

Adsorption of Ionic Surfactants at Liquid–Liquid Interfaces in the Presence of Salt: Application in Binary Coalescence of Drops

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Binary coalescence of water drops in organic liquids has several commercial applications that are related to the stabilization of emulsions. The stability of the emulsion is dependent on adsorption of the surfactant molecules at the water/organic interface. In this work, the adsorption of ionic surfactants at water/organic interfaces, both in the presence and absence of salt, and its effect on binary coalescence were studied. The ionic surfactants used were sodium dodecyl sulfate and cetrimide. The organic phase was constituted from either toluene or carbon tetrachloride. Adsorption was studied by measuring the interfacial tension. The presence of salt had a strong effect on the interfacial tension in the presence of these surfactants. In the absence of surfactant, salt had little effect on interfacial tension. The data were fitted using a surface equation of state that was developed from the Gibbs adsorption equation and the Langmuir isotherm. Binary coalescence of water drops in toluene was studied in a specially designed coalescence apparatus. Coalescence time did not have a single value but a stochastic distribution of coalescence time was observed in each case. The addition of salt had a significant effect on coalescence time. A stochastic model was used to characterize the distributions.

Introduction

The adsorption of a surfactant at a liquid/liquid interface is important in deciding the stability of emulsions. Surfactant molecules adsorb at the interfaces and prevent the droplets from coalescing with each other. If coalescence occurs readily, the droplets grow in size and ultimately the two phases separate. Many commercial applications involve the presence of salt along with surfactant. Examples of such applications are petroleum dewatering, liquid–liquid extraction, off-shore oil recovery, cleaning, and preservation of food and medicine.^{1,2} Therefore, it is important to understand how the presence of salt affects the adsorption and coalescence of drops.

There have been several studies on the effect of salt on the adsorption of ionic surfactants at air/water interfaces.^{3–5} The extent of the adsorption of surfactant molecules is quantified in terms of “surface excess”. The amount of surface excess can be estimated in two steps. In the first step, the surface tension of the solution at different concentrations of the surfactant is measured. A surface equation of state (EOS), which correlates surface excess with surface tension, is then used to estimate the surface excess. If the experimental data on the variation of surface tension with the concentration of surfactant are available, the Gibbs adsorption equation can be used to estimate the surface excess. There are several models for estimating surface excess. The Langmuir adsorption isotherm and the Frumkin isotherm are often used to quantify it. The method described above is known as an “indirect method”. Apart from this indirect method, it is possible to determine the density of the adsorbed surfactant molecules at the surface by direct experimental methods. Some of the researchers have used radiotracer,⁶ neutron reflection,⁷ and IR-reflection–absorption spectroscopy.⁸

Although much work has been performed on the adsorption of surfactants at air/water interfaces, comparatively less work has been done on the adsorption of surfactants at liquid/liquid interfaces in the presence of salt.^{9,10} Very recently, Gurkov et

al.¹¹ studied the adsorption of sodium dodecyl sulfate (SDS) at water/hexadecane and water/soybean oil interfaces in the presence of NaCl. At dilute concentrations of the surfactant, the interfacial tension was expressed as a third-order polynomial in the logarithm of the squared mean ionic activity of the solution. At higher concentrations of the surfactant, an extension of the Langmuir model with provisions for counterion binding was used. The resulting model for interfacial tension had four fitted parameters.

As mentioned previously, the stability of emulsions (and, hence, the coalescence of drops) is closely related to the adsorption of surfactants. A large amount of theoretical and experimental work has been performed on the coalescence of drops.^{12,13} Most of these works focused on coalescence at a flat interface. Relatively few works have been conducted on the binary coalescence of drops.^{14–16} The theoretical works on coalescence can be divided into two categories: film-drainage models^{17–25} and a stochastic model.²⁶ The film-drainage models predict the mean value of the stochastic distribution of coalescence time. A comparative study of the film-drainage models has been presented by Ghosh.²⁷ However, the film-drainage models do not give the distribution of coalescence time, which is omnipresent. The distribution of coalescence time has been shown to be very important in the design of emulsification equipment.²⁸ However, such distributions of binary coalescence time have not been reported so far in the literature.

The objective of the present work was to study the adsorption of ionic surfactants at the interface of water and either a nonpolar or polar organic liquid. An anionic surfactant and a cationic surfactant were used. Carbon tetrachloride and toluene were used as nonpolar and polar organic liquids, respectively. Small quantities of sodium bromide (NaBr) were added to the aqueous phase, to study its effect on adsorption of surfactants. The interfacial tension data at low surfactant concentrations were fitted using a surface EOS that was derived from the Gibbs adsorption equation and a Langmuir isotherm. Binary coalescence of water drops in toluene in the presence of these surfactants and salt was studied. This work presents the

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coalescence time distributions and demonstrates how the presence of salt affects coalescence time.

General Theory

Surfactant Adsorption. For a symmetric univalent surfactant, such as sodium dodecyl sulfate (SDS) and cetrinide, the Gibbs adsorption equation gives the surface excess (Γ) as²⁹

$$\Gamma = -\frac{1}{2RT} \frac{d\gamma}{d \ln(c)} \quad (1)$$

where γ is the interfacial tension and c is the concentration of surfactant in the bulk. According to the Langmuir isotherm, the surface excess is related to the concentration of surfactant in the bulk solution as follows:

$$\Gamma = \frac{\Gamma_{\infty} K_L c}{1 + K_L c} \quad (2)$$

Here, Γ_{∞} is the adsorption capacity, and its value is dependent on the minimum surface area per adsorbed molecule. The equilibrium constant, K_L , is the ratio of the rate constants for adsorption and desorption. From eqs 1 and 2, we obtain

$$d\gamma = -2RT\Gamma_{\infty} \left(\frac{K_L c}{1 + K_L c} \right) d \ln(c) \quad (3)$$

If the interfacial tension in pure (surfactant-free) solvent is represented by γ_0 , integration of eq 3 gives

$$\gamma = \gamma_0 - 2RT\Gamma_{\infty} \ln(1 + K_L c) \quad (4)$$

Now, consider a univalent salt that has the same counterion as the surfactant. If the concentration of salt is given as c_s , eq 3 is modified to (see Appendix A)

$$d\gamma = -RT\Gamma_{\infty} \left(\frac{K_L c}{1 + K_L c} \right) [d \ln(c + c_s) + d \ln(c)] \quad (5)$$

Integrating eq 5, we obtain the following surface EOS:

$$\gamma = \gamma_0 - \left(\frac{RT\Gamma_{\infty}}{K_L c_s - 1} \right) \times \left[(K_L c_s - 2) \ln(1 + K_L c) + K_L c_s \ln \left(\frac{c + c_s}{c_s} \right) \right] \quad (6)$$

A few assumptions were made in deriving the aforementioned equations. The activity coefficients were taken to be unity, which correspond to ideal solutions. This is justified because the concentrations of surfactants studied in the work were <0.01 M and the maximum concentration of salt was 0.1 M. At these concentrations, the deviation from ideality would be insignificant.^{30,31} We have assumed further that the salt is indifferent to adsorption at the interface (inorganic salts sometimes exhibit negative surface activity). When ionic surfactants adsorb at the interface, a potential is developed. The Langmuir model does not account for this potential. Furthermore, when the charged surfactant headgroups are adsorbed on the interface, a diffuse layer of counterions lies in very close proximity. It is likely that these ions will have interactions with the adsorbed ions. This is known as the “binding of counterions”. The classical Langmuir model (which corresponds to an ideal interface) does not account for these interactions. The advantage of this model is its simplicity and wide applicability. There are sophisticated

extensions of the Langmuir model. These models usually have more fitted parameters. Their agreement with experimental data at high surfactant concentrations is sometimes better.

Coalescence of Drops. According to the film-drainage theory of coalescence, when two drops approach each other under the application of a force such as gravity or shear applied by a stirrer, the film that separates the drops drains. The lubrication force separates the drops. As the distance between the drops decreases, the hydrodynamic resistance increases without bound. In the later stages of drainage, repulsive forces of interfacial origin, such as electrostatic double layer force, prevent the drops from coming closer, in addition to the hydrodynamic resistance. When the thickness of the film becomes very small (a few nanometers), the van der Waals force causes the film to rupture. The film-drainage models for the coalescence of drops describe the evolution of the profile of the thin liquid film over time. However, only a few expressions are available in the literature from which coalescence time can be calculated. The model of Li²⁴ gives the following equation for binary coalescence time:

$$t_c = 0.729 \frac{\mu R_b^{1.68}}{\gamma^{0.54} B^{0.46}} \left(\frac{R_{d1} R_{d2}}{R_{d1} + R_{d2}} \right) \quad (7)$$

Here, μ is the viscosity of continuous phase, R_b the radius of the barrier ring, and B the London–van der Waals constant. R_{d1} and R_{d2} are the radii of the two drops. This model was developed for small drops that have a Bond number ($\Delta \rho g R_{di}^2 / \gamma$, for $i = 1, 2$) that is far less than unity. This model neglects the electrostatic double layer repulsion between the two drops in contact. Therefore, the coalescence time that is predicted by this model in ionic surfactant solutions may not be accurate. The following equation was proposed by Chen and Pu:¹⁶

$$\ln \left[k_f \gamma \left(\frac{1}{R_{d1}} - \frac{1}{R_{d2}} \right) \right] = k_b t_c + b' \quad (8)$$

where k_f is the film coefficient, and k_b and b' are constants.

To account for the wide distribution of coalescence time observed in all experiments, Ghosh and Juvekar²⁶ proposed a stochastic model of coalescence in which the variation in coalescence time was attributed to the variation in surface excess at the liquid/liquid interface. The distribution of surface excess was assumed to be Gaussian. They discussed the factors responsible for the variation, and that discussion is not repeated here. The model was developed for the coalescence of a drop at a flat liquid/liquid interface, but it can be readily used in binary coalescence as well when the drops are pressed together in a resting position by a constant force. The theory is concerned with the surfactant distribution in the thin liquid film trapped between the drops. When two drops approach each other with a high velocity, the liquid film that is trapped between the drops drains fast. During the drainage of the film, the surfactant molecules adsorbed on the surface of the drops are swept toward the rim of the film, which is known as the “barrier ring”. The stress can be so large that the surfactant molecules are likely to form a liquid-condensed (LC) phase. Colloidal forces such as double layer, steric, and solvation forces repel the drops. The nature of these forces is dependent on the type of surfactant adsorbed at the interfaces. During the approach of the drops, a dimple forms in the film such that the thickness of the film is maximum at the center and minimum at the periphery. However, asymmetry in the thickness of the film may exist. The repulsive force generated by the surfactant molecules prevents the drops from coalescing with each other. The repulsion is largest at the

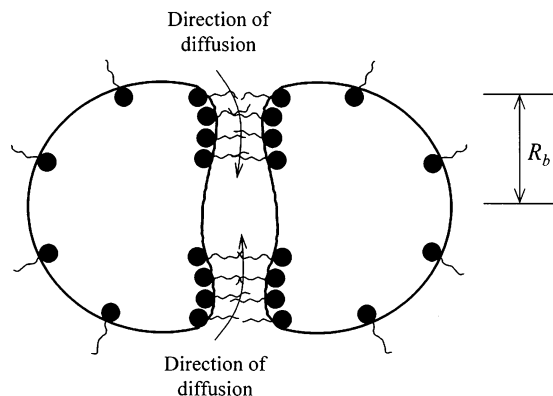


Figure 1. Two water drops in organic medium in contact before coalescence.

barrier ring, where the separation between the two drops (i.e., the thickness of the film) is minimum, because of the dimple at the central part of the film (which may flatten to some extent afterward). Once the surfactants are concentrated at the barrier ring, they diffuse back toward the center of the film driven by the concentration gradient (see Figure 1). This reduces the concentration of surfactant at the barrier ring, which leads to the depletion in the repulsive force. When the repulsion diminishes, the drops come closer to each other. At a certain point of separation, the thickness of the thin film at the barrier ring becomes very small and the van der Waals attraction between the two drops overpowers the repulsion, resulting in coalescence. Therefore, the coalescence is likely to occur at the barrier ring, which has been supported experimentally.^{32,33} Based on this physical description of the coalescence process, the following expression for cumulative distribution of coalescence time was developed:

$$F(\tau_R) = \frac{1}{2} \left\{ \operatorname{erf} \left[\frac{1}{S_\Gamma \sqrt{2}} \left(\frac{P_\Gamma}{1 + \sum_{i=1}^{\infty} e^{-\lambda_i^2 \tau_R}} - 1 \right) \right] + \operatorname{erf} \left(\frac{1}{S_\Gamma \sqrt{2}} \right) \right\} \quad (9)$$

Here, $\operatorname{erf}(x)$ represents the error function. λ_i are the roots of the Bessel function of the first type and order one (J_1). τ_R is the dimensionless coalescence time, which is defined as ($\tau_R = t/\bar{t}$) where \bar{t} is the characteristic diffusion time, which is given by

$$\bar{t} = \frac{R_b^2}{D_\Gamma} \quad (10)$$

D_Γ is the surface diffusivity of the adsorbed surfactant molecules at the interfaces. Its value was taken to be equal to 1×10^{-10} m²/s for the surfactants used in this study. The radius of the barrier ring, R_b , can be estimated from the equation³⁴

$$R_b = 2R_d^2 \sqrt{\frac{\Delta \rho g}{3\gamma}} \quad (11)$$

where R_d is the radius of the drop. This equation was derived considering weight-induced deformation of a drop on a flat deformable interface. The effects of interfacial tension and density difference between the two liquid phases were taken into account in eq 11. Li²⁴ suggested a simple equation for estimating the radius of barrier ring, based on experimental observations in systems where the effects of repulsion by the electrostatic double layer were important.

$$R_b = 0.5 \left(\frac{R_{d1} R_{d2}}{R_{d1} + R_{d2}} \right) \quad (12)$$

During the period in which the drops remain in contact, the barrier ring may expand or shrink. Because the model of Ghosh and Juvekar²⁶ does not take into account this possibility, R_b remains constant with time. P_Γ is the dimensionless coalescence threshold. It is given by

$$P_\Gamma = \frac{\Gamma_m}{\alpha \bar{\Gamma}} = \frac{R_d}{(w_b f_r \alpha) \bar{\Gamma}} \sqrt{\frac{\Delta \rho g \gamma}{6}} \quad (13)$$

where Γ_m represents the minimum value of surfactant concentration at the barrier ring required to prevent coalescence and $\bar{\Gamma}$ is the mean value of surface excess in the film. The value of the latter parameter is taken to be equal to the surface excess (Γ) given by eqs 1 and 2, α represents the fraction of the total surfactant molecules that remains at the barrier ring after the second drop strikes the first drop, w_b is the width of the barrier ring, and f_r is the repulsive force generated by one mole of the adsorbed surfactant molecules. It is dependent on the type of surfactant used. It can be affected by the presence of salt in the solution. $\Delta \rho$ is the density difference between the two phases, g is acceleration due to gravity, and γ is the interfacial tension. Equation 13 was derived by a simple force balance on the drops in contact, as shown schematically in Figure 2. S_Γ is the normalized standard deviation in surface excess, given by

$$S_\Gamma = \frac{\sigma_\Gamma}{\bar{\Gamma}} \quad (14)$$

Therefore, this model has two unknown parameters, P_Γ and S_Γ , that need to be fitted using the coalescence time distributions obtained experimentally. The variation of P_Γ with the physical properties of the system can be explained from eq 13.

Experimental Section

Materials Used. The anionic surfactant, sodium dodecyl sulfate (SDS, C₁₂H₂₅O₄SNa), was procured from EMD Biosciences (Merck, Germany). It had a purity of 99.8%. The cationic surfactant, cetrimeride (C₁₇H₃₈BrN), was procured from Merck (India). It had a purity of 99.3%. Sodium bromide (NaBr) was procured from Merck (Germany). It had a purity of 99.995%. Toluene and carbon tetrachloride (CCl₄) were procured from Merck (India). They had 99.8% purity (high-performance liquid chromatography (HPLC) grade). All these chemicals were used as received from their manufacturers. The water used in this study was purified from a Millipore water purification system. Its conductivity was 1×10^{-7} Ω⁻¹ cm⁻¹, and the surface tension was 72.5 mN/m (at 25 °C).

Experimental Conditions. All experiments on interfacial tension and coalescence were performed in an air-conditioned room, where the temperature was maintained at 25 °C. The variation of temperature in the room was within 0.5 °C. Neither interfacial tension nor coalescence time was determined to be affected by this small fluctuation in temperature.

Measurement of Interfacial Tension. Interfacial tension was measured using a computer-interfaced tensiometer [manufacturer: GBX (France), model: ILMS, precision: 0.01 mN/m]. The Du Nöuy ring method was used to measure interfacial tension. The sample vessel and the ring were scrupulously cleaned after each measurement. Following the equipment manufacturer's instructions, they were cleaned with chromic

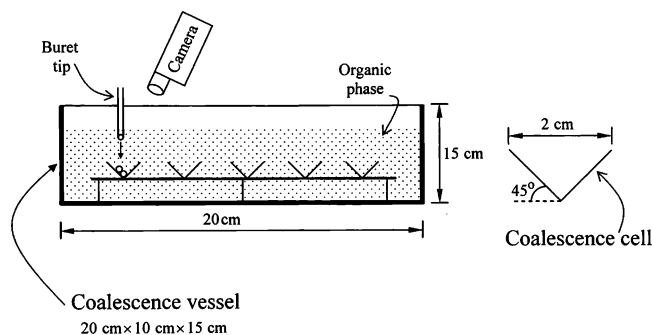


Figure 2. Experimental setup for studying coalescence.

acid, acetone, and Millipore water. The platinum ring was burned to red-hot conditions with a Bunsen burner. A very slow speed of $100 \mu\text{m/s}$ was used to move the sample vessel during the measurements. The aqueous and organic phases were equilibrated before the experiments. The ring was dipped inside the heavier phase, the lighter phase was poured over the heavier phase and allowed to settle for at least 1 h before interfacial tension was measured.

Study of Binary Coalescence. Binary coalescence of drops was studied in a specially designed coalescence setup (see Figure 2). The setup consisted of a coalescence vessel that was composed of glass, conical coalescence cells that were made of Teflon, a support that was also made of Teflon, a glass buret, and a digital video camera [manufacturer: Sony (Japan), model: DCR-HC32E, optical zoom: $20\times$]. The cells were placed, in inverted positions, on the Teflon support and placed inside the vessel such that all of them were completely immersed within the organic phase. The level of liquid was raised 5 cm beyond the height of the cells. The drops were formed using a specially fabricated glass buret that had a delicate long capillary end. Tips that had different diameters were fixed on the end of the buret, to generate drops of different size. Drops that have a diameter in the range of 2–3 mm were studied. The tip of the buret was dipped into the organic phase, and the aqueous drop was slowly formed at the end of the tip. The drop was equilibrated with its surrounding liquid for 1 min. It then was released so that it fell with its terminal velocity inside the coalescence cell placed beneath it. After the first drop settled inside the cell, the second drop was released. The second drop, after some initial movement due to its inertia, rested on the first drop, leaning against the inclined side of the cell. The drops formed in this manner were almost equal in size. The size of a drop was determined by two methods. In the first method, the drop was formed inside the organic liquid in a flat-walled glass vessel. Photographs of the pendant drop were taken from outside. The images of the drop were analyzed and its volume was determined. In the second method, the weight of 100 water drops formed inside the organic liquid was measured. From the total weight, the volume of a single drop was calculated. The diameter of an undeformed drop was calculated from its volume. The values obtained from these two methods agreed well.

The conical Teflon coalescence cells were 2 cm in diameter at the base and their inclined side made a 45° angle with their base. Teflon is inert to all chemicals used in this work. Because the drops had no chance to separate from each other, they could be kept together for a long period of time. Therefore, long coalescence times could be studied. This is the advantage of the present experimental technique over the methods used in the past for studying binary coalescence. The symmetry of the conical cell ensured that all pairs of drops were contacted in

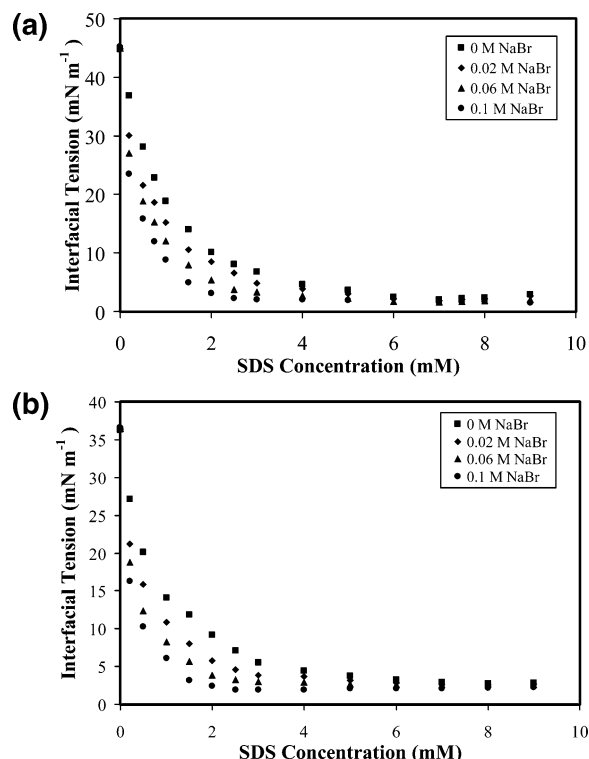


Figure 3. Effect of sodium bromide (NaBr) on interfacial tension in the presence of sodium dodecyl sulfate (SDS): (a) water/ CCl_4 interface and (b) water/toluene interface.

identical manner. A battery of 10 coalescence cells was used. After the coalescence of each pair of drops, the cell was cleaned up discarding the new drop formed by coalescence. The cells and the vessel were cleaned following a procedure similar to that used for the measurement of interfacial tension.

Seventy-five pairs of drops were studied in each experiment. Cumulative distribution of coalescence time was generated using these experimental values. The coalescence process was recorded using the digital video camera, which had an internal timer. The time count began as soon as the second drop collided with the first drop.

Results and Discussion

Effect of Salt on Interfacial Tension. The addition of salt decreased interfacial tension significantly. The results for the water– CCl_4 and water–toluene systems with SDS and cetrimide are presented in Figures 3 and 4. The concentration of salt was varied from 0.02 M to 0.1 M. In a pure system (i.e., in the absence of any surfactant), the addition of salt in this range of concentration had a negligible effect on interfacial tension. In the presence of surfactants, the graphs show a sharp decrease in interfacial tension with increasing salt concentration. However, when the concentration of surfactant approached the critical micelle concentration ($\text{CMC} \approx 8 \text{ mM}$ for SDS and $\text{CMC} \approx 1.2 \text{ mM}$ for cetrimide), the interfacial tension changed very slowly. Therefore, the decrease in interfacial tension was more pronounced in dilute concentrations of the surfactants, up to $\sim 3 \text{ mM}$ for SDS and 0.5 mM for cetrimide. The addition of salt reduced the electrostatic double layer repulsion between the surfactant ions, which augmented their adsorption at the interface. In addition, with increased salt concentration, the CMC was attained early. Therefore, at a lower concentration of the surfactant, the interfacial tension almost ceased to change with concentration. At higher concentrations of the surfactant, it was

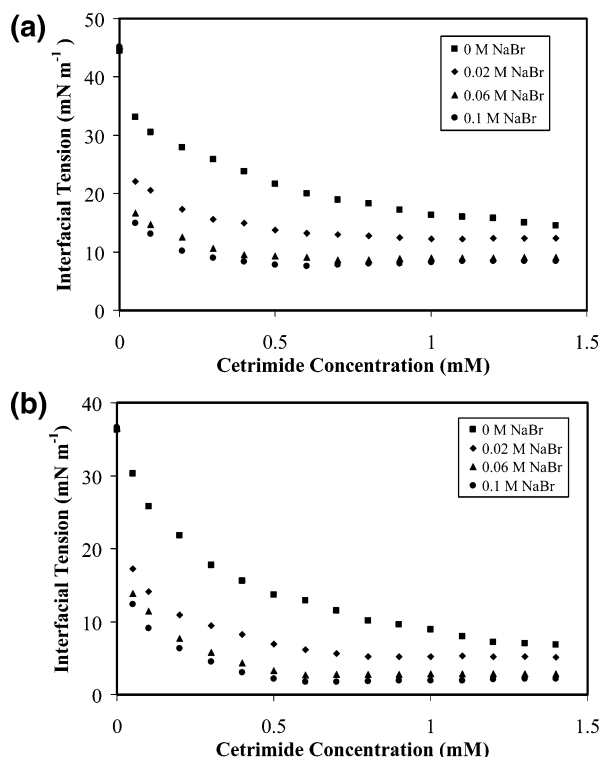


Figure 4. Effect of NaBr on interfacial tension in the presence of cetrimide: (a) water/ CCl_4 interface and (b) water/toluene interface.

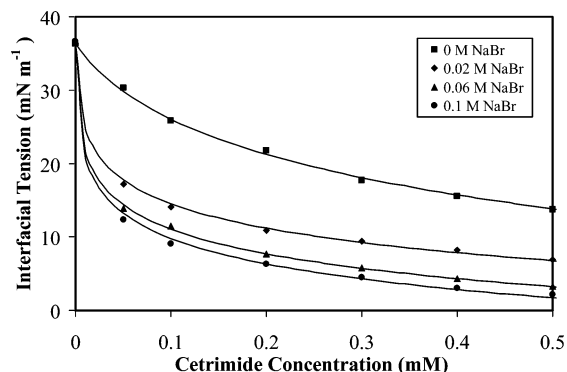


Figure 5. Fit of the surface equation of state (EOS) to the interfacial tension data for the water-toluene-cetrimide-NaBr system.

observed that interfacial tension sometimes increased slightly. This is probably because of the repulsion between the surfactant headgroups when the interface became almost saturated. An interesting observation from Figure 4 is, in cetrimide systems, the addition of salt reduced the interfacial tension even beyond the CMC. This observation supports the results from the neutron reflection studies at air/water interfaces that further adsorption is possible, even after reaching the CMC.³⁵ Another important observation from Figures 3 and 4 is that the reduction of interfacial tension in the water- CCl_4 -cetrimide system was less than that observed with other systems.

To characterize the interfacial tension data in the low-concentration region, the Langmuir model was applied. The data were fitted using eqs 4 and 6. It was observed that the Langmuir model fitted the data well in this range of surfactant concentration. Figure 5 depicts the fit of the surface EOS to the interfacial tension data for the water-toluene-cetrimide-NaBr system. The two parameters, Γ_∞ and K_L , are listed in Table 1 for all four systems. The mean square average deviation between the

Table 1. Parameters of the Langmuir Adsorption Isotherm

NaBr concentration (M)	$\Gamma_\infty \times 10^6$ (mol/m ²)	K_L (m ³ /mol)	$\Delta\gamma$ (mN/m)
Water-CCl_4-SDS-NaBr System			
0.00	3.06	4.34	0.83
0.02	3.56	27.77	0.75
0.06	3.66	36.49	0.65
0.10	3.73	46.00	1.02
Water-Toluene-SDS-NaBr System			
0.00	1.78	9.90	0.36
0.02	2.50	61.73	0.47
0.06	2.54	87.79	0.60
0.10	2.56	114.00	0.99
Water-CCl_4-Cetrimide-NaBr System			
0.00	1.22	93.14	0.82
0.02	1.26	33015.00	0.76
0.06	1.50	35795.00	0.50
0.10	1.56	40119.00	0.84
Water-Toluene-Cetrimide-NaBr System			
0.00	1.93	19.89	0.40
0.02	1.96	961.00	0.35
0.06	1.99	1900.00	0.46
0.10	2.06	2080.00	0.76

experimental values and the values predicted by the model was minimized to obtain these two parameters:

$$\Delta\gamma = \left[\frac{\sum (\gamma_{\text{exp}} - \gamma_{\text{model}})^2}{n} \right]^{1/2} \quad (15)$$

In eq 15, the summation was performed over n experimental observations. It can be observed from Table 1 that the value of Γ_∞ increased slightly as the salt concentration increased. As per the Langmuir theory, its value should be constant. However, this variation can be considered to be small. The values of Γ_∞ are lower in cetrimide systems, as compared to the SDS systems. This is because of the fact that a cetrimide molecule occupies a larger area at the interface than does an SDS molecule and, therefore, they saturate the interface at a lower concentration. As expected, K_L increased as the salt concentration increased. The value of $\Delta\gamma$ was less than unity in almost all systems, which suggests that the fit of the surface EOS to the experimental data was good. From Table 1, it is observed that the values of K_L are exceptionally high for the water- CCl_4 -cetrimide-NaBr system, compared to the values in other systems. These high values suggest that Γ is invariant with surfactant concentration at high concentrations.

The surface excess computed from the Langmuir model for the water-toluene-cetrimide-NaBr system is shown in Figure 6. In this figure, the effect of salt in saturating the interface at a lower concentration of surfactant is apparent. In the absence of salt, the surface excess curve monotonically increased with surfactant concentration. With the addition of salt, the surface excess reached its near-saturation value at a lower concentration of surfactant. Beyond this point, any further increase was very gradual.

Effect of Salt on Binary Coalescence. The addition of salt is expected to produce two counteracting effects on coalescence. The first effect is that adsorption of the surfactant at the surface of the drops is facilitated by the presence of salt, as evident from the foregoing discussion. This increases the surfactant concentration at the drop surface. The result is more surfactant molecules accumulate at the barrier ring (see Figure 1), which can exert greater repulsion between the drops. This phenomenon prevents coalescence. On the other hand, the presence of salt reduces the double layer repulsion between the two drops,

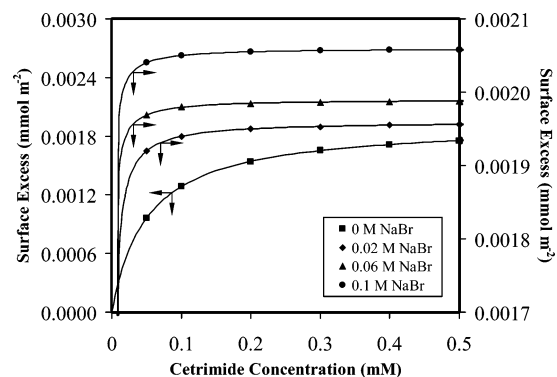


Figure 6. Surface excess computed from the Langmuir isotherm for the system shown in Figure 5.

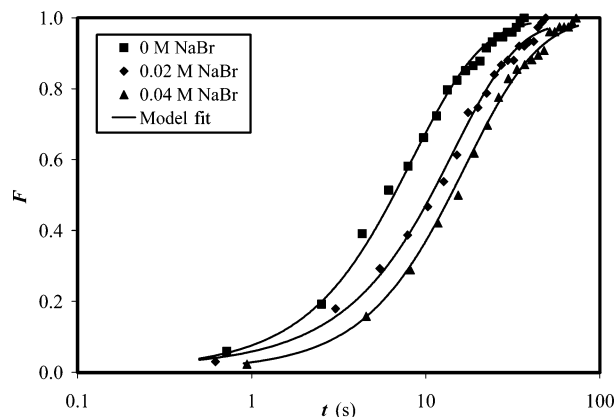


Figure 7. Coalescence time distributions in the water-toluene-SDS system. (SDS concentration = 1 mM.)

allowing them to approach closer to each other. This favors coalescence. From eq 13, it is evident that, as surface excess increases, P_{Γ} should decrease, which should result in a longer coalescence time. At the same time, if f_r is reduced, P_{Γ} would increase, which would make coalescence faster. Thus, the relative magnitude of these effects determines whether the coalescence time will be shorter or longer.

While conducting the experiments on coalescence, special precautions were taken for maintaining the size of the drops, which changes with changes in the interfacial tension. Because the decrease in interfacial tension with an addition of salt was large, the drops became very small. This difficulty was avoided to some extent through the use of buret tips of different diameters. However, at relatively higher salt concentrations (0.06 M and above), this experimental strategy was no longer suitable. Therefore, the coalescence studies were conducted at lower salt concentrations (0.02 and 0.04 M). Results on the binary coalescence of water drops in toluene in the presence of SDS and NaBr are presented in Figure 7. As shown in the figure, broad distributions of coalescence time were observed. As the salt concentration increased, coalescence time increased. The two model parameters obtained by fitting the distributions (P_{Γ} and S_{Γ}) are listed in Table 2. The values of \bar{t} are also listed in Table 2. Note that eq 10 provides an approximate value of \bar{t} , because the estimates of the radius of the barrier ring and the diffusivity of surfactant molecules are approximate. The fitted value of P_{Γ} is indeed affected by a change in the value of \bar{t} . However, as discussed by Ghosh and Juvekar,²⁶ the trend in the variation of P_{Γ} remains similar as long as the model for the estimation of \bar{t} is used consistently. P_{Γ} was determined to decrease as the salt concentration increased. This parameter is dependent on the drop radius (R_d), the interfacial tension (γ), the surface excess (Γ), the repulsive force (f_r), the loss of

Table 2. Parameters of the Stochastic Model

NaBr (M)	D (mm)	γ (mN/m)	\bar{t} (s)	P_{Γ}	S_{Γ}
(i) Water-Toluene-SDS-NaBr System					
0.00	2.4	14.14	2493.6	6.8	0.40
0.02	2.3	10.83	2746.1	5.9	0.40
0.04	2.2	9.40	2648.5	5.2	0.36
(ii) Water-Toluene-Cetrimide-NaBr System					
0.00	2.5	25.80	1609.1	5.2	0.34
0.02	2.4	14.13	2495.4	4.8	0.30
0.04	2.3	12.31	2415.9	3.3	0.24

surfactant molecules from the film during the collision of the drops (α), and the width of the barrier ring (w_b). In the present case, the overall effect was a decrease in the value of P_{Γ} with increases in surfactant concentration.

The magnitude of the repulsive double layer force at a liquid/liquid interface is often estimated using the theory for colloids. Therefore, the repulsive “disjoining” pressure between two flat interfaces in aqueous medium in the presence of NaBr can be computed from the equation that has been given by Hiemenz and Rajagopalan:³⁶

$$\Pi = 5.32 \times 10^5 T c_s \tanh^2 \left(\frac{e\psi}{4k_B T} \right) \exp(-\kappa h) \quad (16)$$

where κ is the Debye-Hückel parameter, which is defined as

$$\kappa = \left[\frac{2 \times 10^3 e^2 N_A c_s}{\epsilon \epsilon_0 k_B T} \right]^{1/2} \quad (17)$$

Here, e is the electronic charge, h the separation between the interfaces, k_B the Boltzmann constant, N_A Avogadro's number, T the absolute temperature, ϵ the dielectric constant of the medium, ϵ_0 the permittivity of vacuum, and ψ the potential developed at the interface. The concentration of salt in eqs 16 and 17 is expressed in units of mol dm^{-3} . The inverse of κ is known as the Debye length. From eqs 16 and 17, it can be demonstrated easily that the double layer repulsion is strong enough to support two drops of organic liquid in aqueous media in the arrangement shown in Figure 2. However, in the experiments reported here, the water drops were separated by a continuous medium of toluene. The double layer repulsion between the drops is expected to be small, because the dielectric constant of toluene is very small ($\epsilon \approx 2.4$). Therefore, the major repulsion between the drops was caused by the alkyl tails of the surfactant molecules adsorbed at the barrier ring. They were probably associated with each other in the presence of salt by hydrophobic interaction, providing a steric repulsive force of entropic origin that prevented the drops from approaching each other close enough for the van der Waals force to cause coalescence. From the fitted values of P_{Γ} , it is possible to study the variation of α , f_r , and w_b with the addition of salt, because the values of other parameters (i.e., R_d , γ , and Γ) are known. From eq 13, we can write

$$\frac{(P_{\Gamma})_0}{(P_{\Gamma})_{0.02}} = \left[\frac{(R_d)_0}{(R_d)_{0.02}} \right] \left[\frac{(\bar{\Gamma})_{0.02}}{(\bar{\Gamma})_0} \right] \left[\frac{(\alpha f_r w_b)_{0.02}}{(\alpha f_r w_b)_0} \right] \left[\frac{(\gamma)_0}{(\gamma)_{0.02}} \right]^{1/2} \quad (18)$$

The subscripts in eq 18 refer to the concentrations of NaBr. We can use the values of R_d , γ , and P_{Γ} presented in Table 2. The values of $\bar{\Gamma}$ were computed from eq 2. Therefore, we obtain

$$\frac{(\alpha f_r w_b)_{0.02}}{(\alpha f_r w_b)_0} = 0.64 \quad (19)$$

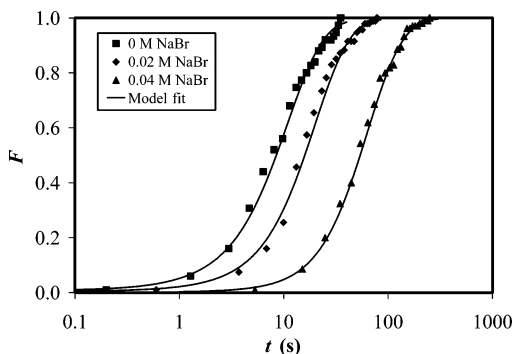


Figure 8. Coalescence time distributions in the water–toluene–cetrimide system. (Cetrimide concentration = 0.1 mM.)

The width of the barrier ring (w_b) is likely to increase as the reduction in interfacial tension increases, because the drops become more deformable. We have previously discussed that f_r might increase as the salt concentration increases. Therefore, from the aforementioned results, it seems that a significant portion of the surfactant molecules were desorbed when the drops collided. This is expected because the interface between water and the organic liquid becomes gradually saturated with surfactant molecules with the addition of salt and the barrier ring may not be able to accommodate all surfactant molecules. Therefore, some of the surfactant molecules are likely to be desorbed from the interface.

The effect of salt concentration on the coalescence of water drops in toluene, in the presence of cetrimide and NaBr, is shown in Figure 8. In this system also, the addition of salt increased the coalescence time. With increasing salt concentration, P_Γ decreased, as a result of enhanced adsorption at the water/toluene interface. As the salt concentration was increased from 0 M to 0.02 M, the interfacial tension decreased from 25.8 mN/m to 14.13 mN/m (see Table 2). This reflects strong adsorption. However, the decrease in the value of P_Γ was rather small (viz., from 5.2 to 4.8). On the other hand, as the salt concentration was increased from 0.02 M to 0.04 M, the decrease in interfacial tension was comparatively small but the coalescence time increased by a large extent and the value of P_Γ was reduced significantly. This is probably because of the entangling effect of the surfactant tails at the higher density of the surfactant molecules at the interface, which increased f_r , to a significant extent.

The normalized standard deviations (S_Γ) for the three distributions presented in Figure 7 were reduced slightly as the salt concentration was increased. This indicates that the fluctuations in the concentration of surfactant at the interfaces were diminished by the addition of salt. An interesting observation in the distributions shown in Figure 8 is that S_Γ was reduced significantly as the salt concentration increased. This means that, as the interface became increasingly covered by the surfactant molecules, the fluctuations in the concentration of the surfactant molecules at the interface were reduced. Cetrimide molecules saturated the interface at a much lower concentration than the SDS molecules. With increasing concentration at the interface, the surfactant tails oriented themselves such that their movement became more restricted. This is the likely reason for reduction of S_Γ with increases in the salt concentration.

Conclusion

Adsorption of a cationic surfactant and an anionic surfactant at water/carbon tetrachloride and water/toluene interfaces was studied in the presence (as well as in the absence) of a monovalent salt (sodium bromide, NaBr). The presence of salt

reduced the electrical repulsion between the charged headgroups of the surfactant molecules, thereby enhancing adsorption at the interface. In the presence of the cationic surfactant, cetrimide, it was observed that adsorption was not entirely complete, even after reaching the critical micelle concentration. A surface equation of state (EOS) derived from the Langmuir adsorption isotherm was used to fit the interfacial tension data at low concentrations of the surfactants. The agreements were generally good. The surface excess values that have been computed from the EOS seem to be reasonable. They are comparable to the values reported in the literature for the adsorption of similar surfactants at air/water interfaces.

The binary coalescence of water drops in toluene was studied in a specially designed coalescence setup. Coalescence time was measured at dilute concentrations of surfactant and salt. Broad stochastic distributions of coalescence time were observed. The addition of salt increased coalescence time significantly for both surfactants. A stochastic model developed earlier fitted the distributions well. Generally, the variation of the two fitted model parameters was commensurate to the variation in the physical properties of the systems. The dimensionless coalescence threshold, P_Γ , obtained by fitting the distributions followed the expected trend. Cetrimide, because of the association of the tails of the surfactant molecules, rendered the distribution of surface excess narrow when the interface became increasingly saturated; this observation was reflected in the coalescence time distributions.

Nomenclature

- b' = constant in eq 8
- B = London–van der Waals constant (J m)
- c = concentration of surfactant (mol/m³)
- c_s = concentration of salt (mol/m³)
- D = diameter of the drop (m)
- D_Γ = surface diffusivity (m²/s)
- e = electronic charge (C)
- f_r = repulsive force generated by one mole of the surfactant molecules at the barrier ring (N/mol)
- $F(\tau_R)$ = cumulative probability distribution of coalescence time
- g = acceleration due to gravity (m/s²)
- h = thickness of the thin liquid film lying between the drops (m)
- k_b = constant in eq 8 (s⁻¹)
- k_B = Boltzmann constant (J/K)
- k_f = film coefficient in eq 8 (Pa⁻¹)
- K_L = equilibrium constant in the Langmuir isotherm (m³/mol)
- n = number of data points used to determine the parameters of the surface equation of state
- N_A = Avogadro's number (mol⁻¹)
- P_Γ = dimensionless coalescence threshold
- R = universal gas constant (J mol⁻¹ K⁻¹)
- R_b = radius of barrier ring (m)
- R_d = radius of the drop (m)
- R_{d1} = radius of the first drop (m)
- R_{d2} = radius of the second drop (m)
- S_Γ = normalized standard deviation
- t = time (s)
- t_c = binary coalescence time (s)
- \bar{t} = characteristic diffusion time (s)
- T = temperature (K)
- w_b = width of the barrier ring (m)

Greek Letters

- α = fraction of Γ that remains at the barrier ring after the displacement of surfactant molecules to the barrier ring

γ = interfacial tension (N/m)
 γ_0 = interfacial tension in the absence of surfactant (N/m)
 γ_{exp} = interfacial tension obtained experimentally (N/m)
 γ_{model} = interfacial tension predicted by the model (N/m)
 Γ = surface excess of the surfactant (mol/m²)
 $\bar{\Gamma}$ = mean value of the surface excess (mol/m²)
 Γ_{∞} = adsorption capacity (mol/m²)
 Γ_m = minimum value of the surfactant concentration at the barrier ring required to prevent the drops from coalescence (mol/m²)
 $\Delta\gamma$ = mean square average deviation in γ (N/m)
 $\Delta\rho$ = density difference between the aqueous and organic phases (kg/m³)
 ϵ = dielectric constant
 ϵ_0 = permittivity of vacuum (C² J⁻¹ m⁻¹)
 κ = Debye–Hückel parameter (m⁻¹)
 λ_i = roots of the Bessel function of the first type and order one (J_1)
 μ = viscosity of the continuous phase (Pa s)
 Π = repulsive disjoining pressure (N/m²)
 σ_{Γ} = standard deviation in the distribution of Γ (mol/m²)
 τ_R = dimensionless coalescence time
 ψ = potential developed at the interface (V)

Appendix A. Change in Equilibrium Interfacial Tension with the Change in Concentration of Surfactant and Salt in the Solution

Let us consider the adsorption of sodium dodecyl sulfate (SDS) in the presence of NaBr. We represent the organic ion as R⁻. The common counterion in this case is Na⁺. It is represented as A⁺. The bromide ion is represented as X⁻. The adsorption of the bromide ion is negligible, in comparison with that of R⁻. Because the ions are completely dissociated in solution, we have



The Gibbs adsorption equation gives the following relation between the change in equilibrium interfacial tension and the change in composition of the solution:

$$d\gamma = -RT \sum_i \Gamma_i \ln(c_i) \quad (\text{A2})$$

The summation is over all ionic species in the solution. The solution has been assumed to be ideal because the surfactant and salt concentrations studied in this work were low. Therefore, the activity coefficients are unity and they also are invariant with concentration. We represent the ion concentrations in terms of the bulk concentration as follows:

$$c_{\text{R}^-} = c \quad (\text{A3a})$$

$$c_{\text{X}^-} = c_s \quad (\text{A3b})$$

At the interface,

$$\Gamma_{\text{R}^-} = \Gamma \quad (\text{A4a})$$

$$\Gamma_{\text{X}^-} = 0 \quad (\text{A4b})$$

The requirement of electroneutrality gives

$$c_{\text{A}^+} = c_{\text{R}^-} + c_{\text{X}^-} \quad (\text{A5})$$

in the bulk and

$$\Gamma_{\text{A}^+} = \Gamma_{\text{R}^-} \quad (\text{A6})$$

at the interface. Therefore, from eq A2, we obtain

$$d\gamma = -RT[\Gamma_{\text{A}^+} d \ln(c_{\text{A}^+}) + \Gamma_{\text{R}^-} d \ln(c_{\text{R}^-}) + \Gamma_{\text{X}^-} d \ln(c_{\text{X}^-})] \quad (\text{A7})$$

Substituting Γ_{A^+} from eq A6, c_{A^+} from eq A5, Γ_{R^-} from eq A4a, Γ_{X^-} from eq A4b, and c_{R^-} from eq A3 into eq A7, we obtain

$$d\gamma = -RT\Gamma[d \ln(c + c_s) + d \ln(c)] \quad (\text{A8})$$

Substituting $\Gamma = \Gamma_{\infty} K_L c / (1 + K_L c)$ into eq A8, we obtain

$$d\gamma = -RT\Gamma_{\infty} \left(\frac{K_L c}{1 + K_L c} \right) [d \ln(c + c_s) + d \ln(c)] \quad (\text{A9})$$

For cetrimide and NaBr, a similar procedure can be followed to derive eq A9.

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