

# On the Induction Criterion of the Marangoni Convection at the Gas/Liquid Interface

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Some spreading solutes were found to be effective in enhancing the absorption rate by provoking interfacial turbulence at the gas–liquid surface. In this work, the induction criterion of the Marangoni convection is explored experimentally and theoretically by using aqueous solutions of normal alcohols and surfactants as spreading liquids. The experimental results show that aqueous solutions of methanol, ethanol, *n*-propanol, *n*-butanol, and *n*-pentanol may induce significant interfacial turbulence, and, on the other hand, aqueous solutions of *n*-hexanol, *n*-octanol, SDS, DTMAC, and Triton X-100 do not provoke noticeable interfacial turbulence. A dimensionless Marangoni number, *Ma*, based on film thickness  $\delta$  is satisfactorily developed to evaluate the potentiality of a spreading liquid to produce interfacial turbulence. The critical Marangoni number, *Ma*, *c*, for the occurrence of the Marangoni convection is also determined.

## Introduction

The importance of the Marangoni convection on heat and mass transfer processes has been recognized and, consequently, has led to many investigations over several years (Sternling and Scriven, 1959; Bakker et al., 1966, 1967; King, 1980; Berg, 1982). The Marangoni convection, which is artificially provoked by the addition of a low surface tension liquid at the gas/liquid interface, 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., 1996).

In our previous paper (Lu et al., 1996), the effectiveness of absorption enhancement by continuously dissolving aqueous solution of methanol, ethanol, and *n*-propanol at the water surface were studied theoretically (by following the model of Ruckenstein and his collaborators) and experimentally. The results revealed that mass transfer rates with artificially provoked Marangoni convection can be as much as 3–4 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

$$Sh = 0.74Ma^{0.35}Sc^{-0.35}Sc'^{0.5} \quad (1)$$

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

$$Sh = \overline{K}_L(R/D_g) \quad (2)$$

$$Ma = (\Delta\sigma R)/(\mu D_s) \quad (3)$$

$$Sc = \mu/(\rho D_s) \quad (4)$$

$$Sc' = \mu/(\rho D_g) \quad (5)$$

A problem among others which pertain to this approach for enhancing absorption rates emerges as to whether a diversity of “initiators” of the Marangoni convection is possible. Two specific questions concerned with this problem may arise from our previous study as:

1. It is known that the alcohol with higher number of carbon atoms has the higher ability of surface tension depression and, on the other hand, has the lower solubility in water. Then, what extent of the Marangoni convection can the partially soluble alcohols in a homologous series and their aqueous solutions provoke?

2. A minute quantity of surfactants is known to be able to decrease the surface tension of water drastically. Then, what should one expect if aqueous solutions of these powerful surface tension depressors are used for provoking the Marangoni convection?

Attempting to find answers to these questions is the purpose of this paper. To achieve the goals implies that the induction mechanism and induction criterion of the Marangoni convection should be elucidated. In this work, aqueous solutions of normal alcohols—including *n*-butanol, *n*-pentanol, *n*-hexanol, and *n*-octanol—and surfactants—including SDS, DTMAC, and Triton X-100—were studied experimentally and theoretically for the inducement of the Marangoni convection and their effects on absorption of CO<sub>2</sub> by water.

## Theoretical Section

**Surface Concentration and Velocity Profiles along the Interface and Liquid Phase Mass Transfer Coefficient with Artificially Provoked Marangoni Convection.** Although the theoretical analysis by Ruckenstein and his collaborators is not an accurate description of the complex flow with induced Marangoni convection, it contains, nevertheless, qualitatively correct ingredients. The details of the solution procedure for various variables in the mathematical model are referred to Lu et al. (1996). However, a brief description of it is as follows.

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The low surface tension spreading liquid is assumed to be fed at a small constant flow rate through a capillary tube with its tip somewhat above the surface of the high surface tension supporting liquid. A region of low surface tension, and hence surface tension sink, on the gas/liquid interface thus constitutes the source of the Marangoni convection. The dissolution process, then, takes place at the very leading edge of the drop. The film that begins to spread outward from the leading edge is assumed to consist of water saturated with spreading liquid. It forms a ring of small thickness,  $\delta$ , around the drop. The spreading liquid in the spreading layer dissolves into the main body of the water, and the concentration field of the spreading liquid can be described by the convective-diffusion equation. The spreading of the film is due to the surface tension gradient. From a macroscopic point of view, the gradient produces a shear stress at the interface that induces motion in the interface and the liquid layer in its vicinity. The hydrodynamics of this process may be described by the Navier–Stokes equations. The most important boundary condition is provided by the balance between the radial surface tension gradient (dependent on the concentration gradient along the interface) and the shear stress. For this reason the convective-diffusion equation must be solved together with the Navier–Stokes equations subjected to the above boundary condition.

The simplified governing equations and the corresponding boundary conditions are listed as follows (Ruckenstein et al., 1970):

$$u_i \frac{\partial C_s}{\partial r} = D_s \frac{\partial^2 C_s}{\partial y^2} \quad (6)$$

$$u_i \frac{\partial u}{\partial r} = \nu \frac{\partial^2 u}{\partial y^2} \quad (7)$$

The boundary conditions are

$$\begin{aligned} r &= r_0, \quad u = 0, \quad \text{and} \\ C_s &= C_{s0}, \quad 0 < y < \delta \\ C_s &= 0, \quad \delta < y < \infty \end{aligned} \quad (8)$$

$$y = 0, \quad \frac{\partial u}{\partial y} = -\frac{1}{\mu} \frac{\partial \sigma}{\partial r}, \quad \frac{\partial C_s}{\partial y} = 0 \quad (9)$$

$$y \rightarrow \infty, \quad u = 0; \quad C_s = 0 \quad (10)$$

Consequently the distributions of concentration and velocity along the interface can be obtained.

concentration profile:

$$C_s = \frac{C_{s0}}{2} \left[ \operatorname{erf} \left( \frac{\delta - y}{2\sqrt{D_s t}} \right) + \operatorname{erf} \left( \frac{\delta + y}{2\sqrt{D_s t}} \right) \right] \quad (11)$$

velocity profile:

$$u = (\nu/\pi)^{1/2} \int_0^{tF(t-\lambda)} \frac{e^{-y^2/4\nu\lambda}}{u(t-\lambda)} \frac{d\lambda}{\lambda^{1/2}} \quad (12)$$

where

$$t = \int_{r_0}^r \frac{dr}{u_i} \quad (13)$$

$$F(t) = -\frac{1}{\mu} \frac{d\sigma}{dC_{si}} \frac{C_{s0}\delta}{2\sqrt{\pi D_s}} t^{-3/2} e^{-\delta^2/4D_s t} \quad (14)$$

It should be noted that surface concentration ( $C_{si}$ ) and surface velocity ( $u_i$ ) profiles can be obtained by setting  $y = 0$  in eqs 11 and 12.

The mathematical description of the surface velocity field produced by a surface tension sink also opened the possibility of calculating the mass transfer coefficient through such moving interfaces. The simplified convective-diffusion equation and corresponding boundary conditions for the absorption of gas solute into water have the forms

$$u \frac{\partial C_g}{\partial r} - \frac{y}{r} \frac{\partial(ur)}{\partial r} \frac{\partial C_g}{\partial y} = D_g \frac{\partial^2 C_g}{\partial y^2} \quad (15)$$

$$y = 0, \quad C_g = C_{gi} \quad (16)$$

$$y = \infty, \quad C_g = C_{g0} \quad (17)$$

The solutions for above equations were obtained by Smigelschi et al. (1969) as

local liquid phase mass transfer coefficient:

$$K_L = \sqrt{\frac{D_g}{\pi}} \frac{u_i r}{(\int_{r_0}^r u_i r^2 dr)^{1/2}} \quad (18)$$

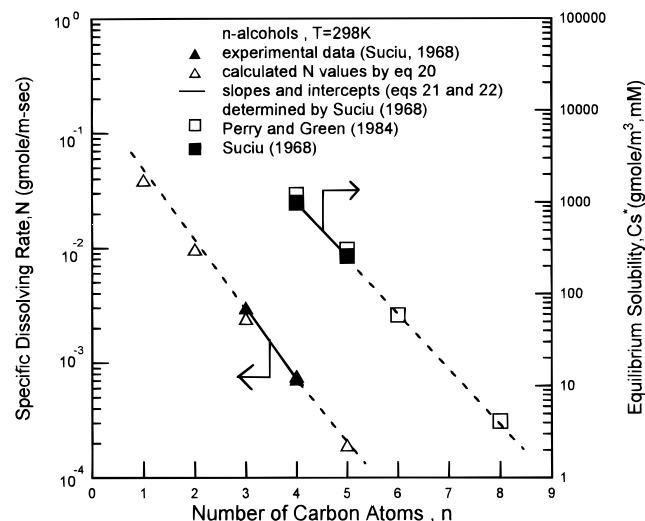
average mass transfer coefficient:

$$\bar{K}_L = \frac{\int_{r_0}^R 2K_L r dr}{R^2 - r_0^2} = \frac{\int_0^R 2K_L r dr}{R^2} \quad (19)$$

**Dissolving Rate and Film Thickness ( $\delta$ ) of a Spreading Solute.** The quasisteady dissolving of a thin film fed continuously from a point source on a flat water surface was examined by Suci et al. (1967). They found that the film had a definite contour. And for some organic substances, the diameter of the film is dependent on certain properties of the liquid–liquid system and increases linearly with the flow rate. It should be noted that the linear dependence of film contour diameter on flow rate implies that rapid dissolution takes place mainly along the film contour rather than beneath the film-forming liquid. The Marangoni effect, of course, provides an explanation for it. The slope of the best straight line obtained when representing the flow rate versus film diameter (at small flow rates) for a given dissolving substance was termed specific dissolving rate  $N$  ((g mol)/(m s)) and studied further by Suci (1968) for the mass transfer equation:

$$N = \beta \Delta C_s \quad (20)$$

where  $\beta$  ( $\text{m}^2/\text{s}$ ) is the mass transfer coefficient across the contour and  $\Delta C_s$  ((g mol)/ $\text{m}^3$ ) is the driving force. For the cases of pure supporting liquid,  $\Delta C_s$  equals  $C_s^*$ , the equilibrium solubility of the partially soluble spreading solute in the supporting liquid, or  $C_{s0}$ , the initial concentration of the aqueous spreading liquid.



**Figure 1.** Dependence of specific dissolving rate and equilibrium solubility on the number of carbon atoms in the molecule for normal alcohols.

As shown in Figure 1, Suci (1968) correlated the variation of the equilibrium solubility and specific dissolving rate with the number of carbon atoms in the molecule,  $n$ , by the following equations

$$\log C_s^* = \log C_0 - An \quad (21)$$

$$\log N = \log N_0 - Bn \quad (22)$$

where  $\log C_0$ ,  $\log N_0$ , and  $A$ ,  $B$  are the intercepts and the slopes of the corresponding straight lines, respectively. By eliminating  $n$  and taking  $A/B = 1$ , one obtained

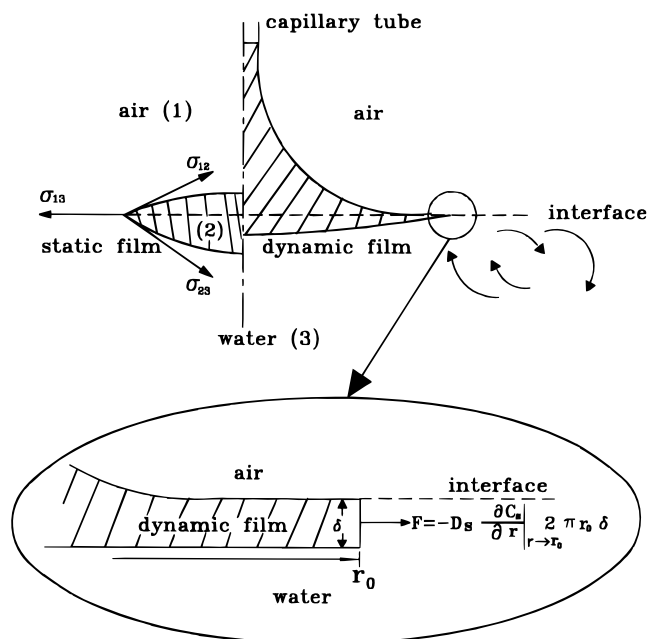
$$\frac{C_s^*}{C_0} - \left(\frac{N}{N_0}\right)^{A/B} \approx \frac{N}{N_0} \quad (23)$$

Equation 20 then yields

$$\beta = \frac{N_0}{C_0} \quad (24)$$

From experimental data of  $C_0$  and  $N_0$ ,  $\beta = 6.32 \times 10^{-7} \text{ m}^2/\text{s}$  was found for  $n$ -propanol and  $n$ -butanol. Since  $C_0$  and  $N_0$  are constants for the homologous series, Suci (1968) came to the conclusion that in the condition of the experiment, the mass transfer coefficient  $\beta$  depends only on the homologous series. It should be noted that the  $\beta$  value mentioned above is valid only in the conditions where the Marangoni convection is present. The specific dissolving rates of methanol, ethanol,  $n$ -propanol,  $n$ -butanol, and  $n$ -pentanol were calculated by eq 20 with  $\beta = 6.32 \times 10^{-7} \text{ m}^2/\text{s}$  and are shown also in Figure 1. The relationship between  $N$  and  $n$  seems to be in good agreement with what Suci (1968) observed experimentally.

The actual structure of dissolving thin liquid film was investigated experimentally by Suci et al. (1969) and is shown schematically in Figure 2. Owing to the Marangoni effect, the interfaces are subjected to stretching, and for this reason the structure of a dynamic film is different from that of a static one. Three regions of film thickness were noted. In the first region (near the capillary tip) the thickness decreases rapidly. It becomes practically constant in the middle region and

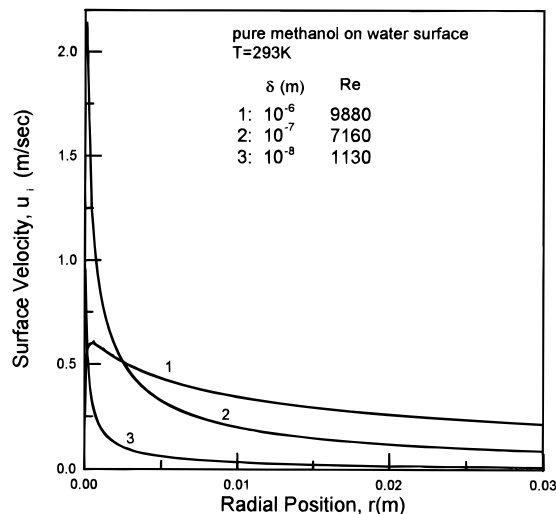


**Figure 2.** Schematic diagram of the structure of dissolving liquid thin film on the water surface.

decreases again gradually near the film contour in the third (border) region.

As also shown in Figure 2, however, a simplified model was proposed to approximate the structure of the dissolving film in the vicinity of the border. It assumes that a cylindrical thin film of uniform thickness is formed at the leading edge. This thickness in fact constitutes important boundary conditions of the mathematical model by Ruckenstein et al. (1970). As dictated in eq 8, finite thickness and thermodynamic equilibrium are assumed. The former assumption is necessary since otherwise the velocity at the leading edge of the drop would have an infinite value. The thickness  $\delta$  is of the order of magnitude of the zone in which the surface forces are acting. Thermodynamic equilibrium assumes that at the boundary the concentration of the spreading solute is maintained at the saturation concentration (equilibrium solubility),  $C_s^*$ , for partially soluble alcohol or at the initial concentration,  $C_{s0}$ , for aqueous solution of alcohol and surfactant. This latter assumption, however, may fail to be fulfilled for slightly soluble solutes and surfactant solutions and will be discussed later. From the measured solute flow rate, lengths of the contour of the surface drops, and radial surface velocity immediately outside the contour,  $\delta$  was estimated to be about  $10^{-6} \text{ m}$  (Suci et al., 1970). On the other hand, fitting the experimental velocity distributions with the theoretical ones yielded information concerning the thickness  $\delta$  of the spreading film. The values of  $\delta$  thus obtained were found to be in the range of  $(0.64-1.35) \times 10^{-6} \text{ m}$  (Ruckenstein et al., 1970).

In order to elucidate the role the thickness  $\delta$  may play in the induction process of the Marangoni convection, a parametric study of it is conducted for the case of pure methanol as a spreading liquid on water surface. As shown in Figure 3, the theoretical velocity distributions reveal that the velocity increases rapidly near the leading edge, attains a maximum, and then decreases slower. The smaller the value of  $\delta$ , the more confined the region at the interface, on which the interfacial turbulence prevails. As also shown in Figure 3, the



**Figure 3.** Effect of film thickness on surface velocity and the corresponding Reynolds number.

Reynolds numbers of interfacial turbulence defined as

$$Re = \frac{\rho \int_0^R u_i dr}{\mu} \quad (25)$$

In this work, a different approach for estimating  $\delta$  is used as follows. The mass balance of the dissolving solute between feed and dissolution rates yields

$$F = -D_s \left( \frac{\partial C_s}{\partial r} \right)_{r=r_0} 2\pi r_0 \delta \quad (26)$$

and then the specific dissolving rate becomes

$$N \equiv \frac{F}{2r_0} = -D_s \left( \frac{\partial C_s}{\partial r} \right)_{r=r_0} \pi \delta \quad (27)$$

Substituting eq 20 in eq 27, one obtains

$$\delta = \frac{\beta \Delta C_s}{\left[ -D_s \left( \frac{\partial C_s}{\partial r} \right)_{r=r_0} \right] \pi} \quad (28)$$

Thickness  $\delta$  for a specific spreading liquid, which induces the Marangoni convection, thus can be estimated by eq 28 with known mass transfer coefficient across the contour  $\beta$  and concentration profile  $C_s$ .

**Induction Criterion of the Marangoni Convection.** In order that a simple induction criterion of the Marangoni convection can be found, a dimensional analysis of the equations of change and the corresponding boundary conditions (eqs 6–10) has been done as follows. For the problem under consideration,  $\delta$  and  $C_{s0}$  were selected as the characteristic length and concentration, respectively. Once this choice has been made, the following dimensionless variables and equations can then be defined:

$$\bar{r} = \frac{r}{\delta}, \quad \bar{y} = \frac{y}{\delta}, \quad \bar{C}_s = \frac{C_s}{C_{s0}}, \quad \bar{u} = \frac{u\delta}{D_s} \quad (29)$$

$$\frac{\partial \bar{C}_s}{\partial \bar{r}} = (\bar{u}_i)^{-1} \left( \frac{\partial^2 \bar{C}_s}{\partial \bar{y}^2} \right) \quad (30)$$

$$\frac{\partial \bar{u}}{\partial \bar{r}} = (\bar{u}_i)^{-1} Sc \left( \frac{\partial^2 \bar{u}}{\partial \bar{y}^2} \right) \quad (31)$$

$$\bar{r} = \frac{r_0}{\delta}, \quad \bar{u} = 0, \quad \text{and}$$

$$\bar{C}_s = 1, \quad 0 < \bar{y} < 1$$

$$\bar{C}_s = 0, \quad 1 < \bar{y} < \infty \quad (32)$$

$$\bar{y} = 0, \quad \frac{\partial \bar{u}}{\partial \bar{y}} = - \left[ \frac{\left( C_{s0} \frac{\partial \sigma}{\partial C_s} \right) \delta}{\mu D_s} \right] \left( \frac{\partial \bar{C}_s}{\partial \bar{r}} \right)$$

$$\frac{\partial \bar{C}_s}{\partial \bar{y}} = 0 \quad (33)$$

$$\bar{y} \rightarrow \infty, \quad \bar{u} = 0, \quad \bar{C}_s = 0 \quad (34)$$

It is noteworthy that one of the boundary conditions (eq 33) results from the Marangoni effect. A Marangoni number based on thickness  $\delta$  is then proposed as

$$Ma = \frac{\Delta \sigma \delta}{\mu D_s} \quad (35)$$

where  $\Delta \sigma$  is the total surface tension difference between those of spreading and supporting liquids.

It should be noted that the Marangoni number defined by eq 35 is dimensionless and is distinguished from the Marangoni number (eq 3) by replacing  $R$ , the radius of gas–liquid surface, with  $\delta$ , the film thickness of the spreading liquid. The  $\delta$ -based Marangoni number then allows one to evaluate the ability of inducing the Marangoni convection by a spreading liquid. While  $\Delta \sigma$ ,  $\mu$  and  $D_s$  can be obtained straightforwardly, the acquirement of  $\delta$ , however, needs much effort. In this work, for the spreading liquids which provoke the Marangoni convection, eq 28 associated with eq 11 is used to calculate the film thickness for the system by trial-and-error. For those which do not provoke the Marangoni convection, experimental absorption mass transfer coefficients are fitted with the theoretical ones (eq 19) to get the  $\delta$  values.

## Experimental Section

The experimental gas–liquid contacting apparatus used in this work is basically that which was constructed by Lu et al. (1996). The readers are referred to that paper for the details of the apparatus and the experimental data uncertainty. The absorption cell was formed from two concentric Plexiglass tubes which were soldered to the same base. The interior and exterior tubes have radii of 50 and 55 mm and heights of 70 and 140 mm, respectively. Distilled water (supporting liquid) with a specific conductance of  $7.26 \pm 0.5$  ( $\mu\Omega^{-1}$ )/cm centered the bottom of the inner tube, risen, 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 system. The spreading liquids, which generate the surface motion, were 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

**Table 1. Physical Properties of the Liquids at 293 K**

diffusivity in pure water <sup>a-e</sup> (m <sup>2</sup> /s) × 10 <sup>9</sup>	methanol	1.45
	ethanol	1.15
	<i>n</i> -propanol	0.98
	<i>n</i> -butanol	0.97
	<i>n</i> -pentanol	0.79
	<i>n</i> -hexanol	0.57
	<i>n</i> -octanol	0.49
	SDS	0.5
	DTMAC	0.5
	Triton X-100	0.26
	CO <sub>2</sub>	1.92
viscosity (kg/(m s)) × 10 <sup>4</sup> <sup>f</sup>	pure water	9.93
density (kg/m <sup>3</sup> ) <sup>f</sup>	pure water	998.2
solubility in pure water <sup>a,f</sup> ((g mol)/m <sup>3</sup> )	CO <sub>2</sub>	33.6
	<i>n</i> -butanol	1214
	<i>n</i> -pentanol	306.3
	<i>n</i> -hexanol	58.7
	<i>n</i> -octanol	4.15
surface tension (mN/m) and parameters in Szyszkowski equation: <sup>g</sup>	pure methanol	24.3
$\sigma = \sigma_w - a \ln(1 + bC_s)$	pure ethanol	23.8
$\sigma_w = 72.2$	pure <i>n</i> -propanol	24
$C_s$ in mM	pure <i>n</i> -butanol	24.5
	pure <i>n</i> -pentanol	26.4
	pure <i>n</i> -hexanol	26.8
	pure <i>n</i> -octanol	31.1
	<i>n</i> -butanol solution	$a = 14.62, b = 0.021$
	<i>n</i> -pentanol solution	$a = 17.05, b = 0.0602$
	<i>n</i> -hexanol solution	$a = 15.86, b = 0.19$
	<i>n</i> -octanol solution	$a = 15.59, b = 2.4$
	SDS solution	$a = 9.826, b = 24.74$
	DTMAC solution	$a = 14.11, b = 6.04$
	Triton X-100 solution	$a = 8.956, b = 473.5$

<sup>a</sup> Defay and Hommelen (1959). <sup>b</sup> Hayduk and Laudie (1974). <sup>c</sup> Lin et al. (1990). <sup>d</sup> Vazquez et al. (1990). <sup>e</sup> Vazquez et al. (1993). <sup>f</sup> Perry and Green (1984). <sup>g</sup> Reid et al. (1988).

surface so that the disturbance caused by the drippings of spreading liquid could be avoided. The flow rate of spreading liquid was fixed at 1 mL/min during the periods of all experiments. It is to be noted that the flow rate of spreading liquid is relatively small as compared with that of supporting liquid. Pure normal alcohols and their aqueous solutions with concentrations up to the equilibrium solubilities were used as the spreading liquids. Aqueous solutions of water soluble surfactants with various concentrations were also used as the other type of spreading liquids. The surfactants used are sodium dodecyl sulfate (SDS), dodecyl trimethyl ammonium chloride (DTMAC), and polyoxy-ethylated *tert*-octylphenol (Triton X-100, CH<sub>3</sub>C(CH<sub>3</sub>)<sub>2</sub>-CH<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>(OCH<sub>2</sub>CH<sub>2</sub>)<sub>*n*</sub>OH, *n* = 9–10). 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 24 ± 2 °C.

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

$$\overline{K_L}A = \frac{r_a}{(C_g^* - C_g)} \quad (36)$$

where  $C_g^*$  is the solubility of CO<sub>2</sub> in water and  $C_g$  is the concentration of CO<sub>2</sub> in the bulk liquid. This concentration is one-half of 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 the ideal gas law, eq 30

becomes

$$\overline{K_L}A = \frac{1}{\frac{RTC_g^*}{P\Delta V} - \frac{1}{2Q}} \quad (37)$$

The pressure in the absorption cell was considered to be equal to atmospheric pressure.

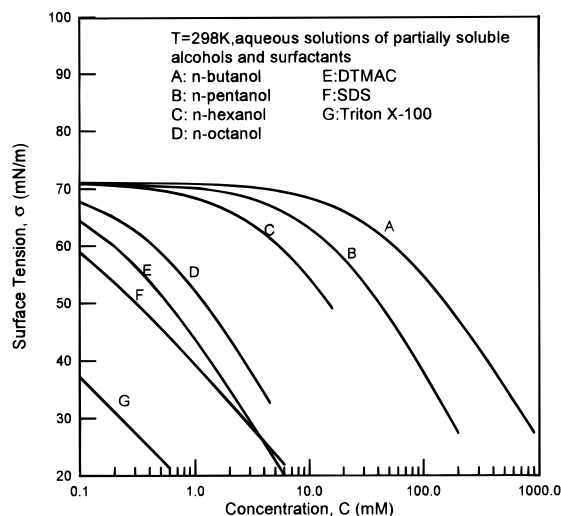
Surface tensions of the aqueous solutions of partially soluble alcohols and surfactants were measured at room temperature (24 ± 2 °C) with commercial equipment (CBVP-A3 Type, Kyowa Interface Science Co., Ltd.) by the Wilhelmy plate method.

## Results and Discussion

**Physical Properties.** The physical properties that are important for this study are the diffusivity ( $D_s$ ), viscosity ( $\mu$ ), density ( $\rho$ ), equilibrium solubility ( $C_s^*$ ), and surface tension ( $\sigma$ ). They are summarized in Table 1. The experimentally measured surface tension data of the aqueous solutions of partially soluble alcohols and surfactants are correlated by the Szyszkowski equation (Reid et al., 1988):

$$\sigma = \sigma_w - a \ln(1 + bC_s) \quad (38)$$

The fitted parameters  $a$  and  $b$  are also shown in Table 1 for the aqueous solutions studied. Figure 4 shows the corresponding variations of surface tension with concentration.



**Figure 4.** Surface tension with respect to concentration for aqueous solutions of partially soluble normal alcohols and surfactants.

**Gas Absorption Enhancement.** The experimental overall mass transfer coefficients ( $\overline{K_L}A$ ) resulting from the addition of spreading liquids at the gas-liquid surface reveal that pure *n*-butanol, *n*-pentanol, and their aqueous solutions may induce severe interfacial turbulence and enhance the mass transfer rate significantly. It should be noted that this behavior is similar to that caused by the addition of aqueous solutions of methanol, ethanol, and *n*-propanol as reported in Lu et al. (1996). The addition of *n*-hexanol, *n*-octanol, aqueous solutions of them, and aqueous solutions of SDS, DTMAC, Triton X-100, however, exhibits unnoted effect on mass transfer across the gas-liquid interface.

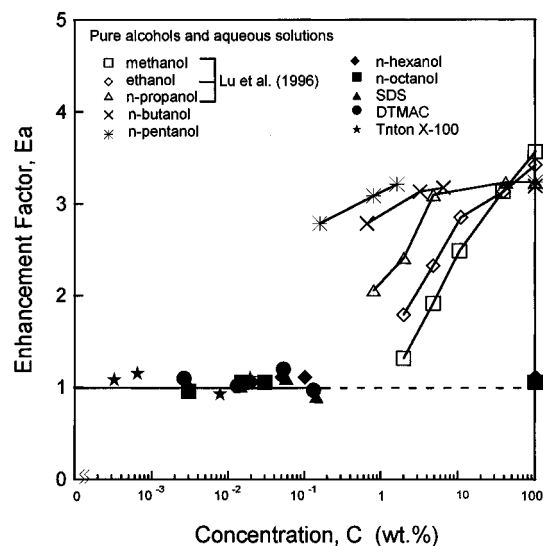
An enhancement factor,  $E_a$ , is defined as the ratio of the experimental overall mass transfer coefficient with artificially induced interfacial turbulence to that without it:

$$E_a = \frac{(\overline{K_L}A)_{\text{with induced turbulence}}}{(\overline{K_L}A)_{\text{without induced turbulence}}} \quad (39)$$

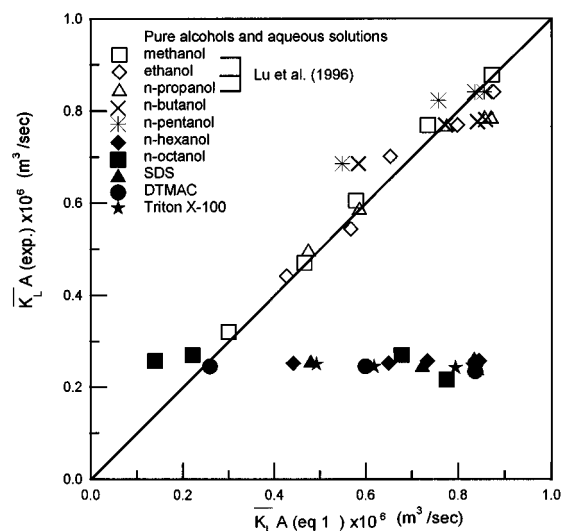
As shown in Figure 5, pure *n*-butanol, *n*-pentanol, and aqueous solutions of them verify themselves as effective absorption enhancement agents by inducing the Marangoni convection. On the other hand, neither the pure normal alcohols with a number of carbon atoms in the molecule more than five (i.e. for *n*-hexanol and *n*-octanol) nor the aqueous solutions of them succeed in inducing interfacial turbulence. Aqueous solutions of SDS, DTMAC, and Triton X-100 are also found to fail in inducing interfacial turbulence.

As shown in Figure 6, the dimensionless equation (eq 1), which was proposed for correlating the experimental data of the aqueous solutions of methanol, ethanol, and *n*-propanol in the presence of interfacial turbulence, is found to also satisfactorily describe the data of *n*-butanol, *n*-pentanol, and aqueous solutions of them. This correlation, of course, fails to predict the ill absorption enhancement by pure *n*-hexanol, *n*-octanol, and aqueous solutions of these two alcohols and all surfactants used in this work. Obviously, the interesting phenomena mentioned above are worthy of receiving further study.

**Film Thickness ( $\delta$ ) of a Spreading Solute.** For the spreading liquids which provoke the Marangoni



**Figure 5.** Absorption enhancement caused by the addition of pure alcohols and aqueous solutions.

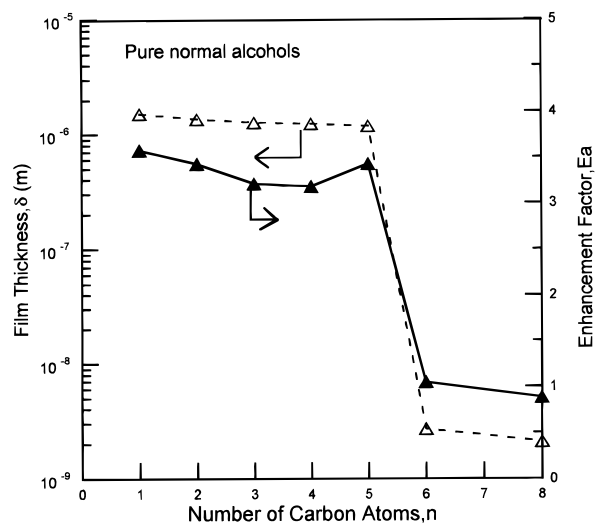


**Figure 6.** Comparison between experimental and calculated (eq 1) overall mass transfer coefficients.

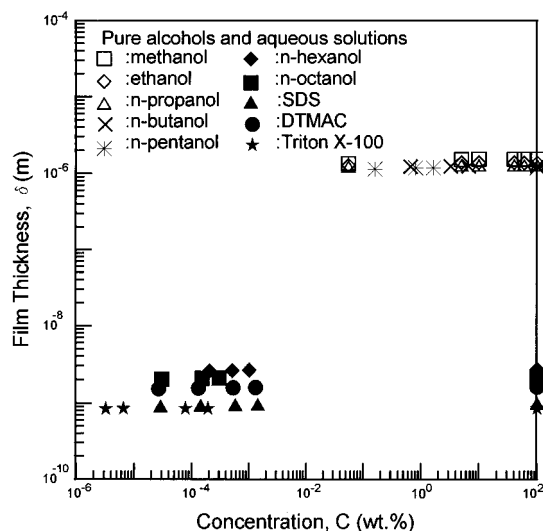
convection, it is proposed that the film thickness ( $\delta$ ) can be estimated by using eqs 11 and 28 with a known  $\beta$  value of  $6.32 \times 10^{-7} \text{ m}^2/\text{s}$  for normal alcohols. Film thickness values for pure methanol through *n*-pentanol were thus calculated and are shown in Figure 7. The results reveal that they do not differ much with one another and are around the value of  $1.3 \times 10^{-6} \text{ m}$ . This is consistent with the reported values for  $\delta$  by Suciu et al. (1970) and by Ruckenstein et al. (1970) as mentioned before. Particularly, this does also verify the appropriateness of using a  $\delta$  value of  $1.35 \times 10^{-6} \text{ m}$  for methanol, ethanol, and *n*-propanol in predicting the induced Marangoni convection (Lu et al., 1996).

For those which do not provoke the Marangoni convection, the above approach is not adequate. Hence, the film thickness values of *n*-hexanol and *n*-octanol should be estimated by fitting the experimental mass transfer coefficients with the theoretical predictions (eq 19). The results show that  $\delta$  values for *n*-hexanol and *n*-octanol are about 3 orders of magnitude smaller than those for methanol through *n*-pentanol.

The drastic reduction in  $\delta$  values is explained by the decrease in equilibrium solubility with increase of carbon atom numbers in the molecule of normal alcohols. As shown in Figure 1, the much lower equilibrium



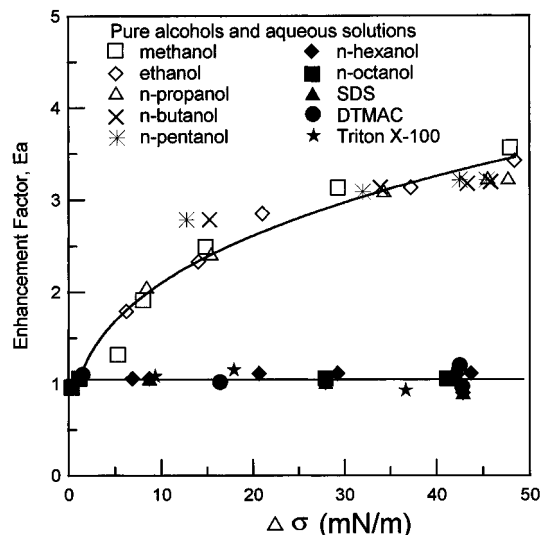
**Figure 7.** Film thickness and enhancement factor with respect to the number of carbon atoms in the molecule for pure normal alcohols.



**Figure 8.** Film thicknesses of pure alcohols and aqueous solutions with various concentrations.

solubilities of *n*-hexanol and *n*-octanol may result in lower enough dissolving rates of them in water, and such that the thermodynamic equilibrium at the boundary (eq 8) as assumed by the model of Ruckenstein and his collaborators may then not be satisfied. The  $\delta$  values obtained in this way may be deemed as those for the "pseudoequilibrium" film thickness by which the assumption of thermodynamic equilibrium at the boundary is still effective. As has been shown in Figure 3,  $\delta$  plays an important role in determining the surface velocity field and consequently the effectiveness of absorption enhancement. The similarity between  $\delta$  versus  $n$  and  $E_a$  versus  $n$  relations (as shown in Figure 7) strongly indicates this point.

Figure 8 shows the estimated film thickness for all spreading liquids studied in this work. It is interesting to note that they can roughly be classified into two distinct categories:  $10^{-6}$  and  $10^{-9}$  m. The actual figures of them range from  $1.13 \times 10^{-6}$  to  $1.53 \times 10^{-6}$  m for methanol through *n*-pentanol and  $0.84 \times 10^{-9}$  to  $2.61 \times 10^{-9}$  (m) for *n*-hexanol, *n*-octanol, and surfactants. The former value of film thickness is consistent with that estimated by Suci et al. (1970) and Ruckenstein et al. (1970) and is of the order of magnitude of the zone



**Figure 9.** Dependence of enhancement factor on the surface tension difference between spreading liquids and supporting liquid (water).

in which the surface forces are acting and bestow the potential on a spreading liquid for provoking the Marangoni convection. The latter value of film thickness, however, is too small to provoke significant turbulence at the surface. The small values of film thickness for aqueous solutions of *n*-hexanol, *n*-octanol, and surfactants imply that the solute molecules in the dilute solutions cannot diffuse fast enough to the boundary to maintain the thermodynamic equilibrium as assumed by the model with large enough film thickness.

**Critical Marangoni Number for the Induction of the Marangoni Convection.** The determination of the Marangoni number, as defined by eq 35, calls for the knowledge of  $\delta$ ,  $\Delta\sigma$ ,  $\mu$ , and  $D_s$ .

Although  $\delta$  values cannot be known a priori, the results of this work seem to support the argument that normal alcohols with less than six carbon atoms in the molecule (equilibrium solubility  $> 58.7$  (g mol)/m<sup>3</sup>,  $C_s^*$  of *n*-hexanol) and aqueous solutions of them would possess roughly a film thickness of  $10^{-6}$  m and may provoke the interfacial turbulence. On the other hand, normal alcohols with higher or equal to six carbon atoms in the molecule (equilibrium solubility  $\leq 58.7$  (g mol)/m<sup>3</sup>) would possess roughly a much smaller film thickness of  $10^{-9}$  m and are destined to never provoke the interfacial turbulence. Of course, the inability to induce the interfacial turbulence by the aqueous solutions of them and surfactants is due to the same reasoning of possessing a much smaller film thickness.

So long as the film thickness for a spreading liquid can be estimated, the other key property of the spreading liquid which determines the effectiveness of provoking the Marangoni convection is the surface tension difference between the spreading and supporting liquids  $\Delta\sigma$ . Figure 9 shows values of  $\Delta\sigma$  for all spreading liquids studied in this work. The values range from 0.3 to 48.4 mN/m. Aqueous solutions of methanol through *n*-pentanol may enhance the absorption rates considerably. As shown in Figure 9, the enhancement factor depends on the value of  $\Delta\sigma$ . Pure *n*-hexanol, pure *n*-octanol, and aqueous solutions of them and surfactants, however, cannot provoke significant interfacial turbulence regardless of the large values of  $\Delta\sigma$  they may have.

In this work, the viscosity  $\mu$  of the supporting liquid is that of water and has the value of  $9.93 \times 10^{-4}$  kg/m

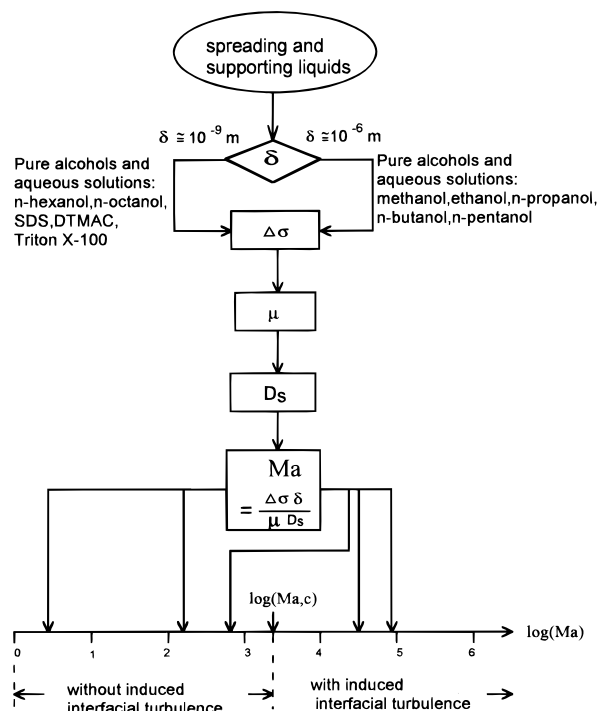


Figure 10. Calculation procedure for the Marangoni number.

s, and the diffusivities  $D_s$  of the spreading solutes in water range from  $0.26 \times 10^{-9}$  to  $1.45 \times 10^{-9}$  m<sup>2</sup>/s. A flow chart showing the evaluation procedure of the Marangoni numbers can then be constructed as shown in Figure 10. Table 2 shows the calculated values of the Marangoni number for various spreading liquids on the water surface.

As also shown in Figure 10, pure alcohols and aqueous solutions of methanol through *n*-pentanol may result in indexes above the threshold of inducing interfacial turbulence. On the other hand, the Marangoni number of pure alcohols and aqueous solutions of *n*-hexanol, *n*-octanol, SDS, DTMAC, and Triton X-100 are below the threshold value, and no interfacial turbulence can be induced. This threshold value can be termed the critical Marangoni number,  $Ma, c$ . Figure 11 shows that

$$Ma, c = 2500 \quad \text{or} \quad \log(Ma, c) = 3.4 \quad (40)$$

and the relationship between enhancement factor  $E_a$  and  $\log(Ma)$  can be correlated as

$$E_a = -4.82 + 1.72 \log(Ma) \quad \text{for} \quad \log(Ma) > 3.4 \quad (41)$$

$$E_a = 1 \quad \text{for} \quad \log(Ma) < 3.4 \quad (42)$$

Equation 40 is a criterion to determine the occurrence

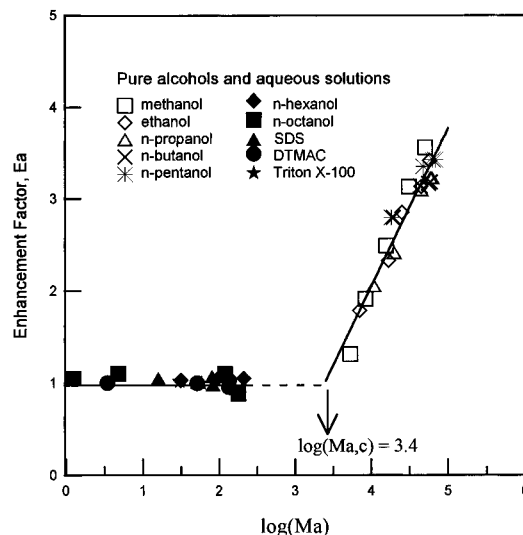


Figure 11. Dependence of enhancement factor on the Marangoni number and the determined critical Marangoni number.

of the Marangoni convection, and eq 41 provides a different means for predicting the effect of the Marangoni convection on absorption.

## Conclusions

The experimental results show that aqueous solutions of methanol, ethanol, *n*-propanol, *n*-butanol, and *n*-pentanol may induce significant interfacial turbulence and consequently enhance the absorption rate considerably. On the other hand, aqueous solutions of *n*-hexanol, *n*-octanol, SDS, DTMAC, and Triton X-100 do not provoke noticeable interfacial turbulence.

In order that a simple induction criterion of the Marangoni convection can be found, a dimensionless Marangoni number based on thickness  $\delta$ ,  $Ma = (\Delta\sigma\delta)/(\mu D_s)$  as defined by eq 35, is proposed to evaluate the ability of inducing the Marangoni convection by a spreading liquid. While  $\Delta\sigma$ ,  $\mu$ , and  $D_s$  can be obtained straightforwardly,  $\delta$  values were estimated in this work either by eq 28 associated with eq 11 for spreading liquids which induce the Marangoni convection or by fitting the experimental absorption mass transfer coefficients with the theoretical ones for those which do not provoke the Marangoni convection. The analyses result in two distinct categories of film thickness:  $10^{-6}$  and  $10^{-9}$  m. The much smaller value of the "pseudoequilibrium" film thickness, and consequently unnoted interfacial turbulence, is caused by invalidation of the thermodynamic equilibrium at the boundary as assumed by the theoretical model. This invalidation is either due to the much lower equilibrium solubility

Table 2. Ranges of Values of the Marangoni Number,  $Ma$ , Based on Thickness  $\delta$  for Various Spreading Liquids on the Water Surface,  $T = 24 \pm 2$  °C

spreading liquids	concentration	$Ma$	$\log(Ma)$	enhancement factor ( $E_a$ )
methanol	2–100 wt %	5301–50516	3.72–4.70	1.31–3.58 <sup>a</sup>
ethanol	2–100 wt %	7058–57832	3.85–4.76	1.80–3.43 <sup>a</sup>
<i>n</i> -propanol	0.8–100 wt %	10790–62349	4.03–4.79	2.79–3.18 <sup>a</sup>
<i>n</i> -butanol	0.7–6.58 wt %, pure	19445–58936	4.29–4.77	2.80–3.18
<i>n</i> -pentanol	0.2–1.63 wt %, pure	18389–68422	4.26–4.83	2.80–3.43
<i>n</i> -hexanol	2.0–10 mM, pure	31–208	1.49–2.32	1.03–1.05
<i>n</i> -octanol	0.2–2.3 mM, pure	1–177	0.093–2.25	0.88–1.10
SDS	0.1–5 mM	16–83	1.20–1.92	0.98–1.07
DTMAC	0.1–5 mM	3–135	0.54–2.13	0.96–1.02
Triton X-100	0.005–0.3 mM	30–137	1.48–2.14	0.98–1.02

<sup>a</sup> Lu et al. (1996).



( $\leq 58.7$  (g mol)/m<sup>3</sup>), and hence the much lower dissolving rate, of *n*-hexanol and *n*-octanol in water or due to the slowness of molecular diffusion in dilute aqueous solutions of *n*-hexanol, *n*-octanol, SDS, DTMAC, and Triton X-100. The results reveal that the values of  $\log(Ma)$  range from 0 to 4.83 for the spreading liquids studied in this work, and the value of the critical Marangoni number,  $Ma_c$ , for the occurrence of the Marangoni convection is determined to be 2500 (eq 40).

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## Nomenclature

$a, b$  = constants in Szyskowski equation  
 $A$  = interfacial area, m<sup>2</sup>; constant in eq 21  
 $B$  = constant in eq 22  
 $C_s$  = concentration of spreading solute in liquid phase, wt %, (g mol)/m<sup>3</sup>  
 $C_s^*$  = equilibrium solubility of partially soluble solute in water, (g mol)/m<sup>3</sup>  
 $C_g$  = concentration of gas solute in liquid phase, (g mol)/m<sup>3</sup>  
 $C_g^*$  = equilibrium solubility of gas solute in water, (g mol)/m<sup>3</sup>  
 $C_0$  = constant in eq 21  
 $D_s$  = diffusivity of spreading solute in liquid phase, m<sup>2</sup>/s  
 $D_g$  = diffusivity of gas solute in liquid phase, m<sup>2</sup>/s  
 $E_a$  = enhancement factor  
 $F$  = feed rate of spreading solute, (g mol)/s  
 $K$  = local mass transfer coefficient, m/s  
 $\bar{K}$  = average mass transfer coefficient, m/s  
 $Ma$  = Marangoni number,  $(\Delta\sigma R)/(\mu D_s)$ , eq 3;  $(\Delta\sigma\delta)/(\mu D_s)$ , eq 35  
 $N$  = specific dissolving rate, (g mol)/(m s)  
 $N_0$  = constant in eq 22  
 $n$  = number of carbon atoms in the molecule  
 $P$  = pressure, atm  
 $Q$  = flow rate of supporting liquid, m<sup>3</sup>/s  
 $R$  = radius of gas-liquid surface, m; gas constant, (atm m<sup>3</sup>)/(g mol K)  
 $Re$  = Reynolds number of interfacial turbulence, eq 25  
 $r$  = radial coordinate  
 $r_0$  = radius of steady drop of spreading liquid around the capillary tip, m  
 $r_a$  = absorption rate, (g mol)/s  
 $Sc$  = Schmidt number,  $\mu/(\rho D_s)$   
 $Sc'$  = Schmidt number,  $\mu/(\rho D_g)$   
 $Sh$  = Sherwood number,  $(K_L R)/D_g$   
 $t$  = variable, eq 13, s  
 $T$  = temperature, K  
 $u$  = radial component of velocity, m/s  
 $y$  = normal coordinate  
 $\Delta V$  = difference of the volumetric flow rates between the inlet and outlet gas streams, m<sup>3</sup>/s

## Greek Letters

$\beta$  = mass transfer coefficient across the contour, m<sup>2</sup>/s  
 $\nu$  = kinematic viscosity, m<sup>2</sup>/s  
 $\delta$  = film thickness of the spreading liquid at the leading edge of the dynamic drop, m  
 $\sigma$  = surface tension, mN/m  
 $\Delta\sigma$  = the surface tension difference between the spreading liquid and supporting liquid, mN/m  
 $\mu$  = viscosity of supporting liquid, kg/(m s)  
 $\rho$  = density of supporting liquid, kg/m<sup>3</sup>  
 $\lambda$  = a dummy variable

## Subscripts

0 = initial  
 i = interfacial  
 L = liquid phase  
 ave = average  
 c = critical  
 w = water

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