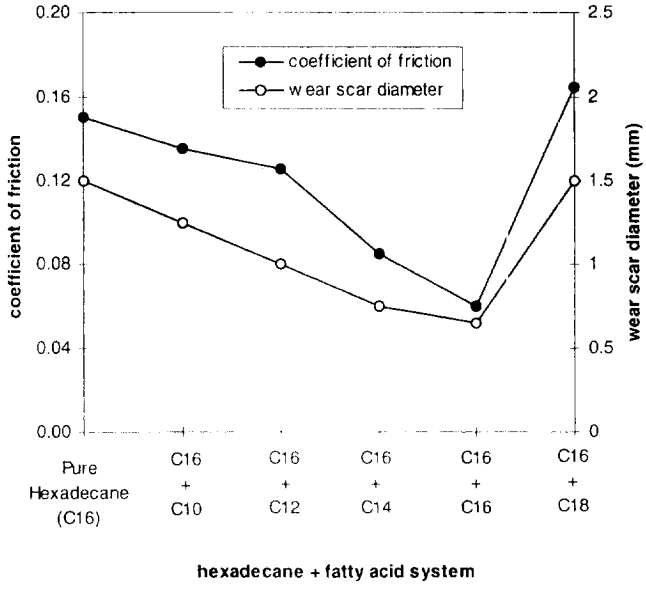

Fig. 14. The coefficient of friction and wear scar diameter of varying chain length hexadecane–fatty acid systems.

8. Environmental remediation

The concept of thermal motion of hydrocarbon chains at the air–liquid interface has been known for some time [23]. The thermal motions generated by the difference in chain lengths of adjacent molecules is believed to reduce the packing of these molecules at the interface. This leads to an increase in the area/molecule in the mixed monolayer. For cosurfactants of equal chain lengths, the thermal disturbances generated due to chain–chain interaction are minimized. Thus, the surface properties of mixed surfactant systems are influenced by the compatibility of the alkyl chains of the surfactants.

The surface tension and surface viscosity of mixed surfactant systems are clearly affected by the chain length compatibility. As the difference in chain lengths is increased, the packing of the molecules at the interface is reduced, the surface tension is increased and surface viscosity is decreased. When the chain length of both the components is similar, the surface viscosity is the highest (close packing of molecules at interface) and the surface tension is minimum.

Previous research has shown that the chain length compatibility of mixed surfactant systems plays an important role in understanding foaming systems, in particular for applications in enhanced oil recovery and environmental remediation of contaminated aquifer sites [18]. As the packing of surfactant molecules increases at the air–liquid interface (similar chain length components), the surface viscosity increases. This in turn causes the drainage of the liquid out of the lamellae in

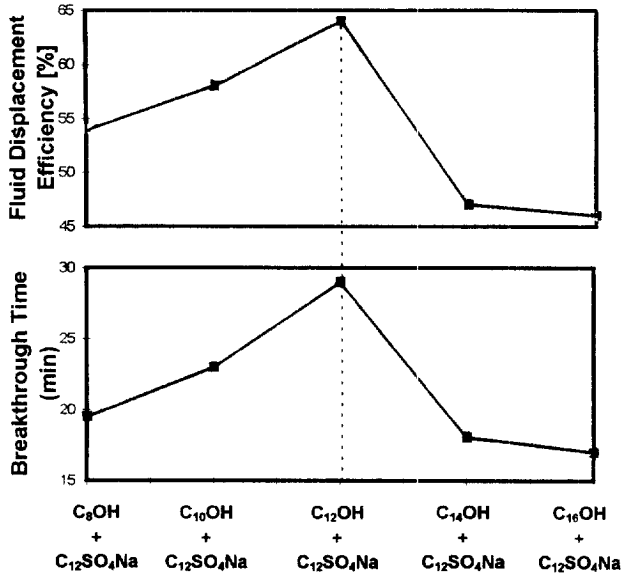

Fig. 15. Chain length (alcohol/SDS) effect on breakthrough time and fluid displacement efficiency for removal of residual trapped oil in the porous media.

foams to decrease. A decrease in the film drainage rate causes the stability of the film to increase. Higher foam/film stability leads to better foam displacement in porous media. Experiments for enhanced recovery of petroleum products in the presence of surfactants showed that surfactant foam is an efficient displacement process for residual oil. Moreover, an optimum foam flushing process is observed for mixed surfactant systems of similar chain lengths. The higher foam stability increases the breakthrough time for the gas phase and the effective air mobility is minimum. The increased breakthrough time results in an increase in the fluid displacement efficiency (Fig. 15).

9. Effect of chain length compatibility in rust prevention

The nature of adsorbed mixed films may be very important in understanding the nature of surfactants as additives in lubricants, fuels or other systems. The retention of hydrocarbon solvents by fatty acids was shown earlier in radio-tracer-adsorption and film-balance studies. In these studies the molecular geometry was considered significant. The chain length compatibility between additives (fatty acids) and solvents in rust prevention has been investigated by Ries et al. [24]. The compatibility was investigated using ASTM rust experiments and film-tenacity tests. The results from the rust tests, presented in Table 1, showed that a C_{16} acid added to *n*-hexadecane, at three concentrations of 0.1, 0.2 and 0.4 wt.%, is

Table 1
Rust tests on fatty acids in n-hexadecane

Fatty acid additive	wt.%	ASTM rust	Film-tenacity rust
Myristic (C_{14})	0.1	Severe	
	0.2	Severe	
	0.4	Moderate	Severe
Palmitic (C_{16})	0.1	Slight	Severe
	0.2	Very slight	Moderate
	0.4	None	Slight
Stearic (C_{18})	0.1	Severe	
	0.2	Moderate	Severe
	0.4	Slight	Slight

considerably superior when compared to the C_{14} and C_{18} acids. Fatty acids of varying chain length were then added to a pentadecane (C_{15}) solvent. Again, the combination of fatty acid and solvent of matching chain length ($C_{15\ acid}$–$C_{15\ solvent}$) 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 film combinations form readily on the metal surface, they 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 [25]. 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 peptisation 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 geometrical and chain length compatibility.

10. Effect of chain length compatibility in microemulsions

The effect of chain length compatibility in emulsion systems has been studied in systems involving surfactants, cosurfactants and oils [26]. The effect of chain length is particularly important to microemulsion systems in which the interfacial tension must remain extremely low ($< 10^{-3}$ dyn/cm) in order to maintain stability [26]. In microemulsion systems, surfactant as well as a cosurfactant (usually an alcohol) are generally required. The effect of the alcohol chain length relative to the soap chain length and oil chain length has been shown to be very important. One of the most revealing methods of observing this phenomena is to measure the water solubilization capacity of a water-in-oil microemulsion as shown in Fig. 16. The data in Fig. 16 for butanol show that the quantity of water solubilized in the microemulsion prior to phase separation decreased as the oil chain length increased. This effect is

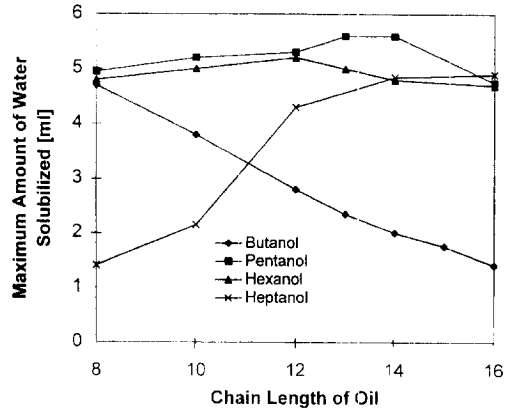

Fig. 16. Water solubilization capacity of water in oil microemulsions produced using 4 ml of the specified alcohol with 1 g of sodium stearate and 10 ml of the specified straight chain hydrocarbon oil.

attributed to the partitioning at the interface. As water is added to the system, the concentration of butanol in the aqueous phase decreases. The decrease in activity in the aqueous phase makes the butanol less available to stabilize the interface. The decrease in butanol activity in the aqueous phase is, however, offset with a short chain oil due to the butanol solubility in the oil phase. As the oil chain length increases, however, it is likely that more of the butanol partitions to the aqueous phase taking with it additional soap, thus decreasing the stability of the interface. In contrast, the data in Fig. 16 for heptanol show the opposite trend that is attributed to the chain length of heptanol that dictates different partitioning behavior than butanol [26]. The longer heptanol hydrocarbon chain allows for greater heptanol solubility in the oil phase. Conversely, the longer chain in heptanol decreases its solubility in water. As more water is added to the system, the low concentration of heptanol in the aqueous phase remains relatively constant due to the availability of heptanol in the oil phase. However, as the oil chain length increases, the solubility of the heptanol in the oil phase decreases, forcing the heptanol to the interfacial region, thereby increasing the stability 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 the quantity of butanol, pentanol and hexanol is doubled, the quantity of water solubilized increases as shown in Fig. 17. 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 = length of 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

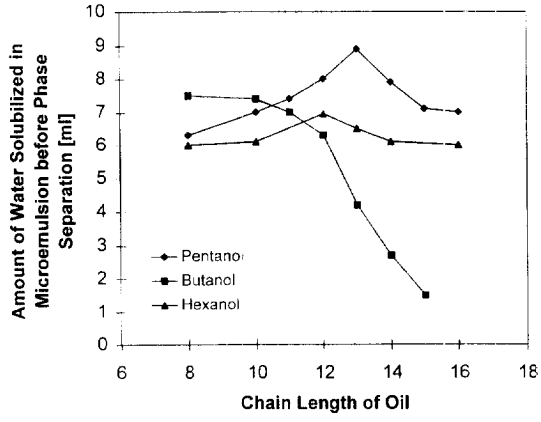

Fig. 17. Water solubilization capacity of water in oil microemulsions produced using 8 ml of the specified alcohol with 1 g of sodium stearate and 10 ml of the specified straight chain hydrocarbon oil.

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. 18.

The effect of alcohol partitioning can also be evaluated by maintaining a constant molar ratio of soap to water while increasing the oil and alcohol concentrations according to the method of Bowcott and Schulman [27] as shown in Fig. 19 for the pentanol/water/oil/sodium stearate system. Although this method assumes all the surfactant is at the interface and that the alcohol is insoluble in water, it provides useful comparative information. From Fig. 19 it is apparent that

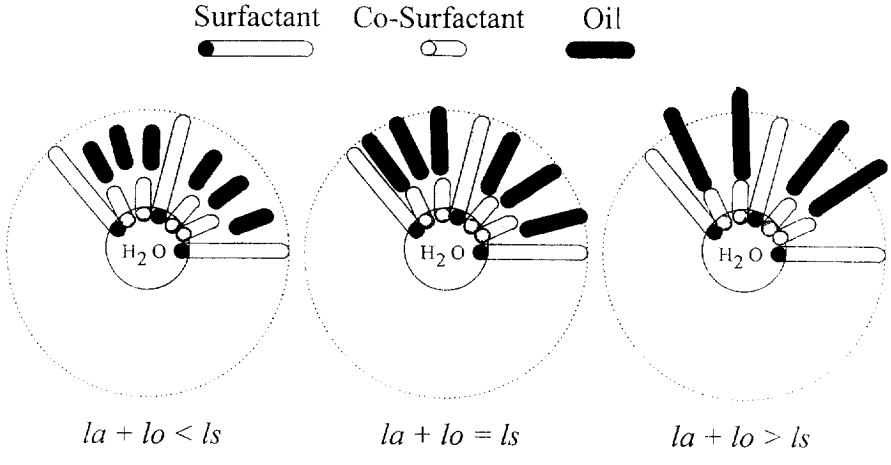

Fig. 18. Schematic diagram showing the effect of surfactant, oil and cosurfactant (alcohol) chain lengths at the water–oil interface.

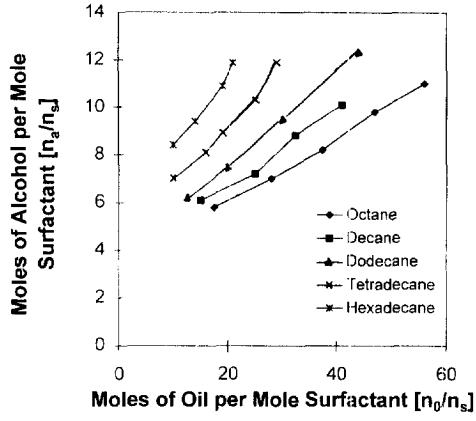

Fig. 19. Effect of oil chain length in oil/alcohol titrations of microemulsions for the system pentanol/water/oil/sodium stearate ($n_w/n_S = 51$).

the ability for the microemulsion system to remain stable with higher oil/soap ratios, it is necessary to add more alcohol. When octane is the oil phase, the extra quantity of pentanol necessary to stabilize additions of octane is smaller than when the oil consists of hexadecane due to the lower solubility of pentanol in hexadecane. In other words, the slope of the lines in Fig. 19 become steeper as the solubility of pentanol in the oil phase decreases.

The data in Fig. 19 also provide an indication of the partitioning of the pentanol at the oil/water interface as evidenced by the intercept on the ordinate axis as the ratio of oil to soap approaches zero. The value of the intercept, which represents the molar ratio of alcohol to soap at the interface, increases as the chain length of the oil increases from eight carbons to 16 carbons, thus confirming that the alcohol is increasingly forced to the interface as its solubility in the oil phase decreases.

The tighter interfacial packing with a higher alcohol to soap ratio observed with longer oil chain length microemulsions is also associated with a higher degree of soap ionization. With more alcohol chains present at the interface, the overall packing of molecules at the interface increases. The packing between the stearate molecules increases, allowing for greater ionization [26]. Corroborative evidence for this phenomenon is presented in Fig. 20 which shows that the dielectric constant of the microemulsion increases as the oil chain length increases until a critical water to oil ratio is reached. The increase in the dielectric constant of the microemulsion with increasing oil chain length is likely due to enhanced carboxylate ionization that occurs due to the presence of additional pentanol at the interface.

Additional evidence for the effect of increasing oil chain length is illustrated in Fig. 21, which shows how electrical resistance in microemulsions varies with both oil chain length and pentanol concentration. As the pentanol concentration increases, the electrical resistance increases until a critical value is reached. As the

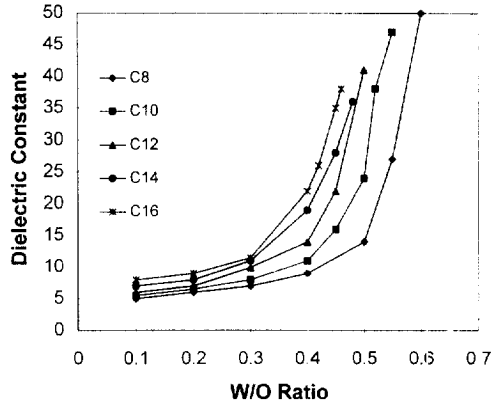

Fig. 20. Comparison of dielectric constants of microemulsions with varying oil chain lengths and oil to water ratios (system: 1 g sodium stearate, 8 ml pentanol, 10 ml oil).

chain length of the oil increases, the electrical resistance decreases and the amount of pentanol needed to maintain the microemulsion increases. As discussed previously, the increase in oil chain length increases the quantity of pentanol at the interface, increasing the spacing between carboxylate head groups, which eventually leads to greater ionization and reduced resistance (relative to shorter chain oils). The overall increase in resistance with increasing pentanol concentration may

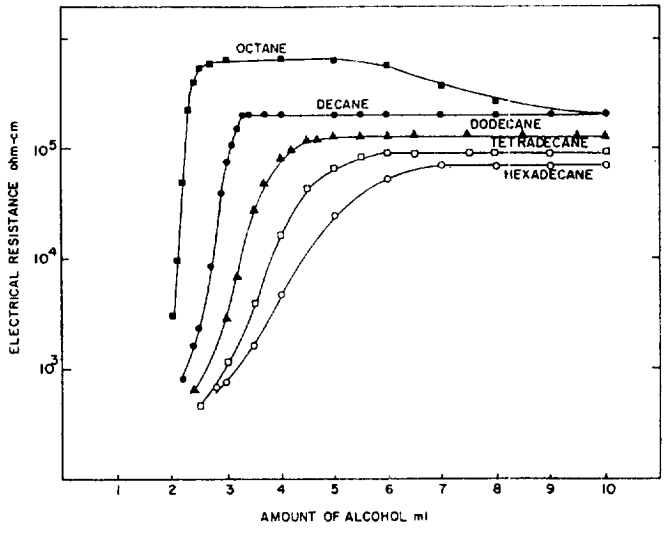

Fig. 21. Comparison of pentanol concentration and oil chain length on electrical resistance in microemulsions (system: 1 g sodium stearate, pentanol, 10 ml oil, 3 ml water).

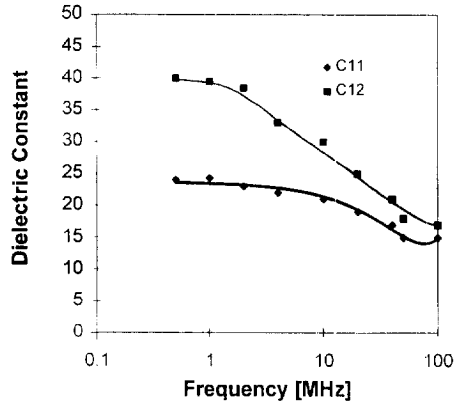

Fig. 22. Effect of increasing the oil chain length on the dielectric constant of microemulsions at various frequencies (system: 1 g sodium stearate, 8 ml pentanol, water/oil = 0.5).

be due to disruption in the percolation mechanism of microemulsion electrical conductivity [28].

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 interfacial properties as illustrated in Fig. 22. Increasing the oil chain length from 11 to 12 carbon atoms results in a near doubling of the dielectric constant at 0.5 MHz.

Although not with emulsion systems, Meakins [29] has also studied the chain length compatibility in binary mixtures of polar long chain compounds with hydrocarbons using dielectric properties. In his study the dielectric absorption of binary mixtures of various long chain ketones with *n*-octacosane was measured to indicate if the polar molecules (ketones) are dispersed to form a solid solution in the hydrocarbon. Meakins [29] showed that the magnitude of the dielectric absorption decreases with increasing discrepancy between the chain length of ketone and hydrocarbon, indicating a decreasing tendency of the ketone molecules to disperse as solid solutions in the hydrocarbon. It was concluded that the dispersal of long chain polar molecules in the crystal lattice of a hydrocarbon occurs most readily when their chain lengths are similar or equal.

Other research on the effect of chain length and compatibility in emulsion systems has been evaluated and compared to the work by Bansal et al. [26]. The chain length compatibility approach has been used to interpret the solubilization behavior of some W/O microemulsions composed of cationic surfactants, water and aromatic solvents and of the same systems in the presence of alcohols or carboxylic acid [30–33] as cosurfactant. The BSO equation ($lo + la = ls$) was reexamined by Li et al. [34]. They showed that this equation is valid for anionic (sulfates and carboxylates) surfactants. However, it did not hold for mixtures of cetyltrimethylammonium bromide (CTAB)/(C_3–C_{12}) *n*-aliphatic alcohols/*n*-octane/water. The authors attributed this discrepancy due to the repulsion of the

cationic head-group of the surfactant and the electropositive hydrogen of the hydroxyl group of alcohol. Another exception to the BSO equation is sodium dioctylsulfosuccinate (Aerosol OT). Aerosal OT has proven to be more efficient than expected, which is ascribed to its double-chain configuration [35].

Garti et al. [36] have investigated the validity of the BSO equation for non-ionic microemulsions in several systems based on following components: ethoxylated alcohols/C_{10}–C_{16} n-alkanes/C_2–C_{12} n-aliphatic alcohols/water. They have 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, their representation is also quite common, particularly among solubilization researchers [36–40]. In their phase diagrams, the alcohols have been considered, formally at least as a cosolvent [41], rather than a cosurfactant. Garti et al. [36] have shown for the first time that the BSO equation and the concept of chain length compatibility [26,42] can predict, within some limits, conditions for maximum water solubilization in the presence of non-ionic 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 [43,44].

John and Rakshit [45] 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 alkanols 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 counting system. The conductivity studies in the mixed alkanols systems 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 two components.

Berr et al. [46] have examined the influence of counterions on micelle structure for a series of alkyl trimethyl ammonium halide surfactants $C_nTAX = C_nH2_{n+1}N(CH_3)_3^+X^-$ ($X = NO_3$, Br, CH_3SO_4, Cl and OH) by small-angle neutron scattering. They have also studied the variation of micelle structure as a function of chain length (n = 12, 14 and 16) and surfactant concentration. They have observed that the aggregation number, N, increases in the order of $NO_3 > Br > CH_3SO_4 > Cl \gg OH$. They have roughly correlated this order to the fractional micellar charge, β, which follows the order $OH > Cl > CH_3SO_4 \sim Br \sim NO_3$.

Yu et al. [47] have studied the solution behaviors of equimolar mixtures of tetrabutylammonium bromide and sodium alkyl sulfate (B_4NC_nS, n = 8–18). They have proposed a method for calculating the content of organic-ions in micelles at the CMC using the Gibbs–Duhem equation. The results show that the content of B_4N in the alkyl sulfate micelles at the CMC and in surface adsorption layer

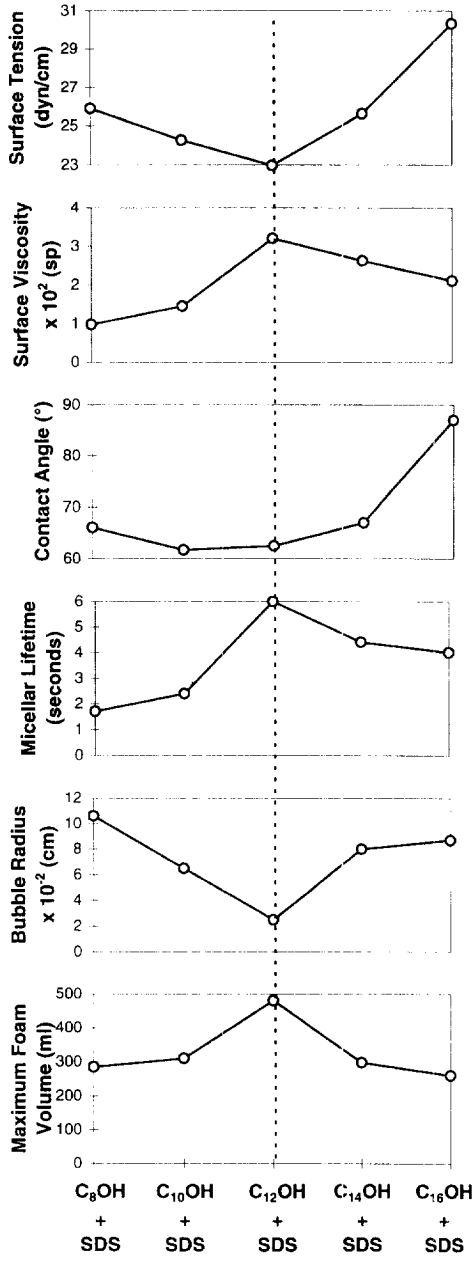

Fig. 23. Effect of chain length compatibility on interfacial-related properties for the sodium dodecyl sulfate/alkanol systems shown.

decreases with increasing alkyl sulfate chain length, which they have shown arises from the increase of hydrophobicity asymmetry between B_4N and the surfactant with increasing surfactant chain length. They have also shown that the Krafft point of alkyl sulfate salt is reduced considerably in the presence of B_4N. They have also observed that the Krafft point decreases with increasing micellar concentration in the presence of inorganic salt concentration and the chain length of surfactant.

Panitz et al. [48] 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 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 occur by a hopping process in which the associated rate decreases with the surfactant chain length.

11. 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 show 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 a consequence of this packing there is also a corresponding minimum in the surface tension, contact angle and bubble radius (Fig. 23). In microemulsion systems, it has been shown that for some systems the chain length compatibility is important to the stability of microemulsions with the stability occurring when the sum of the alcohol and oil chain lengths equals the surfactant chain length. Finally, on a practical note it has been shown that chain length compatibility has an important direct influence in technologies such as lubrication, evaporation control, corrosion, oil recovery, environmental remediation, foaming and microemulsion stabilization, in addition to many other technologies that utilize surfactants.

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