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Diffusion of Gases Through Surfactant Films: Interfacial Resistance to Mass Transfer

A model is proposed for mass transfer of gases across surface-active films and into an aqueous phase. The interfacial region 1) obeys local equilibrium conditions, 2) has a capacity for the dissolved gases greater than the solubility in water, and 3) has a diffusion coefficient three orders of magnitude less than for that in water. The model is solved for and compared with three different experiments: the transient diffusion through monomolecular films into quiescent liquids studied by Plevan and Quinn (1966), the gas absorption through surfactant films into falling liquid films investigated by Emmert and Pigford (1954), and the frequency response of concentration pulses in surfactant films reported by Whitaker and Pigford (1966). The model consistently describes these experiments previously explained by three different models that either ignored the capacitance of the film or assumed local non-equilibrium.

L.-A. NGUYEN LY
R. G. CARBONELL
and
B. J. MC COY
Department of Chemical Engineering
University of California
Davis, California 95616

SCOPE

The presence of surfactants at a gas-liquid interface affects the rate of transfer of a solute from the gas to the liquid. The surfactant alters the interfacial region and provides additional resistance to diffusion even when the liquid is quiescent. Attempts to quantitatively describe this effect have been varied: models have been proposed with empirical overall mass transfer or permeability coefficients, with molecular accommodation coefficients, or with empirical rate constants for adsorption and desorption processes occurring in the interfacial region.

The objective here is to evaluate a quantitative model for this interfacial resistance, a model similar to those for

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* Present address for Nguyen-Ly: Cortis-Dow Corp., Walnut Creek, Calif.

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simple diffusion in biological or polymer membranes. That is, the interfacial region has a non-zero thickness, a capacity for the gas solute molecules, and a diffusion coefficient different from the bulk aqueous solution. We studied the consequences of this model in light of experimental data on gas transport through liquid-gas interfaces, in the presence of surfactants. We estimated the value of the parameters in the model necessary to obtain reasonable agreement with the available experimental data.

CONCLUSIONS AND SIGNIFICANCE

The model here proposes that the interfacial region of the surfactant film is of finite thickness and requires a diffusion coefficient to describe mass flux. Local equilibrium solubility conditions exist at either side of the film: a Henry's law constant for the gas-surfactant interface, and a distribution coefficient at the plane between the interfacial region and the bulk phase. This assumption of local equilibrium at continuum interfaces seems preferable to assumptions of local non-equilibrium, as implied by the use of accommodation coefficients or rate constants for adsorption processes. The present model consistently describes three experiments and yields parameters of the following magnitude: thickness of interfacial region $\delta \lesssim 2000$Å, diffusion coefficient $D_I \sim 10^{-8}$ cm^2/sec, and distribution coefficient for solute in water and in interfacial region $K = 0.008$ to 0.08. This diffusion model is an alternate approach for interpreting interfacial mass transfer resistance. The relative simplicity of the theory and of the mathematical procedure reinforces its usefulness.

The presence of surfactants at an interfacial region can offer significant resistance to the transfer of a solute between a gas and a liquid phase. One effect is that surfactants increase the rigidity of the interface and reduce convective motion. Surfactants reduce surface motion of the liquid at the interface by lowering the surface tension. A quiescent liquid in contact with a soluble gas will begin to exhibit surface convective motion after a sufficient lapse of time. This convective motion is usually interpreted as being caused by surface tension gradients at the interface, and results in a considerable enhancement in mass transfer rates (Sherwood et al. 1975). In addition to reducing interfacial motion, surfactants also contribute their own intrinsic resistance to mass transfer, by changing the nature of the properties of the interface. This effect is the main focus of this article.

Thompson (1970) was able to restrict surface motion by applying fine mesh screens to the liquid surface; he still found a considerable decrease in mass transfer rates in the presence of surfactants. Emmert and Pigford (1954) reduced surface rippling in wetted-wall columns and found that the mass transfer resistance in the presence of surfactant was 5 to 25% higher than what would be expected for a clean surface film. Caskey and Barlage (1972) established, by a study of the effects of surfactants on gas absorption in laminar jets, that even very expanded monolayers offered a measurable resistance to mass transfer. Similar conclusions about non-hydrodynamic interfacial mass transfer resistances caused by surfactants have been reached by other investigators: Hawke and Alexander (1962), Harvey and Smith (1959), Goodridge and Bricknell (1962).

Insoluble monolayers occurring naturally in bodies of water, or introduced occasionally by man to retard evaporation, are of concern in water conservation (La Mer 1962, La Mer and Healy 1965). Because surfactants reduce the rate of vaporization of small drops, their use has been proposed to reduce evaporation of fogs that protect crops from frost damage (Mihara 1966). Interfacial resistance and hydrodynamic effects due to surface-active materials can be an important factor in the design of mass transfer equipment. This is particularly true in instances in which the liquid side and gas side diffusional resistances are small, and in situations such as the dispersion of gas bubbles in liquids or liquid droplets in gases. Of special interest are applications of the theory of interfacial resistance to transport of respiratory and toxic gases through natural membranes in the lung (Danielli et al. 1964).

Several molecular models have been proposed to explain the diffusive resistance of surfactant films. Emmert and Pigford (1954) suggest that a factor contributing to interfacial resistance was the lack of thermodynamic equilibrium between the gas and liquid phases. They introduced a mass transfer coefficient containing an accommodation coefficient based on kinetic theory. Recently Sherwood, Wilke and Pigford (1975) suggest that such non-equilibrium effects are not likely to be important in usual studies of gas-liquid mass transfer. They will only contribute when the mass transfer through the interface is extremely rapid, as in the evaporation of liquids in a near vacuum.

Blank's experimental studies (Blank and Roughton 1960, Blank 1961, 1962a, 1962b, 1964) for transport of gases through different monolayers lead him to suggest that monolayer permeabilities can be explained by fluctuations in the density of the interface at equilibrium. These fluctuations are estimated from statistical mechanics. This same point of view is espoused by Bockman (1969) who compares Blank's theory with the potential energy barrier model for interfacial transfer suggested by Goodridge and Robb (1965).

Different types of continuum models have also been proposed to account for the effect of interfacial resistance. Plevan and Quinn (1966) express the flux of solute through the surfactant film in terms of an overall mass transfer coefficient multiplied by a concentration difference. Similar "surface transmission" or "surface transfer" coefficients have been used by Hawke and Parts (1964), Sada and Himmelblau (1967), and Goodridge and Bricknell (1962). Such models assume that the film is of infinitesimal thickness and has no capacitance for the solute.

Whitaker and Pigford (1966) had to account for the temporary storage of solute molecules at the interface to explain their experimental results. They do this by proposing a four rate constant constitutive equation for the rate of adsorption of SO_2 at the interface. This constitutive equation describes the adsorption process as occurring in four steps: adsorption and desorption from the gas phase and adsorption and desorption from the liquid phase. Thermodynamic constraints provides a relation between the rate constants. Implicit in the assumptions of the Whitaker-Pigford model is that the interface is of infinitesimal thickness, and that diffusion or mass transfer resistance is described entirely by a non-equilibrium adsorption-desorption mechanism.

In this article, we adopt a different continuum model of the interface, to examine the nature of the gas-liquid mass transfer process in the presence of surfactants. The simple mass transfer coefficient models do not allow for the storage of molecules at the interface. The more complex constitutive equations assume non-equilibrium at the interface and do not yield information about the thickness of the interfacial region and the values of basic transport parameters within the interface. In our model, we assume that the gas can both dissolve in and diffuse through the interfacial region. Including the equilibrium solubility of gas in the film of a finite thickness has a precedent in models of mass transfer through biological membranes.

Permeation of nonelectrolytes across biological membranes is the result of two processes: partitioning between the liquid and the membrane and diffusing within the membrane (Lieb and Stein 1971). Similar to the present model, the overall process has been characterized by an *equilibrium distribution coefficient* K between membrane and external phase and the membrane diffusion coefficient D_1. The diffusion process closely resembles diffusion in polymers, in that diffusion coefficients are three or four powers of ten less than diffusion coefficients in liquids. Biological membranes are bimolecular lipid leaflets to which proteins may be adsorbed (Mueller et al. 1964).

While monolayers lack the obvious structural features to serve as realistic models of biological membranes, they do have the close-packed molecular nature of the bilayers. Thus it does not seem unreasonable to treat monolayers, as well as thicker surface active films, as having a capacity for diffusing molecules denoted by the distribution coefficient, K, and having a diffusion coefficient D_1 of the order 10^{-8} cm^2/sec.

By treating the diffusion of a solute through the interfacial region *as if it is diffusion in a separate phase*, our objective is to gain information about the values of the interfacial thickness and the molecular diffusivity of the solute at the interface. In general, calculations using available experimental data may be expected to yield interfacial thicknesses that are somewhat larger than the thickness of the surfactant monolayer. This is so because of the rather high degree of orientation of water molecules in the vicinity of the charged ends of the surfactant molecules (Davies and Rideal 1963, Drost-Hansen 1971). One likewise expects that diffusion coefficients for the solute in the interfacial region would reflect both the nature of the surfactant and of the oriented molecules in the bulk liquid.

In the section that follows, we describe in detail the model for diffusion of a solute through the interface. This model is then applied to the experimental data of Whitaker and Pigford (1966), Plevan and Quinn (1966), and Emmert and Pigford (1954) to calculate the appropriate parameters in the interfacial region. It is significant that the present model consistently describes the three experiments, which heretofore were described by three separate and different models. The application of the model to evaporation of water through surfactant films will be reported in a separate communication.

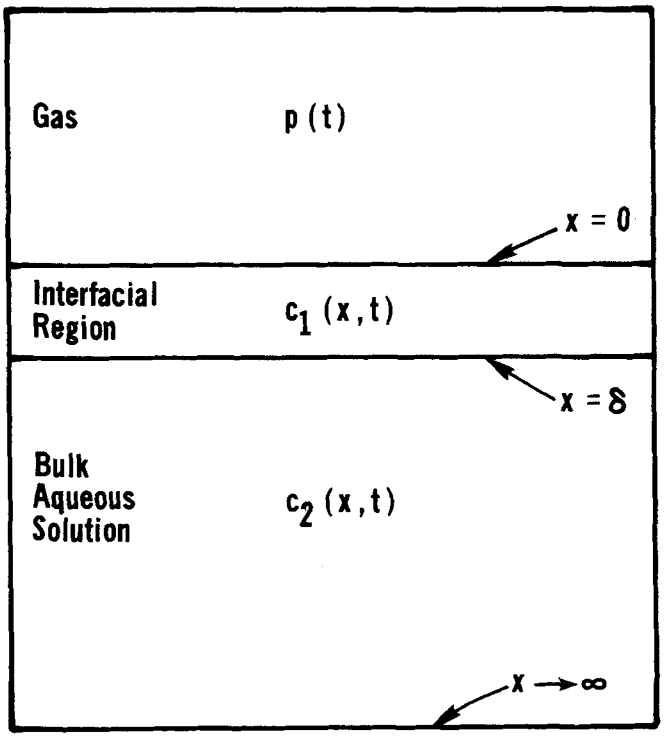

Figure 1. Diagram of model for gas diffusing through the interfacial region of a surface active film.

MODEL FOR INTERFACIAL DIFFUSION

Figure 1 shows a diagram of the present model for interfacial diffusion. We consider a pure gas of partial pressure $p(t)$ to be in contact with a surfactant film located at $x = 0$. The interface is treated as a separate phase of thickness δ. We assume that there is a Henry's Law constant H_s that relates the concentration of the gas dissolved in the interface at $x = 0$ and the gas partial pressure. Further, we assume that there is a partition coefficient, K, that relates the solute concentration in the interfacial region and the solute concentration in the bulk liquid region at $x = \delta$. This is consistent with the idea that the interface and the bulk liquid are separate phases. The diffusion coefficients and concentrations for the solute in the interfacial region and in the bulk fluid are D_1, D_2 and c_1, c_2 respectively. Fick's Law of diffusion is assumed to hold in both phases and equilibrium is assumed to be maintained between the gas and the interfacial region and between the interfacial region and the bulk liquid.

If the liquid and the interface are taken to be stationary so that the transport of gas is only through molecular diffusion, we can write the governing differential equations for the concentrations, c_1, c_2, with the appropriate boundary conditions,

$$\frac{\partial c_1}{\partial t} = D_1 \frac{\partial^2 c_1}{\partial x^2} \quad 0 \leq x \leq \delta \tag{1}$$

$$\frac{\partial c_2}{\partial t} = D_2 \frac{\partial^2 c_2}{\partial x^2} \quad \delta \leq x < \infty \tag{2}$$

$$c_1 = H_2 p \quad @ \quad x = 0 \tag{3}$$

$$c_2 = K c_1 \quad @ \quad x = \delta \tag{4}$$

$$-D_1 \frac{\partial c_1}{\partial x} = -D_2 \frac{\partial c_2}{\partial x} \quad @ \quad x = \delta \tag{5}$$

$$c_2 = c_i \quad @ \quad x = \infty \tag{6}$$

where c_i is the solute concentration in the bulk aqueous phase initially. Here we have taken the bulk fluid phase to be semi-infinite and we have adopted the initial conditions

$$c_1 = K^{-1} c_i \qquad @ \quad t = 0 \quad 0 < x \leqq \delta \tag{7}$$

$$c_2 = c_i \qquad @ \quad t = 0 \quad \delta \leqq x < \infty \tag{8}$$

This model will also hold when the solute reacts instantaneously with the liquid. The transport of the product of the reaction will then be governed by Equations (1) and (2). This is important in the study of the absorption of CO_2 and SO_2, which forms ions extremely fast in the presence of water. At equilibrium, the chemical potential of the solute must be the same in all three phases, gas, interface, and bulk liquid. This requires that

$$K = H/H_s \tag{9}$$

where H is the Henry's Law constant for direct contact of the gas with the bulk liquid.

Equations (1-8) can be solved subject to several functions $p(t)$ and initial conditions c_i corresponding to experimental arrangements used in previous investigations. We next analyze the data of three rather different experiments using the model described by Equations (1-8). We attempt to ascertain that the values of the parameters evaluated here are consistent with what is known about the interfacial region. Because of the difficulty associated with independent measurements of δ, K, or D_1, the quantitative estimates based on the experiments can only be judged to be of the correct order of magnitude.

THE WHITAKER AND PIGFORD (1966) EXPERIMENTS

Whitaker (1959) and Whitaker and Pigford (1966) used a frequency response technique to study the absorption of SO_2 in water covered with a film of surface-active material. They measured the response of a 0.004 in. thick liquid layer to a sinusoidally varying SO_2 pressure for frequencies ranging from 1 to 10 hertz. The total quantity of SO_2 dissolved was measured by the amount of light absorbed by the water layer, which contained a colored hydrogen ion indicator, cresol red. They used an aqueous solution of cresol red old enough that the water surface was covered with a layer of adsorbed surface-active cresol red molecules.

To explain the resistance of the surface phase and its apparent capacity of temporary storage of the molecules, they proposed a constitutive equation with four rate constants to describe the rate of adsorption

$$\frac{dc^*}{dt} = k_1 p - k_2 c^* + K_2 c(0, t) - K_1 c^* \tag{10}$$

where c^* and $c(x, t)$ are the concentrations in the surface phase and the bulk phase. For the bulk of the liquid phase the diffusion equation applies,

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \tag{11}$$

with the boundary conditions

$$-D\left(\frac{\partial c}{\partial x}\right) = K_1 c^* - K_2 c \quad @ \quad x = 0 \tag{12}$$

$$c(x \rightarrow \infty) = 0 \tag{13}$$

where D is the diffusion coefficient of solute in the bulk phase. The Henry's Law constant is related to the four constants by

$$H = k_1 K_1 / k_2 K_2,$$

so that only three rate constants are independent.

Since the gas pressure fluctuation is sinusoidal, the solution to the diffusion Equation (11), $c(x, t)$, is likewise sinusoidal. If the light signal is assumed proportional to the average concentration, then one can write

$$\int_0^\infty c(x, t)\, dx = A(\omega)\, e^{i(\omega t - \theta)} \tag{14}$$

and the amplitude of the recorded signal and the phase lag angle, i.e., $A(\omega)$ and $\theta(\omega)$, are observed experimentally as functions of frequency. Whitaker and Pigford (1966) used the solution of the diffusion equation $c(x, t)$ in Equation (11) to obtain expressions for $A(\omega)$ and $\theta(\omega)$, in terms of the parameters of the model, which were then evaluated from the experimental data.

The alternate approach we propose is to use diffusion Equations (1) and (2) for the surface active and water phases, respectively. The boundary conditions for these equations change slightly since we displace the x axis for convenience

$$c_1 = a_c\, e^{i\omega t} + c_{01} \quad @ \quad x = -\delta \tag{15}$$

$$-D_1 \frac{\partial c_1}{\partial x} = -D_2 \frac{\partial c_2}{\partial x} \quad @ \quad x = 0 \tag{16}$$

$$c_2 = K c_1 \qquad @ \quad x = 0 \tag{17}$$

$$c_2 = c_{02} \qquad @ \quad x \rightarrow \infty \tag{18}$$

Here c_{01} and c_{02} are the initial concentrations of solute in the surfactant layer and in the bulk of the liquid phase, respectively, and a_c denotes the amplitude of concentration fluctuations at the gas-surfactant interface.

To solve the partial differential equations, we substitute

$$c_1(x, t) = g_1(x)\, e^{i\omega t} + c_{01} \tag{19}$$

$$c_2(x, t) = g_2(x)\, e^{i\omega t} + c_{02} \tag{20}$$

into Equations (1) and (2) and apply the boundary conditions (15) through (18), we obtain after rearrangement

$$\begin{aligned} c_2(x, t) = {} & \frac{1}{\Omega}(A' + iB') \\ & [\cos(\omega t - x\phi_2) + i \sin(\omega t - x\phi_2)]\, e^{-x\phi_2} \\ & + c_{02} \end{aligned} \tag{21}$$

where

$$\begin{aligned} A' = {} & (\alpha\, e^{-2\delta\phi_1} - \beta\, e^{2\delta\phi_1})\, c_0 \cos \omega t \\ & - (\alpha\, e^{-\delta\phi_1} - \beta\, e^{\delta\phi_1})\, 2a_c K \cos \delta\phi_1 \\ & + \alpha\, c_0 \cos(\omega t - 2\delta\phi_1) - \beta\, c_0 \cos(\omega t + 2\delta\phi_1) \end{aligned} \tag{22}$$

$$\begin{aligned} B' = {} & -(\alpha\, e^{-2\delta\phi_1} - \beta\, e^{2\delta\phi_1})\, c_0 \sin \omega t \\ & - (\alpha\, e^{-\delta\phi_1} + \beta\, e^{\phi_1\delta})\, 2a_c K \sin \delta\phi_1 \\ & - \alpha\, c_0 \sin(\omega t - 2\delta\phi_1) + \beta\, c_0 \sin(\omega t + 2\delta\phi_1) \end{aligned} \tag{23}$$

$$\Omega = (\alpha^2 e^{-2\delta\phi_1} + \beta^2 e^{2\phi\delta_1} - 2\alpha\beta \cos 2\delta\phi_1)\sqrt{D_2/D_1} \tag{24}$$

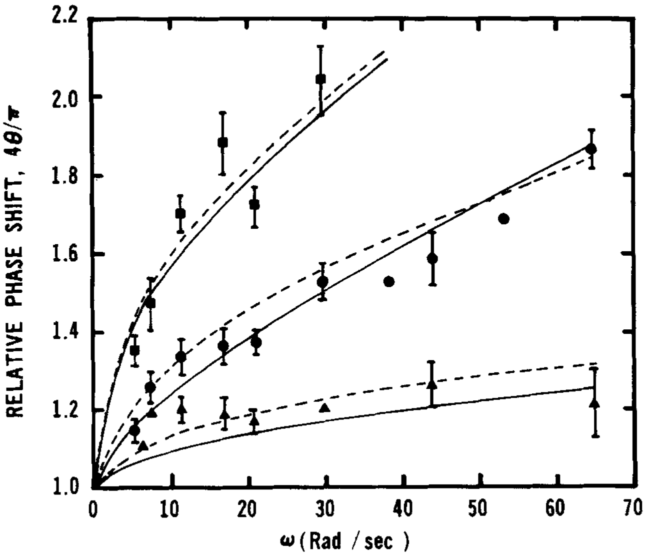

Figure 2. Phase lag as a function of frequency: Solid line is present model, dashed line is the Whitaker-Pigford model; ▲ 2.0 × 10^{-4} molar cresol red, 23.8°C, ● 2.7 × 10^{-4} molar cresol red, 26.3°C, ■ 2.7 × 10^{-4} molar cresol red, 23.5°C.

$$\alpha = K - \sqrt{D_1/D_2} \tag{25}$$

$$\beta = K + \sqrt{D_1/D_2} \tag{26}$$

$$\phi_1 = \sqrt{\omega/2D_1} \tag{27}$$

$$\phi_2 = \sqrt{\omega/2D_2} \tag{28}$$

$$c_0 = c_{02} - K c_{01} \tag{29}$$

To obtain expressions for the amplitude $A(\omega)$ and phase lag $\theta(\omega)$, we take the average of the real part of $c(x, t)$ over the depth l as follows

$$c_{\text{avg}}(t) = \frac{1}{\gamma l} \int_0^l [A' \cos(\omega t - x\phi_2) - B' \sin(\omega t - x\phi_2)]\, e^{-x\phi_2}\, dx + c_{02} \tag{30}$$

After rearranging we finally obtain

$$c_{\text{avg}}(t) = A(\omega) \cos(\omega t - \theta) \tag{31}$$

where

$$A(\omega) = \sqrt{p^2 + q^2} \tag{32}$$

$$\theta(\omega) = \frac{\pi}{2} - \tan^{-1}(p/q) \tag{33}$$

$$\begin{aligned} p = \frac{a_c}{2l\gamma\phi_2} \{ & [(\alpha\beta + \beta^2)\, e^{\delta\phi_1} - (\alpha\beta + \alpha^2)\, e^{-\delta\phi_1}] \\ & [(-\cos l\phi_2 + \sin l\phi_2) e^{-l\phi_2} + 1] \cos \delta\phi_1 \\ & - [(\alpha\beta + \beta^2)\, e^{\delta\phi_1} + (\alpha\beta + \alpha^2)\, e^{-\delta\phi_1}] \\ & [(-\cos l\phi_2 - \sin l\phi_2) e^{-l\phi_2} + 1] \sin \delta\phi_1 \} \end{aligned} \tag{34}$$

$$\begin{aligned} q = \frac{a_c}{2l\gamma\phi_2} \{ & [(\alpha\beta + \beta)\, e^{\delta\phi_1} + (\alpha\beta + \alpha^2)\, e^{-\delta\phi_1}] \\ & [(-\cos l\phi_2 + \sin l\phi_2) e^{-l\phi_2} + 1] \sin \delta\phi_1 \\ & + [(\alpha\beta + \beta^2)\, e^{\delta\phi_1} - (\alpha\beta + \alpha^2)\, e^{-\delta\phi_1}] \\ & [(-\cos l\phi_2 - \sin l\phi_2) e^{-l\phi_2} + 1] \cos \delta\phi_1 \} \end{aligned} \tag{35}$$

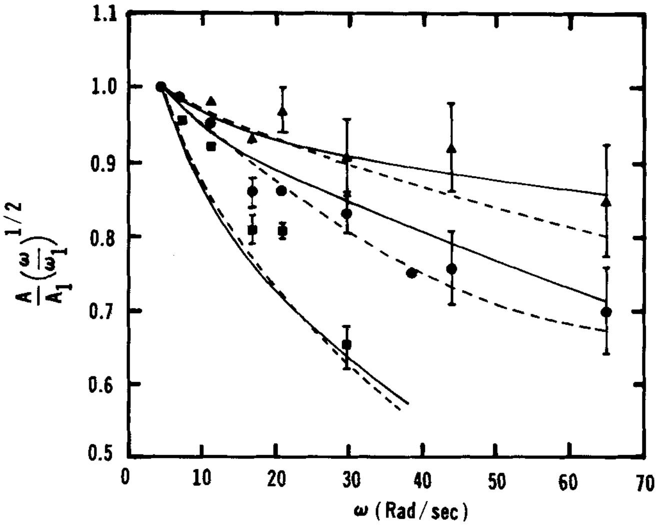

Figure 3. Relative amplitude as a function of frequency: Symbols same as in Figure 2.

Table 1. Parameter Values for the Present Model Calculated from Frequency Response Experiments of Whitaker and Pigford (1966)

Temperature (°C)	Cresol red concentration (gmole/liter)	Parameters δ (cm)	D_1 (cm²/sec)	K
23.5	2.7 × 10^{-4}	1.7 × 10^{-5}	7.5 × 10^{-9}	0.02
26.3	2.7 × 10^{-4}	1.3 × 10^{-5}	9.0 × 10^{-9}	0.008
23.8	2.0 × 10^{-4}	0.3 × 10^{-5}	7.5 × 10^{-9}	0.02

The independent parameters appearing in Equations (32-35) are δ, D_1, and K. We used a numerical search technique to find values fitting experimental data. Results are presented in Figures 2 and 3 as plots of the relative amplitude function $[A(\omega)/A_r(\omega)]\sqrt{\omega/\omega_r}$ and of the relative phase shift $4\theta/\pi$ against $\sqrt{\omega}$. The reference amplitude and frequency, $A_r(\omega)$ and ω_r, are chosen at the lowest recorded frequency, ω_r = 0.83 hertz. The error bars show the standard deviation from the mean value. The observed phase angles in Figure 2 are always greater than $\pi/4$, indicating that a resistance to mass transfer exists at the interface. The computed values of the parameters δ, D_1, and K are given in Table 1. The theoretical curves in Figures 2 and 3 fit the data at least as well as those of Whitaker and Pigford's model.

The values of D_1 in Table 1 are of the order of magnitude of diffusion coefficients of small gas molecules in non-porous biological and polymer membranes, namely 10^{-8} cm²/sec (Leib and Stein 1971).

The surfactant film thickness, δ, increases with an increase in cresol red concentration in the aqueous solution, Table 1. This is consistent with measurements of surface concentrations of cresol red, which increase with increasing bulk concentrations (Whitaker and Pigford 1966).

Frequency response experiments were performed at two slightly different temperatures, ~24°C and ~26°C, and at two different concentrations of cresol red (see Table 1). The estimated value of the diffusion coefficient D_1 of SO_2 in the surfactant film correctly increases with temperature, and is unaffected by the concentration change. The energy of activation for D_1 is calculated to be (12 ± 7) kcal/mole, which agrees with E_{act} for diffusion of gases within natural rubber and polyisobutylene (Lieb and Stein 1971).

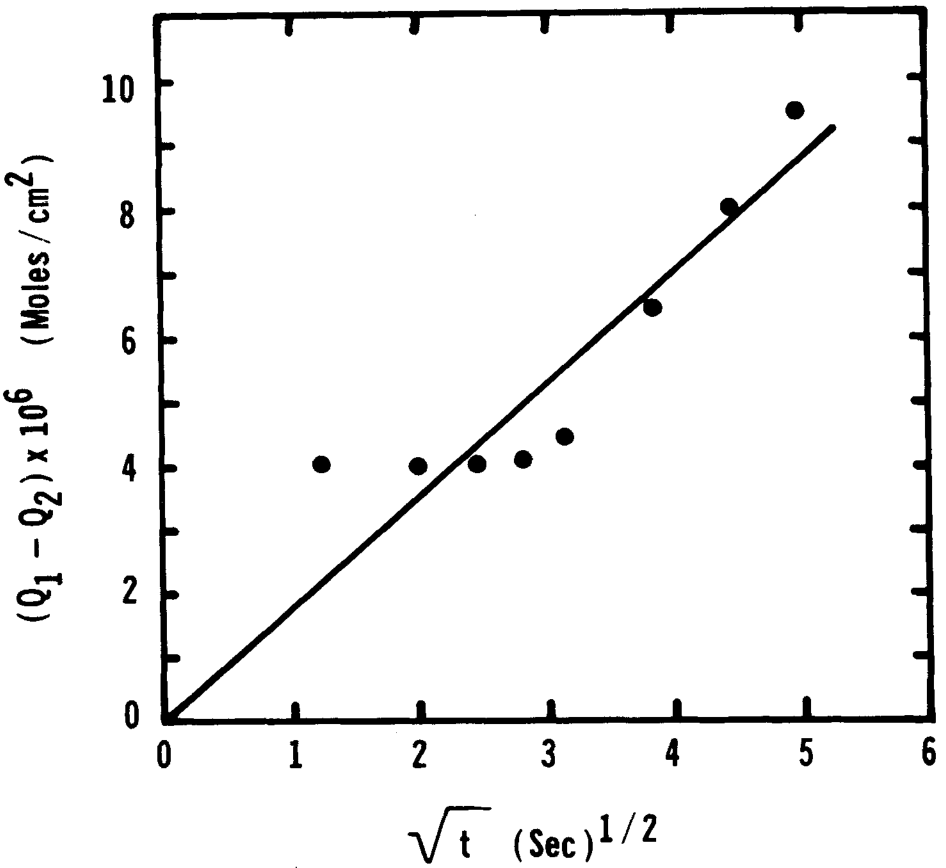

Figure 4. Effect of hexadecanol on SO_2 adsorption into water, from Plevan and Quinn (1966).

Of the three different experiments we analyze, only that of Whitaker and Pigford allows us to estimate the film thickness δ, which has values of 300, 1300 and 1700Å. Since these film thicknesses are of the order of magnitude of wave lengths of visible light, one might expect the films to be observable. However, because of the large solubility of cresol red compared to other surfactants, the diffuse nature of the cresol red — H_2O interface could make observing interference patterns difficult. It is also possible that micellar structures are formed at the liquid surface, since cresol red exists in ionic form in solution and micelle formation has been reported for numerous ionic substances when the surfactant concentration exceeds the critical micellar concentration (Fendler and Fendler 1975).

Moreover, it may not be correct to consider the region of high resistance to diffusion to be limited to the actual surfactant film. In their classic volume on interfacial phenomena Davis and Rideal (1963) recognize that a surfactant forming a monolayer at the interface will drastically change the properties of the liquid in the vicinity of the interface. For example, ionic groups in the surfactant will give rise to an electrical double layer. This, in turn, can affect the transport of ionic species through the interfacial region. Furthermore, water molecules in the vicinity of the interface are highly oriented, giving rise to very large local values of the viscosity. The interfacial region has a finite thickness of influence whose properties differ quite radically from those of the bulk liquid. Thus, the large resistance of the interfacial region may extend beyond the surfactant film, so that D_1 and K are essentially average values within the region of high molecular orientation.

THE PLEVAN AND QUINN (1966) EXPERIMENTS

The experiment performed by Plevan and Quinn (1966) consists of measuring simultaneously the total amount of gas absorbed into two liquid layers, one containing a monomolecular film of a non-ionic surfactant, and the other completely free of surfactant. A step function in pressure of the absorbing gas was imposed simultaneously on the two liquid layers in adjoining cells. The difference between the total amount of gas absorbed at a given time in the two cells gives information on the interfacial resistances. Plevan and Quinn express the flux into the liquid in terms of a mass transfer coefficient k_S for the surfactant film, namely,

$$-D_2 \frac{\partial c_2}{\partial x} = k_S \left[Hp(t) - c_2 \right] \quad \text{at interface} \qquad (36)$$

Here H is the Henry's Law constant for the liquid, and $p(t)$ is the partial pressure of gas above the liquid. Implied in this model is that the film is of negligible thickness. For a step change in pressure,

$$p(t) = \Delta p \, u(t) + p_i \qquad (37)$$

where Δp is the change in the gas partial pressure in the cell. For times $t > 0$,

$$p(t > 0) = \Delta p + p_i = p_0 \qquad (38)$$

In the surfactant-free cell, the boundary condition used by Plevan and Quinn was

$$c_2 = HP_0 \quad t > 0 \qquad (39)$$

The difference in the total amount of gas absorbed for large times between the pure liquid and the surfactant-covered liquid is calculated with Laplace transforms,

$$\lim_{t \to \infty} (Q_1 - Q_2) = \frac{D_2}{k_S} [HP_0 - c_i] \tag{40}$$

Here c_i is the concentration of solute in the water layer for times $t \leqq 0$. Note that Equation (40) predicts that $Q_1 - Q_2$ should approach a constant value inversely proportional to k_S. Typical experimental results for SO_2 absorption into water with octadecanol as the surfactant are shown in Figure 4. Note that $Q_1 - Q_2$ is apparently constant in the time range $1 \leqq t \leqq 10$ secs, but increases significantly for longer times. This is attributed to the effect of convection in the surfactant-free liquid layer.

To apply our model to the Plevan and Quinn experiments, we solved Equations (1-8) by Laplace transforms using $p(t)$ from Equation (37) (Ly 1977). Carslaw and Jaeger (1947) solved a similar problem for heat conduction through composite solids. The results for the concentration of SO_2 in the interfacial region and in the bulk aqueous region are

$$c_1(x, t) = (H_s p_0 - c_i/K) \sum_{n=0}^{\infty} (-1)^n \left(\frac{a}{b}\right)^n \left[\frac{a}{b} \operatorname{erfc}\left(\frac{-x + 2\delta(n+1)}{2\sqrt{D_1 t}}\right) + \operatorname{erfc}\left(\frac{x + 2\delta_n}{2\sqrt{D_1 t}}\right)\right] + c_i/K \tag{41}$$

$$c_2(x, t) = \frac{2}{b} (KH_s p_0 - c_i) \sum_{n=0}^{\infty} (-1)^n \left(\frac{a}{b}\right)^n \operatorname{erfc}\left(\frac{(x-\delta)}{2\sqrt{D_2 t}} + \frac{2\delta n}{\sqrt{D_1 t}}\right) + c_i \tag{42}$$

where

$$a = 1 - K\sqrt{D_2/D_1} \tag{43}$$

$$b = 1 + K\sqrt{D_2/D_1} \tag{44}$$

For the cell containing the surfactant-free liquid the concentration of SO_2 in the water is given by

$$c(x, t) = (Hp_0 - c_i) \operatorname{erfc}\left(\frac{x}{2\sqrt{D_2 t}}\right) + c_i \tag{45}$$

The difference in the total amount of gas absorbed after time, t, in the surfactant-free cell and the cell containing surfactant is

$$Q_1 - Q_2 = \int_0^t \left[-D_2 \frac{\partial c_2(0, t')}{\partial x} + D_1 \frac{\partial c_1(0, t')}{\partial x} \right] dt' \tag{46}$$

After calculating the derivatives with respect to x of $c(x, t)$ arnd $c_1(x, t)$, and integrating with respect to time, we obtain an approximate expression for $Q_1 - Q_2$ valid for $\delta^2/D_1 t << 1$

$$Q_1 - Q_2 \approx A\, t^{1/2} + B\, t^{-1/2} + C\, t^{-3/2} + D \tag{47}$$

where

$$A = 2(Hp_0 - c_i)\sqrt{\frac{D_2}{\pi}} + 2(H_s p_0 - c_i/K)\sqrt{\frac{D_1}{\pi}}\left(1 - \frac{a}{b}\right)^2 \tag{48}$$

TABLE 2. CALCULATED VALUES OF K FOR THE PLEVAN AND QUINN (1966) EXPERIMENTS WHEN $D_1 = 10^{-8}$ CM²/SEC IS ASSUMED

Surfactant	$A \times 10^6$ (moles/cm²)	K
1-hexadecanol	1.7 ± 0.2	0.08 ± 0.01
1-octadecanol	1.0 ± 0.3	0.06 ± 0.01
Stearic acid	0.4 ± 0.1	0.04 ± 0.01
Oleic acid	0.3 ± 0.2	0.04 ± 0.01

$$B = 4(H_s p_0 - c_i/K)\sqrt{\frac{D_1}{\pi}}\,\eta\left[2\left(\frac{a}{b}\right) - 4\left(\frac{a}{b}\right)^2\right] \tag{49}$$

$$C = \frac{16}{3}(H_s p_0 - c_i/K)\sqrt{\frac{D_1}{\pi}}\,\eta^2\left[\left(\frac{a}{b}\right) - 8\left(\frac{a}{b}\right)^2\right] \tag{50}$$

$$D = 2(H_s p_0 - c_i/K)\sqrt{D_1 \eta}\left[\left(\frac{a}{b}\right) - 1\right] \tag{51}$$

and

$$\eta = \delta^2/D_1 \tag{52}$$

Note that even for values of δ as large as 1000Å and values for D_1 as small as 10^{-8} cm²/sec, Equation (47) would be valid for times $t > 1$ sec, since $\delta^2/D_1 t \leqq 0.01$. Clearly, Equation (47) predicts that $Q_1 - Q_2$ will continue to increase as $\sqrt{t}$ for large times. This is in contrast to the Plevan and Quinn model that indicates, according to Equation (40), that this quantity should approach a constant as $t \to \infty$. The difference between the two models is primarily the effect of the capacitance of the interfacial region δ, in particular, the effect of the parameters H_s and K. The experimental results in the region of time t between 1 and 10 sec indicates a plateau or constant value of $Q_1 - Q_2$.

Plevan and Quinn obtained these constant values after subtracting the results of blank runs with the two cells, each filled with surfactant-free liquid. This became necessary due to a large temperature rise, 20°C, in each cell at the beginning of the experiment caused by the sudden increase in gas pressure. Further details can be found in Plevan and Quinn's (1966) article. It is conceivable that this correction could have masked the correct time-dependent behavior of $Q_1 - Q_2$ for $1 < t < 10$ sec. For $t > 10$ sec, Plevan and Quinn argue that convective effects were of importance and that Equation (40) should not apply.

Another argument can be made that the time dependence of $Q_1 - Q_2$ should be governed by a model having film capacity. Plevan and Quinn assume that the Henry's Law constant at the surfactant film surface is identical to that of water. This can be strictly true only for a zero thickness film. If the film has a capacity for the solute different from that of water, which is the hypothesis of the present work, then $H_s \neq H$ should be substituted for H in Equation (10). It is not difficult to show that the Laplace transform solution for this problem yields instead of Plevan and Quinn's result,

$$Q_1 - Q_2 = 2p_0(H - H_s)\sqrt{D_2 t/\pi} + (H_s p_0 - c_i)(D_2/k_s) \times (1 - e^{k_s^2 t/D_2} \operatorname{erfc} k_s \sqrt{t/D_2}) \tag{53}$$

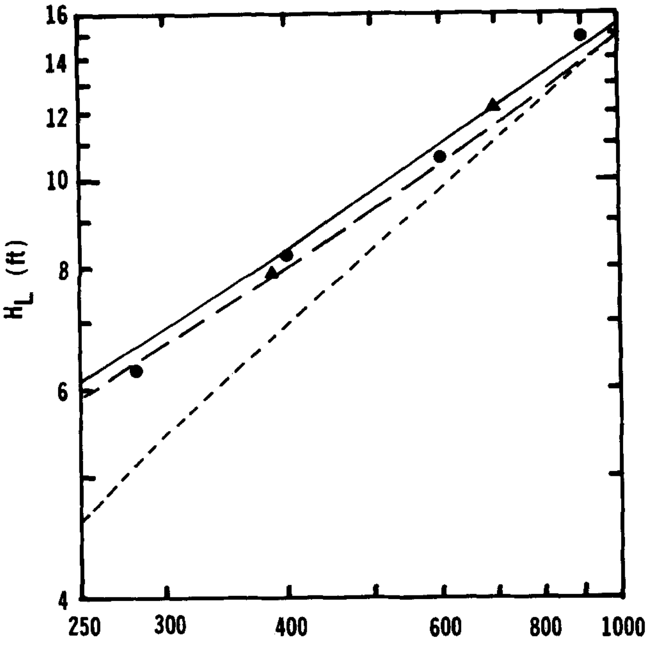

Figure 5. Absorption and desorption of CO_2 in a falling liquid film with wetting agent (data of Emmert and Pigford 1954), ● absorption, ▲ desorption. Solid line is present theory, long and short dashed lines are Eqs. (13) and (6) of Emmert and Pigford.

When $k{s}^2t/D_2$ becomes large, the second term on the right-hand side of Equation (22) becomes negligible, and the $\sqrt{t}$ time dependence remains, i.e.

$$Q_1 - Q_2 \sim 2p_0(H - H_s)\sqrt{D_2t/\pi} \qquad (54)$$

Only when $H = H_s$ identically will the $\sqrt{t}$ dependence disappear, leaving the constant term, which is Equation (40). Thus the Plevan and Quinn result is a consequence of the assumption that the Henry's Law constant for the surfactant is identical to that of water.

In Equation (47) the terms with B, C, and D are very much smaller than the leading term $A\,t^{1/2}$, so that

$$Q_1 - Q_2 \simeq A\,t^{1/2}$$

Because A is independent of δ, we cannot use our model to estimate the thickness of the interfacial region for the monolayers of the Plevan and Quinn experiments. Our approach is to estimate the slope A of $Q_1 - Q_2$ plotted against $t^{1/2}$, and to calculate K based on the value $D_1 = 10^{-8}$ cm²/sec. We used values of $H = 1.52 \times 10^{-3}$ gmoles/cm³ atm, $D_2 = 1.5 \times 10^{-5}$ cm²/sec, $c_i = 1.52 \times 10^{-3}$ gmoles/cm³, and $p_0 = 2$ atm, as given by Plevan and Quinn (1966). Figure 4 shows data for 1-hexadecanol. The plots for the other surfactants are of similar quality. Choosing $D_1 = 10^{-8}$ cm²/sec, we calculate the values of K shown in Table 2. Although one certainly expects D_1 to vary with the chemical nature of the surfactant, as well as K, in the absence of further detailed knowledge we must be content with the order of magnitude estimates of Table 2.

THE EMMERT AND PIGFORD (1954) EXPERIMENTS

Emmert and Pigford (1954) studied the absorption of O_2 and CO_2 into water in a wetted wall column. A wetting agent, Petrowet R, was added to the water film to eliminate interfacial rippling. To describe the absorption process, they use a model of unsteady-state diffusion into a flowing liquid in laminar flow. For short times of contact, the parabolic velocity profile may be replaced by the surface velocity, u_S, in calculating the absorbed gas concentration in the liquid film. Under these conditions, i.e., assuming a uniform velocity within the falling film, Emmert and Pigford (1954) obtained an expression for the logarithmic mean mass transfer coefficient in the liquid,

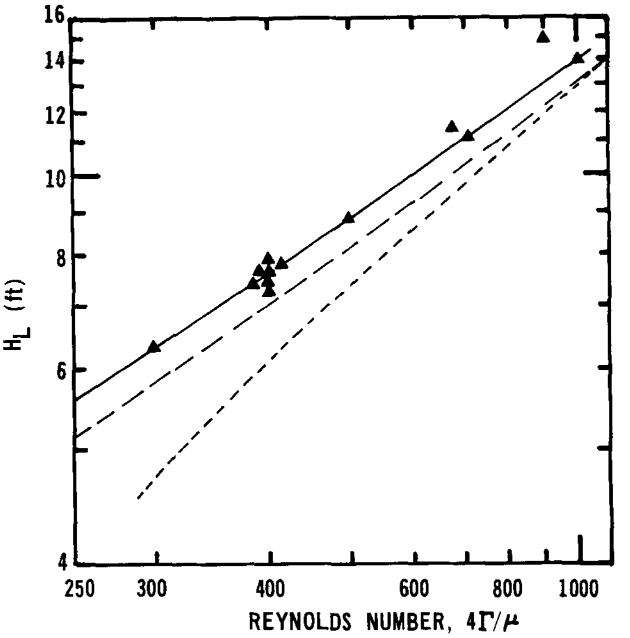

Figure 6. Absorption and desorption of O_2 in a falling liquid film with wetting agent (data of Emmert and Pigford 1954). Solid line is present theory, long and short dashed lines are Eqs. (13) and (6) of Emmert and Pigford.

$$k_{Lm} = \sqrt{\frac{6D_2\Gamma}{\pi\rho L\delta_F}} \qquad (55)$$

where $\delta_F >> \delta$ is the liquid film thickness, L is the wetted wall column length, and Γ is the mass flow rate per unit length of wetted perimeter,

$$\Gamma = \rho\delta_F\langle u\rangle = \frac{2}{3}\rho\delta_F u_S \qquad (56)$$

Here we have noted that in a falling liquid film with parabolic velocity profile, the area-averaged velocity of the liquid is 2/3 the surface velocity. The liquid film thickness can be shown to be related to Γ by

$$\delta_F = \left(\frac{3\mu\Gamma}{g\rho^2}\right)^{1/3} \qquad (57)$$

The height of a transfer unit is defined as

$$H_L = \frac{\Gamma}{\rho k_{Lm}} \qquad (58)$$

Substituting Equation (55) into Equation (58), Emmert and Pigford found

$$H_L = \gamma\,Re^{2/3}\,L^{1/2} \qquad (59)$$

where the Reynolds number is given by

$$Re = \frac{4\Gamma}{\mu} \qquad (60)$$

and

$$\gamma = \left(\frac{\mu^5}{18{,}432\,\rho^5 g}\right)^{1/6}\sqrt{\pi D_2} \qquad (61)$$

Data of H_L versus Re from Emmert and Pigford's work is plotted in Figures 5 and 6 for absorption and desorption of CO_2 and O_2. Also included is a plot of Equation (59), together with H_L values calculated by using the full parabolic velocity profile, rather than the surface velocity. The full solution to the problem deviates from Equation (59) and lies considerably below the data especially for $Re < 700$. At $Re = 700$, Equation (59) exhibits a 10% higher H_L value than the full solution and the difference gets larger for the lower Re.

It is of interest that the theory for constant film velocity provides better agreement with the experimental data than the theory including the full velocity profile. Evidently, the surfactant film distorts the velocity profile by causing it to be more uniform, and there is evidence to support this explanation. The retarding effect of surfactants on surface velocities of falling films and rising gas bubbles is well known (Davies and Rideal 1963, p. 316). Also the work of Cerro and Whitaker (1971) on the effect of surfactant on the hydrodynamic development of thin liquid films shows that heptanoic acid was capable of significantly retarding the establishment of the velocity profile. Thus, the assumption of uniform velocity in the falling film may not be totally unrealistic.

To analyze the Emmert and Pigford data using our model of the interfacial region, we consider the diffusion equation within the interfacial region as

$$u_S \frac{\partial c_1}{\partial z} = D_1 \frac{\partial^2 c_1}{\partial x^2} \qquad 0 < x < \delta \tag{62}$$

where δ is considered small enough that the velocity of the interface is u_S. Within the liquid, we write the diffusion equation with the usual laminar profile for generality

$$u_S \left[1 - \left(\frac{x}{\delta_F} \right)^2 \right] \frac{\partial c_2}{\partial z} = D_2 \frac{\partial^2 c_2}{\partial x^2} \qquad \delta < x < \delta_F \tag{63}$$

In both Equations (62) and (63), z is the direction of flow and x is the direction normal to it. Diffusion in the direction of flow is neglected relative to the convective term. For short contact times, Equation (63) may be modified by changing the velocity term to u_S. This makes Equations (62) and (63) identical to Equations (1) and (2), with t replaced by z/u_S. Since the boundary and initial conditions to Equations (62) and (63) are of the same form as Equations (3-8), the solutions for c_1 and c_2 are identical to Equations (41) and (42), with $t = z/u_S$.

If we average Equation (63) in the x direction from δ to δ_F, and Equation (62) in the x direction from 0 to δ and then in the z direction from 0 to L, we obtain an equation for the average flux of gas into the liquid

$$N_{\text{avg}} = \frac{1}{L} \int_0^L \left(-D_1 \frac{\partial c_1}{\partial x} \bigg|_{x=0} \right) dz$$

$$= \frac{u_S \delta_F}{L} [<\bar{c}>_L - <\bar{c}>_0] \tag{64}$$

where

$$<\bar{c}> = \frac{\delta}{\delta_F} <c_1> + \frac{2}{3} \left(1 - \frac{\delta}{\delta_F} \right) c_{2b} \simeq \frac{2}{3} c_{2b} \tag{65}$$

$$<c_1> = \frac{1}{\delta} \int_0^\delta c_1 \, dx \tag{66}$$

$$c_{2b} = \frac{1}{(\delta_F - \delta) <u>} \int_\delta^{\delta_F} u_S \left[1 - \left(\frac{x - \delta}{\delta_F - \delta} \right)^2 \right] c_2 \, dx \tag{67}$$

$$<u> = \frac{1}{\delta_F - \delta} \int_\delta^{\delta_F} u_S \left[1 - \left(\frac{x - \delta}{\delta_F - \delta} \right)^2 \right] dx \tag{68}$$

We define a log-mean mass transfer coefficient in terms of a driving force between the gas-liquid interface where the actual concentration is c^*, and the bulk concentration in the water film,

$$k_{lm} = \frac{u_S \delta_F}{L} \ln \left(\frac{Kc^* - (c_{2b})_0}{Kc^* - (c_{2b})_L} \right) \tag{69}$$

Since the argument of the logarithm is large, we can show that

$$k_{lm} = N_{\text{avg}} / [Kc^* - (c_{2b})_0] \tag{70}$$

To calculate N_{avg} we let $t = z/u_S$ and make the identification of the present system with that described by Equations (1-8). The major approximation is that the velocity profile in the water film is considered to be constant u_S. We let

$$c_1(x = 0) = c^* = H_s p_0 \tag{71}$$

and

$$c_i = H \, p_i \tag{72}$$

in terms of p_i, the partial pressure of solute gas before the liquid enters the film region, and p_0, the partial pressure of solute gas in contact with the surfactant film. After calculating $\partial c_1/\partial x$ at $x = 0$ and integrating over z as shown in Equation (64), we obtain an expression for the mass transfer coefficient. When it is substituted into Equation (58), we get

$$H_L = \gamma \, Re^{2/3} L^{1/2} \Big/ \frac{3}{2} \psi \sqrt{D_1/D_2} \, (1 - a/b) \tag{73}$$

We use the relation $\delta^2/D_1 t << 1$, and define

$$\psi = \frac{H_s p_0 - c_i/K}{Kc^* - (c_{2b})_0} \tag{74}$$

Since $K << 1$, we have

$$\psi \simeq (1 - p_i/p_0)/K \tag{75}$$

For values of D_1 and K that are of the order of those in earlier sections of this paper, one may show that H_L calculated from Equation (73) is larger than H_L calculated from Equation (59).

To fit Equation (73) to the data presented by Emmert and Pigford in Figures 5 and 6, we use the following equations for lines through the data

for CO_2, $\quad H_L = 0.155 \, N_{Re}^{2/3}$

for O_2, $\quad H_L = 0.141 \, N_{Re}^{2/3}$

For μ and D_2 respectively we used 0.74 cp and 1.96×10^{-5} cm^2/sec for CO_2 and 0.74 cp and 2.5×10^{-5} cm^2/sec for O_2. We let p_i be 0.00 and 0.21 for CO_2 and O_2, respectively. As previously, we let $D_1 = 10^{-8}$ cm^2/sec. We found $K = 0.05$ for CO_2 and $K = 0.03$ for O_2. These values of K are within the range of values of K in Tables 1 and 2, namely, 0.008 to 0.08. Because K is defined as the ratio of the solubility of the gas in the film to the solubility in the bulk liquid, small values of K indicate a preference of the solute molecules for the interfacial region.

NOTATION

$A(\omega)$ = amplitude of the sinusoidal response
A', B' = constants in Equation (21)
A, B, C, D = constants in Equation (46)
a, b = constants in Equations (41), (42)
c = bulk liquid concentration in Whitaker and Pigford model

c^* = interfacial concentration in Whitaker and Pigford model

c_i = solute concentration in the bulk region at $t = 0$

c_1, c_2 = solute concentration in the interfacial and bulk regions

c_{01}, c_{02} = initial solute concentration in the interfacial and bulk regions

$<c_1>$ = area-averaged concentration in the interfacial region

$<c_{2b}>_L, <c_{2b}>_0$ = bulk average concentrations in fluid film at exit and entrance to column

$<\bar{c}>_L, <\bar{c}>_0$ = average solute concentrations at exit and entrance to the column

c_0 = constant in Equation (21)

D_1, D_2 = molecular diffusivities of solute in the interfacial and bulk regions respectively

g_1, g_2 = functions of x in Equations (19), (20)

g = gravitational acceleration

H = Henry's Law constant for the bulk liquid

H_s = Henry's Law constant for the interface

H_L = height of a transfer unit

k_S = mass transfer coefficient in Plevan and Quinn model

k_{Lm} = logarithmic mean mass transfer coefficient

k_1, k_2, K_1, K_2 = constants in the Whitaker and Pigford constitutive equation

K = distribution coefficient, interfacial to bulk region

l = depth of liquid layer in Whitaker and Pigford experiment

L = length of wetted wall column

N_{avg} = average flux into liquid film

$p(t)$ = partial pressure of the solute above the interface

p, q = constants in Equation (32)

p_0 = pressure for $t > 0$ in Plevan and Quinn experiments

p_i = initial pressure

Δp = pressure change

Q_1, Q_2 = total amount of adsorbed solute in pure liquid and with surfactant

Re = Reynolds number

t = time

$u(t)$ = step function

$<u>$ = average fluid velocity

u_S = surface velocity

x = position normal to the interface

z = axial position in column

Greek Letters

$\alpha, \beta, \phi_1, \phi_2, \Omega$ = constants in Equation (21)

γ = constant in Equation (61)

δ = thickness of the interfacial region

δ_F = liquid film thickness, Emmert and Pigford experiment

$\theta(\omega)$ = phase lag angle of the sinusoidal response

ω = frequency

ω_r = reference frequency

η = δ^2/D_1

Γ = mass flow rate

ρ = density of liquid

μ = viscosity of the liquid

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