Adsorption Behavior of Surfactants and Mass Transfer in Single-Drop Extraction

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Three surfactants—SDS, Triton X-100, and DTMAC—were used to study effects of surfactants on the mass transfer in liquid–liquid extraction. Single-drop extraction apparatus was used to obtain the mass-transfer coefficient of acetic acid from dispersed CCl_4 *droplets to the continuous water phase. The excess mass-transfer resistance was related to the adsorption behavior of surfactants on the interface. All of these surfactants significantly reduced the mass-transfer rate. Mass-transfer coefficient,* K_R*, decreases rapidly with increasing surfactant concentration and reaches a minimum at concentrations less than 0.04 mM. The effectiveness of the surfactants in decreasing the mass-transfer rate increases in the order:* $DTMAC < SDS = Triton\ X\text{-}100$*. This effectiveness has no direct relation with the ionic types of surfactants, but is affected by the adsorption rate and adsorbed surface concentration on the interface. A slight increase in the mass-transfer coefficient was found at higher concentrations of Triton X-100 due to its higher adsorption kinetics. The excess mass-transfer resistance exerted by the surfactant mainly resulted from the obstruction of the adsorbed barrier layer. The contribution of the inhibition of interfacial flow to the mass-transfer resistance was considered to be minor.*

Introduction

The presence of a surface active agent in a mass-transfer system is known to reduce the mass-transfer coefficient markedly and has been studied by many authors using a single-drop extraction process (Garner and Hale, 1953; Garner and Skelland, 1956; Lindland and Terjesen, 1956; Boye-Christensen and Terjesen, 1958, 1959; Lee et al., 1998). In these studies, the variation of the mass-transfer coefficient, K, with surfactant concentration may be classified into two types: the mass-transfer coefficient decreases rapidly with surfactant concentration to a constant value (Lindland and Terjesen, 1956; Boye-Christensen and Terjesen, 1958, 1959; Lee et al., 1998), and the mass-transfer coefficient decreases to a minimum value rapidly, but increases slowly and slightly with further addition of surfactants (Garner and Hale, 1953; Garner and Skelland, 1956).

The excess mass-transfer resistance exerted by the surfactants has been attributed to either the hydrodynamic effect or to the formation of an interfacial barrier layer. The effects of surfactant on the hydrodynamic behavior of a moving droplet may include changes in internal circulation velocities, interfacial mobilization, and the inhibition of interfacial movement due to the gradient of interfacial tension along the drop surface (Garner and Skelland, 1956; Bakker et al., 1967; Beitel and Heideger, 1971; Jeng et al., 1986; Lee et al., 1998). On the other hand, the concept of the barrier layer, also called the physicochemical effect, was usually attributed to the interaction between solute and adsorbed surfactant across the interface (West et al., 1952; Lindland and Terjesen, 1956; Boye-Christensen and Terjesen, 1958; Huang and Kinter, 1969; Mudge and Heideger, 1970). Although a great deal of effort was made to identify the mechanisms of mass transfer in the presence of surfactants, no consistent conclusion has been drawn.

In an extraction process, the movement of dispersed droplets through the continuous phase causes surface convection and stretching and compressing on the drop surface. For a surfactant-containing system, the concentration profile of

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surfactants on the drop surface is a competing result of the surface convection, and the diffusion, adsorption, and desorption of the surfactants to and from the drop surface. To better understand the effects of surfactants on the mass transfer coefficient, we must look at the adsorption kinetics of the surfactant on the interface. In recent years, Stebe and her coworkers used a three-phase periodic fluid particle flow to study the surfactant effects on surface mobility (Stebe et al., 1991; Stebe and Maldarelli, 1994). They found that for surfactants that have fast adsorption kinetics, the surface mobility was decreased at low concentrations, while increased well above the critical micelle concentration (CMC). Although their studies gave no direct information about the mass-transfer coefficient, it seemed to have effects similar to the two types of variations of mass-transfer coefficients previously mentioned.

In our previous study (Lee et al., 1998), a single-drop extraction apparatus was used to study the surfactant effects on the mass-transfer coefficient and the fluid flow behavior along the extraction column. In the present work, three types of surfactants (anionic, cationic, and nonionic) were used and the equilibrium and dynamic interfacial tensions of the surfactants were measured. The influence of the adsorption behavior of surfactants on mass transfer was studied in order to better understand the surfactant mechanism in reducing the mass-transfer coefficient.

Experimental Studies

Materials

Acetic acid was used as the solute that was originally contained in the dispersed phase (carbon tetrachloride) and extracted by the continuous phase (water). The initial concentration of acetic acid in the carbon tetrachloride was 0.2 M for all of the experiments. The anionic, cationic, and nonionic surfactants used are sodium dodecyl sulfate (SDS, 95%) supplied by Sigma Chemical Company, dodecyl trimethyl ammonium chloride (DTMAC) supplied by TCI Co. Ltd., and polyoxyethylated t-octylphenol (Triton X-100) supplied by Aldrich Chemical Company, respectively. All of these surfactants are water soluble and used without further purification.

Method

The single-drop extraction apparatus, shown in Figure 1, is similar to that constructed by Lee et al. (1998). The drop volume is controlled at 0.02 ± 0.001 mL by changing inside diameters of the drop former for various concentrations of surfactant solutions. The dispersed drops were formed within water and the formation times were kept to between 0.8 and 1.2 s per drop. The experimental results showed that within this time range, the rate of drop formation had no obvious effect on the mass-transfer coefficient. The drops fell by the force of gravity from the top of the extraction column through the stagnant continuous phase and were collected at the bottom of the column (B) after passing the valve (C). The mass transfer proceeded during this process, and the overall mass-transfer coefficient was evaluated for the main extraction column (A) by analyzing the amount of acetic acid in the column (B). The extraction column had an inside diameter of 3 cm and the lengths of the main extraction column (A) and collection column (B) were 70 and 14 cm, respectively. The time of extraction, t_f, was estimated using a stopwatch to measure the average traveling time of the drops through column (A). After the extraction process, the content of column (B), including the water and carbon tetrachloride, was removed for analysis. For every experimental condition, an average value was obtained from four different runs, in which duplicated experiments were performed for the drop numbers for 100 and 200, respectively.

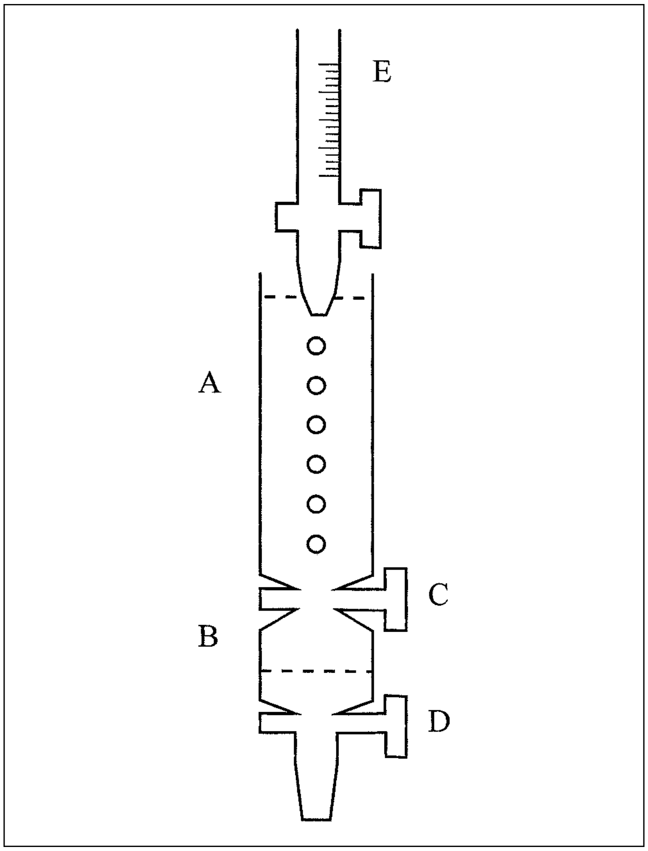

Figure 1. Experimental apparatus for single-drop extraction process.

A, main extraction column; B, collection column; C and D, controlling valves; E, drop former.

The distribution ratio, m, of acetic acid between CCl_4 and water is defined as $m = X_R/X_E$, where X_R and X_E are the equilibrium mole fractions of acetic acid in CCl_4 and water, respectively. The value of m was found to increase linearly with X_E ($m = 2.9X_E + 0.026$) and was nearly independent of the surfactant concentration. Because the acetic acid concentration in the extracted phase is very dilute, the value of m is much smaller than 0.1 in the concentration range used. The concentration of acetic acid in the CCl_4 phase was analyzed by mixing the sample with an excess amount of water and then determined by titration with NaOH.

The overall mass transfer coefficient, K_R, can be evaluated from the equation (Lee et al., 1998)

$$K_R = (V_d/t_f a_d) \ln (X_{R1}/X_{R2}), \tag{1}$$

where a_d and V_d are the surface area and volume of a drop, respectively; t_f is the extraction time; and X_{R1} and X_{R2} are the measured mole fractions of solute in the feed and raffinate solutions, respectively. Since the volume of a drop is very small (about 0.02 mL), for calculating the surface area, a_d, all drops were considered to be spherical in shape.

Measurement of interfacial tension

The dynamic interfacial tensions between the aqueous solution of surfactant and the carbon tetrachloride were measured at 298 K by a drop volume tensiometer (TVT1, Lauda Co.). A quasi-static mode is used in this measurement. When a surfactant is present, the interfacial tension will decrease with increasing adsorption time. An equilibrium interfacial tension corresponding to the equilibrium state of adsorption is theoretically established only at an infinite time. To obtain the equilibrium interfacial tension, an approximate method is always used by using the plot of interfacial tension vs. $(t)^{-1/2}$ and extrapolating t to infinity (Fang and Joos, 1992; Hunsel et al., 1986). The last 3 to 5 points of the dynamic interfacial tension data show a good linear relation in the plot of interfacial tension vs. $(t)^{-1/2}$, and were taken to make a linear extrapolation.

Theoretical Model

Surface mobility

When a drop is settling under gravity in a continuous phase, the viscous force will drag the interfacial liquid backward. This promotes the internal circulation and interfacial mobility of drops, and thus enhances the mass-transfer rate. However, if a surfactant is present, the interfacial mobility will be inhibited significantly by the Marangoni stress (Scriven and Sternling, 1960; Gibbs, 1961; Levich, 1962). The fluid dynamic of a moving drop at the presence of a surfactant had been studied by Levan and Newman (1976), Sadhal and Johnson (1983), Oguz and Sadhal (1988), and Chen and Stebe (1996).

As a droplet settles in a surfactant solution, surfactant molecules that adsorb on the interface are convected toward the rear of the droplet, where they accumulate and reduce the local interfacial tension. At the leading pole of the falling drop, the stretch and renewing of surface cause the surfactant concentration to decrease, and thus, the local interfacial tension will be higher than those of the surroundings. The interfacial layer of the drop, which pulled from the low-tension region toward the leading pole, exerts a Marangoni stress and thus increases the drag resistance of the interfacial flow. As a consequence, the interfacial mass-transfer rate will be decreased. This effect has been taken as the main reason, from the hydrodynamic point of view, for the decrease in the mass transfer rate by the surfactant. The mobility of the interface can range from a state of stress-free motion to partial, or even to complete stagnation. This is controlled by the concentration gradient of surfactants on the drop surface, which is built by the competitive mechanisms of surface convection, bulk diffusion and convection, and the adsorption−desorption kinetics of surfactant molecules.

The surface mobility leads to variations in the terminal velocity of a falling drop, and other effects, such as drop distortion and oscillation, that are responsible for the mass-transfer efficiency across the interface of the droplet.

Adsorption of surfactants on the interface

The surfactant molecules in the bulk phase have a tendency to adsorb on the interface, and thus decrease the interfacial tension. For a surfactant solution, the equilibrium tension is essentially constant when the surfactant concentration is above the critical micelle concentration (CMC), because only the monomeric surfactant molecule contributes to the reduction of interfacial tension. For surfactant concentrations below the CMC, the equilibrium surface concentration, Γ, on the interface can be estimated by the Gibbs adsorption equation:

$$\Gamma = -\frac{1}{nRT}\left(\frac{d\sigma}{d\ln C}\right), \tag{2}$$

where R is the gas constant, T is the temperature, σ is the interfacial tension, and C is the bulk concentration of surfactant. The factor n represents the number of species constituting the surfactant and adsorbing at the interface. For a nonionic surfactant (Triton X-100), $n = 1$, and for uni-univalent ionic surfactant (SDS, DTMAC), $n = 2$. With a proper $\Gamma(C)$ isotherm, one can derive a corresponding surface equation of state, $\sigma(C)$. In this article, the Langmuir isotherm is used:

$$\Gamma = \Gamma_m \frac{K_L C}{1 + K_L C}, \tag{3}$$

where Γ_m is the maximum surface concentration, and K_L is the Langmuir equilibrium adsorption constant. The corresponding surface equations of state for Langmuir isotherm are the Szyszkowski equation (Eq. 4) and Frumkin equation (Eq. 5):

$$\sigma = \sigma_o - nRT\ \Gamma_m \ln(1 + K_L C) \tag{4}$$

$$\sigma = \sigma_o + nRT\ \Gamma_m \ln(1 - \Gamma/\Gamma_m), \tag{5}$$

where σ_o is the interfacial tension between the pure water and pure oil. The equilibrium adsorption parameters, Γ_m and K_L, can be estimated by fitting the experimental data with these equations.

When a new surface is created in a surfactant solution, the surfactant molecules will move from the bulk phase to the interface to reach equilibrium between the surface and bulk concentrations. A finite time is required to approach this state. The transport of the surfactant is governed by two mechanisms (Defay and Petre, 1971): (1) the transfer of the molecules between the bulk solution and the subsurface (the region a few molecular thicknesses adjacent to the interface); and (2) the adsorption−desorption process of molecules between the interface and subsurface. During the surfactant transport stage, the nonequilibrium interfacial tension varies with the variation in the surface concentration, and is called dynamic surface tension (DST). The DST is always measured from a static drop or bubble (such as the drop volume or pendant drop techniques), in which the effect of bulk convec-

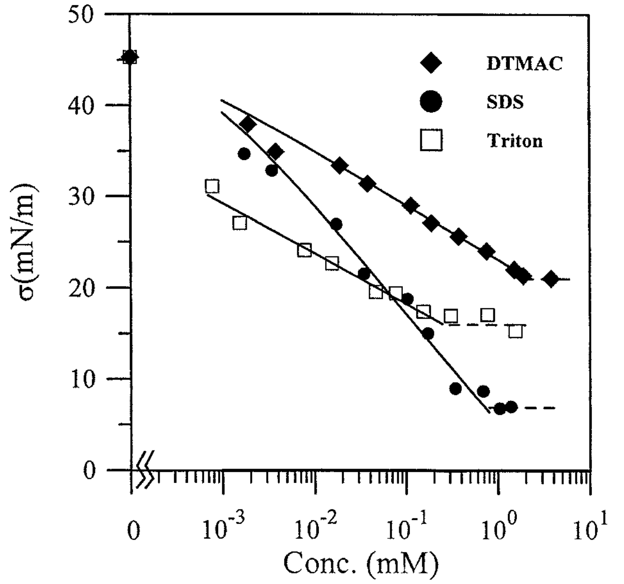

Figure 2. Equilibrium interfacial tensions of aqueous solutions of surfactants against CCl_4 obtained from the drop weight method.

The solid lines are the predicted values using the Langmuir isotherm.

tion is inconsequential to the transport of surfactants in the bulk phase.

For a moving drop in an extraction process, the convection flux at the leading pole is more important than the diffusion flux, and thus the equilibrium interfacial tension should be established more quickly than that measured from a static condition. This problem was solved approximately by considering a diffusion-controlled adsorption with a diffusion layer of thickness l between the bulk solution and the subsurface (Chang et al., 1992). An infinite diffusion length corresponds to a stagnant system when the effect of convection flux is negligible. However, when the convection becomes important, the diffusion length is decreased and a finite value of l should be considered. This problem can only be solved numerically, but two asymptotic cases were derived (Chang et al., 1992): When $l/(\Gamma_m K_L) \ll 1$,

$$t_x = C_x\left[l(\Gamma_m K_L)/D\right]; \tag{6}$$

for $l/(\Gamma_m K_L) \gg 1$

$$t_x = C_x^*\left[(\Gamma_m K_L)^2/D\right], \tag{7}$$

the time t_x is the time required for the surface concentration to reach x% of the equilibrium surface concentration. The parameters C_x and C_x^* are dependent on the dimensionless concentration of a surfactant solution, $K_L C_0$, and were obtained numerically by Chang et al. (1992).

The group $\Gamma_m K_L$, which has a dimension of length, is the characteristic length for adsorption. This value is important in evaluating the equilibrium time needed for adsorption. Equations 6 and 7 show that the higher the value of $\Gamma_m K_L$, the larger the adsorption time scale to reach a given limit of the equilibrium surface concentration.

Results and Discussion

Adsorption properties of surfactants

The equilibrium interfacial tensions of aqueous solutions of Triton X-100, SDS, and DTMAC against CCl_4 are shown in Figure 2. The Langmuir isotherm is used to correlate the dependence of interfacial tension on the bulk surfactant concentration. These results are shown by the solid lines in this figure, and the adsorption parameters are listed in Table 1, as are other equilibrium properties. The CMC occurs at 0.3 mM for Triton X-100, 0.7 mM for SDS, and 1.9 mM for DTMAC. For surfactant concentrations below CMC, the ability of surfactants to reduce the interfacial tension increases in the following order: DTMAC < SDS < Triton X-100. At higher concentrations, however, the ability of SDS to reduce the interfacial tension is more significant than that of Triton X-100, and a smaller interfacial tension is obtained, as shown in Figure 2. The maximum surface concentrations, Γ_m, for the three surfactants have the same order. Similar values of Γ_m were found for Triton X-100 and SDS, but a smaller value was obtained for DTMAC. The K_L value for Triton X-100 was two orders of magnitude larger than those for SDS and DTMAC, which reflects the greater efficiency (surface activity) of Triton X-100, over that of the others.

Figure 3 shows the typical data of dynamic interfacial tensions for the three surfactant solutions. Several hundred to several thousand seconds are needed for a new surface to approach equilibrium in a static measuring condition. But this time is reduced at elevated surfactant concentrations. The level curves for the Triton X-100 indicate that its adsorption rate is more rapid than the others. It is difficult to obtain the kinetic parameters of surfactants without a complicated numerical simulation of the theoretical model. Instead of the complicated calculation, the adsorption kinetics of the three surfactants was compared quantitatively using the decreasing ratio of interfacial tension for 5 s, that is, $(\sigma_o - \sigma_{5s})/(\sigma_o - \sigma_e)$. A higher value of the ratio represents rapid adsorption kinetics. These ratios are shown in Figure 4 for the three surfac-

Table 1. Equilibrium Adsorption Parameters and Properties of Surfactants

Surfactant	Γ_m (mol/m^2)	K_L (m^3/mol)	CMC (mM)	σ_{CMC} (mN/m)	$\Gamma_m K_L$ (m)	Γ_e/C_0^* (m)
Triton X-100	9.6×10^{-7}	8.5×10^{5}	0.3	15.7	8.16×10^{-1}	9.6×10^{-6}
SDS	9.7×10^{-7}	3.6×10^{3}	0.7	6.9	3.49×10^{-3}	9.7×10^{-6}
DTMAC	5.2×10^{-7}	4.7×10^{3}	1.9	21.1	2.44×10^{-3}	5.2×10^{-6}

$^*C_0 = 0.1$ mM.

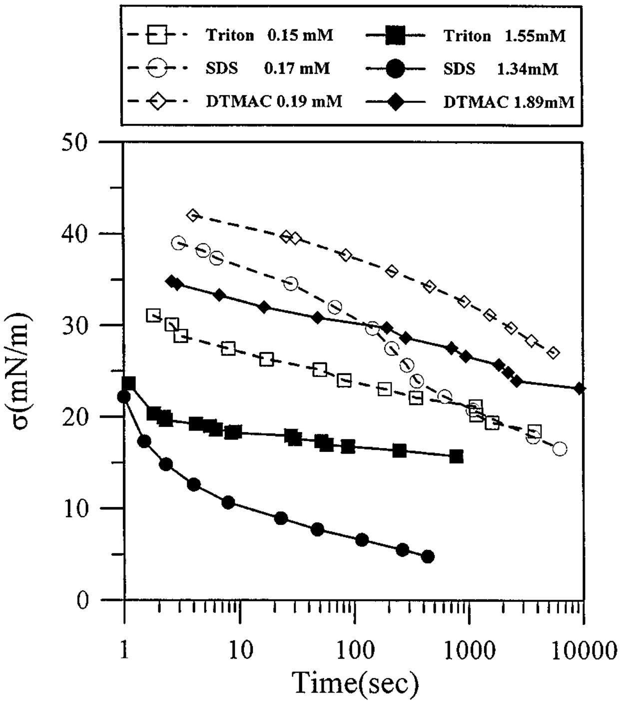

Figure 3. Experimental data of the dynamic interfacial tension of surfactant solutions against CCl_4 as obtained from the drop-weight method.

tants. Triton X-100 was found to have rapid adsorption kinetics, and DTMAC had the slowest one.

The characteristic adsorption length, $\Gamma_m K_L$, for the three surfactants is also shown in Table 1. A highest value of $\Gamma_m K_L$ was obtained for Triton X-100 due to its large K_L value. According to Eqs. 6 and 7, since the diffusion coefficients for the three surfactants are of the same order (approximately 5×10^{-6} cm^2/s), Triton X-100 should have a larger adsorption time scale (slower equilibrium) than the others. This paradox between the theoretical inference and the experimental result is attributed to the use of Eqs. 6 and 7, which were derived for the diffusion-controlled adsorption model. The adsorption of Triton X-100 was found to follow the diffusion-controlled mechanism either at the air/water or the water/oil interface (Lin et al., 1990; Stebe et al., 1991). So, the lower adsorption kinetics of SDS and DTMAC, compared with the theoretically predicted rate, is due to the intrinsic adsorption–desorption mechanism between interface and subsurface.

Another characteristic length for adsorption was defined as Γ_e/C_0, which corresponds to the distance normal to the surface, which contains as many surfactant molecules as those adsorbed onto the surface at equilibrium. At an elevated bulk concentration, C_0, the value of Γ_e/C_0 approaches zero. In this context, the diffusion rate is rapid and the surfactant transport is adsorption–desorption controlled. The Γ_e/C_0 values are shown in Table 1 for a surfactant concentration of 0.1 mM. At this concentration, since Γ_e approaches Γ_m, the Γ_e/C_0 values were close to Γ_m/C_0 and vary little for the three surfactants. Compared with SDS and DTMAC, the rapid adsorption rate of Triton X-100, shown in Figure 4, at this concentration implies its faster adsorption–desorption kinetics.

Surfactants effects on the mass transfer

The effects of surfactant concentration on the overall mass-transfer coefficient, K_R, are shown in Figure 5 for SDS, Triton X-100, and DTMAC. All of these surfactants have significant effects on reducing the mass-transfer rate. The values of K_R decrease rapidly and reach a minimum at concentrations of less than 0.04 mM. For the SDS and DTMAC, a

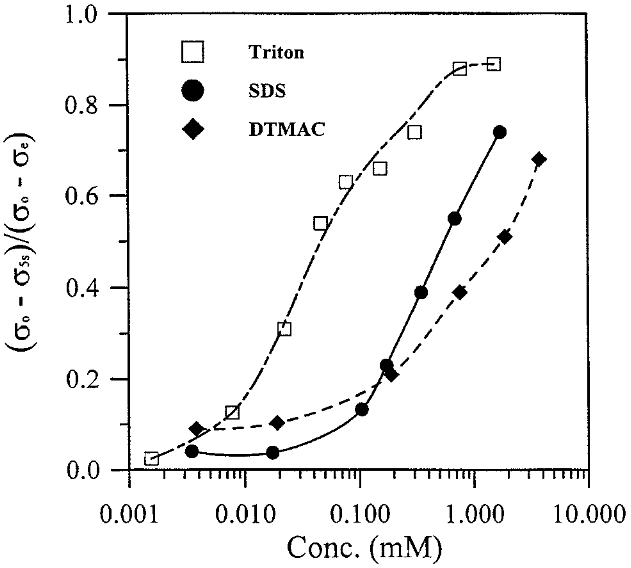

Figure 4. Decreasing ratio of dynamic interfacial tensions within 5 s as a function of surfactant concentrations.

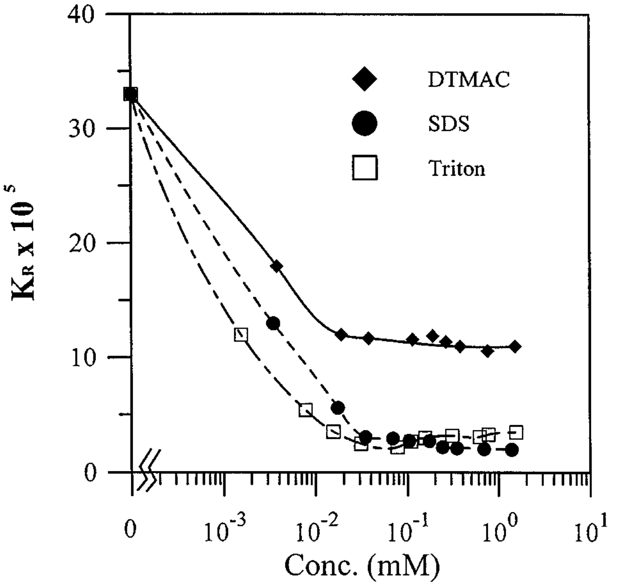

Figure 5. Variations of K_R as functions of surfactants concentration.

further increase in the surfactant concentration gives no appreciable variation to the K_R value. However, for Triton X-100, the value of K_R increases slowly and slightly with the addition of more surfactant. The experimental results also revealed that the effectiveness of the surfactants in decreasing the mass-transfer rate is more significant for Triton X-100 and SDS. The minimum values of K_R for the two surfactants are about 7% of the value when no surfactants are present. Compared with Triton X-100 and SDS, DTMAC is less effective, and the minimum value of K_R is 30% of the value obtained for a surfactant-free system.

The ability of the three surfactants to reduce the mass-transfer coefficient is about the same as their ability to reduce interfacial tension. However, since K_R approaches the minimum value at much smaller concentrations (less than 0.04 mM) than the CMC, the decrease in the mass-transfer coefficient cannot be attributed directly to the lessening of interfacial tension. Besides, the traveling time of a drop through the extraction column was always less than 5 s, which is much less than the time it takes for static measuring equipment to approach equilibrium tension.

During the actual extraction process, due to the transport of surfactants by the forced convection at the leading edge of a falling drop and the sweep by the surface convection along the drop surface, the equilibrium adsorption state should be established much earlier than shown in Figure 3. This is doubtless for two reasons: (1) the magnitude of convective velocity at the leading edge of a falling drop (about order of 10 cm/s) is much higher than the magnitude of diffusion transport (about order of 10^{-4} cm/s), so the transport of surfactants from bulk to the subphase is greatly accelerated and the equilibrium is only controlled by the adsorption–desorption process of molecules between interface and subsurface; and (2) the adsorbed surfactants at the leading pole are rapidly swept to the back of the drop, which enhances the adsorption rate at the leading boundary.

For a droplet falling in a solution of Triton X-100, the dimensionless length $l/(\Gamma_m K_L) \ll 1$, so Eq. 6 can be used to estimate the time it takes for the surfactants to be adsorbed onto the interface. Because of convection, the adsorption depth, Γ_e/C_0, was used as an approximation of the diffusion length, l. When $x = 95\%$, an empirical formula of $C_{0.95}$ is $C_{0.95} = 1/K_L C_0$ for $K_L C_0 > 1$ (Chang and Franses, 1995). The adsorption times required for the surface concentration to reach 95% of the equilibrium surface concentration are listed in Table 2. At bulk concentrations of 0.01 and 0.1 mM, the values of $t_{0.95}$ for Triton X-100 are 18.6 and 0.186 s, respectively. These time scales are much smaller than the experimental values shown in Figure 3, which were obtained when the bulk convection was absent. The estimated results also show that the equilibrium adsorption time is greatly decreased at elevated bulk concentrations. The estimated value of $t_{0.95}$ at $C_0 = 0.01$ mM was slightly higher than the descending time of a droplet in the extraction process. However, since the value of l was always taken to be about 100 μm in a stagnant system, the real value of l should be smaller than that estimated by Γ_e/C_0. That is, adsorption time in the actual case should be smaller than that predicted here, and the assumption that the equilibrium adsorption is established during the drop-falling period should be true. The values of $t_{0.95}$ estimated for SDS and DTMAC are of the same order as that for Triton X-100.

Table 2. Estimated Adsorption Time Required for Surface Concentration to Reach 95% of the Equilibrium Surface Concentration

Surfactant	C_0 (mol/m^3)	$K_L C_0$	$C_{0.95}$*	l** (m)	$t_{0.95}$† (s)
Triton X-100	0.01	8.5×10^3	1.18×10^{-4}	9.6×10^{-5}	18.6
	0.1	8.5×10^4	1.18×10^{-5}	9.6×10^{-6}	0.186
SDS	0.01	3.6×10	2.8×10^{-2}	9.4×10^{-5}	18.4
	0.1	3.6×10^2	2.8×10^{-3}	9.7×10^{-6}	0.189
DTMAC	0.01	4.7×10	2.1×10^{-2}	5.1×10^{-5}	5.2
	0.1	4.7×10^2	2.1×10^{-3}	5.2×10^{-6}	0.053

*$C_{0.95}$ is evaluated by an empirical formula $C_{0.95} = 1/K_L C_0$.

**The value of diffusion length l is approximately estimated by the adsorption depletion length, Γ_e/C_0.

†Calculated by Eq. 6, and a value of 5×10^{-10} m^2/s was taken for the diffusion coefficients of the three surfactants.

Hydrodynamic behavior

From the hydrodynamic point of view, the inhibition of the internal circulation of a moving droplet by the Marangoni stress in a system containing surfactant has been thought to be the main cause of excess mass-transfer resistance. A simultaneous and well-recognized effect resulting from the inhibition of surface mobility is a reduction in the traveling velocity. These data were obtained by measuring the traveling time of droplets along the column. The traveling time was found to have a linear relation to the traveling distance for distances greater than 15 cm. The average velocities were calculated from the linear curves, and are shown in Figure 6. The results showed that Triton X-100 is the most effective in

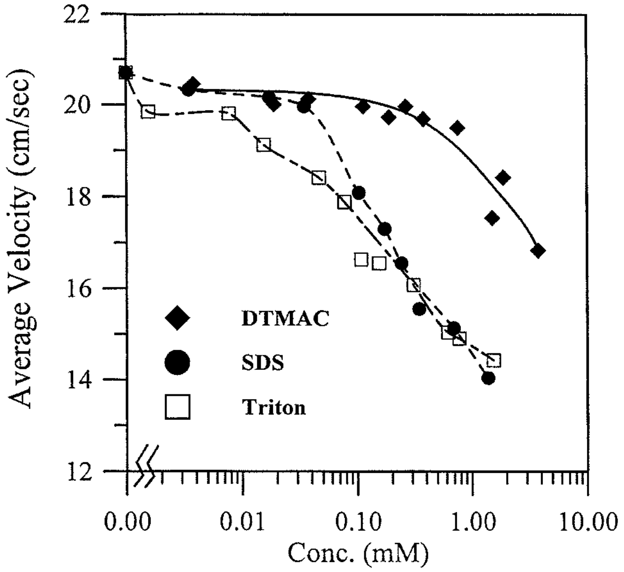

Figure 6. Average falling velocity of CCl_4 drop in aqueous surfactant solutions.

The drop volume of CCl_4 is 0.02 ± 0.001 mL.

reducing the terminal velocity at low concentrations, while DTMAC is the least effective. But at high concentrations, the effectiveness of SDS becomes more significant than that of Triton X-100. The reduction in terminal velocity when surfactants are present has been attributed either to the formation of a spherical cap on the surfactant layer (Huang and Kintner, 1969; Sadhal and Johnson, 1983; He et al., 1991), or to the Marangoni stress resulting from the concentration gradient along the interface (Levich, 1962; Davies and Rideal, 1963; Schechter and Farley, 1963). No matter what is dominant, both models have an intimate relation with the adsorption rate and the amount of surfactant adsorbed onto the interface. The slow adsorption rate and small Γ_m value of DTMAC result in a less effective reduction of terminal velocity, mass-transfer rate, and interfacial tension. On the other hand, the greater effectiveness of Triton X-100 is attributed to its rapid adsorption kinetics.

It has been proposed that the decreases in the mass-transfer rate are associated with the inhibition of surface mobility. When Figure 5 and Figure 6 are compared, at the concentration when the minimum K_R value is approached (about 0.03–0.04 mM), only a slight decrease in the terminal velocity can be found for SDS and DTMAC. Since the terminal velocity indicates the degree of surface mobility, the K_R values approach a minimum value at a state when the surface mobility is not completely inhibited. Besides, when the results of Triton X-100 and SDS at 0.04 mM are compared, the degrees of surface mobility are different, which can be concluded from their distinct terminal velocity values, but their K_R values are similar. Both of these phenomena indicate that the inhibition of surface mobility is not the main cause of the excess mass-transfer resistance by the surfactants.

Recently, the effects of surfactants on the surface mobility with a three-phase periodic fluid particle flow were studied by Stebe et al. (1994). Surface mobility was measured by the pressure drop needed to drive the fluid flow. The pressure drop was found to increase (due to a decrease in surface mobility) with the increase in surfactant concentration of up to CMC. Their results also showed that the surface mobility is not completely stopped at concentrations as low as 0.04 mM.

While the drop falls, drop oscillation and distortion, which depend on the surfactant concentration and falling distance, can be observed. The oscillations were not found at low surfactant concentrations, and occurred near the lower end of extraction column at 0.03 mM (Triton X-100), 0.07 mM (SDS), and 0.11 mM (DTMAC). At a higher surfactant concentration, the oscillation occurs earlier or immediately after the drop leaves the drop former. The criteria for the onset of droplet oscillation were reviewed by Skelland et al. (1987), who concluded that a lower interfacial tension enhances the oscillation. For the surfactant effects on the drop deformation, SDS was found to be the most effective one. The shape of a moving drop is determined by the viscous stresses that deform the drop and the interfacial tension that resists the deformation. Pawar and Stebe (1996) recently studied these phenomena using the capillary number, *Ca*, which is the ratio of viscous stresses to interfacial tension. When the interfacial tension is reduced, the viscous stresses are more effective at distorting the droplet. As a result, the droplet distortion was more significant in an SDS solution, because SDS reduced the interfacial tension more than did the others.

The drop oscillation and distortion are supposed to enhance the mass-transfer rate. Contrary to this assumption, however, the enhancing effect was not found to be associated with the variation in the hydrodynamic state of the droplet. Based on the preceding assumptions, another mass-transfer resistance barrier should exist with the addition of surfactants; this barrier plays a dominant role, compared to the variation in hydrodynamic behavior, in resisting the mass transfer.

Evidence to the barrier-layer resistance

In the barrier-obstruction model, the adsorbed surfactant molecules on the interface accumulate to form a condensed monolayer. The adsorption-free area for the mass transfer is thus decreased. When the solute transports across the adsorbed layer on the interface, the interaction between the solute and surfactant molecules becomes an additional resistance and the mass-transfer rate is reduced. According to this assumption, the mass-transfer resistance will increase with the increase in surface concentration. This inference is first verified by the values of Γ_m shown in Table 1. The small Γ_m value for DTMAC leads to a lower mass-transfer resistance and a higher limiting value of K_R, and similar Γ_m values for Triton X-100 and SDS give similar limiting values of K_R.

Because the K_R values of the three surfactants approach their minimum values at very small concentrations, their maximum surface concentrations, Γ_m, should also be approached at the corresponding concentrations in the model of the barrier layer. The surface concentration can be estimated from the Langmuir isotherm (Eq. 3). This result is represented by the ratio of surface concentration to its maximum value (Γ/Γ_m), and is shown in Figure 7. Due to the high values of

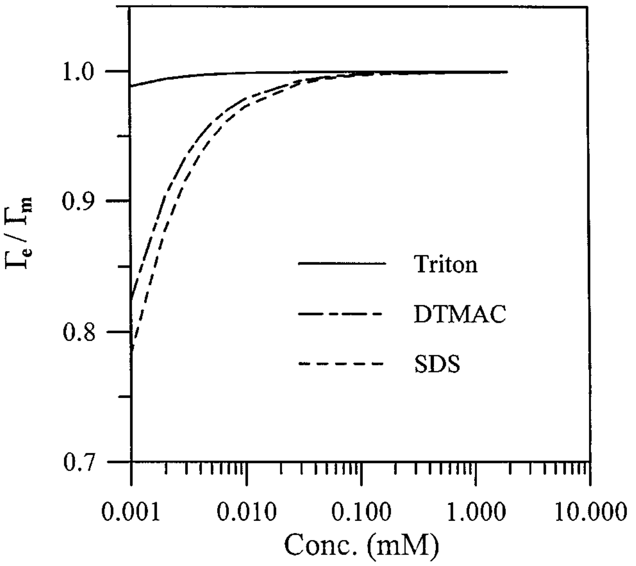

Figure 7. Ratio of equilibrium surface concentration, Γ_e, to the maximum value of corresponded surfactant, Γ_m, as a function of surfactant concentration.

K_L, the maximum surface concentration is approached at very small concentrations. More than 95% of the maximum adsorption amount has been attained at a concentration of 0.01 mM. Thus, the rapid decrease in the K_R value with surfactant concentration can reasonably be explained by the increase in surface concentration.

Variation of K_R at high surfactant concentration

At high surfactant concentrations, when the interfacial tension is greatly reduced, the oscillation and distortion behavior of the droplets becomes more significant. This phenomenon is especially obvious for SDS, which can attain lower interfacial tension. This effect increases the interfacial turbulence, which means that a higher mass-transfer rate can be expected. However, an increase in K_R is not found for SDS and DTMAC, and only a slight elevation is observed for Triton X-100. This result shows that the obstruction of the barrier layer in mass transfer is more than can be enhanced by interfacial turbulence. The slight increase in K_R at high concentrations of Triton X-100 can be attributed to the partial remobility of the surface, as found by Stebe et al. (1991, 1994). In their studies, the criteria for a surfactant to remobilize the interface were studied, and Triton X-100 was found to be a good one due to its fast adsorption−desorption kinetics. When the drop interface is remobilized, the terminal velocity is supposed to increase. This phenomenon was not found in Figure 6, because the simultaneous effects of drop oscillation and distortion at elevated concentration will cause a decrease in terminal velocity.

Conclusions

The adsorption behavior of three surfactants was studied, as were their effects on the mass-transfer rate in a single-drop extraction column. The mass-transfer coefficient, K_R, is found to decrease markedly when only a tiny amount of these surfactants is added, and approaches a minimum value at concentrations of less than 0.04 mM. When more surfactants are added, the K_R values almost remain constant for SDS and DTMAC, but increase slightly for Triton X-100. At low surfactant concentrations, the effectiveness of the three surfactants in reducing K_R, interfacial tension, and terminal velocity is similar and increases in the order: DTMAC $<$ SDS $<$ Triton X-100. But at high concentrations, the effectiveness of SDS is more significant than that of Triton X-100. The additional mass-transfer resistance in the presence of surfactants is found to result mainly from the obstruction of the adsorbed surfactant layer and is related to the value of surface concentration. Triton X-100 has a faster adsorption kinetics than the others, which is responsible for its higher effectiveness at low concentrations and for the slight increase of K_R at elevated concentrations. The contribution of the hydrodynamic behavior of a drop in the mass-transfer rate is thought to be small when surfactants are present.

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