Surfactants Effects on Mass Transfer During Drop-Formation and Drop Falling Stages

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Three types of surfactants were used to study their effects on the inhibition of mass transfer in liquid–liquid extraction. A single-drop extraction apparatus was used to obtain the extraction percentage of acetic acid from dispersed CCl_4 droplets to the aqueous phase. By using various lengths of extraction column, the extraction amounts were estimated during the drop-formation and drop-falling stages. Effects of these surfactants on the mass transfer during various stages were related to the adsorption behavior of these surfactants. The results of dynamic and equilibrium tensions show that the transport of Triton X-100 is a diffusion-controlled mechanism, which shows a fast adsorption kinetic at elevated concentrations. By comparing the effectiveness of the three surfactants in decreasing interfacial tension and in mass-transfer inhibition, the mass-transfer inhibition during the drop-formation and drop-falling stages can be related, respectively, to the properties of dynamic and equilibrium interfacial tensions. For surfactant concentrations below CMC, a surfactant that is most effective in decreasing the interfacial tension always exhibits the highest effectiveness in mass-transfer inhibition. When the surfactant concentration is small (about 10^{-3} mM), the mass-transfer inhibition of SDS and DTMAC is significant in the drop-formation stage, but not in the drop-falling stage. As the concentration is increased, the effectiveness of Triton X-100 increases more quickly than the others in both the formation and falling stages. The mass-transfer rate increased slightly when the Triton X-100 concentration is elevated near CMC, due to the surface remobilization caused by the fast adsorption–desorption rate of Triton X-100 at elevated concentrations. The mass-transfer inhibition of surfactant also was caused mainly by the hydrodynamic effect in the drop-formation stage, but from the obstruction of the barrier layer in the drop-falling stage.

Introduction

The presence of trace amounts of surface-active contaminants is always unavoidable in commercial extraction equipment. These materials will affect the extraction efficiency both by increasing the mass-transfer area and by reducing the mass-transfer coefficient across the interface. It was reported that the reduction of the mass-transfer coefficient is the predominant effect in determining the overall extraction efficiency, especially when the surfactant concentration is as small as several to several tens ppm (Chu et al., 1950; Ruskan, 1974; Chen and Lee, 1999).

Many researchers have studied the effects of surfactants on the reduction of the mass-transfer rate. All of these results show that the mass-transfer coefficient K will decrease rapidly as the surfactant concentration increases. The K value either approaches a constant value at specific concentrations (Lindland and Terjesen, 1956; Boye-Christensen and Terjesen, 1958, 1959; Lee at al., 1998), or decreases to a minimum value first and then increases slightly and slowly with the further addition of surfactants (Garner and Hale, 1953; Garner and Skelland, 1956; Chen and Lee, 2000).

Two models are widely accepted to explain the excess mass-transfer resistance exerted by the surfactants. The first is that the surfactant adsorbed on the interface may form an interfacial barrier layer due to the interaction between the solute and the adsorbed surfactant, which is also called as the physicochemical effect (West et al., 1952; Lindland and Terjesen, 1956; Boye-Christensen and Terjesen, 1958; Huang and Kintner, 1969; Mudge and Heideger, 1970; Chen and Lee, 2000). The second is based on the hydrodynamic point of view (Garner and Skelland, 1956; Bakker et al., 1967; Beitel and Heideger, 1971; Jeng et al., 1986; Lee et al., 1998). That is, the adsorbed surfactants may modify the hydrodynamic behavior of a moving droplet, including: reducing the internal circulation velocity in a droplet, decreasing the terminal velocity, damping the interfacial waves or oscillations, and inhibiting the interfacial turbulence (Levan and Newman, 1976; Sadhal and Johnson, 1983; Oguz and Sadhal, 1988; Chen and Stebe, 1996). These effects are caused by the exertion of the Marangoni stress (Scriven and Sternling, 1960; Gibbs, 1961; Levich, 1962), that is, the interfacial tension gradient along the drop surface, taken as being responsible for the mass-transfer resistance across the interface of a droplet. Although a great deal of work has been done to identify the roles of surfactants in the mass-transfer process, the mass-transfer mechanism in the presence of surface active materials is not completely clear.

In the literature, the effects of surfactants on mass-transfer resistance are always studied in terms of the equilibrium interfacial tension of the surfactant solution, or the tension-related parameters. However, the time required to approach an equilibrium interfacial tension by a commercial tensiometer, such as the drop-volume method or the pendent-drop method, is much longer than the time the droplets are present in the extraction column. So, in addition to the equilibrium interfacial tension, the dynamic interfacial tension, which shows the variation of nonequilibrium interfacial tension with time, should be considered to take care of the effects of surfactants. Although the adsorption kinetic of the surfactants has been studied by many authors (Chang and Franses, 1995; Lin et al., 1990; Hunsel et al., 1986), few studies related this property to the practical process. In recent years, Stebe and her coworkers have studied the surfactant effects on the surface mobility through a three-phase flow system and related their results to the adsorption kinetic of surfactants (Stebe et al., 1991; Stebe and Maldarelli, 1994). In our previous work, three types of surfactants were used to study their effects on mass-transfer resistance (Chen and Lee, 2000), which may be the first article to discuss these effects in terms of the adsorption kinetic of surfactants.

It was known that the mass transfer during the drop-formation stage is very important in the extraction process. As reported in the literature, over 40% of the total extraction amount can occur in the drop-formation stage (West et al., 1951; Skelland and Caenepeel, 1972; Lee et al., 1998). So, it is indispensable to look into the drop-formation stage when one tries to identify the surfactant effects on the mass-transfer rate. The mass-transfer mechanisms involved in the drop-formation stage are very complicated, as it combines simultaneous effects of area creation, interface renewing, shape variation, and the interfacial turbulence associated with the growing and detachment of droplets. Although the droplet behavior and mass transfer during the formation stage have been studied by a few authors (Skelland and Huang, 1979; Skelland and Vasti, 1985), studies concerning the surfactant effect on the drop-formation stage are still few (Skelland and Caenepeel, 1972; Skelland et al., 1987; Lee et al., 1998). Because the drop-formation time is always shorter than 1–2 s, it is more reasonable to study the surfactant effects by the property of dynamic interfacial tension, rather than by the equilibrium data.

In our previous work (Chen and Lee, 2000), three types of surfactants were used to study the relationship between their adsorption behavior and the mass-transfer inhibition in a single-drop extraction process. In the present study, the mass transfer during the drop-formation and drop-falling stages are estimated by using extraction columns of various lengths. The effects of the three surfactants on the mass transfer during the two stages are studied separately and related to the adsorption behavior of these surfactants.

Experimental Studies

Materials

The extraction system consists of the solute, acetic acid ($>99\%$, Osaca Chemical Co., Japan), diffusing from drops of carbon tetrachloride (99%, Acros Organics, USA) into the continuous phase (water). The initial concentration of acetic acid in the carbon tetrachloride was controlled at 0.2 M for all of the experiments. The three types of surfactants used in this study are sodium dodecyl sulfate (SDS, 95%, anionic) supplied by Sigma Chemical Company, dodecyl trimethyl ammonium chloride (DTMAC, cationic), supplied by TCI Co. Ltd., and polyoxyethylated *t*-octylphenol (Triton X-100, nonionic), supplied by Aldrich Chemical Company. All of these surfactants are water soluble and used without further purification. The water used in all the experiments was purified by a Milli-Q plus purification system with a resistivity of 18.2 $\text{M}\Omega\cdot\text{cm}$.

Method

The extraction apparatus and experimental methods were similar to those used in the previous work (Lee et al., 1998; Chen and Lee, 2000). The single-drop extraction apparatus, shown in Figure 1, is used to estimate the extraction percentage and related mass-transfer coefficient in the main extraction column (A). The CCl_4 drops fell down after leaving the drop former, passed through the stagnant continuous phase (water), and were collected at the bottom of the column (B). By analyzing the amount of acetic acid in the column (B), including the water and carbon tetrachloride, the extraction percentage and the overall mass-transfer coefficient in column A can be evaluated. The drop volume is controlled at 0.02 ± 0.001 mL/drop by changing the inside diameter of the drop former for various concentrations of surfactant solutions. The dispersed drops were formed within the water and the formation times were controlled between 0.8 and 1.2 s per drop. The extraction column has an inside diameter of 3 cm. Five different lengths (10, 20, 30, 45, and 70 cm) of the main extraction column (A) were used to study the mass transfer during drop falling and drop formation. The time of extraction t_f was estimated by measuring the average traveling time of drops through column (A) with a stopwatch. A drop number of 100 was used for all the extraction experiments, and an average value was obtained from four different runs for every experimental condition. All experiments were carried out at 25°C.

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

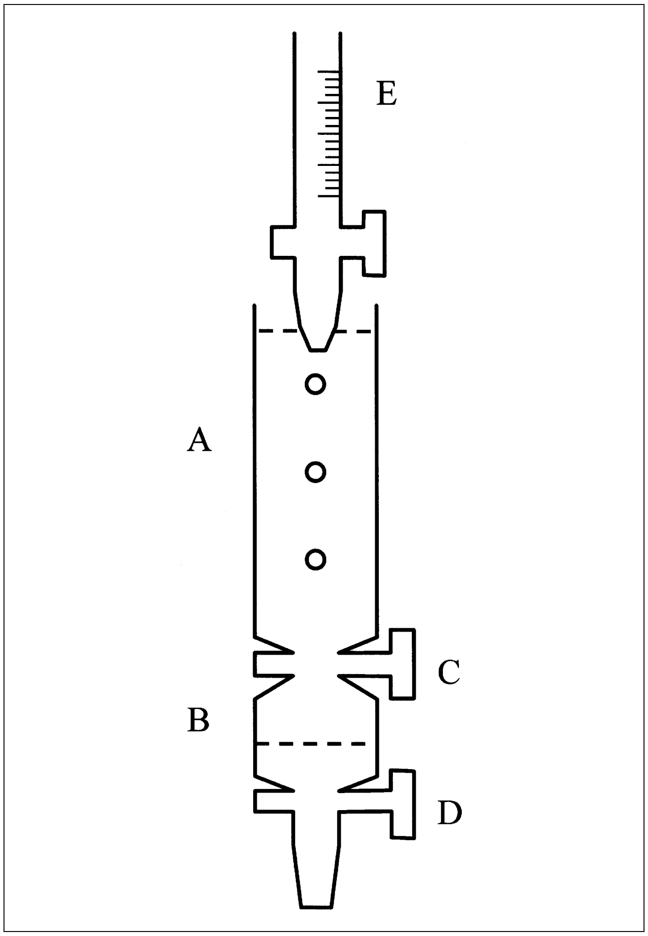


Figure 1. Experimental apparatus for single-drop extraction process.

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

with X_E ($m = 2.9\ X_E + 0.026$) 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. Thus, in estimating the mass-transfer coefficient, the equilibrium concentration of the raffinate phase corresponding to the concentration of the extraction phase X_R^* ($X_R^* = m\ X_E$) is negligibly small. Since X_E is very closed to zero, the effects of the ionization of acetic acid on the mass-transfer rate can also be neglected.

Because the solubility of acetic acid in CCl_4 is much smaller than in water, the concentration of acetic acid in the CCl_4 phase was analyzed by mixing the sample with the excess amount of water and then determined by titration with an NaOH solution. 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; X_{R1} and X_{R2} are the measured mole fractions of the solute in feed and raffinate solutions, respectively. All drops were considered to be spherical in shape for calculating the surface area a_d.

Estimation of extraction percentage during drop-formation stage

To obtain the extraction percentage during the drop-formation stage, a plot of the extraction percentage to the column height (or extraction time) was always constructed first and then extrapolated to zero column length (West et al., 1951; Lee et al., 1998). However, some authors have reported that this method is invalid due to the nonlinear relationship or to the presence of a moving wake in a fluid field behind a liquid drop (Skelland and Minhas, 1971; Magarvey and Maclatchy, 1968). In this article, the extrapolation was carried out by using the nearest 2–3 points of data close to the zero length. For these data, the falling time is very short and the fluid field is not completely developed. Thus, the effect of the moving wake, if any, should be small, especially when surfactant is present. The variation of the hydrodynamic state of a drop along the column, as well as the decrease in the concentration driving force, are the main effects caused to the nonlinear relationship between the extraction amount and the column length. For the data of short columns, both effects of the two factors just mentioned should be decreased greatly. Thus, they are more corrected and it is more reasonable to use them to obtain the extraction percentage of the drop-formation stage than to use all the data.

Measurement of interfacial tension

A drop volume tensiometer (TVT1, Lauda Co.) was used to measure the dynamic interfacial tensions between the aqueous solution of surfactant and carbon tetrachloride. A quasi-static mode is used in this measurement. An equilibrium interfacial tension corresponding to the equilibrium state of adsorption is estimated from the dynamic data, like the method described in the previous article (Chen and Lee, 2000; Fang and Joos, 1992).

Results and Discussion

Adsorption properties of surfactants

The equilibrium interfacial tension between the aqueous solution of surfactants and CCl_4, as well as part of the data of dynamic interfacial tension, have been shown in our previous article (Chen and Lee, 2000). For a discussion of the relationship between the adsorption properties and the mass-transfer effects, some of the adsorption properties are reviewed briefly at this section. The equilibrium adsorption parameters of the three surfactants on the water/CCl_4 interface are listed in Table 1. The critical micelle concentration (CMC) occurs at 0.3 mM for Triton X-100, 0.7 mM for SDS, and 1.9

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)
Triton X-100	9.6×10^{-7}	8.5×10^{5}	0.3	15.7
SDS	9.7×10^{-7}	3.6×10^{3}	0.7	6.9
DTMAC	5.2×10^{-7}	4.7×10^{3}	1.9	21.1

mM for DTMAC. The ability of the three surfactants to reduce the interfacial tension increases in the following order: DTMAC < Triton X-100 < SDS. However, at small concentrations (smaller than 0.1 mM), the ability of Triton X-100 is higher than SDS. The Szyszkowski equation (Eq. 2) of the Langmuir isotherm is used to correlate the dependence of interfacial tension on the bulk concentration

$$\sigma = \sigma_o - nRT\,\Gamma_m \ln(1 + K_L C) \tag{2}$$

where Γ_m is the maximum surface concentration and K_L is the Langmuir equilibrium adsorption constant. The two parameters are also listed in Table 1. The values of Γ_m for the three surfactants are of the same order. However, the K_L value for Triton X-100 was two order larger than those for SDS and DTMAC, which reflects the greater efficiency (surface activity) of Triton X-100 than the others.

Figure 2 shows the typical data of dynamic interfacial tensions for the three surfactant solutions. When the surfactant concentrations are small (1.5×10^{-3}–3.8×10^{-3} mM), the interfacial tension for Triton X-100 is higher than that for SDS at short adsorption time (< ca. 50 s). That is, the adsorption kinetic of Triton X-100 is slower than SDS at the initial stage. However, the situation is different when the concentrations were elevated to 0.15–0.19 mM. The lower curve for Triton X-100 indicates that Triton X-100 can decrease the interfacial tension more rapidly than the others, although its equilibrium tension is higher than SDS, which can also be seen in this figure. The two results indicate that when the bulk concentration is increased, the transportation rate of Triton X-100 can be more greatly enhanced than that of SDS, which shows the characteristic of diffusion-controlled mechanism for Triton X-100. Because the molecular weight of Triton X-100 (646.9) is higher than the other two, its diffusion coefficient should be smaller than SDS and DTMAC. As a consequence, the initial transport rate of Triton X-100 is slower and the interfacial tension is higher when the bulk concentration is small. As the concentration is increased, the diffusion rate will be enhanced for all surfactants and the dynamic interfacial tension of Triton X-100 will be quickly decreased due to its diffusion-controlled mechanism. However, for SDS, because of the limitation of the later adsorption–desorption step, its transport rate cannot be accelerated as quickly as for Triton X-100 by increasing the bulk concentration.

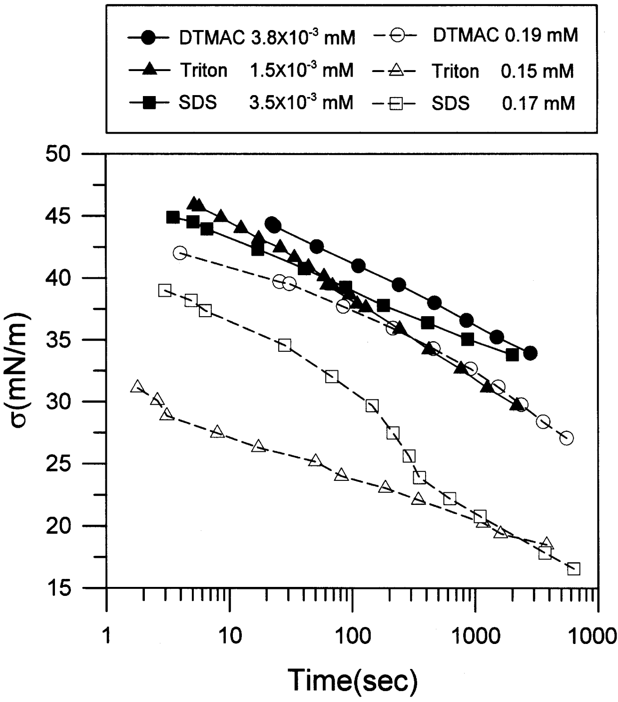


Figure 2. Dynamic interfacial tension data of the surfactant solutions against CCl_4 as obtained from the drop-weight method.

The diffusion-controlled mechanism of Triton X-100, either at the air/water or the oil/water interface, has also been found in the literature (Lin et al., 1990; Stebe et al. 1991). Besides, SDS was reported to follow the adsorption-rate-limited mechanism at the air/water interface (Chang and Franses, 1995). Based on the present result, this mechanism can also be applied at the CCl_4/water interface. As for the DTMAC, the dynamic interfacial tension shows that the adsorption kinetic of DTMAC is similar to that of SDS, that is, the adsorption-rate-limited mechanism.

Surfactant effects on overall extraction percentage

The variations in the extraction percentages of acetic acid with the column length are shown in Figure 3 for various surfactant concentrations. It is found that the extraction percentage will increase as the column length increases due to a longer extraction time. As for the effects of surfactants, the extraction percentage decreases notably when only a tiny amount of surfactant is present. When the surfactant concentration is increased, the extraction percentage decreases steadily and then levels off for SDS and DTMAC; however, for Triton X-100, it decreases to a minimum value first, and then increases when the concentration is further increased. For small concentrations, Triton X-100 is the most effective in inhibiting the mass transfer, and DTMAC is the least effective. However, at high concentrations, the effectiveness of SDS will surpass that of Triton X-100. The effectiveness of these surfactants in decreasing the overall extraction percentage is found to have a similar tendency as their effects in decreasing the interfacial tension, as shown in Table 1.

Mass transfer during drop formation

To study the effects of the surfactants on the mass transfer during the drop-formation stage, the curves in Figure 3 were extrapolated to the zero position of the column length to estimate the extraction percentage during drop formation. These results are shown in Table 2, along with other related parameters. For the surfactant-free system, the extraction percentage during drop formation is estimated to be 39.0%, which is 41% of the total extraction amount for a column length of 70 cm. So, the drop-formation stage plays an important part in the extraction process.

At a surfactant concentration of 3.79×10^{-3} mM (about 1 ppm for DTMAC and SDS), the extraction percentage at the drop-formation stage decreases to 11.1%, 17.3%, and 21.5%, respectively, for SDS, DTMAC, and Triton X-100. That is, at

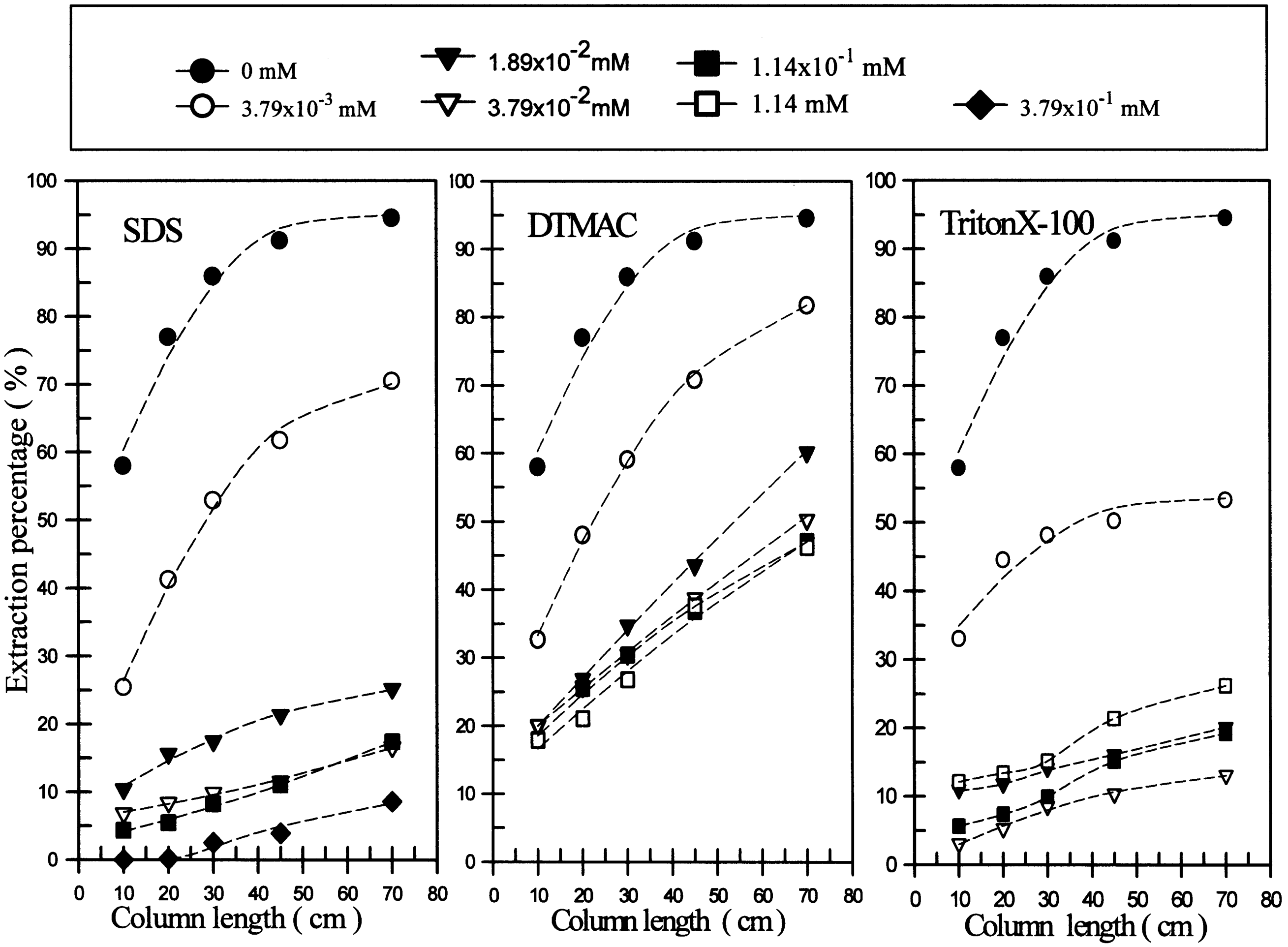
Table 2. Extraction Percentage During Periods of Drop Formation and Drop Falling for a Column of 70-c$_{\min}$ Length

Surfactant	Conc. (mM)	P_{70}* (%)	P_0** (%)	P_f† (%)
Water	0	94.5	39.0	55.5
SDS (95%)	3.79×10^{-3}	70.5	11.1	59.4
	1.89×10^{-2}	25.2	6.5	18.7
	3.79×10^{-2}	16.6	5.9	10.7
	1.14×10^{-1}	19.4	2.6	16.8
	0.379	8.6	0.0	8.6
DTMAC	3.79×10^{-3}	81.8	17.3	64.5
	1.89×10^{-2}	60.1	12.9	47.2
	3.79×10^{-2}	50.2	14.5	35.7
	1.14×10^{-1}	47.1	11.9	35.2
	1.14	46.2	10.4	35.8
Triton X-100	3.79×10^{-3}	53.3	21.5	31.8
	1.89×10^{-2}	20.1	10.2	9.9
	3.79×10^{-2}	13.1	0.8	12.3
	1.14×10^{-1}	19.2	3.9	15.3
	1.14	26.1	10.8	15.3

*P_{70}:extraction percentage in a column of 70 cm in length.
**P_0:extraction percentage in the drop-formation stage.
†P_f:extraction percentage in the drop-falling stage of the 70-cm column.

this concentration, SDS is the most effective one in inhibiting the mass transfer at the drop-forming stage, and Triton X-100 is the least effective. However, during the falling stage, the extraction percentage for a column of 70 cm in length, P_f, increases in the presence of SDS and DTMAC, but decreases to 31.8% with Triton X-100. That is, at such concentration, SDS and DTMAC have no effect in inhibiting the mass transfer of the drop-falling period, but Triton X-100 has a significant effect. These results indicate that SDS and Triton X-100 have the opposite effect on mass transfer during the drop-formation and drop-falling stages.

The contribution of the two stages in the mass transfer may change with the variation in the surfactant concentration. For the system containing SDS, the value of P_0 decreases as the SDS concentration increases and approaches zero at 0.379 mM. That is, at elevated SDS concentrations, the mass transfer during drop formation is completely inhibited, and the mass transfer is mainly carried out in the drop traveling period. For the DTMAC system, the value of P_0 also decreases with increasing DTMAC concentration, but the mass transfer cannot be inhibited completely, so a minimum value of about 10% will be approached. For the Triton X-100 system, a min-



(a) (b) (c)

Figure 3. Variation of extraction percentage with the column length for surfactants of (a) SDS, (b) DTMAC, and (c) Triton X-100.

imum value of P_0 (about 1%), as well as the overall extraction percentage (P_{70}), is approached at about 3.79×10^{-2} mM. When the concentration of Triton X-100 is increased further, both P_0 and P_{70} increase instead, although only to a certain extent. This result is consistent with that of a previous study, which found a minimum value of the overall mass-transfer K_R) at a Triton X-100 concentration of about 0.03–0.08 mM (Chen and Lee, 2000). When the concentration increases from 3.79×10^{-2} mM to 1.14 mM, the value of P_0 increases over 10 times. On the other hand, the P_f value increases only slightly. The increase in the mass-transfer rate at a high concentration of Triton X-100 has been attributed to the interfacial remobilization caused by the fast adsorption kinetic of Triton X-100 (Chen and Lee, 2000). The present result demonstrates that this increase in the mass-transfer rate is mainly due to the enhanced effect in the drop-formation stage. Because the drop-formation time was controlled at about 1 s/drop, this result also implies that the surfactant effect would occur in a very short time which is far from the equilibrium state corresponding to the equilibrium interfacial tension.

Effects of adsorption kinetic of surfactants on the mass transfer

For comparing the effects of surfactants on decreasing interfacial tension and on inhibition of the mass-transfer rate, the related results are summarized in Table 3. It is found that the mass transfer during the drop-formation stage can be related to the property of dynamic interfacial tension, while the drop-falling stage is related to the equilibrium tension. A regular rule found in the table is that the surfactant with the most effectiveness in decreasing the interfacial tension always exhibits the highest effectiveness in the mass-transfer inhibition.

The different effectiveness of the three surfactants on various concentration ranges can be related to their distinct adsorption kinetic. For a surfactant concentration as small as $(1.5-3.8) \times 10^{-3}$ mM, the initial adsorption rate of Triton X-100 is smaller than the other, due to its slower diffusion rate (as verified from the dynamic interfacial tension of Figure 2 and Table 3). As a consequence, Triton X-100 is the least effective one in the drop-formation stage. However, at the drop-falling stage, the transport rate of Triton X-100 can be accelerated by forced convection at the leading edge of a falling drop. That is, the diffusion-rate limitation can be eliminated and the equilibrium surface concentration can be obtained quickly. Although the same accelerating mechanism can also occur in SDS solution, the overall transport rate is limited by the later adsorption–desorption mechanism. As shown in Figure 2, for a long adsorption time, the interfacial tension can be decreased to a smaller value by Triton X-100 at such a concentration range. As a consequence, in the drop-falling stage, Triton X-100 is the most effective one in the inhibition of mass transfer, which is attributed to its higher surface activity and fast transport rate. It is interesting to see that the P_f values for SDS and DTMAC at this concentration range ($(1.5-3.8) \times 10^{-3}$ mM) are higher than in the surfactant-free system. This result demonstrates that, at such a concentration, the two surfactants have no effect on the inhibition of mass transfer during the drop-falling period, which confirms the previous inference.

When the surfactant concentration is increased, the initial diffusion rate of the three surfactants will be enhanced, but this effect is especially prominent for Triton X-100 due to its diffusion-controlled mechanism. This phenomenon can be observed from Figure 2, which shows that the dynamic interfacial tension of Triton X-100 solution (0.15–0.19 mM) has the smallest value at short adsorption time. At the concentration range of $(1.9-3.8) \times 10^{-2}$ mM, shown in Table 3, the solution of Triton X-100 also has the lowest values of dynamic and equilibrium tensions. The fast initial transport rate of Triton X-100 enhances its effect on both the drop-formation and drop-falling stages. A minimum P_0 value of about 0.8% was obtained at 3.8×10^{-2} mM, which is higher than the effect of SDS and DTMAC at the same concentration. For the Triton X-100 system, the minimum value of P_f approaches at a smaller concentration (1.9×10^{-2} mM) than the P_0 does. This is also a consequence of the acceleration effect by force convection of a moving drop.

For high surfactant concentration (0.1–0.2 mM), although Triton X-100 has the lowest dynamic interfacial tension, its effect on the mass-transfer inhibition is less than SDS due to the surface remobilization.

Table 3. Effectiveness of Surfactants in Interfacial Tension and Mass-Transfer Inhibition

Surfactant Conc. Range	Surfactant	Interface Tension		Mass-Transfer Inhibition Effect	
		Dynamic ($t < 5$ s)	Equilib.	Drop-Formation Stage	Drop-Falling Stage
Small: $(1.5 \sim 3.8) \times 10^{-3}$ mM	SDS	Lowest		Most Effective	No Effect
	DTMAC		Highest		No Effect
	Triton	Highest	Lowest	Least Effective	Most Effective
Middle: $(1.9 \sim 3.8) \times 10^{-2}$ mM	SDS				
	DTMAC				
	Triton	Lowest*	Lowest*	Most Effective	Most Effective
High: $(1 \sim 2) \times 10^{-1}$ mM	SDS		Lowest	Most Effective	Most Effective
	DTMAC	Highest	Highest	Least Effective	Least Effective
	Triton	Lowest		**	**

*Data shown in Chen and Lee (2000).
**Mass-transfer resistance decrease due to interface remobilization.

Proposed mechanism of mass-transfer inhibition

Because the drop-formation process in the drop-volume tensiometer is similar to that of the mass-transfer experiments, the dynamic interfacial tension obtained by the drop-volume method can be used to evaluate the adsorption condition of the surfactant during the drop-formation stage of the extraction process. From the dynamic interfacial tension data shown in Figure 2, at small surfactant concentrations, the initial interfacial tension ($t < 5$ s) is close to that of a surfactant-free system. That is, few surfactant molecules are adsorbed on the interface and the surface concentration of surfactant Γ is very small at short adsorption time. Thus, the barrier–obstruction model cannot be used to explain the excess mass-transfer resistance exerted by the surfactants during the drop-formation stage. And, thus, the significant decrease of P_0 can only be attributed to the hydrodynamic effect, because this effect is dominated by the concentration gradient of the surfactant on the interface, but not by the magnitude of concentration.

For the surfactant-free system, the high mass-transfer rate during drop formation had been related to the internal circulation of drop, and the interfacial turbulence accompanied by the mass transfer across an interface. At the presence of surfactant, the interfacial mobility will be inhibited by the Marangoni stress (Scriven and Sternling, 1960; Gibbs, 1961; Levich, 1962). Although the surface concentration of the surfactant is small for an adsorption time as short as the drop-formation interval, the surfactant molecules on the drop surface can be compressed (or expanded) locally by the movement of the interface. Thus, a meaningful concentration gradient is supposed to be constructed, which is responsible for the inhibition of the interfacial mobility during the drop-formation stage.

For surfactants with an adsorption–desorption controlled mechanism, such as SDS and DTMAC, the adsorption becomes the rate-determining step at higher concentrations, and, thus, the transport rate of surfactant molecules from the subsurface cannot be increased fast enough to replenish those that are swept away by the surface convection. A concentration gradient is built as a consequence. However, for Triton X-100, which has a diffusion-controlled mechanism, the surfactant transport rate can be increased steadily by increasing the bulk concentration, and, thus, it is possible to replenish the molecules swept by the surface convection of the drop-formation stage. That is, the Marangoni stress can be decreased or eliminated. This model can be used to explain the slight increase in the P_0 value at elevated concentrations of Triton X-100.

According to the model proposed by Stebe and Maldarelli (1994) for a drop moving in a surfactant solution, a cap region with uniform surface concentration will form at the trailing end of this drop. In this cap region, no Marangoni stress is exerted, and, thus, the surface becomes remobilized. It was suggested that this remobilized cap region forms at the surfactant concentration slightly below the CMC, and develops its size as the surfactant concentration is increased. That is, the mobility of the drop interface can be enhanced from a state of stagnation to partial or complete mobility by increasing the surfactant concentration. The CMC of Triton X-100 in the H_2O/CCl_4 system was reported to be about 0.3 mM (Chen and Lee, 2000), and the concentration of Triton X-100 at which the P_0 starts to increase is 0.114 mM, as shown in Table 1. Both results agree with Stebe's model that the surface remobilization will occur below CMC, and sustain the contribution of the hydrodynamic effect on the mass-transfer inhibition during drop formation. However, when the concentration of Triton X-100 is increased above CMC, which in an interfacial state is said to be completely remobilized, the P_0 cannot retain a value as high as that of a surfactant-free system. This is due to the increase in the barrier resistance of the adsorbed monolayer to the mass transfer since the surface concentration becomes higher at high bulk concentration.

The increase in the P_f value (drop-falling period) at elevated concentrations is also found for Triton X-100, which is also a consequence of surface remobilization, as mentioned earlier. However, the mass transfer enhanced by the surface remobilization during the drop-falling stage is not as significant as for the drop-formation stage. This is because the mass-transfer inhibition of surfactant in the drop-falling stage is mainly caused by the resistance of the barrier layer for the reasons discussed in the previous article (Chen and Lee, 2000).

Development of a drop-flowing state along the column

To trace the development of the drop-flowing state, the instantaneous velocity of a drop along the traveling path should be recorded. Due to the lack of equipment to measure the instantaneous velocity of drops, the mean velocity of a drop traveling for a short distance (ca. 10 cm) was measured instead to evaluate the variation in flowing condition. The mean velocities for five regions of a drop-traveling path —0–10, 10–20, 20–30, 30–45, and 45–70 cm—were measured; they are given in Figure 4. These data show that the drop velocity is relatively smaller at the first 10 cm of traveling path, which implies the undeveloped flowing state of the

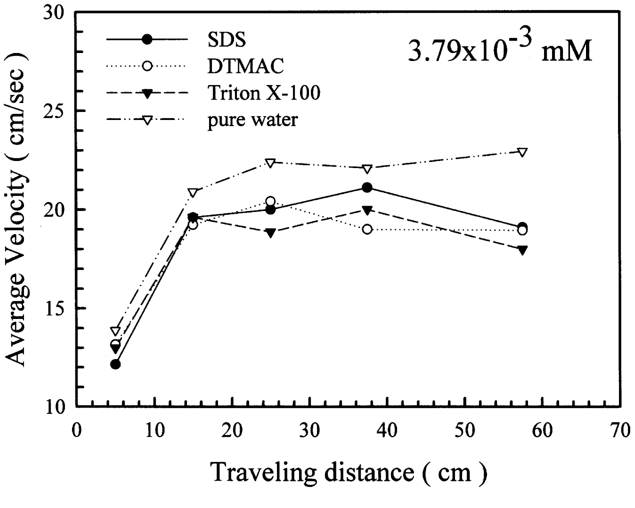


Figure 4. Variation of mean velocities of a drop in various regions of the drop-falling path.

The points for each curve represent successively the mean velocities between traveling distance of 0–10, 10–20, 20–30, 30–45, and 45–70 cm.

Table 4. Physical Properties of Water and CCl_4 Used to Estimate the Reynolds Number and Terminal Velocity of Drop

Liquid	Density (g/cm^3), 25°C	Viscosity (cp), 25°C	Interfacial Tension against CCl_4 (dyne/cm), 25°C
Water	0.9969	0.8937	45.0
CCl_4	1.59	—	—

drop. The velocity increases gradually as the traveling distance increases, and approaches the terminal velocity at a distance between 20 and 45 cm. For the surfactant-free system, the terminal velocity is about 23.0 cm/s, which has an equivalent Reynolds number of 864.7. To estimate the theoretical terminal velocity, the related physical properties of liquids were listed in Table 4. For the flowing condition with the Reynolds number just shown, the Stokes' law cannot be used and a traditional method described in McCabe et al. (2001) was applied. If the drop is taken to be a sphere of 0.336 cm diameter (corresponding to a drop volume of 0.02 mL used in this work), the theoretical value predicted is 23.2 cm/s. Although good agreement is found between the experimental and theoretical values, it may have occurred by chance. As an alternate method, an empirical correlation proposed by Hu and Kintner (1955) was also used and a smaller value, 20.7 cm/s, is predicted.

When a tiny amount of surfactant is present, the velocity decreases significantly as a result of the decreasing interfacial tension and the Marangoni effect. In the surfactant-containing system, the variation of drop velocity with the traveling path is similar to that in pure water, except that a slight decrease was found at the lower end of its falling path. This phenomenon is more significant for systems containing SDS and Triton X-100, which have higher surface activity. The decrease in the drop-traveling velocity at the lower end of the extraction column can be attributed to the effects of drop oscillation and distortion, which depends on the surfactant concentration and the drop-falling distance, and was discussed in a previous article (Chen and Lee, 2000).

To study the effects of surfactant concentrations on the traveling velocity, the mean velocities in two falling regions, 0–10 and 30–45 cm, were measured for SDS and Triton X-100. Figure 5 shows that the average velocities decrease with increasing surfactant concentrations in both regions. For the average velocity at the initial falling period (0–10 cm), the drop velocity in the SDS system is smaller than that in the Triton X-100 system. However, at the later falling stage (30–45 cm), where the terminal velocity is supposed to be approached, the velocity of the Triton X-100 system is smaller. That is, SDS is more effective in inhibiting the surface mobility at the initial falling period. However, Triton X-100 becomes more significant at a later stage. The distinct effects of SDS and Triton X-100 in the two falling regions can also be related to the behaviors of adsorption kinetic. A lower velocity implies a lower interfacial tension or higher Marangoni stress, which resulted from a higher surfactant concentration or concentration gradient, respectively. At the initial falling stage, where force convection effect is not significant, the mass transfer is mainly dominated by the diffusion, and, thus, SDS is supposed to have a higher diffusion rate due to its lower molecular weight and the lower surface coverage at the interface. As a consequence, a lower velocity results for the SDS system. This phenomenon is coincident with the increased effectiveness of SDS in mass-transfer inhibition at the drop-formation stage. When the surfactant concentrations are increased, the diffusion rate will be enhanced, which increases the surface concentrations and surface coverage of the surfactant at the interface. However, due to the limitation of the SDS adsorption rate at high surface coverage, the increasing rate of mass transfer due to the concentration increase of the SDS is less than that of Triton X-100. As a result, the velocity difference for drops in the two systems becomes smaller and smaller with increasing surfactant concentrations, as shown in the lower part of Figure 5.

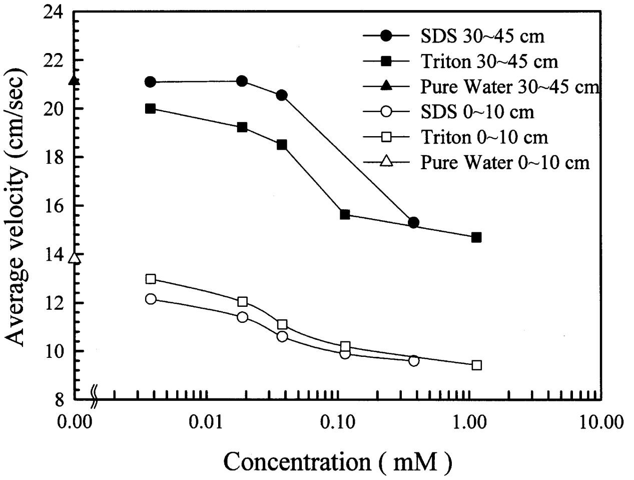


Figure 5. Variation of drop velocity as a function of surfactant concentration.

The velocities are mean values measured in two regions of the traveling distance of 0–10 and 30–45 cm.

At a later falling stage, the surfactant transfer rate is notably enhanced by the force convection, and, thus, the surface coverage is increased. The reduced effectiveness of SDS in the inhibition of drop flow, compared with Triton X-100, is also attributed to its adsorption–desorption mechanism. This phenomenon is caused by the same mechanism as that leading to the higher equilibrium interfacial tension of SDS, as described in the previous sections. The surfactant effects on the drop velocity of this region also coincide with their effects on the mass-transfer inhibition of the drop-falling stage.

Mass transfer along the drop-falling period

In the drop-falling period, the mass-transfer rate may vary along the column due to the following reasons: (1) the concentration driving force may be decreased along the column, which reduces the mass-transfer rate; (2) the interfacial concentration of the surfactant and the concentration gradient may vary due to the adsorption of the surfactant from the bulk solution and the sweeping effect by convection along the drop surface; (3) the variation in the hydrodynamic state of droplets discussed in the previous section.

To get rid of the concentration driving-force effect, one should look at the mass-transfer coefficient. The overall mass-transfer coefficients in the drop-falling stage, K_{Rf}, less the mass-transfer amount of the drop-formation stage, can be calculated from Eq. 1, where X_{R1} is the larger portion of acetic acid in the CCl_4 phase following the drop-formation stage. The dependence of the K_{Rf} value on the surfactant concentration is shown in Figure 6 for the column that is 70 cm in length. The variation of K_{Rf} with the surfactant concentration has a similar tendency as that shown in the earlier work that considered simultaneously both the drop-formation and drop-falling stages (Chen and Lee, 2000). The K_{Rf} value decreases rapidly with the surfactant concentration when the concentration is small. However, at higher concentrations, various tendencies were found for the three surfactants. The distinct effects of the three surfactants on the mass transfer can be observed more clearly by the values of the mass-transfer resistance discussed below.

The mass-transfer resistance across an interface R is always defined as the reciprocal of the mass-transfer coefficient K_R. That is, $R \equiv 1/K_R$. The extra mass-transfer resistance exerted by the addition of surfactants R_i can thus be estimated by the difference between resistances with (R) and without (R_o) the presence of surfactant $(R_i = R - R_o)$. The extra mass-transfer resistances exerted by the three surfactants, which are equivalent to the K_{Rf} values shown in Figure 6, are calculated and given in Figure 7. It is found that DTMAC offers a much smaller resistance than the other two due to its low surface activity. The resistance increases with the increase in the DTMAC concentration and approaches a constant value quickly at concentrations as small as 0.038 mM. For SDS, the mass-transfer resistance also increases with increasing concentration, but no constant value was approached at the concentrations studied here. Of the three surfactants, Triton X-100 offers the highest resistance at the low-concentration range. The mass-transfer resistance reaches a maximum value at 0.038 mM of Triton X-100 and decreases with a further increase in concentration. Surface remobilization has been taken as the reason for the decrease in resistance. From the present analysis, it is found that over 50% of the resistance can be decreased by the surface remobilization effect.

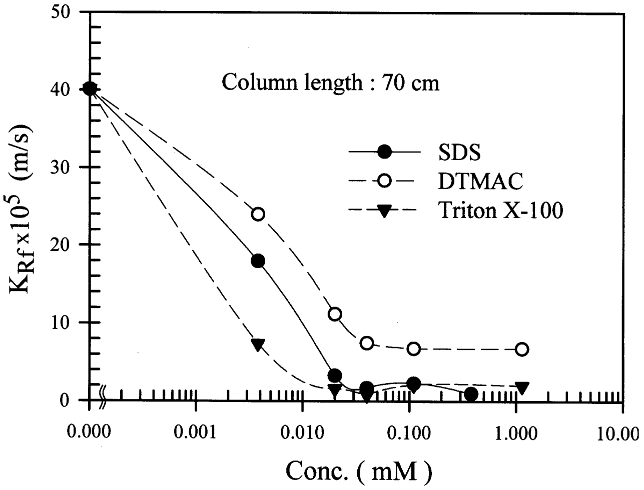


Figure 6. Variation of overall mass-transfer coefficient in the drop falling stage K_{Rf}, as functions of surfactant concentration.

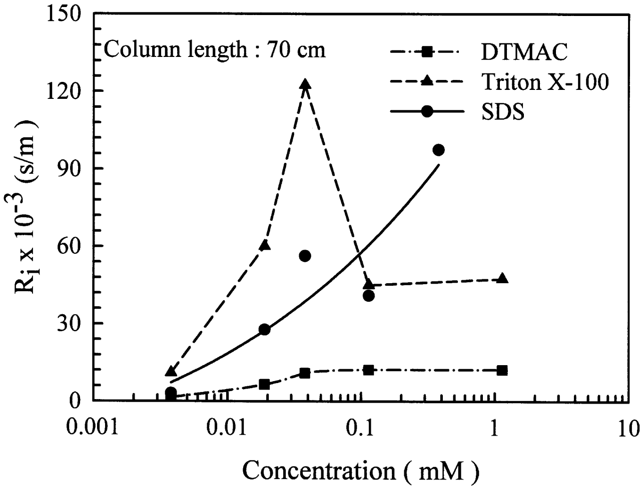


Figure 7. Effects of surfactant concentrations on the extra mass-transfer resistances (R_i) exerted by the addition of surfactants.

The mass-transfer resistances are equivalent to the overall mass-transfer coefficients shown in Figure 6.

To estimate the instantaneous mass-transfer coefficient along the column, the variation of $-\ln(X_{R2})$ with traveling time (t_f) are polated and shown in Figure 8. The slope of the curve in Figure 8, $d(-\ln X_{R2})/dt_f$, can agree with the instantaneous value of K_R. For the surfactant-free system, the slope of the curve increases before the column length of 20 cm as a result of the development of the terminal velocity and the related interfacial turbulence. However, because the concentration driving force is very small at the later falling stage, the slope decreases slightly as a consequence.

At the surfactant concentration of 3.79×10^{-3} mM, an increasing slope period was also found at the initial falling stage for the three surfactants. When the traveling distance is more than 20 cm, the slope remains nearly constant for DTMAC, decreases slightly for SDS, but decreases significantly for Triton X-100. This fact implies that the mass-transfer coefficient is the highest and remains nearly constant in the DTMAC system. For Triton X-100, the leveling curve after 20 cm shows that the mass transfer is greatly depressed and the mass transfer of the falling period is carried out mainly at the early falling stage when the surfactant-adsorption is far from the equilibrium state. The leveling curves of Triton X-100 in Figure 8c sustains the previous inference that the surfactant-adsorption equilibrium state can be obtained quickly under the acceleration effect of surface convection. Based on the present data, the equilibrium state would be approached within 1–2 s.

When the surfactant concentration is increased further, the first increasing period of the mass-transfer coefficient becomes insignificant gradually for the three surfactants. That is, the surfactant transfer rate is greatly enhanced by the increase in surfactant concentration, and the accompanying mass-transfer resistance overcomes the enhancing effect by the development of terminal velocity. For the SDS system, the slope of the curve decreases gradually with increasing surfactant concentration and remains nearly constant at the lower part of the extraction column. For the DTMAC system, which has the highest mass-transfer rate, the mass-transfer coefficient also is nearly constant along the falling period and, besides, the curves are indistinguishable for concentrations greater than 3.79×10^{-2} mM. For the Triton X-100 system with concentrations on the order of 10^{-2} mM order, the mass-transfer coefficient is the lowest among the three systems and remains nearly constant along the column. However, for concentrations greater than 1.14×10^{-1} mM, the slope increases slightly after 30 cm of the column length. This phenomenon can be observed more obviously from Figure 3c, and can be used to sustain the inference that the interface is remobilized at increased concentrations of Triton X-100. Figure 8c also shows that the remobilization occurs at the later falling stage, since a finite time is required for the transport of surfactant in order to eliminate the concentration gradient on the drop surface.

Conclusions

At low surfactant concentrations, the dynamic interfacial tension of Triton X-100 is higher at the initial stage than SDS and DTMAC, but lower at a longer adsorption time. When the concentration is increased, the dynamic interfacial tension of Triton X-100 decreases more rapidly and lower than that of the others, which demonstrates the diffusion-controlled mechanism of Triton X-100. For concentrations as small as 10^{-3} mM, the effect of surfactants on the inhibition of the mass transfer of the drop-formation stage increases in the following order: Triton X-100 < DTMAC < SDS. On the other hand, at the drop-falling stage, Triton X-100 becomes the most effective, but SDS and DTMAC have no significant effect. When the concentration is increased, the effectiveness of Triton X-100 increases more quickly than the others in both the formation and falling stages, which is attributed to the diffusion-controlled mechanism of Triton X-100. This characteristic also leads to the slight increase in the mass-

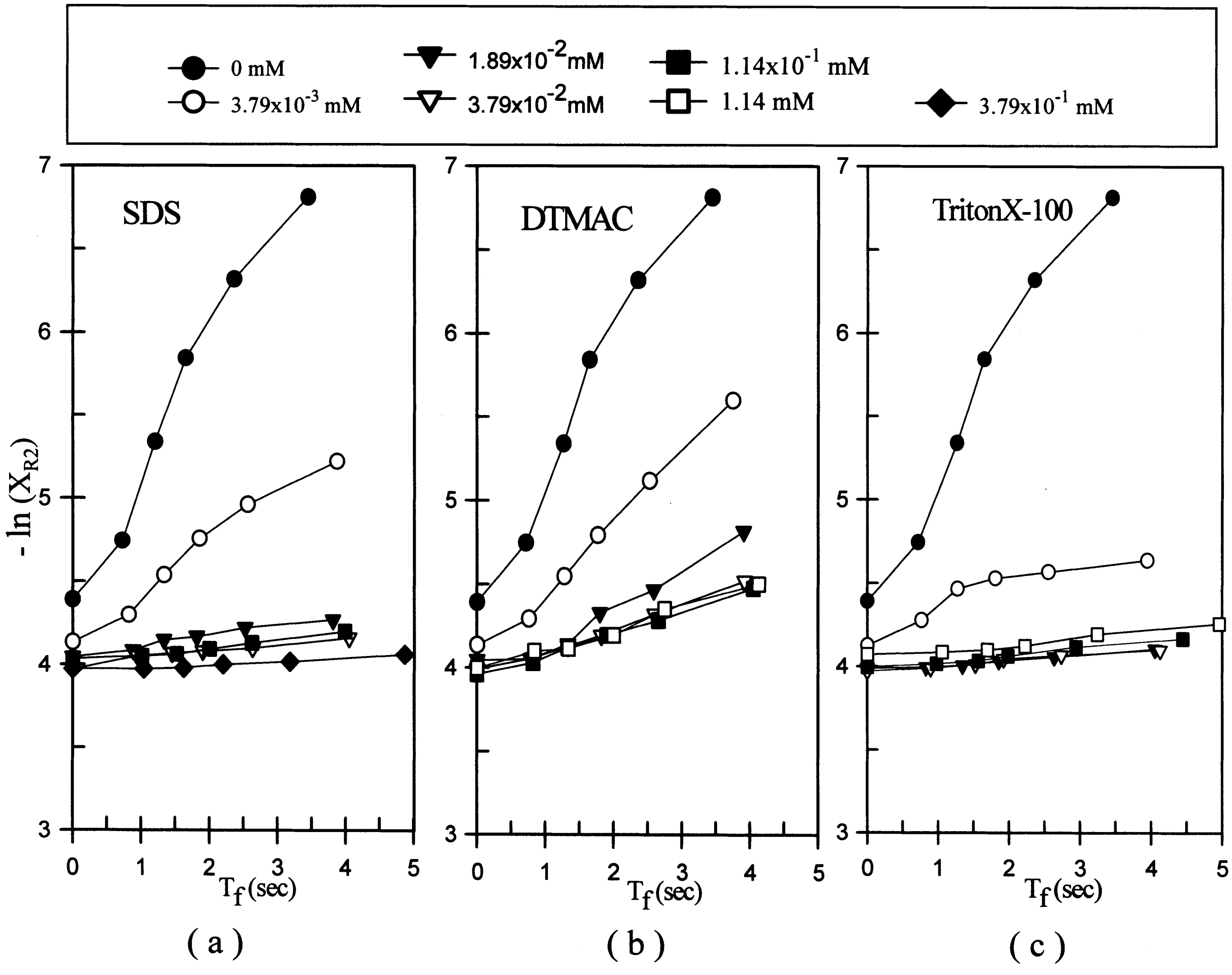


Figure 8. Variation of ($-\ln X_{R2}$) with the traveling time of a droplet for various surfactant concentrations.

The points on each curve, from left to right, correspond to the traveling time of droplets in the column of 0, 10, 20, 30, 45, and 70 cm in length, respectively.

transfer rate when the Triton X-100 concentration is increased up near CMC. Due to the insignificant surfactant surface concentration at an adsorption time as small as the drop-formation interval, the mass-transfer inhibition of the surfactant in the drop-formation stage is inferred to be mainly caused by the hydrodynamic effect. On the other hand, the mass-transfer resistance during the drop-falling stage is mainly caused by the obstruction of the adsorbed barrier layer.

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Literature Cited

Bakker, C. A. P., F. H. Fentener Van Vlissingen, and W. J. Beek, "The Influence of the Driving Force in Liquid-Liquid Extraction—A Study of Mass-Transfer with and without Interfacial Turbulence Under Well-Defined Conditions," *Chem. Eng. Sci.*, **22**, 1349 (1967).

Beitel, A., and W. J. Heideger, "Surfactants Effects on Mass Transfer from Drops Subject to Interfacial Instability," *Chem. Eng. Sci.*, **26**, 711 (1971).

Boye-Christensen, G., and S. G. Terjesen, "On the Mechanism of Interfacial Resistance to Mass Transfer in Liquid-Liquid Extraction," *Chem. Eng. Sci.*, **7**, 222 (1958).

Boye-Christensen, G., and S. G. Terjesen, "On the Action of Surface Active Agents on Mass Transfer in Liquid-Liquid Extraction," *Chem. Eng. Sci.*, **9**, 225 (1959).

Chang, C. H., and E. I. Franses, "Adsorption Dynamic of Surfactants at Air/Water Interface: A Critical Review of Mathematical Model, Data, and Mechanisms," *Colloids Surf. A: Phys. Eng. Aspects*, **100**, 1 (1995).

Chen, J., and K. J. Stebe, "Marangoni Retardation of the Terminal Velocity of a Settling Droplet: The Role of Surfactant Physico-Chemistry," *J. Colloid Interface Sci.*, **178**, 144 (1996).

Chen, L. H., and Y. L. Lee, "Surfactant Effects on the Equipment Performance of Extraction Column," *J. Chem. Eng. Jpn.*, **32**, 138 (1999).

Chen, L. H., and Y. L. Lee, "Adsorption Behavior of Surfactants and Mass Transfer in Single-Drop Extraction," *AIChE J.*, **46**, 160 (2000).

Chu, J. C., C. C. Taylor, and D. J. Levy, "Liquid-Liquid Extraction Correlation of H.T.U. with Interfacial Tension," *Ind. Eng. Chem.*, **42**, 1157 (1950).

Fang, J. P., and P. Joos, "The Dynamic Surface Tension of SDS-Dodecanol Mixtures. 1. The Submicellar Systems," *Colloids Surf.*, **65**, 113 (1992).

Garner, F. H., and A. R. Hale, "The Effects of Surface Active Agents in Liquid Extraction Processes," *Chem. Eng. Sci.*, **2**, 157 (1953).

Garner, F. H., and A. H. P. Skelland, "Effects of Surface Active Agents on Extraction from Droplets," *Ind. Eng. Chem.*, **48**, 51 (1956).

Gibbs, J. W., *The Scientific Papers*, Vol. 1, Dover, New York, p. 302 (1961).

Hu, S., and R. C. Kintner, "The Fall of Single Liquid Drops through Water," *AIChE J.*, **1**, 42 (1955).

Huang, W. S., and R. C. Kintner, "Effects of Surfactants on Mass Transfer Inside Drops," *AIChE J.*, **15**, 735 (1969).

Hunsel, J. V., G. Bleys, and P. Joos, "Adsorption Kinetics at the Oil/Water Interface," *J. Colloids Interface Sci.*, **114**, 432 (1986).

Jeng, J. J., J. R. Maa, and Y. M. Yang, "Surface Effects and Mass Transfer in Bubble Column," *Ind. Eng. Chem. Process Des. Dev.*, **25**, 974 (1986).

Lee, Y. L., J. R. Maa, and Y. M. Yang, "The Effects of Surfactant on the Mass Transfer in Extraction Column," *J. Chem. Eng. Jpn.*, **31**, 340 (1998).

Levan, M. D., and J. Newman, "The Effect of Surfactant on the Terminal and Interfacial Velocities of a Bubble or Drop," *AIChE J.*, **22**, 695 (1976).

Levich, V. G., *Physicochemical Hydrodynamics*, Prentice-Hall, New York (1962).

Lin, S. Y., K. McKeigu, and C. Maldarelli, "Diffusion-Controlled Surfactant Adsorption Studied by Pendent Drop Digitization," *AIChE J.*, **36**, 1785 (1990).

Lindland, K. P., and S. G. Terjesen, "The Effect of a Surface-Active Agent on Mass Transfer in Falling Drop," *Chem. Eng. Sci.*, **5**, 1 (1956).

Magarvey, R. H., and C. S. Maclatchy, "Mass Transfer and Wake Phenomena," *AIChE J.*, **14**, 260 (1968).

McCabe, W. L., J. C. Smith, and P. Harriott, *Unit Operations of Chemical Engineering*, 6th ed., McGraw-Hill, New York, p. 162 (2001).

Mudge, L. K., and W. J. Heideger, "The Effect of Surface Active Agents on Liquid-Liquid Mass Transfer Rates," *AIChE J.*, **16**, 602 (1970).

Oguz, H. N., and S. S. Sadhal, "Effects of Soluble and Insoluble Surfactants on the Motion of Drops," *J. Fluid Mech.*, **194**, 563 (1988).

Ruskan, R. P., "The Effect of a Surfactant on a Mechanically Agitated Extraction Column," *Ind. Eng. Chem. Process Des. Dev.*, **13**, 203 (1974).

Sadhal, S. S., and R. E. Johnson, "Stokes Flow Past Bubbles and Drops Partially Coated with Thin Films," *J. Fluid Mech.*, **126**, 237 (1983).

Scriven, L. E., and C. V. Sternling, "The Marangoni Effects," *Nature*, **187**, 186 (1960).

Skelland, A. H. P., and C. L. Caenepeel, "Effects of Surface Active Agents on Mass Transfer During Droplet Formation, Fall, and Coalescence," *AIChE J.*, **18**, 1154 (1972).

Skelland, A. H. P., and N. C. Vasti, "Effects of Interaction Between Circulating or Oscillating Droplets on Drop Formation, Free Fall, and Mass Transfer," *Can. J. Chem. Eng.*, **63**, 390 (1985).

Skelland, A. H. P., and S. S. Minhas, "Dispersed Phase Mass Transfer During Drop Formation and Coalescence in Liquid-Liquid Extraction," *AIChE J.*, **17**, 1316 (1971).

Skelland, A. H. P., S. Woo, and G. G. Ramsay, "Effects of Surface-Active Agents on Drop Size, Terminal Velocity, and Droplet Oscillation in Liquid-Liquid Systems," *Ind. Eng. Chem. Res.*, **26**, 907 (1987).

Skelland, A. H. P., and Y. F. Huang, "Continuous Phase Mass Transfer During Formation of Drops from Jets," *AIChE J.*, **25**, 80 (1979).

Stebe, K. J., S. Y. Lin, and C. Maldarelli, "Remobilizing Surfactant Retarded Fluid Particle Interface I," *Phys. Fluids*, **A3**, 3 (1991).

Stebe, K. J., and C. Maldarelli, "Remobilizing Surfactant Retarded Fluid Particle Interfaces II," *J. Colloid Interface Sci.*, **163**, 177 (1994).

West, F. B., A. J. Herrman, A. T. Chong, and L. E. K. Thomas, "Addition Agents and Interfacial Barriers in Liquid-Liquid Extraction," *Ind. Eng. Chem.*, **44**, 625 (1952).

West, F. B., P. A. Robinson, A. C. Morgenthaler, T. R. Beck, and D. K. McGregor, "Liquid-Liquid Extraction from Single Drops," *Ind. Eng. Chem.*, **43**, 234 (1951)

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