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Chemical Engineering Journal 73 (1999) 77–81

Chemical Engineering Journal

Short communication

# The effects of a surfactant on the mass transfer in spray-tower extraction column

Liang-Huei Chen, Yuh-Lang Lee*

*Department of Applied Chemistry, Chia-Nan College of Pharmacy and Science, Tainan 717, Taiwan*

Received 2 June 1998; received in revised form 28 December 1998; accepted 4 January 1999

## Abstract

For an extraction process, the overall efficiency of mass transfer is determined by the mass transfer coefficient and the interfacial area. A small amount of surfactant has the effect of decreasing the mass transfer coefficient while increasing the interfacial area. The extraction efficiency thus varies in a complex manner with the concentration of surfactant due to the two competing factors. To obtain a better understanding of these effects, the two factors were studied individually. A single-drop extraction apparatus was used to study the effects of a surfactant on the mass transfer coefficient in a previous work. In this work, the effects of a surfactant on the overall efficiency and mass transfer area were investigated in a spray-tower extraction column. The results show that sodium lauryl sulphate (SLS) has a negative effect on the overall efficiency. The value of $K_Ra$ decreases rapidly with increasing SLS concentration, approaches a minimum at about 10 ppm, and then increases monotonically with further addition of SLS. With increasing surfactant concentration, the interfacial area increases more rapidly at a low SLS concentration, which is mainly due to the inhibition of drop coalescence by the dynamic surface effect. However, the slower increasing rate of mass transfer area at higher SLS concentrations results from a decrease in drop size with decreasing interfacial tension. © 1999 Elsevier Science S.A. All rights reserved.

*Keywords:* Extraction; Mass transfer coefficient; Interfacial area; Surfactant; Dynamic surface effects

## 1. Introduction

The extraction column is a useful tool for various liquid–liquid mass transfer operations. In the extraction column, the discontinuous phase is dispersed into small droplets in order to increase the two-phase contact area. As the dispersed droplets travel through the continuous phase, convection in both phases is promoted and the mass transfer coefficient is enhanced. The overall mass transfer efficiency is thus determined by the mass transfer coefficient and the interfacial area. If a small amount of surfactant is added to the extraction system, the two factors are affected. The effects of a surfactant on mass transfer in an extraction column have been studied by many workers. Some have studied the effects of a surfactant on the mass transfer coefficient in single-drop extraction [1–6], and others have investigated its effect on the overall efficiency of the equipment [7–11]. The results indicate that surfactants often reduce the mass transfer coefficient but increase the mass transfer area per unit volume.

In studies performed on single-drop extraction, the decrease in the mass transfer coefficient by surfactant was attributed either to the decrease in interfacial mobility and internal circulation [1,2] or to the blocking action of surfactant molecules at the interface [3,4]. In the studies on equipment performance, the overall efficiencies were found to increase or decrease with the addition of surfactant. This is due to the competitive effects of surfactant on the mass transfer coefficient, *K*, and mass transfer area, *a*. The net effect of surfactant on the operation efficiency of the extraction column or the value of the product, *Ka*, is rather complicated. To identify the competitive effects, it is more appropriate to study the two factors individually.

In a previous study [6], a single-drop extraction apparatus was used to study the effects of a surfactant on the mass transfer coefficient and the fluid flow behaviour along the extraction column. In the present work, the experiments were carried out in a spray-tower to obtain the overall performance. In addition, the effects of a surfactant on the overall mass transfer efficiency and mass transfer area were investigated.

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*Corresponding author. Tel.: +886-6-266-4911/extn. 245; fax: +886-6-266-6411; e-mail: jleeyl@chna.chna.edu.tw

PII: S1385-8947(99)00028-5

## 2. Experimental method and apparatus

Acetic acid was used as solute, which originally contained a dispersed phase (carbon tetrachloride) that was extracted by a continuous phase (water). The surfactant used was sodium lauryl sulphate (SLS, $C_{12}H_{25}OSO_3Na$), which is a water-soluble, anionic surfactant. The initial concentration of acetic acid in carbon tetrachloride was 0.1 M for all of the experiments.

Fig. 1 shows a schematic diagram of the experimental set-up used in this work. The extraction column (A) has an inside diameter of 35 mm and a height of 1.0 m. The distributor (G), made of stainless steel, has four 2 mm diameter holes which are separated by 4 mm.

For all of the experiments, the flow rates of the water phase and the $CCl_4$ phase were kept at 160 and 80 ml $min^{-1}$, respectively. The output flow rate of the $CCl_4$ phase was adjusted by a valve (E) to control the two-phase interface at a constant level, and steady state could be reached within 30 min.

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 $m$ increases linearly with $X_E$ ($m = 2.9X_E + 0.026$) and is nearly independent of surfactant concentration. As the acetic acid concentration in this study is very dilute, the value of $m$ is much smaller than 0.1 during the operation range. The concentration of acetic acid in the CCl4 phase was analysed by mixing the sample with an excess amount of water, followed by titration with NaOH.

For the continuous counter-current extraction column, the volumetric overall mass transfer coefficient, $K_Ra$, was obtained by Lee [12] as follows:

$$K_Ra = \frac{F_R(X_{R1} - X_{R2})}{AC_{RM}H(\Delta X)_{ln}} \tag{1}$$

where $(\Delta X)_{ln}$ is the logarithmic mean mole fraction difference defined by

$$(\Delta X)_{ln} = \frac{(X_{R1} - X^*_{R1}) - (X_{R2} - X^*_{R2})}{\ln(X_{R1} - X^*_{R1}/X_{R2} - X^*_{R2})} \tag{2}$$

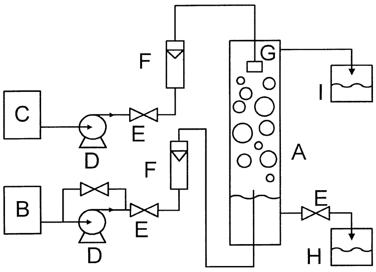

Fig. 1. Flow diagram of the spray-tower extraction apparatus: A, extraction column; B, water phase feed tank; C, $CCl_4$ phase feed tank; D, feeding pump; E, flow rate controlling valves; F, rotameters; G, distributor; H, $CCl_4$ phase collection tank; I, water phase collection tank.

where $a$ is the mass transfer area per unit volume ($m^2$ $m^{-3}$). As it is not easily estimated, it is always combined with $K_R$. $F_R$ is the molar flow rate, $A$ and $H$, respectively, are the cross-sectional area and height of the extraction column, $X_{R1}$ and $X_{R2}$ are the mole fractions of the solute in the $CCl_4$ phase at the top (input) and bottom (output) of the column, respectively, and $X^*_{R1}$ and $X^*_{R2}$ are the mole fractions of the solute in equilibrium with the extraction phase, i.e. $X^*_R = mX_E$. In this work, the value of $X^*_R$ is negligibly small for two reasons: (i) the value of $X_E$ is very small due to the small holdup of the dispersed phase (less than 10%) and, in addition, the initial concentration of the solute is very dilute; and (ii) the value of $m$ is much smaller than 0.1 during the operation range. $C_{RM}$ is the mean concentration of the raffinate phase along the extraction column. Since the acetic acid concentration is dilute, $C_{RM}$ is equivalent to the molar concentration of $CCl_4$.

## 3. Dynamic surface effect and drop coalescence mechanism

The local difference in solute concentration or temperature at the interface causes a local increase or decrease in surface tension, and thus induces fluid flow at the interface (or interfacial turbulence). This phenomenon is known as the Marangoni effect, discussed by Scriven and Sternling [13] and Levich [14]. For a system containing surfactant, when the surface is being stretched, a new surface is created constantly and surfactant molecules should be supplied from the bulk phase to the interface so as to satisfy the need for adsorption. The concentration in the vicinity of the interface is lower than that in the bulk phase due to the limitation of the diffusion rate. The surface concentration of surfactant is in equilibrium with this lower concentration and is lower than that at a static surface without stretching of the interface. As a result, the interfacial tension of a stretching interface will be higher than that of a static one. The local difference in surface tension caused by the stretching of the interface exerts a Marangoni stress which prevents the surface from being stretched further, and the surface motion will be retarded. When the interface is being compressed, surfactant has a similar effect of retarding further compression. The Marangoni stress induced by a stretching (or compressing) surface is termed the dynamic surface effect [15]. This effect hampers interfacial turbulence and surface convection, and the mass transfer coefficient of an extraction system is thus reduced.

As two drops come into contact in the coalescence process shown in Fig. 2, the liquid between them flows outwards and simultaneously stretches the drop surface. In a surfactant containing solution, the interfacial tension in the region between the two drops would be higher due to the stretching of the interface. The surface convection sweeps adsorbed surfactant molecules on the drop surface towards the outside surface of the two drops, where they accumulate,

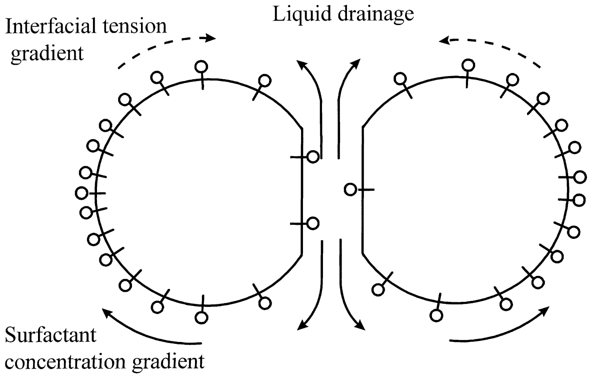

Fig. 2. The interfacial flow of two approaching drops in surfactant solution.

further reducing the interfacial tension there. The net force on the interface, pulling from this low-tension region towards the contact region between the drops, exerts a Marangoni stress which increases the drag resistance of the drainage of the liquid. As a result, coalescence is prevented or obstructed [16,17].

A liquid film always forms between two drops (or bubbles) during the process of coalescence. Thinning and final rupturing of the thin liquid film are the processes by which the two drops coalesce. The thinning process was proposed to occur in two stages by Marrucci [18]. The first stage involves very rapid stretching of the liquid film down to a quasi-equilibrium thickness, $h_0$, where the increase in interfacial tension is balanced by the internal pressure. The value of this thickness was calculated as a function of physical properties, as shown by Marrucci [18]:

$$\frac{Qrk^2}{\sigma} = \frac{1}{kh_0} + (kh_0)^2 \tag{3}$$

$$k = \left(\frac{12\pi\sigma}{A_0 r}\right)^{1/3} \tag{4}$$

$$Q = \frac{2C}{RT}\left(\frac{\mathrm{d}\sigma}{\mathrm{d}C}\right)^2 \tag{5}$$

where $r$ is the drop radius, $A_0$ the Hamaker London constant and $\sigma$ the interfacial tension of the solution at the surfactant concentration $C$. The second stage involves further thinning of the quasi-equilibrium film down to a thickness of the rupture, $h_f$, which can be expressed by

$$\frac{Qrk^2}{\sigma} = \frac{2}{kh_f} - (kh_f)^2 \tag{6}$$

It was shown that the stage which dominates the thinning process is determined by the value of $Qrk^2/\sigma$, i.e. the value of $Qrk^2/\sigma$ is very important for the coalescence of drops. At constant temperature, if we define $M$ by Eq. (7), then $M$ is proportional to $Qrk^2/\sigma$ and can be used to express the degree of ease of coalescence of two drops in dilute surfactant solution [19]:

$$M \equiv C\left(\frac{r}{\sigma}\right)^{1/3}\left(\frac{\mathrm{d}\sigma}{\mathrm{d}C}\right)^2 \tag{7}$$

## 4. Results and discussion

The experimental results of $K_Ra$ are shown in Fig. 3 as a function of the SLS concentration. In this work, surfactant has a negative effect on the overall efficiency of mass transfer. The value of $K_Ra$ decreases rapidly as the concentration of SLS increases and reaches a minimum at about 10 ppm, and then increases monotonically as the concentration is further increased. This result indicates that, below 10 ppm of SLS, the effect of surfactant on the decrease in $K_R$ is more important than that on the increase in interfacial area. However, with further addition of SLS, the increase in $K_Ra$ is caused mainly by the increase in interfacial area.

The effects of SLS on the mass transfer coefficient, $K_R$, of the same system have been studied previously [6]. These results are plotted in Fig. 3, which shows that the value of $K_R$ decreases rapidly as surfactant is added and reaches a constant value at about 20 ppm of SLS. To understand the dependence of the interfacial area on the surfactant concentration in the spray-tower, the values of $K_R$ obtained from the single-drop extraction study were used to substitute for the values in the product, $K_Ra$, and thus the interfacial area was calculated. Although the $K_R$ values for the two processes are not exactly identical, the distinction between them should be small because the mass transfer across the interface is controlled by the transfer within the dispersed phase due to the small value of $m$, and the fluid flow within the dispersed phase is inhibited in the presence of surfactant. Since the dependence of $K_R$ on the SLS concentration is similar in both types of apparatus, the mass transfer area in the spray-tower can be compared relatively. The mass transfer area, $a$, obtained by this calculation is also shown in Fig. 3.

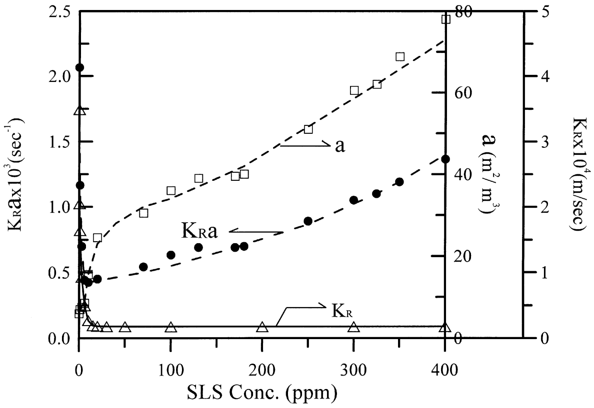

Fig. 3. $K_Ra$, $K_R$, and $a$ as functions of the concentration of SLS in solution. $K_Ra$: obtained from spray-tower extraction column; $K_R$: obtained from single-drop extraction at the same column length (1.0 m); $a$: calculated by substituting the values of $K_R$ into $K_Ra$.

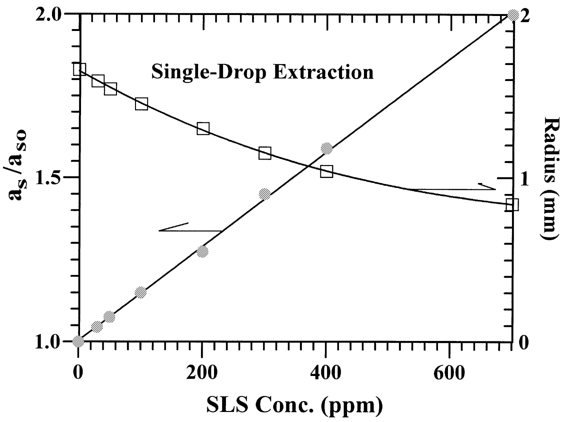

Fig. 4. The drop radius and the ratio of the specific surface area with ($a_s$) and without ($a_{s0}$) surfactant as a function of the SLS concentration.

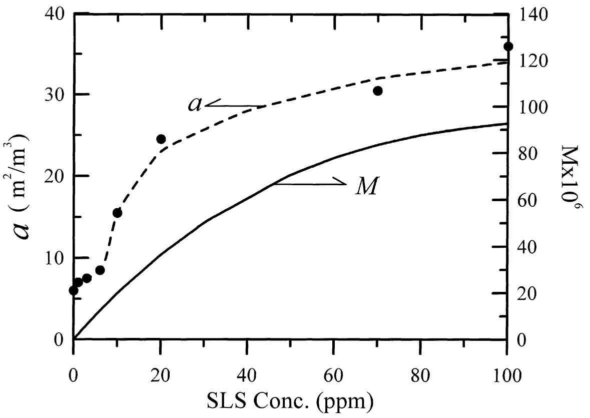

Fig. 5. The mass transfer area, $a$, and $M$ as functions of the SLS concentration.

With increasing SLS concentration, the interfacial area increases rapidly at a low SLS concentration, but slows down when the SLS concentration reaches higher values. A surfactant will increase the interfacial area via two effects: via a decrease in the drop size with decreasing interfacial tension [20,21], and via the prevention of coalescence dispersing droplets by the dynamic surface effect. The first effect can be estimated by measuring the drop sizes at various concentrations of SLS. This experiment was carried out using a drop former made of glass (tip head outside diameter, 3 mm). The drop size decreases with decreasing interfacial tension, which is shown in Fig. 4 as a function of the SLS concentration. The ratio of the specific surface area, $a_s$ (ratio of the surface area of a drop, $a_d$, to the drop volume, $V_d$), to the value in a surfactant free solution ($a_{s0}$) is also shown in Fig. 4.

The linear increase in the specific area ratio ($a_s/a_{s0}$) represents the increase in the interfacial area with no coalescence, and the variation is due to the decrease in drop size with decreasing interfacial tension. When the SLS concentration increases from 0 to 100 ppm, no significant increase in the interfacial area is found in Fig. 4, but the $a$ value in Fig. 3 increases to about six times the initial value. So, we can infer that, at a low SLS concentration, the rapid increase in the mass transfer area in the spray-tower is caused by the inhibition of drop coalescence by the dynamic surface effect. When the SLS concentration increases further, the increase in $a$ slows down, which means that further addition of SLS has little effect on coalescence prevention. The increase in the surface area at a high SLS concentration is thus mainly attributed to the decrease in drop size with the decreasing interfacial tension.

The value of $M$ measures the degree of difficulty of coalescence of dispersing droplets in a surfactant-containing solution. For a system with a large value of $M$, the droplets find it difficult to coalesce. However, when the $M$ value is small, they coalesce easily. The variation in the interfacial tension (between water and $CCl_4$) with SLS concentration, as shown in the previous work, has a relationship of $\sigma = \exp(3.43 - 1.34212C) + 4.14$. This relationship was used for the computation of $M$ values. Fig. 5 shows the values of $a$ and the computed $M$ values as functions of the SLS concentration. The similarity between these two curves verifies that the $M$ value can be used as a measure of the difficulty of drop coalescence.

The effects of surfactants on the overall mass transfer coefficient obtained by other researchers are not identical to our results. Hong and Maa [9], using a mixer–settler apparatus, and Chu et al. [7], using a packed tower, found maximum values of $Ka$, which implies that the increase in the interfacial area is more important than the decrease in the mass transfer coefficient at low surfactant concentrations. In contrast, the minimum values of $Ka$ obtained by Ruskan [8], using an agitated extraction column, and from this work show that the decrease in the mass transfer coefficient is the dominant factor. The discrepancy may be due to the effect of different apparatus. In addition, the solvent–solute systems and surfactants used may also play an important role, which has been demonstrated by the research of Chu et al. [7]. It is still very difficult to predict how the $Ka$ value will change for a particular system.

## 5. Conclusions

A small amount of surfactant has the effect of retarding the coalescence of droplets, and thus causes an increase in the mass transfer area in the extraction process. It also has the effect of retarding the stretching and compression of the interface, therefore, reducing the interfacial disturbance and increasing the mass transfer resistance. For the mass transfer in a spray-tower extraction column, a minimum value of $K_R a$ was obtained due to the competitive effects of these two factors, which demonstrates that the effect of SLS on the decrease in $K_R$ is more important than that on the increase in the mass transfer area.

For a surfactant containing system, the mass transfer area may be increased both by the decrease in drop size with decreasing interfacial tension, and by the coalescence prevention of dispersing droplets. At a low concentration of SLS, the mass transfer area increases more rapidly with increasing SLS concentration, which is mainly due to the prevention of the coalescence of droplets. However, at a high SLS concentration, the slow rate of increase in the mass transfer area is mainly caused by the decrease in drop size with decreasing interfacial tension. The value of $M$ is a measure of the degree of difficulty of coalescence of the dispersing droplets. The variation in $M$ values with SLS concentration agrees satisfactorily with that of the $a$ values at low concentrations of SLS.

## Acknowledgements

The partial support of this research by the National Science Council of the Republic of China through Grant NSC84-2214-E041-001 is gratefully acknowledged. Professor Jer-Ru Maa is also acknowledged for his helpful discussions.

## Appendix

### Nomenclature

| | |
|---|---|
| $a$ | mass transfer area per unit volume ($m^2\ m^{-3}$) |
| $a_d$ | surface area of a drop ($m^2$) |
| $a_s$ | surface area per unit volume of a drop ($m^2\ m^{-3}$) |
| $A$ | cross-sectional area of the extraction column ($m^2$) |
| $A_0$ | Hamaker London constant (J) |
| $C$ | molar concentration ($mol\ m^{-3}$) |
| $C_{RM}$ | mean value of total molar concentration of raffinate phase along the column ($mol\ m^{-3}$) |
| $F$ | molar flow rate ($mol\ s^{-1}$) |
| $h_f$ | film thickness at break (m) |
| $h_0$ | quasi-equilibrium film thickness (m) |
| $H$ | height of extraction column (m) |
| $k$ | defined by Eq. (4) ($m^{-1}$) |
| $K$ | mass transfer coefficient ($m\ s^{-1}$) |
| $K_Ra$ | volumetric overall mass transfer coefficient based on the raffinate phase ($s^{-1}$) |
| $m$ | distribution ratio |
| $M$ | defined by Eq. (7) ($(N\ m)^{5/3}\ mol^{-1}$) |
| $Q$ | defined by Eq. (5) (N) |
| $r$ | drop radius (m) |
| $R$ | gas constant ($J\ K^{-1}\ mol^{-1}$) |
| $T$ | temperature (K) |
| $V_d$ | volume of a drop ($m^3$) |
| $X$ | mole fraction |
| $X_R^*$ | mole fraction of raffinate phase in equilibrium with the extract phase |
| $\Delta X$ | defined by Eq. (2) |
| $\sigma$ | interfacial tension ($N\ m^{-1}$) |

*Subscripts*

| | |
|---|---|
| R | raffinate phase |
| E | extraction phase |
| 1 | feed stream |
| 2 | output stream |

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