Surfactant Effects on Absorption in the Presence of Induced Interfacial Turbulence

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Hydrodynamic phenomena driven by the gradients of surface tension are called Marangoni effects. If the gradients are along the interface of two phases, spatial variations in surface tension can result in added tangential stresses at the interface and hence a surface tractive force that acts on the adjoining fluid, giving rise to fluid motions in the underlying bulk liquid. This motion, which is induced by tangential gradients of surface tension, is usually termed the Marangoni convection.

Specifically, the radial interface motions can be obtained when a single point surface tension sink is generated in which a small drop of a soluble or partially soluble liquid was continuously dissolved at the surface of a liquid substrate layer. The aforementioned drop liquid, which has a smaller surface tension than that of substrate liquid, is called the "spreading liquid" while the substrate liquid is called the "supporting liquid." As a result, severe Marangoni convection due to the Marangoni effect was taking place and led to an intense agitation at the interface. This artificially induced interfacial turbulence is known to effectively enhance the rate of mass transfer across the interface. Reviews of this subject are available (Ruckenstein et al., 1992; Lu et al., 1997).

Most theoretical and experimental investigations on this subject in the literature are concerned with the role the spreading liquids may play in inducing interfacial turbulence. Various low surface tension spreading liquids including alcohols, organic acids, and ketones and so on have been found to be good "initiators" of the Marangoni convection at gas/liquid interface. Water, however, is used mostly as a supporting liquid.

It is well known that the minute quantity of surfactants is able to depress the surface tension of water drastically. An important problem among others which pertain to this approach for enhancing mass-transfer rates is what should one expect if surfactants enter the system in water (supporting liquid)? However, the surfactant effect on gas/liquid mass transfer in the presence of artificially induced interfacial turbulence has seldom, if ever, been reported (Vazquez et al., 1996).

In this work, aqueous solutions of three different types of surfactants (anionic, cationic, and nonionic) over relatively wide ranges of concentrations were used as the supporting (absorbing) liquids. The largest concentrations are high enough to exceed the critical micelle concentration of each surfactant. Absorption rates of CO_2 by absorbing liquids were determined experimentally to indicate the extent of the influence of interfacial turbulence on mass transfer across interface. The identification of the inhibition mechanisms of surfactants on artificially induced interfacial turbulence is to be aimed at. To our knowledge, this is the first systematic study in the literature on surfactant effects which exhausts the artificially induced Marangoni convection to a maximum extent.

Theoretical Studies

Liquid-phase mass-transfer coefficient with artificially induced Marangoni convection in the absence of surfactant

The details of the solution procedure for the variables in the mathematical model, which were proposed by Ruckenstein and coworkers, are referred to in Lu et al. (1996). However, the pertinent relations to the present study are listed as follows (Smigelschi et al., 1969; Ruckenstein et al., 1970).

Concentration Profile Along the Interface

$$C_s = \frac{C_{s0}}{2}\left[\mathrm{erf}\left(\frac{\delta - y}{2\sqrt{D_{st}}}\right) + \mathrm{erf}\left(\frac{\delta + y}{2\sqrt{D_{st}}}\right)\right] \tag{1}$$

Velocity Profile Along the Interface

$$u = (\nu/\pi)^{1/2}\int_0^t \frac{F(t-\lambda)}{u(t-\lambda)} e^{-y^2/4\nu\lambda}\frac{d\lambda}{\lambda^{1/2}} \tag{2}$$

where

$$F(t) = -\frac{1}{\mu}\frac{d\sigma}{dC_{si}}\frac{C_{s0}\delta}{2\sqrt{\pi D_s}}t^{-3/2}e^{-\delta^2/4D_{st}}; \quad t = \int_{r_0}^{r}\frac{dr}{u_i} \tag{3}$$

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where δ is the film thickness of the steady drop of spreading liquid, y is a normal coordinate, D is the diffusivity in liquid phase, t is a variable, ν is a kinematic viscosity, λ is a dummy variable, σ is surface tension, μ is viscosity of supporting liquid, subscript s is spreading liquid, r is a radial coordinate, and subscript 0 is initial. It should be noted that surface concentration (C_{si}) and surface velocity (u_i) profiles can be obtained by setting $y = 0$ in Eqs. 1 and 2.

Local Liquid-Phase Mass-Transfer Coefficient

$$K_L = \sqrt{\frac{D_g}{\pi}}\,\frac{u_i r}{\left(\int_{r_0}^{r} u_i r^2 dr\right)^{1/2}} \tag{4}$$

Average Mass-Transfer Coefficient

$$\overline{K}_L = \frac{\int_{r_0}^{R} 2K_L r dr}{R^2 - r_0^2} \doteq \frac{\int_{0}^{R} 2K_L r dr}{R^2} \tag{5}$$

where subscript g is a gas solute, R is the radius of gas-liquid surface; gas constant; mass-transfer resistance, and r_0 is the radius of steady drop of spreading liquid around the capillary tip.

The effectiveness of absorption enhancement by continuously dissolving an aqueous solution of methanol, ethanol and n-propanol at the water surface was studied theoretically and experimentally (Lu et al., 1996). Results revealed that mass-transfer rates with artificially induced Marangoni convection can be as much as 3 to 4 times larger than those without it. From an engineering design point of view, it is most desirable that the results of mass transfer can be analyzed, generalized, and formulated in a convenient form for calculations. Fortunately, a dimensionless equation for correlating the experimental mass-transfer coefficient data in the presence of interfacial turbulence was satisfactorily developed

$$Sh = 0.74\, Ma^{0.35} Sc^{-0.35} Sc'^{0.5} \tag{6}$$

where the Sherwood number, the Marangoni number, the Schmidt numbers of spreading liquid and gas are defined, respectively, as

$$Sh = \overline{K_L} R / D_g; \quad Ma = \Delta\sigma R / \mu D_s; \quad Sc = \mu / \rho D_s;$$
$$Sc' = \mu / \rho D_g \tag{7}$$

where $\Delta\sigma$ is the surface tension difference between the spreading liquid and supporting liquid, and ρ is the density of supporting liquid.

Resistance to interphase mass transfer in the presence of surfactants

The importance of the effect of surfactants on mass transfer has been recognized and, consequently, has led to many investigations over several years. According to the extended two-film theory, the overall resistance to mass transfer consists of the individual resistances of the two phases and the resistance of the interface itself. As shown in Figure 1a for soluble surfactants, the overall resistance to transfer of solute from gas phase to liquid phase is given by the sum of partial resistances

$$R = R_G + R_I + R_L \tag{8}$$

where R is the overall resistance, R_G and R_L are the resistances in gas phase and liquid phase, respectively, and R_I is the interfacial resistance.

The increase in R due to the presence of surfactants can, in general, occur due to changes in R_G and R_L as well as changes in R_I. The increase in R_I, if it is the case, is usually interpreted in terms of a barrier to transport across interface. The changes in R_G and R_L are due to the alteration of the flow fields near the interface due to positive adsorption of surfactants.

Since pure gas (CO_2) was used in this study, there is no gas-phase resistance, that is, $R_G = 0$. As will be explained later, the interfacial resistance is found to be negligibly small

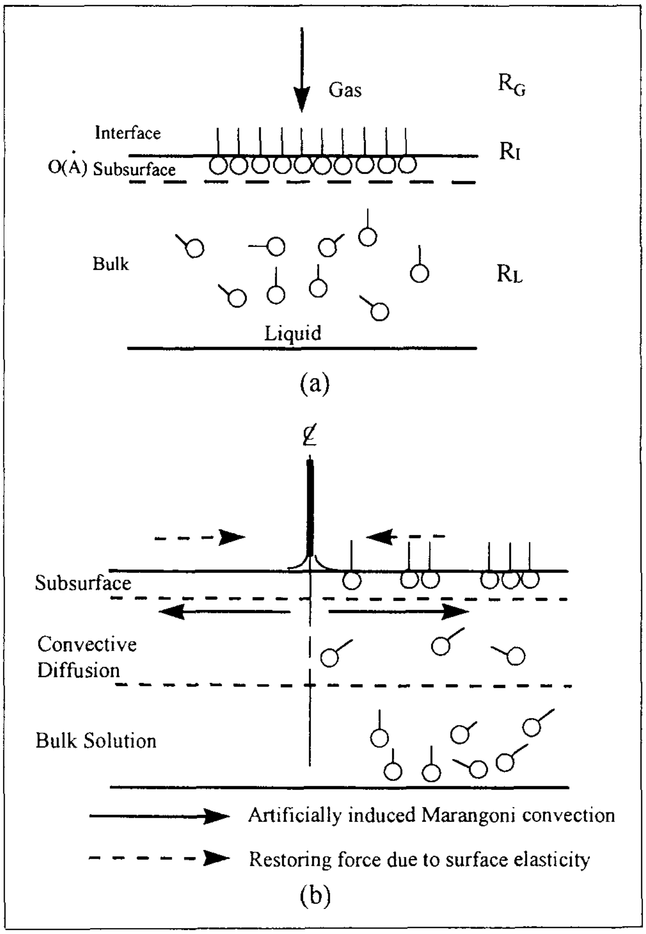

Figure 1. (a) Resistances to mass transport across interface; (b) artificially induced Marangoni convection creating surfactant concentration gradient and restoring force that opposes interfacial flows.

under the conditions of this work, that is, $R_I \equiv 0$. The barrier mechanism of the surfactant may then play no role in the increase of resistance to mass transfer. Liquid-phase hydrodynamic mechanism, therefore, should be propounded to explain the surfactant effects on interphase mass transfer in the presence of artificially induced interfacial turbulence.

Due to the positive adsorption of surfactants at the interface and consequently the depression in surface tension of supporting liquid, the reduction in the driving force for the Marangoni convection and, as a consequence, the intensity of the induced interfacial turbulence is expected. From a macroscopic concept, this effect of surfactants on liquid-phase mass-transfer coefficient can be assessed by Eq. 6 which was obtained by correlating the experimental mass-transfer coefficient data in the presence of induced interfacial turbulence and in the absence of surfactants (Lu et al., 1996).

Surfactant solutions, however, possess a unique effect which is demonstrated in Figure 1b. As the interface is stretched by the induced Marangoni convection, due to the increase of interfacial area, the surfactant molecules to be adsorbed at the interface has to be supplied from the bulk liquid solution to the interface. Since the rate of convective diffusion is finite, the concentration of the surfactant in the vicinity of the stretching interface is lower than that for the case without stretching. The adsorption on the interface is the equilibrium value corresponding to this lower concentration and is thus lower than that of the interface without such stretching. Hence, the local increase in surface tension caused by the stretching of the interface may result in a restoring force which opposes the artificially induced Marangoni convection. These adsorbed films of surfactant molecules, thus, endow the system with the surface elasticity property that distinguishes the system of surfactant solutions from that of pure liquids. An additional inhibiting effect of surfactant on induced interfacial turbulence is then expected. It should be noted, however, that the real situation is extremely complicated in that there is a competitive effect between mass transfer from the spreading liquid (such as ethanol) rich region to the peripheral interface and surfactant from the bulk of the solution to the newly created interface. Rigorous theoretical analysis of this problem is not yet available for the present.

Experimental Studies

Materials

In the preliminary experiments, aqueous ethanol solutions with various concentrations were used as the spreading liquids and tap water and distilled water were used as the supporting liquids for examining the effect of the possible trace surface active impurities in tap water on the induced interfacial turbulence. On the other hand, water soluble surfactants were deliberately introduced in the supporting liquid (distilled water) for systematic study of surfactant effects on the interfacial turbulence induced by dissolving pure ethanol (spreading liquid) at the surface.

The anionic, cationic, and nonionic surfactants used are sodium dodecyl sulfate (SDS) 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. Pure carbon dioxide was used as absorbing gas. The relevant physical properties are referred to in Lu et al. (1996, 1997).

Method

The experimental gas-liquid contacting apparatus used in this work is basically that which was constructed by Lu et al. (1996). Refer to that article for the details of the apparatus and the experimental data uncertainty. The absorption cell was formed from two concentric Plexiglas tubes which were soldered to the same base. The interior and exterior tubes have radii of 50 mm and 55 mm, and heights of 70 mm and 140 mm, respectively. Various concentrations of surfactant solutions (supporting liquids) entered the bottom of the inner tube, rose, and flowed over the brim, fell into the annular space, and left the cell. The flow rate of supporting liquid was able to be well controlled and set at 75 mL/min for all experiments in this work by an overflow liquid supply system. The spreading liquid, which generates the surface motion, was added to the gas/liquid interface through a stainless steel capillary tube of 1 mm outside diameter by a metering pump. The end of the capillary tube was located above the interface as close as possible to the surface so that the disturbance caused by the drippings of the spreading liquid could be avoided. The flow rate of spreading liquid was fixed at 1 mL/min during the periods of all experiments. Note that the flow rate of spreading liquid is relatively small as compared with that of the supporting liquid. Carbon dioxide, previously saturated with water vapor, could flow continuously through the upper half of the cell and into the atmosphere. Experiments were conducted in a room in which the temperature was controlled within 297 ± 2 K.

Surface tensions of the aqueous solutions of surfactants were also measured at a temperature of 298 K with commercial equipment (CBVP-A3 Type, Kyowa Interface Science Co., Ltd.) by the Wilhelmy plate method.

Data analysis

The absorption rate r_a was determined from the difference between the flow rates entering and leaving the cell ΔV under established steady state, and the flow rates were measured by flowmeters. The overall mass-transfer coefficient (product of average mass-transfer coefficient and surface area) was calculated from the equation

$$\overline{K_L A} = \frac{r_a}{(C_g^* - C_g)} \tag{9}$$

where C_g^* is the solubility of CO_2 in water and C_g is the concentration of CO_2 in the bulk liquid. This concentration is one-half that in the liquid leaving the cell and can be written as $C_g = r_a/(2Q)$ by a mass balance, where Q is the flow rate of supporting liquid. Assuming the gas follows ideal gas law, Eq. 9 becomes

$$\overline{K_L A} = \frac{1}{\dfrac{RTC_g^*}{P\Delta V} - \dfrac{1}{2Q}} \tag{10}$$

The pressure (P) in the absorption cell was considered to be equal to the atmospheric pressure. The experimental mass-transfer coefficient $\overline{K_L}$ can then be obtained by dividing Eq. 10 by the geometric area A.

Results and Discussion

Since surfaces are exceptionally sensitive to impurities, preliminary experiments have been carried out to measure the overall mass-transfer coefficients for CO_2-tap water and CO_2-distilled water absorption with and without the presence of artificially induced Marangoni convection. As shown in Figure 2, the experimental results for the tap water are somewhat lower than those for distilled water. However, they do not differ much from each other. (T is temperature.) This outcome is consistent with the fact that the measured surface tension value of the tap water (68.9 mN/m) is very close to that of distilled water (72.0 mN/m) at 298 K. Therefore, the possible impurities in the tap water seem to cause no significant inhibition of the induced interfacial flows. On the other hand, the theoretical prediction of the overall mass-transfer coefficients agrees qualitatively with the experimental results. However, it is seen that the theory (Eq. 5) underpredicts the overall mass-transfer coefficient values. The deviation was estimated to be less than 25%. This discrepancy is due to the inability of the theory to consider the effective interfacial area for the absorption process in the presence of induced interfacial turbulence.

As also shown in Figure 2, it is interesting to note that the curve of distilled water and the horizontal line, which indicates the $\overline{K_L}A$ value of water in the absence of induced Marangoni convection, create a region of possible interfacial turbulence inhibition by impurities. For the possible maximum inhibition, the artificially induced interfacial turbulence should be completely exhausted. In this work, the inhibition of interfacial turbulence is attempted to be realized by deliberately introducing surfactants in supporting liquid. It is noteworthy that the overall mass-transfer coefficient is possible, in theory, to be decreased from 0.89×10^{-6} to 0.25×10^{-6} (m^3/s) by the effect of surfactants for the case of the most severe Marangoni convection, which is artificially induced by dissolving pure ethanol over the distilled water surface.

Figure 3a shows surfactant effects on absorption with and without the induced interfacial turbulence. The negligibly small influence of surfactants on mass transfer in the absence of artificially induced interfacial turbulence indicates that the barrier mechanism of surfactants, as mentioned above, plays a trivial role in the interphase mass-transfer process. R_I is therefore assumed to be zero in this work. Significant effect of surfactants, however, is found, as expected, in decreasing the overall mass-transfer coefficient. 0.5 mM Triton X-100, 5 mM DTMAC, and 6 mM SDS were shown to be able to exhaust about 70% of the absorption enhancement which was caused by the artificially induced interfacial turbulence without the presence of surfactants. For further increase in surfactant concentration, no further appreciable deterioration was observed. The artificially induced interfacial turbulence can never be inhibited completely under the conditions studied in this work. This is due to the reach of the critical micelle concentration above which the surfactant molecules

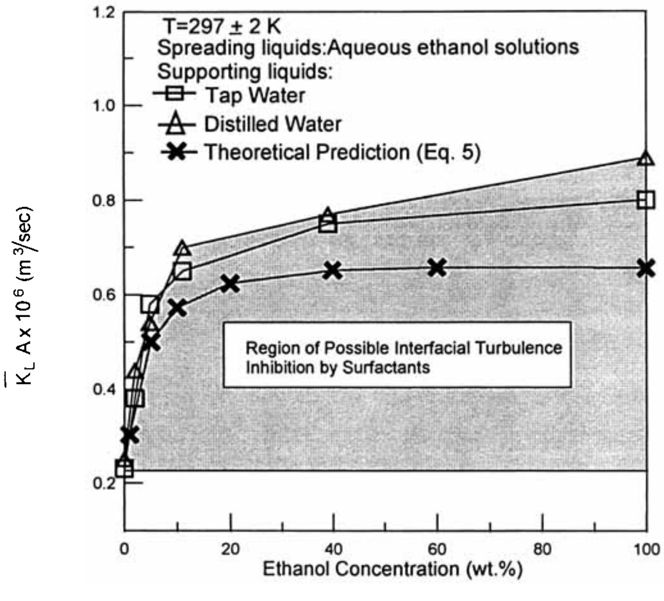

Figure 2. Enhancement of mass transfer by artificially induced interfacial turbulence and the possible interfacial turbulence inhibition by surfactants.

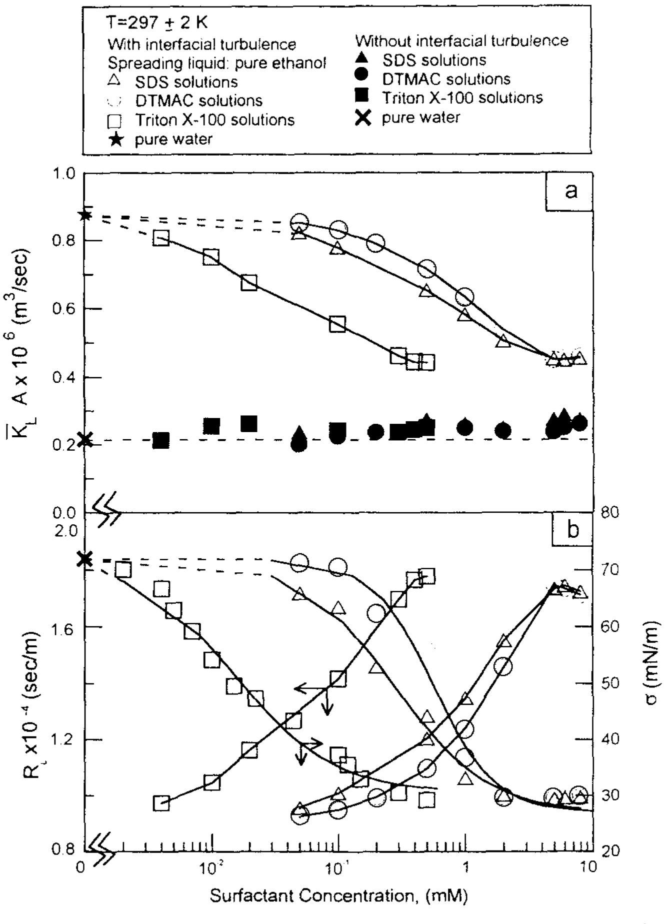

Figure 3. (a) Surfactant effects on absorption with/without artificially induced Marangoni convection; (b) liquid-phase resistance and surface tension of aqueous surfactant solutions.

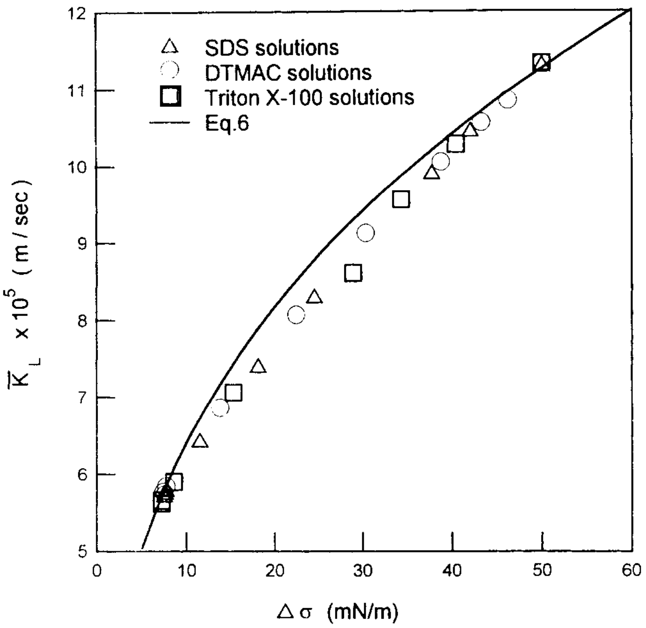

Figure 4. Experimental liquid-phase mass-transfer coefficients vs. predictions by Eq. 6.

aggregate to form micelles and the surface tension of surfactant solutions does not decrease any longer.

Since $R_G = 0$ and $R_I \cong 0$, the overall resistance R, as represented by Eq. 8, is therefore approximated by the liquid phase resistance R_L. If the overall resistance to mass transfer is defined as

$$R \cong R_L = \frac{1}{\overline{K}_{L,\mathrm{exp}}} \tag{11}$$

then the liquid-phase resistance can be evaluated from the experimental absorption results. (exp is experimental.) As shown in Figure 3b, the liquid-phase resistance increases drastically with the increase of surfactant concentration. The experimental results also reveal the fact that the effectiveness of resistance enhancement increases in the order: DTMAC < SDS < Triton X-100. Figure 3b also clearly shows that the decrease in surface tension by the addition of a surfactant and, consequently, the reduction in driving force for the Marangoni convection, results in an increase of interfacial mass-transfer resistance.

Figure 4 shows the comparison between the experimental liquid-phase mass-transfer coefficients and those predicted by Eq. 6, which tacitly assumes that the only effect of surfactants is to depress the equilibrium surface tension. Although the agreement between them is quite satisfactory, nevertheless, a small but systematic deviation from the predictions by Eq. 6 was evidenced by the experimental results. This is due to the surface elasticity which has not been taken into consideration in Eq. 6.

Conclusions

Inhibition of the artificially induced Marangoni convection, and consequently the deterioration of absorption rates, by surfactants in supporting liquid were studied systematically in this work. Experimentally determined absorption rates of CO_2 with and without induced interfacial turbulence reveal that the interfacial resistance R_I, due to the presence of surfactants is negligibly small. However, the liquid-phase resistance R_L is found to increase significantly with the increase of surfactant concentration. 0.5-mM Triton X-100, 5-mM DTMAC, and 6 mM SDS were shown to exhaust about 70% of the absorption enhancement which was caused by the artificially induced Marangoni convection without the presence of surfactants. This inhibiting effect of surfactants on mass transfer was firstly assumed to be due to the reduction in driving force for the Marangoni convection ($\Delta\sigma$) and then assessed by the previously developed dimensionless correlation Eq. 6, which tacitly assumes that the only effect of surfactants is to depress the equilibrium surface tension. Although the agreement is quite satisfactory, a small but systematic deviation from the predictions indicates that the elasticity effect of the surfactant solution surfaces may play a role in interphase mass transfer with induced interfacial turbulence. The later effect was nevertheless estimated to be less than 10% of the total resistance to mass transfer in the presence of surfactants.

Acknowledgment

This study was supported by the National Science Council of the Republic of China through grant No. NSC86-2214-E-006-005.

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Manuscript received Oct. 3, 1996, and revision received Mar. 31, 1997.