Mass Transfer with Interfacial Adsorption

Methyl Chloride into Water

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The rate of transfer of a surface-active solute across an interface may be either greater or less than the rate which would be obtained if the interface had no abnormal properties. Studies of the absorption of methyl chloride, a surface-active gas, by a laminar water jet show that for contact times of 1 msec. or greater the absorption rate is the same as would be predicted for a system with no abnormal interfacial properties. This is in accord with theory which indicates that an abnormally high rate caused by a positive surface excess could only be observed for contact times considerably shorter than those used here.

Mass transfer theory has been based on two assumptions which are independent of the specific intraphase transfer mechanism. The first assumption, usually stated explicitly, is that the boundary between two phases across which transfer is taking place is always close to equilibrium, and the second, usually implied, is that the two phases are homogeneous when at equilibrium.

To show that the assumption of equilibrium homogeneity within a phase is implied in the conventional mass transfer equations consider the transfer of a solute from one phase to a second phase in which the solute is surface active. The conventional rate equation is

$$N_A = k_L(C_i - \overline{C}) \qquad (1)$$

But if the solute is adsorbed at the interface, its concentration at the interface when the two bulk phases are at equilibrium may differ considerably from the bulk concentration, so Equation (1) predicts a finite transfer rate when the rate must actually be zero. Clearly then some modification of the basic mass transfer theory is required if the solute is surface active.

The recent critical examinations of mass transfer theory (*5, 6, 8, 12*) which received their impetus from Danckwerts' (*7*) rediscovery and extension of Higbie's penetration theory (*10*) have been aimed mainly at the first assumption, and the second has received little attention aside from the important study of Auer and Murbach (*2*). They analyzed a transient diffusion model in which the interface was considered to be of finite thickness with an absorption capacity different from either of the two bulk phases. Their very general analysis forms the basis of this work.

THEORY

A surface-active solute is characterized by the condition that at equilibrium its concentration at the surface of the solvent is different from its concentration in the bulk. This equilibrium surface excess is given by Gibbs adsorption isotherm (*1*):

$$\Gamma = \frac{\overline{C}}{RT}\left(\frac{\partial \gamma}{\partial \overline{C}}\right) \qquad (2)$$

The thickness of the interfacial region in which this excess exists appears to be of the order of molecular dimension, and the surface excess may be orders of magnitude greater than the bulk concentration. The solid lines in Figure 1 show the idealized equilibrium concentration profile with the true interface at plane $-a$ and a positive surface excess in the interfacial region bounded by planes $-a$ and a. The transient concentration profiles in this three-region model which have been determined by Auer and Murbach (*2*) are quite complex functions, but a simple picture of the transfer process can be readily obtained by the consideration of the steady state. The equilibrium relationships are

$$C_2 = nC_3 \qquad (3)$$

$$C_1 = qC_2 \qquad (4)$$

so that

$$C_1 = qnC_3 = mC_3 \qquad (5)$$

The last equation is the normal equilibrium relationship between the concentration in the bulk of the liquid and the gas. The first is obtained from the Gibbs equation, Equation (2), and the second calculated from the other two. When $n > 1$ a positive surface excess exists, and when $n < 1$ there is a negative surface excess.

If it is assumed that equilibrium exists at each boundary, Equation (4) holds at plane $-a$ and Equation (3) holds at plane a. The dotted lines sketched in Figure 1 show typical concentration profiles. The transfer rate in the steady state is then given by

$$N_A = k_1(\overline{C_1} - C_1(-a)) = k_2(C_2(-a) - C_2(a)) = k_3(C_3(a) - \overline{C}_3) \qquad (6)$$

Combining Equations (3) to (6) one obtains

$$N_A = K_L\left(\frac{\overline{C}_1}{m} - \overline{C}_3\right) \qquad (7)$$

$$\frac{1}{K_L} = \frac{1}{mk_1} + \frac{1}{nk_2} + \frac{1}{k_3} \qquad (8)$$

It should be noted that $\overline{C_1}/m$ which appears in Equation (7) is the concentration in the bulk phase 3, which would be in equilibrium with phase 1, so the normal over-all driving force is obtained and the effect of the surface excess appears only in the coefficient.

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The apparent liquid-side coefficient is obtained from Equation (8) by letting k_1 approach infinity:

$$\frac{1}{K_L} = \frac{1}{k_L} = \frac{1}{nk_2} + \frac{1}{k_3} \qquad (9)$$

and under the same condition of no gas-side resistance Equation (6) yields $C_1 = C_1(-a)$, so Equation (7) becomes

$$N_A = k_L \left(\frac{C_1(-a)}{m} - \overline{C}_3 \right) \qquad (10)$$

and a partial answer to the question posed earlier is obtained by comparing Equations (10) and (1). The interfacial concentration to be used in the conventional rate equation is not the true value but is $C_1(-a)/m$, the interfacial concentration which would exist if there were no surface excess.

Thus a surface excess modifies k_L. For a given value of k_L a positive surface excess causes an increase in k_L and a negative surface excess causes a decrease. The magnitude of this effect however depends upon the relative values of the resistance in the region of the interface and in the rest of the system. Since the thickness of the interfacial region is probably of the order of molecular dimensions, k_2 would be expected to be very large unless a significant interfacial resistance is present. In the absence of such a resistance the first term in Equation (9) will generally be negligible, and there is negligible effect of surface activity on the absorption rate. If there is an interfacial resistance high enough for k_2 to be the same magnitude as k_3 (or if k_3 is extremely small), then a positive surface excess decreases the resistance to transfer across the interfacial region and consequently increases k_L while a negative surface excess has the opposite effect.

In the above discussion an interfacial resistance has been considered to be present when k_2 was abnormally small. but since both n and k_2 are physicochemical properties of the system, they are really inseparable and one might with better justification say that an interfacial resistance exists only when nk_2 is smaller than the value of k_2 which would exist when the interfacial region has the same properties as the bulk. This is equivalent to stating that an interfacial resistance exists when the transfer rate is abnormally small.

The above conclusions must be modified somewhat when considering unsteady state transfer. The authors consider the following simplified form of the Auer and Murbach problem: At time zero a semi-infinite slab containing no solute is contacted with the external phase 1 which contains pure solute at a concentration C_1. The solute is surface active, the thickness of the interfacial region in which a surface excess exists is $2a$, and Fick's law is assumed to hold both in the interface, region 2, and in the bulk, region 3 (Figure 1 with $D_1 = \infty$). Equilibrium is assumed to exist at all boundaries, so an apparent interfacial resistance caused by nonequilibrium at the gas-liquid interface is not being considered. However if D_2 is smaller than D_3, an interfacial resistance does in a sense exist; if a is small, D_2 is much smaller than D_3, and there is no positive surface excess, this interfacial resistance can be shown to have characteristics similar to one caused by nonequilibrium (5).

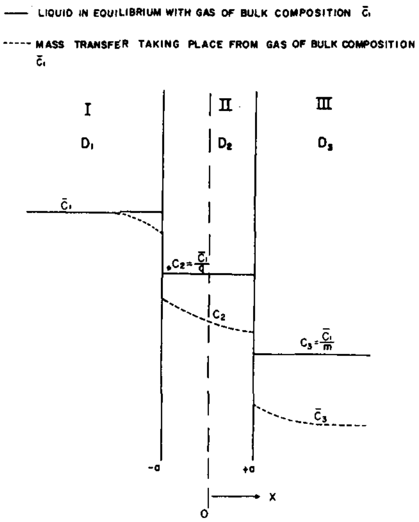

Fig. 1. Three-region model for interfacial transfer.

Thus the equations to be solved are

$$\frac{\partial C_2}{\partial \theta} = D_2 \frac{\partial^2 C_2}{\partial x^2}, -a < x < a \qquad (11a)$$

$$\frac{\partial C_3}{\partial \theta} = D_3 \frac{\partial^2 C_3}{\partial x^2}, x > a \qquad (11b)$$

$$C_2\ (\theta, -a) = \frac{n}{m} C_1 \qquad (11c)$$

$$C_2\ (\theta, a) = n\, C_3\ (\theta, a) \qquad (11d)$$

$$D_3 \frac{\partial C_3(\theta, a)}{\partial x} = D_2 \frac{\partial C_2(\theta, a)}{\partial x} \qquad (11e)$$

$$C_2(0,x) = C_3(0,x) = C_3(\theta, \infty) = 0 \qquad (11f)$$

The time average of transfer was obtained directly from the above equations by use of a Laplace transform (4). The result is

$$\overline{N_A} = 2n \frac{C_1}{m} \sqrt{\frac{D_2}{\pi\theta'}}$$

$$\left[1 + 2\sqrt{\pi} \sum_{j=1}^{\infty} g^j \text{ ierfc} \frac{2ia}{\sqrt{D_2\theta'}} \right] \qquad (12)$$

where

$$g = \frac{\sqrt{D_3} - n\sqrt{D_2}}{\sqrt{D_3} + n\sqrt{D_2}} \qquad (13)$$

and *ierfc* is the first integral of the complimentary error function (3). When g is zero, the absorption rate is given by

$$\overline{N_A} = \overline{N_A}^* = 2 \frac{C_1}{m} \sqrt{\frac{D_3}{\pi\theta'}} \qquad (14)$$

which is the rate in the absence of either a surface excess or an interfacial resistance. But note that g is zero when

$$n = \sqrt{\frac{D_3}{D_2}} \qquad (15)$$

and although this latter condition holds when the interfacial region has the same properties as the bulk, it may also hold when $D_2 < D_3$ and there is a positive surface excess (or when $D_2 > D_3$, and a negative surface excess is present). Thus if D_2 is much less than D_3, there may be an interfacial resistance, but if n is large enough to satisfy

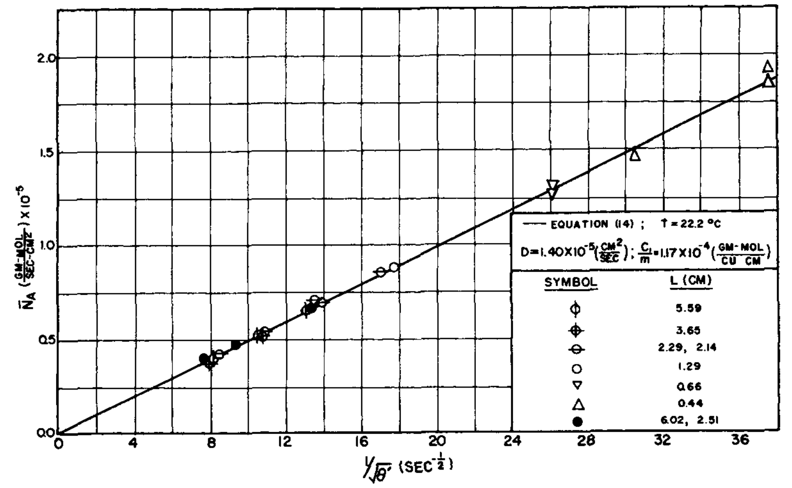

Fig. 2. Rate of methyl chloride absorption into water jets.

Equation (15), the absorption rate is identical to that obtained in the absence of both surface excess and a low interfacial diffusivity.

It may be deduced from the results of Auer and Murbach that when $n\sqrt{D_2}$ is greater than D_3 the transfer is enhanced; $\overline{N_A}$ is greater than $\overline{N_A}^*$. When $n\sqrt{D_2}$ is less than D_3 the transfer is hindered; $\overline{N_A}$ is less than $\overline{N_A}^*$. It seems more reasonable to consider an interfacial resistance to exist when $n\sqrt{D_2}$ is less than D_3 rather than when D_2 is less than D_3.

A clearer understanding of Equation (12) is obtained by considering the limiting cases. For short times ($a/\sqrt{D_2\theta'}$ large) the rate becomes

$$\overline{N_A} = 2n\frac{C_1}{m}\sqrt{\frac{D_2}{\pi\theta'}} \tag{16}$$

which corresponds to times so short that the region of surface excess has not been penetrated. Consequently the diffusion is identical to diffusion into a semi-infinite slab in which the solubility is the interfacial solubility and the diffusivity is the interfacial diffusivity. Since the interfacial solubility is n times the bulk solubility, the diffusion rate given by Equation (16) is merely n times the rate given by Equation (14) (with D_2 replacing D_3). The above limit is approached only at extremely short times if a is of molecular order.

The long time limit is obtained by expanding the *ierfc* function and summing the geometric series in g:

$$\overline{N_A} = \overline{N_A}^* + n\frac{C_1}{m}\frac{2a}{\theta'}\left(1-\frac{D_3}{n^2D_2}\right) \tag{17}$$

If the second term in the brackets is negligible, $n\sqrt{D_2} >> D_3$

$$\overline{N_A} = \overline{N_A}^* + \frac{Q_E}{A\theta'} \tag{18}$$

so the approximate long time rate is the normal rate without surface excess given by Equation (14) plus the total amount of gas needed to saturate a unit area of the interfacial region divided by the time of contact.

Equation (18) is identical to the equation one would derive if it were argued that the interface cannot really be treated as a continuum, but it was merely assumed that the interface instantaneously saturated. The concentration at $x = a$ then immediately attains the value C_1/m, and diffusion into the bulk phase proceeds in the normal manner described by Equation (14). It then follows that the total average rate of transfer across the plane $x = -a$ is given by Equation (18).

For long enough times the second term in Equation (18) is negligible and Equation (14) applies, indicating as before that when the resistance to transfer is mainly in the bulk phase (which is the case for long contact times) the effects of abnormal interfacial conditions are negligible.

When $n\sqrt{D_2} << D_3$, it can be shown that over the ranges of contact time usually measured Equation (17) is a good approximation to the equation for transfer with an interfacial resistance caused by nonequilibrium at the interface (5). The group $nD_2/2a$ then has the characteristics of an interfacial transfer coefficient. This occurs because at long times a quasisteady state is attained in the interfacial region. The above results, as well as those of Auer and Murbach, imply that a positive surface excess will tend to eliminate any decrease in rate caused by a lack of equilibrium at the gas-liquid interface as well as any decrease caused by a low value of D_2.

In order to determine the contact times for which Equations (17) and (14) are valid it is necessary to sum the series in Equation (12). Calculations were carried out on an IBM 650 digital computer since the series converges slowly for long times.

It was found by direct measurement by means of the anchor-ring method that at 22.4°C. the surface tension of water freshly saturated with methyl chloride and in contact with a methyl chloride atmosphere is 14 dynes/cm. less than the surface tension of water in contact with air. If the interface is of molecular thickness, Gibbs equation then yields a value of n of approximately 90. With this value of n, $D_2 = D_3$, and the group $2a/\sqrt{D_2\theta'} = 0.002$, Equations (12) and (17) were found to yield almost identical results. Available evidence indicates that the region of surface excess is of molecular order (*1*) so if a is taken as 10^{-8} cm. and if D_2 and D_3 are 10^{-5} sq. cm./sec., then Equation (17) is valid at least for contact times of 10^{-5} sec. or greater.

At 10^{-3} sec. with the above constants $\overline{N_A}$ is found to be $1.016\overline{N_A}^*$, and D_2 would have to be less than 1/8,100 of the normal bulk diffusivity before an interfacial resistance could exist and considerably less than that value before an interfacial resistance could be detected.

Thus it would be expected that in the absence of any hindering effects at the interface the rate of absorption of methyl chloride by water for contact times of 10^{-3} sec. or greater would be only slightly greater than the rate obtained by neglecting abnormal interfacial effects. The following experiments were carried out in order to test this.

EXPERIMENTAL PROCEDURE

The experimental method used was based on a technique described previously (*12*). A laminar water jet formed by a thin orifice was passed through a methyl-chloride atmosphere saturated with water vapor. Fresh gas was continuously fed to the absorber form a constant-pressure source, while methyl chloride was absorbed, and the rate of absorption was measured directly by timing the displacement of a soap film moving in a calibrated burette which was in the line connecting the absorber and the constant-pressure source.

The orifice plate was made of 0.012 cm. thick brass, and the orifice diameter was 0.0825 cm. This type of thin orifice was shown earlier to give essentially rodlike flow in the jet (*5, 12*). It was also shown that the conditions were such that the diffusion into the jet was essentially the same as diffusion into a semi-infinite slab. Consequently the unsteady state diffusion equations developed above can be applied to the jet.

The jet surface area and the contact time were calculated from measurements of jet length, diameter, and water flow rate. The measured absorption rates were corrected to values corresponding to a total methyl-chloride pressure of 1 atm.

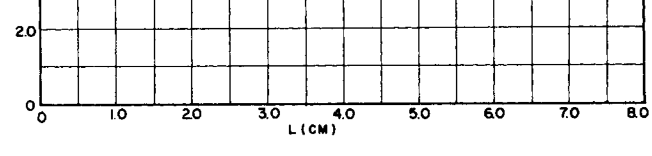

Fig. 3. Comparison of methyl chloride absorbed per unit area at different jet lengths for a fixed contact time.

The water used was distilled water, in which the concentration of methyl chloride was zero. The entire experimental system was situated in a constant-temperature room held at 22.2° ± 0.25°C.

RESULTS

The methyl-chloride absorption was studied for contact times ranging from 0.0007 to 0.012 sec. by varying the jet length from 0.44 to 6.02 cm. and the water flow rate from 0.63 to 2.38 ml./sec. The results are presented in a plot of the average rate of absorption vs. $1/\sqrt{\theta'}$ as shown in Figure 2. The theoretical rate equation with no abnormal interfacial effects, Equation (14), is represented by a straight line, which is based on the physical constants shown in the figures. The value of C_1/m was calculated at a methyl-chloride pressure of 1 atm. from the Henry's law constant given by Glew and Moelwyn-Hughes (*9*). The same authors also reported that the hydrolysis of methyl chloride was a very slow reaction at room temperature so methyl chloride may be regarded as chemically inert to water during a short contact-time absorption. Since there is no reported experimental data on the diffusivity of methyl chloride in water, the value of D_3 was estimated by using Wilke's method (*13*).

DISCUSSION

The maximum deviation among the data shown in Figure 2 is about 5% and the average is less than 2%. A further analysis of the data is shown in Figure 3, where it is seen that the amount of gas absorbed at a fixed contact time is independent of jet length, indicating that the data are self-consistent and confirming earlier conclusions that the jet is in rodlike flow (*5, 12*).

As seen in Figure 2 all experimental data fall very close to the predictions of Equation (14) which is also the long time limit of Equations (12) and (17) if there are no large hindering effects at the interface. Such an agreement between the experimental result and the theoretical prediction strongly suggests that the effects of abnormal surface properties are negligible in the range of constant time studied.

Any further conclusions as to the underlying reasons for the agreement of the results with Equation (14) are not possible, since the agreement is consistent with at least the following possibilities: (1) a is of molecular order, $D_2 = D_3$, and equilibrium exists at the gas-liquid interface, (2) a is of molecular order, D_2 is less than D_3, and/or equilibrium does not exist at the gas-liquid interface, but neither effect is great enough alone or in combination to overcome the effect of the large surface excess, (3) a is greater than molecular order, $n\sqrt{\bar{D}_2} = \sqrt{\bar{D}_3}$, and equilibrium exists at the gas-liquid interface.

When one uses a linear regression method, the best straight line which fits the data is found to be

$$N_A = \left(\frac{4.91}{\sqrt{\theta'}} + 0.504 \right) \times 10^{-7} \quad (32)$$

At the 95% confidence level the limits of the intercept of this straight line are $+2.28 \times 10^{-7}$ and -1.28×10^{-7}. Thus it is highly probable that the best straight line actually passes through the origin. In addition it is found that the limits of the slope of this straight line are 4.81×10^{-7} and 5.02×10^{-7}. The apparent values of the diffusivity evaluated from these limits are 1.33×10^{-5} and 1.45×10^{-5} sq. cm./sec., and since the zero intercept indicates that Equation (14) is valid, these values should correspond to the bulk diffusivity. Based on such statistical evidence it may be concluded that the previously estimated value of the bulk diffusivity, 1.40×10^{-5} sq. cm./sec., is quite reliable.

In the light of these arguments it is concluded that over the range of contact times studied the absorption of methyl chloride, a surface active gas, follows the normal rate equation when the bulk solubility and diffusivity are used. This confirms the theoretical prediction that the effect of a large surface excess on the rate of absorption will generally be negligible for contact times of 10^{-3} sec. or greater if there are no large hindering effects at the interface.

In practice contact times much shorter than those used here are rarely encountered, and if it is assumed, for lack of evidence to the contrary, that large hindering effects do not exist in other surface active systems of this type, then mass transfer of a surface active solute may be treated in practice by using the normal rate equation with the effect of surface activity neglected. This corresponds to using the equilibrium constant corresponding to the bulk solubility in the mass transfer equation which would normally apply to the system of interest.

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NOTATION

a = one half the thickness of interfacial region, (cm.)
A = contact area, (sq. cm.)
C = concentration of solute gas, (g.-mole)/(cc.)
$\bar{C}$ = bulk concentration of solute gas, (g.-mole)/(cc.)
D = diffusivity of solute gas in liquid, (sq. cm.)/(sec.)
g = function defined by Equation (13)
j = index number
k = individual mass transfer coefficient
K = over-all mass transfer coefficient
m,n,q = equilibrium constants
N_A = instantaneous rate of transfer per unit area, (g.-mole)/(sec.)(sq. cm.)
$\overline{N_A}$ = time average rate of transfer per unit area, (g.-mole)/(sec.)(sq. cm.)
Q_E = equilibrium amount of gas absorbed in the interfacial region, (g.-mole)
R = gas constant, 8.32 x 10^7 (dyne) (cm.)/(g.-mole)(°K.)
t = temperature, °C.
T = absolute temperature, °K.
x = distance in the direction of diffusion, cm.
γ = surface tension, dyne/cm.
Γ = surface excess, (g.-mole)/(sq. cm.)
θ = contact time, (sec.)
θ' = total contact time, (sec.)

Subscripts

1,2,3 = regions I, II, and III
i = interface
L = liquid

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