Effect of counterions on surface and foaming properties of dodecyl sulfate

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Abstract

The influence of counterions of surfactant on interfacial properties is studied by measuring foamability, foam stability, equilibrium and dynamic surface tension, and surface viscosity. The surfactant chosen is anionic dodecyl sulfate with various counterions, Li^+, Na^+, Cs^+, and Mg^{++}. Surface tension measurements show a decrease in the following order: $LiDS > NaDS > CsDS > Mg(DS)_2$. Foamability done using shaking method shows similar order as surface tension, i.e., $LiDS > NaDS > CsDS > Mg(DS)_2$. This has been explained in terms of the differences in micellar stability and diffusion of monomers. This is further confirmed by our dynamic surface tension results, which show the same order as equilibrium surface tension (i.e., $LiDS > NaDS > CsDS > Mg(DS)_2$) at low bubble frequencies but the order is $LiDS > NaDS = Mg(DS)_2 > CsDS$ at high bubble frequencies. Foam stability measurements were done at concentrations below and above cmc to elucidate the role of micelles. It was found that there is no significant change in foam stability when counterions are changed for surfactant concentration values below the cmc, but at concentration above cmc the foam stability of CsDS and $Mg(DS)_2$ are much greater than LiDS and NaDS indicating presence of stable micelles are essential to high foam stabilities. Surface viscosity measurements correlated well with the foam stability trends and gave the following order $LiDS < NaDS < CsDS \ll Mg(DS)_2$, indicating that the molecules of CsDS and $Mg(DS)_2$ are tightly packed at the air/water interface.
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1. Introduction

Foamability and foam stability are relevant properties for many industrial applications such as mineral flotation, food processing, foam fractionation, processing of textiles, personal care products, enhanced oil recovery, and fire fighting. The surfactant counterion strongly influences the critical micelle concentration (cmc), micellar catalysis, micelle size, and emulsion size as observed by various researchers [1–3]. The cmc in an aqueous solution is influenced by the degree of binding of counterions to the micelle. For aqueous systems, the increased binding of the counterions to the surfactant causes a decrease in the cmc and an increase in the aggregation number [2]. The extent of binding of the counterion increases with an increase in the polarizability and valence of counterions and decrease with an increase in its hydrated radius [4]. Thus, in aqueous solution, for the anionic dodecyl sulfates, the cmc decreases [2] in the order $Li^+ > Na^+ > Cs^+$. The cmc of LiDS, NaDS, CsDS, and

$Mg(DS)_2$ are reported by Mukerjee [2] to be 8.92, 8.32, 6.09, 0.88 mM, respectively, at 25 °C. Missel et al. [5] have reported that the micellar size is in the order R_h (CsDS) > R_h (NaDS) > R_h (LiDS) at a given ionic strength, detergent concentration, and temperature. Also, the ionized counterions perturb the local ordering or structure of water molecules around the counterions [6]. Several water molecules are bound to counterions due to ion–dipole interaction between counterions and water molecules. The counterion size follows the order $Li^+ < Na^+ < Cs^+$ but the hydrated counterparts show the reverse trend due to the greater hydration of a lithium ion compared to a sodium or cesium ion [6]. The repulsive force between hydrated ions appears to increase [6] in the order $Cs^+–Cs^+ < K^+–K^+ < Na^+–Na^+ < Li^+–Li^+$ (rather than the opposite, as would be expected from the non-hydrated ion radii of the ions). Therefore, the effectiveness of monovalent cations as coagulants decreases according to the so-called lyotropic series [7], viz., $Cs^+ > K^+ > Na^+ > Li^+$. The surface tension of surfactant solutions depends on the number of surfactant molecules per unit area at the surface. For a given surfactant, the greater concentration of surfactant molecules at the surface results in the lower surface tension.

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Many physical factors are involved in control of foamability and foam stability. While foamability depends on surface tension (equilibrium or dynamic) and cmc, the foam stability is determined by bulk and surface viscosities, the Marangoni effect, disjoining pressure and hydrophobic interaction [8–11].

Patist et al. [12] have shown that by using long chain alcohols, the stability of sodium dodecyl sulfate micelles can be tailored to control the dynamic surface tensions achieved and hence the foamabilities. Chattopadhyay et al. [14] reported that the surface viscosity of a monolayer of surfactant, which is a good indicator of foam stability, is sensitive to the concentration and nature of salt. They observed increase in surface viscosity with increase in NaCl concentration in contrast to a decrease in surface viscosity with increase in NH_4NO_3 concentration. The present paper investigates the effect of counterions such as Li^+, Na^+, Cs^+, and Mg^{++} of dodecyl sulfate on interfacial properties in relation to foaming.

2. Experimental procedure

Lithium dodecyl sulfate (99% purity) is purchased from Acros (Orlando, FL), sodium dodecyl sulfate (99% purity) from Sigma Chemical Company (St. Louis, MO), and magnesium dodecyl sulfate (98% purity) from Pfaltz and Bauer (Waterbury, CT). Cesium dodecyl sulfate is prepared in our laboratory with the same procedure as shown by Kim et al. [3]. Chlorosulfonic acid (Aldrich, Milwaukee, WI, 553.5 mM) is added to dodecanol drop by drop with vigorous mixing at 25 °C under a nitrogen atmosphere. The sulfation reaction is performed very slowly (40 min and cooled with ice) since the sulfation process is highly exothermic. After the sulfation process, nitrogen gas is used to purge the reaction mixture to remove HCl produced during the reaction. Aqueous CsOH solution (Aldrich, 50.0 wt%) is added to the reaction mixture in a 1:1 molar ratio to neutralize the acid. The CsDS is recrystallized three times with distilled water, keeping the solution at 5 °C.

Foamability measurements are carried out by shaking at surfactant concentration 50 mM, where 10 ml of the surfactant solution is vigorously shaken 10 times by hand in a 100-ml graduated cylinder and the volume of the foam is recorded immediately after shaking. Each solution is tested at least five times and the reproducibility is about ±5 ml.

For foam stability measurements, the solutions are foamed to the same height (13 cm) by slowly injecting air (100 cm³/min) through a fine capillary (diameter 1 mm) into 25 ml of surfactant solution contained in a quartz column (diameter 3.5 cm, height 80 cm). The time for collapse of the foam to half the initial height is then recorded. Surfactant concentration of 1 mM is chosen for studies below cmc while concentrations of 25 and 50 mM are chosen for studies above cmc (cmc ≈ 1–8 mM depending on the counterion). Appropriate caution (a long funnel that reached the bottom is used to pour the solution) is taken in order to keep the walls dry and to avoid any initial foam formation due to splashing.

The deep-channel surface viscometer [13] is used to measure the surface viscosity of each solution. Two concentric cylinders form the deep channel of the viscometer. The walls of this channel are stationary, while the lower cup moves at a constant angular velocity. To measure the centerline velocity of the air/water (surfactant solution) interface, a small Teflon particle is placed on the surface and the time for that particle to make one revolution is recorded as an average from five such revolutions by visual observation. With this value, the surface viscosity can be determined using the equation [14]

$$\varepsilon = \frac{\eta y_0}{\pi} \left[\frac{8 V_b}{\pi V e^{\pi D}} - 1 \right], \tag{1}$$

where ε is the surface viscosity, η the bulk viscosity of the solution, y_0 the channel width, V_b the plate rotational speed, V the centerline velocity of the air/water interface, and D the ratio of depth to width of the liquid channel.

Equilibrium surface tensions are measured from freshly prepared solutions by the Wilhelmy plate method [15]. Before each measurement, the platinum plate is cleaned by heating it to a red/orange color with a Bunsen burner.

Dynamic surface tension is measured by a similar method as reported in our previous studies [12]. Quantitative estimates of dynamic surface tension of solutions are taken by forcing air into the solutions through a gauge 22 steel needle while measuring the pressure changes as the bubbles are produced using a fast (1-ms) transducer (Omega Instruments) in the maximum bubble pressure instrument [16,17]. To show the importance of micellar break up in the dynamic surface tension measurement a dimensionless parameter θ is introduced [12],

$$\theta = (\gamma_d - \gamma_{eq})/(\gamma_w - \gamma_{eq}), \tag{2}$$

where γ_d is the dynamic surface tension, γ_{eq} is the equilibrium surface tension measured by the Wilhelmy plate method, and γ_w is the surface tension of pure water at 25 °C. The value of $\theta = 0$ (or $\gamma_d = \gamma_{eq}$) indicates that the surfactant adsorption under dynamic condition is the same as that under equilibrium conditions and the micelles are labile as well as the monomers are diffusing fast, whereas $\theta = 1$ ($\gamma_d = \gamma_w$) indicates no surfactant is present at the interface under the dynamic conditions existing during the bubbling process implying either the presence of relatively stable micelles or monomers with high characteristic diffusion time.

3. Results and discussion

Figure 1 shows the equilibrium surface tension values for 50 mM surfactant solutions having different counterions.
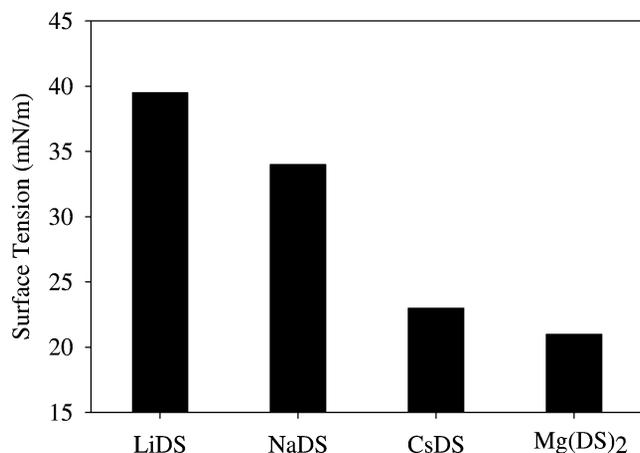
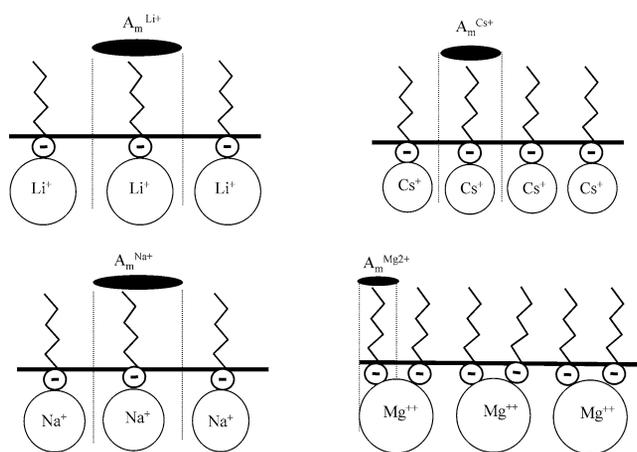Fig. 1. Surface tension as a function of counterion of surfactant, dodecyl sulfate, at 50 mM.

Fig. 2. Effect of counterions on molecular packing of dodecyl sulfate at the air/water interface. Area per molecule (A_m): $A_m^{Li^+} > A_m^{Na^+} > A_m^{Cs^+} > A_m^{Mg^{2+}}$.

Surface tension is related to the number of surfactant molecules per unit area adsorbed at the air/water interface. The surface tension decreases with increasing surface concentration [4]. Figure 1 shows that the surface tension decreases as follows: lithium dodecyl sulfate (LiDS) > sodium dodecyl sulfate (NaDS) > cesium dodecyl sulfate (CsDS) > magnesium dodecyl sulfate (Mg(DS)₂). This can be explained by considering the molecular arrangement at the interface shown in Fig. 2. As one goes down the first group of the periodic table from Li^+ to Cs^+, the ionic radius increases from Li (0.068 nm) to Na (0.095 nm) to Cs (0.169 nm), while the hydrated radius changes as follows: Li (0.38 nm), Na (0.36 nm), Cs (0.33 nm) [6,18]. Thus the positive center (Li^+) in LiDS is at a larger distance from the negative center (DS^-) than in the case of CsDS, resulting in a higher coulombic repulsion between the adjacent sulfate ions in a LiDS monolayer than in a CsDS monolayer. This leads to closer molecular packing and a higher surface concentration of surfactant molecules at the interface in the case of CsDS than for the LiDS adsorbed monolayer. In the case

Table 1
Physical properties and dimensionless dynamic surface tension (θ) of different counterions of dodecyl sulfate

Ion	Ionic radius (Å)	Hydrated radius (Å)	Area per molecule	θ parameter
Li^+	0.60	3.82	61	0.138
Na^+	0.95	3.58	51.5	0.131
Cs^+	1.69	3.29	44.5	0.202
Mg^{++}	0.65	4.28	38.7	0.353

of Mg(DS)₂, the larger separation of positive and negative center [Mg^{++}: ionic radius, 0.066 nm; hydrated radius, 0.428 nm] is countered to some extent because of the bivalency of the cation. This attractive force between a divalent cation and two surfactant molecules probably partially dehydrates the Mg^{2+} ions and hence causes the closest molecular packing at the interface. This is also evident from area per molecule values obtained from Gibbs adsorption equation, in Table 1, where $DS^-_{Mg^{++}}$ occupies the least area followed by $DS^-_{Cs^+}$, $DS^-_{Na^+}$, and $DS^-_{Li^+}$.

3.1. Foamability measurements

Foamability has been studied using shaking method. In this method foam is produced quickly by rapid shaking of cylinder causing a sudden expansion of interfacial area. Simultaneously, due to vigorous shaking, there is a destruction of foam too. Assuming similar bubble size (or bubble size distribution), the foamability experiments (Fig. 3) yielded trends contrary to those as expected from Eq. (3) [19] relating work done in producing foam to interfacial area,

$$W = \gamma \Delta A, \tag{3}$$

where W is the work done, γ is the surface tension at the air/water interface, and ΔA is the change in interfacial area (i.e., the systems with smaller surface tensions, instead of producing larger interfacial areas, produce smaller interfacial areas).
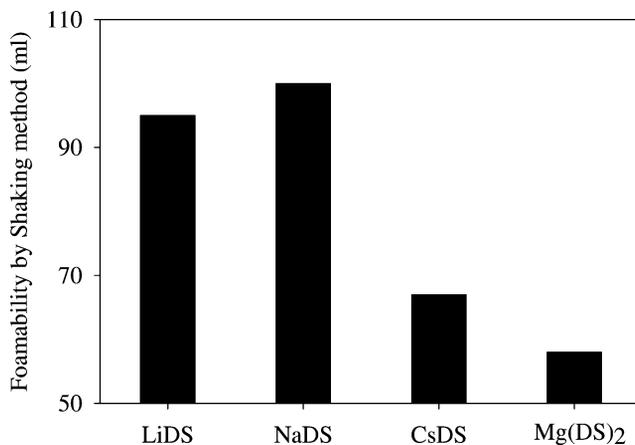

Fig. 3. Foamability (by shaking method) as a function of counterion of surfactant dodecyl sulfate at 50 mM concentration.
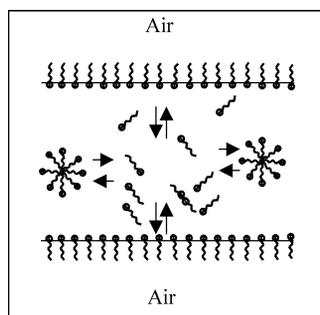
Fig. 4. Schematic representation of adsorption of surfactant on the newly created air/water interface during foam generation. In a thin liquid film, more stable micelles → less monomer flux → lower foamability.

This can be explained on the basis of competitive time scales for interfacial area expansion, the diffusional transport of surfactant monomers, and the ability of micelles to break up in order to provide monomer flux necessary to stabilize the new air/water interface as shown in Fig. 4. Very stable micelles cannot break up fast enough to augment the flux of monomers necessary to stabilize the new air/water interface resulting in higher dynamic surface tension and hence low foamabilities. Simple calculations on lines similar to Oh et al. [20], show that for surfactant with first group counterions (Li^+, Na^+, and Cs^+), the characteristic diffusion time for surfactant monomers is on the order of 10^{-4} s, while for surfactant with Mg^{++} as counterion, it is on the order of 10^{-2} s because of its low cmc as well as least area per molecule at the air/water interface. The characteristic diffusion time for micelles will be approximately an order of magnitude larger because of the slower diffusion (coefficient of diffusion $\propto M_w^{-1}$) of the aggregates. So apparently the breakup of micelles should be a rate-limiting step in the supply of monomers to the new air/water interface for the cases of LiDS, NaDS, and CsDS, while for $Mg(DS)_2$, the resistance should largely come from the diffusion of monomers. From the results in Fig. 3, this further means that the low interfacial area generated in case of CsDS is due to the resistance from micellar stability. For LiDS and NaDS surfactant systems, the micelles appear to be relatively unstable, thus providing all the monomer flux that is required to stabilize the interfacial area.

This is consistent with the dynamic surface tension measurements (Fig. 5). Here, at low flow rates and thus higher bubble lifetimes (∼1 s), the order for the surface tensions is similar to the order for equilibrium surface tensions with different counterions. Apparently, under these conditions, there is no resistance to monomer flux required to stabilize the newly formed bubbles from either the micellar stability or from the diffusion of the monomers. Thus, the bubbles are formed under equilibrium conditions. At higher flow rates and thus smaller bubble lifetimes (∼50 ms), while there is an increase in the surface tension of surfactants as compared to that at low flow rates, the change is higher in magnitude for CsDS or $Mg(DS)_2$ than for LiDS or NaDS, suggesting a larger resistance to monomer flux for CsDS and $Mg(DS)_2$.
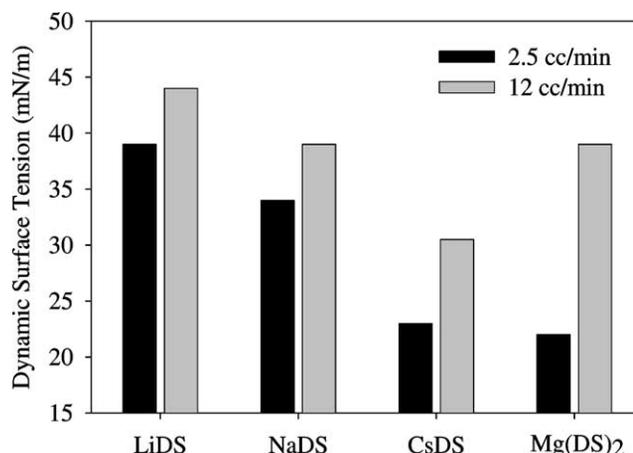

Fig. 5. Dynamic surface tension as a function of counterion of surfactant at 50 mM concentration and 25 °C.

As discussed before, this is probably due to stable micelles in the case of CsDS and larger characteristic diffusion times in the case of $Mg(DS)_2$. Available literature data [21] on relaxation times (τ_2) for NaDS and CsDS systems at surfactant concentration 50 mM (NaDS: $\tau_2 = 1$ ms, CsDS: $\tau_2 = 3000$ ms) further confirms this interpretation.

A more meaningful way to represent the dynamic surface tension might be using the θ parameter as it normalizes the dynamic surface activity (*irrespective* of the mechanisms) with respect to the equilibrium surface activity (see Eq. (2)). Table 1 shows the θ parameter values at a bubble life time of 50 ms. The θ parameter values are lower and similar for LiDS and NaDS while they are higher for CsDS and $Mg(DS)_2$ suggesting a higher dynamic surface activity for LiDS or NaDS than for CsDS or $Mg(DS)_2$ correlating well with the foamability behavior.

3.2. Foam stability measurements

Foam stability can be influenced by two independent factors: (1) molecular packing in adsorbed surfactant film and hence surface viscosity of the film at the air/water interface [22] and (2) layering or structuring of micelles within the bulk water in foam lamellae [12,25–27]. In order to delineate the effect of presence of micellar structuring, the surfactant systems with different counterions are studied systematically below and above the cmc concentration values.

Figure 6 shows the foam stability as a function of counterions at a surfactant concentration of 1 mM. The concentration of 1 mM, which is either close to or below cmc concentration, is chosen to ensure little or no presence of micelles in foam lamellae. Here, one sees that the foam stabilities gradually increase from 10 min for LiDS to 30 min for $Mg(DS)_2$. Foam stability differences are usually explained in terms of the differences in the water drainage rate from the foam lamellae which in itself is influenced by mechanisms such as (i) bulk viscosity, (ii) fluidity of the film, and (iii) Marangoni stabilization mechanism [22] because of the rapid adsorption of surfactants. Mechanism (i) can easily be discounted
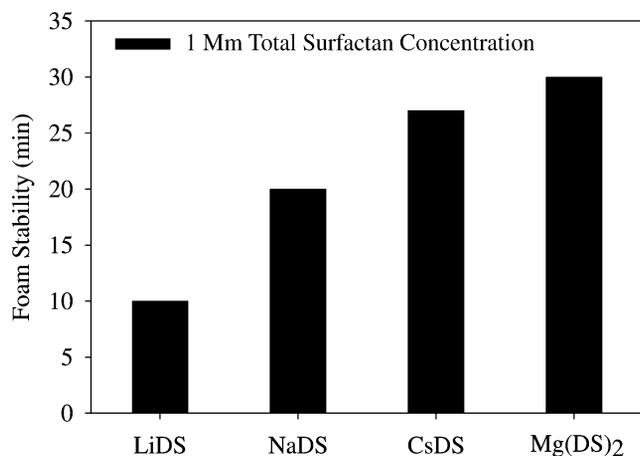
Fig. 6. Foam stability of surfactant dodecyl sulfate with different counterions below critical micellar concentration.

Fig. 7. Foam stability of surfactant dodecyl sulfate with different counterions above critical micelle concentration.

because of the similar bulk viscosities of all four solutions containing different counterions. Mechanism (iii) is also not operative because then a two-orders-of-magnitude smaller adsorption for $Mg(DS)_2$ would have resulted in a significantly more stable foam for $Mg(DS)_2$ than for LiDS, NaDS, or CsDS, where a quicker monomer adsorption would oppose the Marangoni stabilization mechanism, thus promoting the momentary stretch of foam lamella, weakening it further. Thus one can conclude that it is the fluidity of the film that is controlling the drainage rate at this concentration. Apparently, with an increase in crowding of surfactant monomers at the interface, as one changes the counterion from Li^+ to Mg^{++}, the adsorbed film is becoming more rigid (discussed later in Fig. 9), thus retarding the flow of water.

Figure 7 shows the foam stability as a function of counterions at a surfactant concentration of 25 mM. At this concentration, micelles are present in the foam film. Here, it can be observed that foam stabilities are low for LiDS (20 min) and NaDS (60 min) surfactant system, while for CsDS and $Mg(DS)_2$ surfactant system, the foam stabilities are *unusually* high (900 min, 1200 min). This suggests an abrupt change in micellar properties (either their number concentration or their stabilities) for the CsDS and $Mg(DS)_2$ surfactant systems in comparison to the LiDS and NaDS surfactant systems. Except for the widely studied NaDS system, the number concentrations of the micelles cannot be reliably determined because of the unavailability of the aggregation numbers for these surfactant systems. Though one can calculate some bounds for micellar number concentrations assuming the same aggregation number as that of NaDS. The aggregation number for NaDS is reported to be 64 [23]. For the surfactants at two extremes (i.e., LiDS and $Mg(DS)_2$), at 25 mM concentration, the number concentration of micelles is 1.51×10^{20} and 2.26×10^{20}, respectively. These number concentrations come closer if one assumes that the packing in micelles will behave in a way similar to that observed at the air/water interface (i.e., the aggregation number for LiDS should be smaller than 64 and for $Mg(DS)_2$ it should
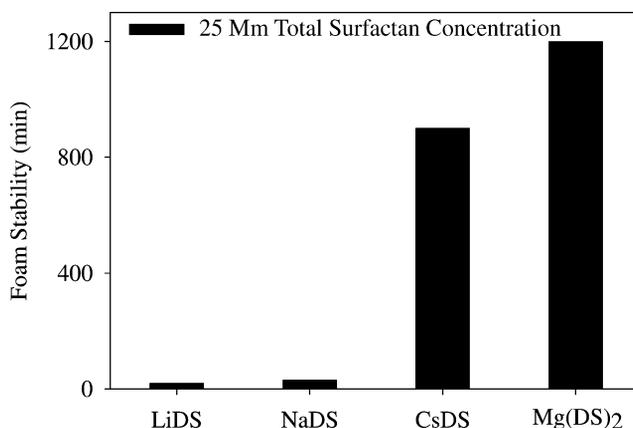
be greater than 64). This is not an unreasonable assumption as such an analogy has been found to be true for mixed systems of NaDS with cationic surfactants of varying chain lengths [24]. Thus the number concentration of micelles is not very different for surfactants with different counterions and the differences in the foam stabilities can be ascribed to the differences in micellar stabilities. From the foamability results shown before (Fig. 3), it is known that the micelles of LiDS and NaDS are unstable in comparison to the micelles of CsDS. Hence one can infer (i) the micellar stability of $Mg(DS)_2$ is very high and (ii) the micellar stability predominantly determines the foam stability (i.e., the higher the micellar stability, the higher is the foam stability).

These issues of structure imparting stability to colloids have been addressed by Wasan and co-workers [25–29], who have shown that polystyrene latices, suspensions of silica particles, and micelles all tend to form ordered or layered colloidal structures in the thin film. One of their results [25] on stepwise film thinning at 30 mM and 100 mM NaDS concentration shows that the time taken for removal of the penultimate micellar layer, before forming a stable film, is highly surfactant-concentration-dependent (i.e., the time required is $\sim$3 min at 30 mM in comparison to $\sim$10 min at 100 mM). The micellar stability of NaDS [30] (1 ms at 25 mM and 100 ms at 100 mM) correlates well with this draining behavior. This observation suggests that it is not just sufficient to have micelles; the micelles must have greater stability to cause enhanced foam stability.

Figure 8 shows the foam stability experiments at 50 mM surfactant concentration. A comparison with Fig. 7 shows that while the foam stabilities for LiDS and NaDS do not change much; the foam stabilities increase *considerably* for CsDS and $Mg(DS)_2$. Thus, one can conclude that the foam stabilities can *only* be enhanced by packing micelles of high stability in the foam lamellae.

In most of our foam stability experiments, lower drainage rates appear to be the requirement for having high foam stabilities. However, the drainage rate measurements (from shaking method) did not correlate well with the foam stabil-
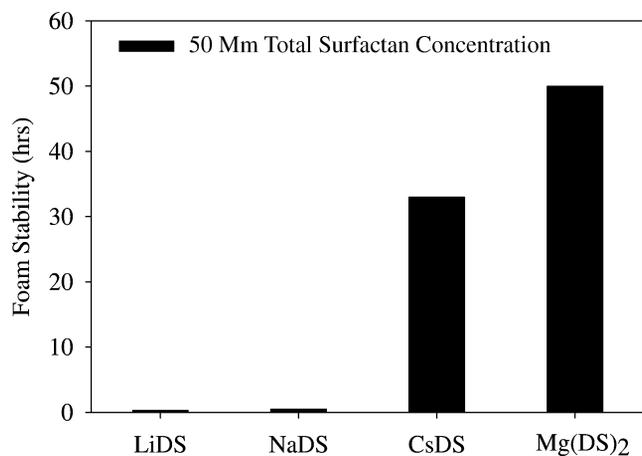
Fig. 8. Foam stability of surfactant dodecyl sulfate with different counterions above critical micellar concentration.
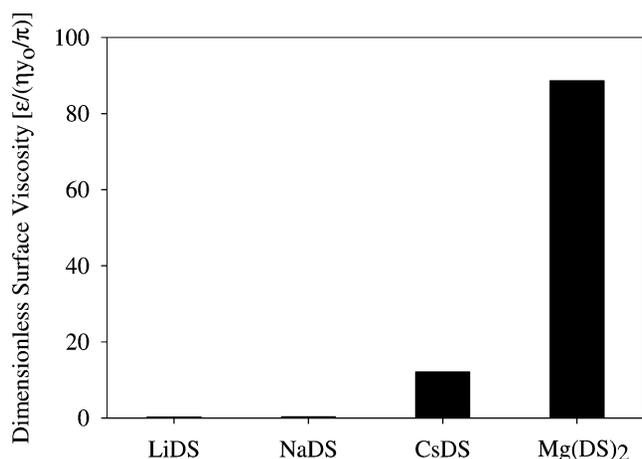

Fig. 9. Dimensionless surface viscosity measurements as a function of counterion of surfactant at concentration 50 mM and 25 °C.

ities. For instance, at surfactant concentration 50 mM, LiDS was found to have a significantly lower drainage rate as compared to NaDS, which is contrary to what is expected from the foam stabilities. Presumably, it is not the bulk drainage but the small residual water drainage from the foam lamellae that can explain the foam stabilities. This phenomenon is also seen in the stepwise thinning of the films, where the majority of the micellar layers drain out quickly. It is only towards the end that one observes the differences in the draining behavior as a function of surfactant concentration [25].

Another useful parameter that correlates well with the foam stabilities is the surface viscosity. The increased stability of foam lamellae with surface viscosity has been shown earlier by various researchers [31–33]. Figure 9 shows the dimensionless surface viscosity measurements for surfactant concentration 50 mM with different counterions. Here, one observes low surface viscosities for LiDS and NaDS, reasonably high surface viscosities for CsDS, and ultrahigh surface viscosities for Mg(DS)$_2$, in good correlation to the foam stabilities shown in Fig. 8. Apparently, the increased binding of
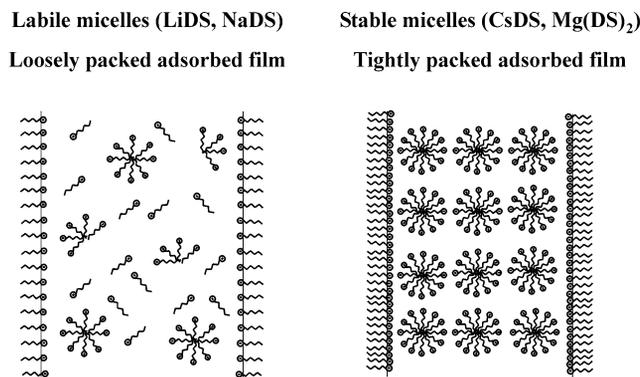

Fig. 10. Diagram showing effect of counterions on packing of surfactant molecule at air/water interface.

counterions in CsDS and Mg(DS)$_2$ decreases the repulsion between adjacent surfactant head groups, causing a more tightly packed film of higher surface viscosity.

Summarily, in the case of cesium and magnesium dodecyl sulfates there is a good contribution to foam stability from structuring effect of micelles while in case of lithium and sodium dodecyl sulfate because of the faster micellar relaxation times, the structural contribution is minimal. Moreover the closer packing of monomers at the air/water interface (Fig. 10) causes higher surface viscosities for cesium and magnesium dodecyl sulfates, which also assists in slowing down the rate of drainage. It might be interesting to study stepwise thinning of film with these surfactants having different counterions. Possibly, one would observe that films with CsDS or Mg(DS)$_2$ systems will squeeze out the micellar layer lot slowly as compared to LiDS or NaDS systems.

4. Conclusions

From the resulted reported in this paper, it can be concluded that

(1) Surface activity of dodecyl sulfate having different counterions is in the order Li < Na < Cs < Mg, while the area per molecule is in the reverse order.
(2) Foamability by shaking method is determined by micellar stability for LiDS, NaDS, and CsDS, while for Mg(DS)$_2$ it is determined by the diffusion of monomers to the air/water interface due to the lower cmc for Mg(DS)$_2$.
(3) Foam stability can be controlled to a certain extent by the molecular packing in the adsorbed film and to a *significantly* larger extent by the presence of *stable* micelles in foam lamellae. The higher the micellar stability, the greater is the foam stability.
(4) The stabilities of the micelles appear to be in the following order: LiDS ∼ NaDS < CsDS ≪ Mg(DS)$_2$.
(5) The surface viscosity is found to be in the order LiDS < NaDS < CsDS ≪ Mg(DS)$_2$ due to the increase in molecular packing at the air/water interface.

(6) Dynamic surface tension at low bubble frequencies shows a trend similar to that for equilibrium surface tension, whereas at higher bubble frequencies, the trend is LiDS > NaDS > CsDS < Mg(DS)$_2$.

Acknowledgment

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