

THE KINETICS OF ADSORPTION OF SURFACE ACTIVE AGENTS AT GAS-LIQUID SURFACES

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Abstract—A general model of adsorption of surfactants at a gas-liquid surface has been developed, which accounts for both the diffusion in the bulk and the barrier to adsorption. In this model, the activation energy barrier to adsorption is accounted for by means of a kinetic expression. A numerical scheme for the solution of the resulting equation of the diffusion-kinetic model is illustrated for the case of the Frumkin isotherm. The model is used to estimate the extent of the adsorption barrier from the dynamic surface tension data of two aqueous surfactant systems reported in the literature. A simplification of the diffusion-kinetic model is proposed which accounts for diffusion in the bulk using diffusion-penetration theory. The simplified model compares very well with the exact model, especially for high barrier resistances.

INTRODUCTION

In general, the surface tension of a freshly formed surfactant solution changes with time until it attains a final equilibrium value. Equilibrium may be attained in a mere fraction of a second or may not be attained for several days. In this paper, attention is focussed on surfactant systems in which the time effect is observable over a period of a few minutes. An informative review of both rapid and slow surface aging phenomena has been given by Moilliet *et al.* [1]. If it is assumed that the orientation of surfactant molecules at the surface does not affect dynamic surface tension, then the dynamic surface tension can be attributed to the changing concentration of surfactant at the surface due to the slow rate of adsorption.

Adsorption may be considered as a two-step process involving: (a) the diffusion of the solute molecules from the bulk to the subsurface (which is the layer immediately below the surface); and (b) the adsorption of the solute molecules from the subsurface onto the surface.

Ward and Tordai [2] have given the general formulation and complete mathematical solution to the problem of diffusion-controlled adsorption in which step (b) is assumed to be instantaneous. Application of their theory to experimental data indicates that, in many cases, diffusion alone is not the cause of dynamic surface tension.

The problem of surfactant transport, which accounts for both the diffusion in the bulk and adsorption from the subsurface, has been examined by several workers [2-9]. In most cases, the second step (b) is represented by a kinetic expression [3-5, 7-9]. Despite several attempts, there is no single treatment of the problem which achieves a general numerical scheme for solving the non-linear set of equations for a general isotherm, without making any simplifying assumptions. In this paper, we critically examine the numerical schemes and the simplifying assumptions of

the earlier investigations. We then present a general formulation of the problem and a simple numerical scheme to solve the resulting equations. This model is called here a "diffusion-kinetic model" as suggested by Miller and Kretzschmar [9], rather than the terminology "barrier-limited" or "adsorption-limited mechanism" used by Hansen [4] and Tsonopoulos *et al.* [5], respectively. We also illustrate the formal procedure for estimating the adsorption barrier from the experimental dynamic surface tension data.

Knowledge of the adsorption process of surfactant systems is of great importance to a complete understanding of mass transfer. Many important phenomena, such as interfacial turbulence, thin film stability, and retardation of drop motion, are consequences of the fact that surface tension varies with surface concentration. In hydrodynamic modelling of any of these phenomena, the hydrodynamics are coupled with mass transfer through the surface stress boundary conditions [10, 11]. Since a barrier to adsorption is known to exist in the case of many surfactant systems, it must be incorporated in the surface conservation equations. A general diffusion-kinetic model is essential to modelling these phenomena, since it will allow us to estimate the extent of this adsorption barrier from experimental dynamic surface tension data.

DIFFUSION-KINETIC MODEL

The diffusion-kinetic model to be presented here takes into account both diffusion in the bulk and the barrier to adsorption, which is represented by a kinetic expression. Kimizuka *et al.* [6] had rejected this two-step approach in favour of the more sophisticated approach wherein the surfactant transport is assumed to be determined by its concentration gradient as well as by the gradient of the potential field at the interface. Their approach, though fundamentally more correct, admits random selection of the gradient of potential and hence has limited usefulness as a model.

From the equilibrium surface tension vs bulk concentration data, the adsorption isotherm and the

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equation of state characteristic of the surfactant system under consideration can be obtained. Once the adsorption isotherm is known, the diffusion-kinetic model can be applied if the corresponding form of the kinetic expression is known. Denbigh[12] presents this correspondence principle in general terms. For the case of an elementary physico-chemical reaction, the principle states that equating the forward and the backward rates in the kinetic expression, should, on suitable rearrangement, yield the equilibrium relationship. Although the adsorption isotherm can be obtained from equilibrium data, the kinetic expression needs to be independently chosen. In most systems of interest here (wherein the dynamics are observable over a period of few minutes only), the adsorption barriers are not very high and considerable resistance in the two-step process is due to the diffusional limitations. Therefore, a diffusion-kinetic model should not be used to decide the form of the kinetic expression, as is a common practice in the kinetic models for chemical reactions. It is assumed instead that the form of the kinetic expression corresponding to the isotherm under consideration is known apriori. Furthermore, the diffusion-kinetic model, as developed below, does not explicitly account for electric charge effects and double layer effects and, hence, may not be directly applicable to the case of ionogenic surfactants.

The diffusion-kinetic model thus yields surface concentration as a function of time for a particular rate constant. The dynamic surface tension can then be calculated using the equation of state corresponding to the isotherm under consideration. The validity of such a procedure has been questioned by Fordham[13]. He believes that concentration gradients should be included in calculating the dynamic surface excess concentration for use in the Gibbs equation. Examination of the validity of his arguments calls for a more direct measurement of the surface excess concentrations. The authors are, however, of the opinion that the surface excess as defined by Gibbs[14] should include the excess over the bulk due to the anisotropy caused by surface activity of the solute and the effects thereof, and should not include

temporary concentration deficiencies due to diffusional concentration gradients. Therefore, the equation of state obtained by application of Gibbs' equation to equilibrium measurements can be used to relate the dynamic surface tension to the dynamic surface concentration.

Theoretical considerations

The first general formulation of the problem is due to Hansen[4] and the formulation presented herein is essentially the same as his. A schematic diagram of the system under investigation is shown in Fig. 1. Since the concentration of the solute is low, Fick's Second Law of Diffusion in one dimension can be used to describe molecular diffusion. The governing equation and the initial and boundary conditions can thus be written as

$$\frac{\partial c}{\partial t}(x, t) = D \frac{\partial^2 c}{\partial x^2}(x, t) \quad 0 < x < \infty, t > 0 \quad (1)$$

$$\text{I.C.:} \quad C(x, 0) = C_0 \quad (2)$$

$$\Gamma(0) = 0 \quad (3)$$

$$\text{B.C.:} \quad \lim_{x \rightarrow \infty} C(x, t) = C_0 \quad (4)$$

$$D \frac{\partial c}{\partial x}(x, t)|_{x=0} = \frac{d\Gamma}{dt}(t) \quad (5)$$

and

$$\frac{d\Gamma(t)}{dt} = r_1 - r_{-1} \quad (6)$$

where $C(x, t)$ is the concentration of the surfactant in the bulk, $\Gamma(t)$ is its concentration at the surface, x is the distance from the surface in the direction normal to it, t is time, D is diffusivity and r_1 and r_{-1} are the forward and backward rates in the kinetic expression. Without loss of generality, eqn (6) can be written as

$$\frac{d\Gamma}{dt}(t) = k[\phi(C(0, t), \Gamma(t))] \quad (7)$$

where k is the rate constant for the forward rate r_1 , and $\phi(C(0, t), \Gamma(t))$ is the remainder of the kinetic expression. The limiting case of diffusion controlled adsorption is realized when $k \rightarrow \infty$, so that

$$\phi(C(0, t), \Gamma(t)) = 0$$

which can be rearranged as

$$C(0, t) = f(\Gamma(t)) \quad (8)$$

and since the sub-surface and the surface are in local equilibrium, by the correspondence principle, eqn (8) must be the adsorption isotherm.

The forward rate is almost always dependent on $C(0, t)$ to its first power and is also dependent on $\Gamma(t)$, while the backward rate is independent of $C(0, t)$. Thus, in view of the equilibrium relationship, we can write

$$\frac{d\Gamma(t)}{dt} = kG(\Gamma(t))[C(0, t) - f(\Gamma(t))]. \quad (9)$$

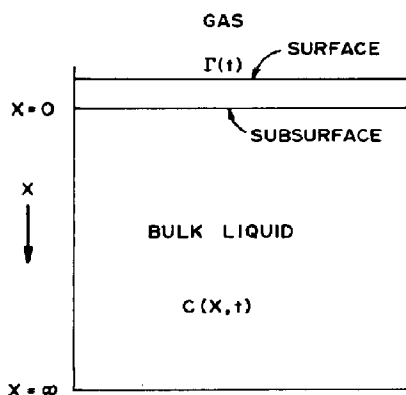


Fig. 1. Schematic diagram of the system, and the co-ordinate system.

It is convenient to write eqn (9) in the form

$$k' \frac{d\Gamma(t)}{dt} = G(\Gamma(t)) [C(o, t) - f(\Gamma(t))] \quad (10)$$

where k' is the reciprocal of the forward rate constant k . The diffusion-controlled case is now realized when $k' \rightarrow 0$. This procedure enables the inclusion of the diffusion controlled case in a general computer program.

By the technique of Laplace transforms, equations (1) to (5) can be solved to give

$$\Gamma(t) = 2C_0 \left(\frac{Dt}{\pi} \right)^{1/2} - \left(\frac{D}{\pi} \right)^{1/2} \int_0^t \frac{C(o, \tau)}{(t-\tau)^{1/2}} d\tau. \quad (11)$$

Equation (11) is one of the several possible integral representations of the system of eqns (1)–(5). Several investigators[9, 15] have used other forms, among them Miller and Kretzschmar[9], who have used the following representation.

$$\Gamma(t) = 2C_0 \sqrt{\frac{Dt}{\pi}} - 2 \left(\frac{D}{\pi} \right)^{1/2} \int_0^t C(o, t-\tau) d\tau^{1/2}. \quad (11a)$$

The basic nature of the integral equation remains the same in any one of these forms, though a particular form may be more suitable for a particular method of solution.

In the case of diffusion-controlled adsorption, eqns (11) and (8) can be combined to give the Ward and Tordai[2] equation:

$$\Gamma(t) = 2C_0 \left(\frac{Dt}{\pi} \right)^{1/2} - \left(\frac{D}{\pi} \right)^{1/2} \int_0^t \frac{[f(\Gamma)]_\tau}{(t-\tau)^{1/2}} d\tau. \quad (12)$$

Several investigators have developed numerical schemes to solve eqn (12) of the diffusion-controlled adsorption for specific isotherms[15–18]. Miller[19] has recently presented a numerical treatment of the diffusion-controlled case using a finite difference scheme to solve eqns (1)–(5) and (8) for any isotherm. Bogaert and Joos[20] and Miller *et al.*[21] have devised numerical schemes to solve integral equations of the diffusion-controlled case when more than one surfactant is present. However, no general numerical scheme for solving eqns (10) and (11) of the diffusion-kinetic model has been presented so far.

The first diffusion-kinetic treatment of the problem of surfactant adsorption is due to Sutherland[3]. He presented an analytical solution for the case of a linear adsorption isotherm with linear kinetics. A slight error in his solution was pointed out by Hansen[4]. Tsionopoulos *et al.*[5] have extended the solution to include the values of the adsorption rate constant when the governing relation becomes a complex variable equation.

The only solution of the exact equations of the diffusion-kinetic model for the case of a non-linear isotherm presented heretofore, is the Miller and Kretzschmar[9] solution for the Langmuir isotherm.

For the Langmuir isotherm, eqn (9) can be written as

$$\frac{d\Gamma(t)}{dt} = k \left[C(o, t)(\Gamma_m - \Gamma(t)) - \frac{\Gamma(t)}{\beta} \right] \quad (9a)$$

where β and Γ_m are constants in the Langmuir isotherm. This equation was integrated analytically by Miller and Kretzschmar[9] over small time intervals, assuming that $C(o, t)$ does not change appreciably over this interval. (This linearization step is not a serious oversimplification if the time intervals used are very small.) They then integrated eqn (11a) using the trapezoidal rule, and solved the resulting equations simultaneously for $C(o, t)$ and $\Gamma(t)$. Their method, however, cannot be directly applied to isotherms which do not have kinetic expressions linear in $\Gamma(t)$ since, in those cases, eqn (9) also needs to be integrated numerically.

The only other work in diffusion-kinetic modelling is that of Fainerman[7, 8]. His work has several shortcomings. His hypothesis that the rate constant varies with surface coverage is contrary to the established practice in kinetic modelling. In the generally accepted approach, the rate constant is considered to be independent of the concentrations, since these are explicitly introduced in the kinetic expression. The dependence he postulates of activation energy on surface coverage can be more correctly introduced into the kinetic expression for the Frumkin isotherm using activity coefficients in the place of concentrations, since Stauff[22] has shown that for the Frumkin isotherm for a non-ideal surface, the solute-solvent interactions are amenable to rationalization using the regular solution theory. Furthermore, Fainerman[7] asserts a dependence of rate constant on surface coverage for the case of Langmuirian adsorption which seems quite unlikely. In the opinion of these authors, this serious discrepancy is entirely attributable to his erroneous simplifying assumption[7] that the "adsorption rate for any degree of adsorption layer filling can be formally expressed as first order reaction, i.e. the inverse rate of adsorption is equal to the sum of the inverse rates of adsorption under diffusion and kinetic control of the process". This assumption of first-order rate process is in direct contradiction to the non-linearity of the adsorption isotherm under consideration and the unsteady nature of the transport process.

Method of solution and the numerical scheme

The technique adopted here to solve eqns (10) and (11) of the generalized diffusion-kinetic model is both general and simple. Between eqns (10) and (11), $C(o, t)$ is eliminated to yield a single integro-differential equation of the Volterra type:

$$\Gamma(t) = 2C_0 \left(\frac{Dt}{\pi} \right)^{1/2} - \left(\frac{D}{\pi} \right)^{1/2} \int_0^t \left\{ k' \frac{d\Gamma}{dt} \frac{1}{G(\Gamma)} + f(\Gamma) \right\}_\tau d\tau \quad (13)$$

The method involves removal of the singularity in the integrand at the upper limit of integration and using the backward difference formula for the derivative. The trapezoidal rule is then applied to evaluate the integral, and the Newton-Raphson method is used to solve the resulting equation in $\Gamma(t)$.

Several isotherms are reported in the literature. For example, Miller[19] has solved the diffusion-controlled case for six isotherms. However, for several of these isotherms, the kinetic expression is not known. Moreover, many of these isotherms may not be common in surfactant systems. A large class of non-ionic surfactants obeys the Frumkin isotherm, of which the Langmuir isotherm is a special case. Therefore, although the numerical scheme outlined above to solve eqn (13) can be used for any isotherm, it will be illustrated here for the Frumkin isotherm only.

The Frumkin isotherm relates the surface concentration Γ to the bulk concentration C with which it is in equilibrium, as follows[23]:

$$C = \frac{1}{\beta} \frac{\Gamma}{\Gamma_m - \Gamma} e^{-A\Gamma/\Gamma_m} \quad (14)$$

where β , Γ_m and A are constants. The constant A is called the interaction parameter and represents the solute-solvent interaction in the non-ideal surface. When A is positive, there is attraction between the molecules; when A is negative, there is repulsion; and when A is zero, the surface is ideal and eqn (14) reduces to that for the Langmuir isotherm. Stauff[22] has derived the Frumkin isotherm by using the analog of regular solution theory to account for the solute-solvent interactions. Using the Eyring's theory of absolute reaction rates, it is possible to derive the rate expression for the Frumkin isotherm[24]. This expression is given as follows:

$$k' \frac{d\Gamma(t)}{dt} = \exp\left(\frac{A}{2} \left(\frac{\Gamma}{\Gamma_m}\right)^2\right) \left[C(o, t)(\Gamma_m - \Gamma) - \frac{\Gamma \exp\left(-A \frac{\Gamma}{\Gamma_m}\right)}{\beta} \right] \quad (10a)$$

Eliminating $C(o, t)$ between eqns (10a) and (11), we

get

$$\Gamma(t) = 2C_0 \left(\frac{Dt}{\pi}\right)^{1/2} - \left(\frac{D}{\pi}\right)^{1/2} \int_0^t \left\{ \frac{k' \exp\left(-\frac{A}{2} \left(\frac{\Gamma}{\Gamma_m}\right)^2\right) \frac{d\Gamma}{dt} + \frac{\Gamma}{\beta} \exp\left(-A \frac{\Gamma}{\Gamma_m}\right) \right\} \frac{d\tau}{(t-\tau)^{1/2}} \quad (15)$$

At this stage, it is convenient to introduce the following dimensionless variables:

$$\mu = \frac{\Gamma}{\Gamma_m}, \quad \psi = \beta C_0, \quad z = \frac{4DtC_0^2}{\pi\Gamma_m^2}, \quad (16)$$

$$\eta = \frac{4D\tau C_0^2}{\pi\Gamma_m^2}, \quad \alpha = \frac{4DC_0 k'}{\pi\Gamma_m^2}.$$

In terms of these dimensionless variables, eqn (15) becomes

$$\mu = z^{1/2} - \frac{1}{2\psi} \int_0^z \left\{ \frac{\alpha \psi \frac{d\mu}{dz} \exp\left(-\frac{A}{2} \mu^2\right) + \mu \exp(-A\mu)}{1 - \mu} \right\} \frac{d\eta}{(z - \eta)^{1/2}} \quad (17)$$

The singularity in the integrand at the upper limit is removed by substituting

$$\eta = z \sin^2 \theta. \quad (18)$$

Thus, equation (17) becomes

$$\mu = z^{1/2} - \frac{z^{1/2}}{\psi} \int_0^{\pi/2} \left\{ \frac{\alpha \psi \frac{d\mu}{dz} \exp\left(-\frac{A\mu^2}{2}\right) + \mu \exp(-A\mu)}{1 - \mu} \right\} \sin \theta \, d\theta. \quad (19)$$

Using the backward difference formula for the derivative and the trapezoidal rule for integration, eqn (19) can be written as

$$\begin{aligned} \mu_n = z^{1/2} - \theta_2 \frac{z^{1/2}}{2\psi} & \left\{ \frac{\psi \alpha \frac{\mu_2 - \mu_1}{\eta_2 - \eta_1} \exp\left(-\frac{A\mu_2^2}{2}\right) + \mu_2 \exp(-A\mu_2)}{1 - \mu_2} \right\} \sin \theta_2 \\ & - \frac{z^{1/2}}{2\psi} \sum_{j=2}^{n-1} \left\{ \frac{\psi \alpha \frac{\mu_{j+1} - \mu_j}{\eta_{j+1} - \eta_j} \exp\left(-\frac{A\mu_{j+1}^2}{2}\right) + \mu_{j+1} \exp(-A\mu_{j+1})}{1 - \mu_{j+1}} \right\} \sin \theta_{j+1} \\ & + \frac{\psi \alpha \frac{\mu_j - \mu_{j-1}}{\eta_j - \eta_{j-1}} \exp\left(-\frac{A\mu_j^2}{2}\right) + \mu_j \exp(-A\mu_j)}{1 - \mu_j} \sin \theta_j \left\{ (\theta_{j+1} - \theta_j) \right\} \end{aligned} \quad (20)$$

where

$$\mu_j = \mu(\eta_j), \eta_1 = 0, \theta_1 = 0, \theta_j = \sin^{-1} \sqrt{\frac{\eta_j}{z}}, \eta_n = z.$$

Although the backward difference cannot be evaluated at $j = 1$, the term does not appear since $\theta_1 = \sin \theta_1 = 0$ at $j = 1$. The procedure is to march in time from time equals zero. In each calculation all the previous evaluations were used as grid points. The result of integration is an algebraic equation in the unknown μ_n . In the case of the Langmuir isotherm the equation is a simple quadratic, while for the Frumkin isotherm the non-linear equation is readily solved using the Newton-Raphson method. A computer program was written and the calculations were performed on I.I.T.'s Prime-400 computer. Before presenting the results of the computer calculations, a simplification of the above diffusion-kinetic model is proposed.

Simplified diffusion-kinetic model

A considerable simplification of the diffusion-kinetic model can be achieved by accounting for the diffusion in the bulk using the diffusion-penetration theory. Such a simplification was used by Bogaert and Joos[18] for the diffusion-controlled case. According to the diffusion-penetration theory, the concentration gradient near the surface can be approximated by[25]

$$\left. \frac{\partial C(x, t)}{\partial x} \right|_{x=0} = \frac{C_0 - C(o, t)}{(\pi D t)^{1/2}} \quad (21)$$

then by eqn (5)

$$\frac{d\Gamma(t)}{dt} = D \left. \frac{\partial C(x, t)}{\partial x} \right|_{x=0} = \left(\frac{D}{\pi t} \right)^{1/2} [C_0 - C(o, t)]. \quad (22)$$

This simplified expression for diffusion in the bulk is then combined with the kinetic expression for adsorption from the subsurface, eqn (10), to yield, upon rearrangement,

$$\frac{d\Gamma(t)}{dt} = \frac{C_0 - f(\Gamma(t))}{\frac{k'}{G(\Gamma(t))} + \left(\frac{\pi t}{D} \right)^{1/2}} \quad (23)$$

For the case of the Frumkin isotherm, equation (23) becomes

$$\frac{d\Gamma(t)}{dt} = \frac{C_0(\Gamma_m - \Gamma) - \frac{\Gamma}{\beta} \exp\left(-A \frac{\Gamma}{\Gamma_m}\right)}{k' \exp\left(\frac{-A}{2} \left(\frac{\Gamma}{\Gamma_m}\right)^2\right) + \left(\frac{\pi t}{D}\right)^{1/2} (\Gamma_m - \Gamma)}. \quad (24)$$

In terms of the dimensionless variables defined by eqn (16), eqn (24) becomes

$$\frac{d\mu}{dz} = \frac{(1 - \mu) - \frac{\mu}{\psi} \exp(-A\mu)}{\alpha \exp\left(\frac{-A}{2} \mu^2\right) + 2(1 - \mu)z^{1/2}}. \quad (25)$$

This equation is an ordinary differential equation and can be integrated using any explicit scheme such as the Runge-Kutta method. The calculations for this simplified theory were also performed on I.I.T.'s Prime-400 computer.

RESULTS AND DISCUSSION

1. Parametric study of the exact diffusion-kinetic model

Computer calculations were performed using the exact diffusion-kinetic model to study the effect of dimensionless bulk concentration ψ , dimensionless reciprocal rate constant α , and the interaction parameter

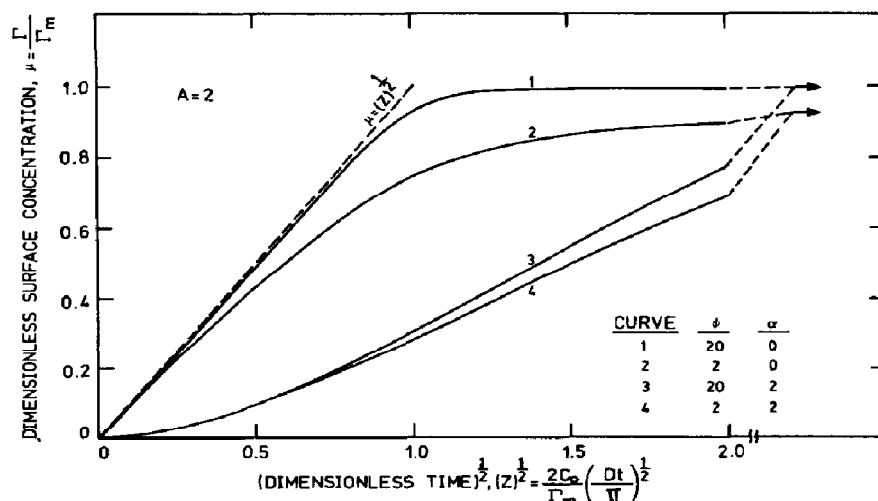


Fig. 2. Dependence of dimensionless surface concentration on square root of dimensionless time for $A = 2$ and various values of ψ and α .

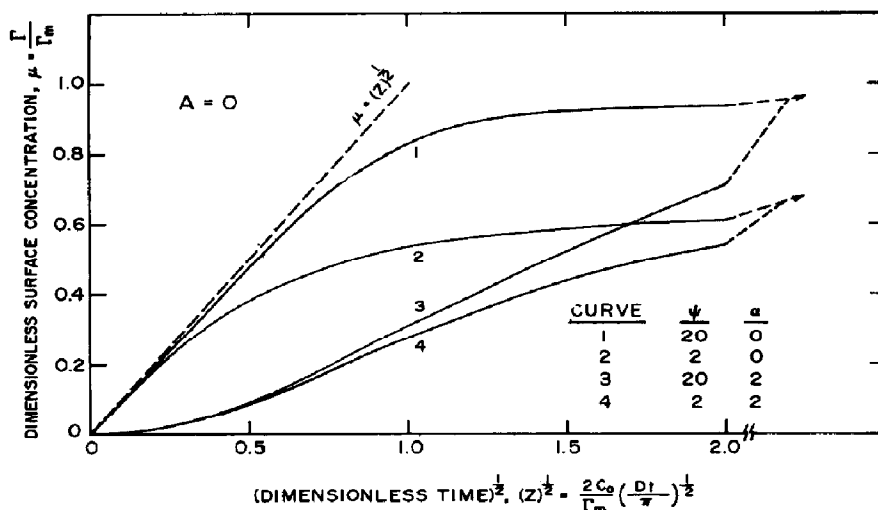


Fig. 3. Dependence of dimensionless surface concentration on square root of dimensionless time for $A = 0$ and various values of ψ and α .

A , on the rate of adsorption. Figures 2–4 show the dependence of dimensionless surface concentration, μ , on the square root of dimensionless time, z , for $A = -2, 0$ and 2 respectively, with ψ and α as parameters. We cite the important conclusions below.

The initial slope of the diffusion-controlled adsorption on a plot of μ vs $z^{1/2}$ is unity (or is infinite on a plot of μ vs z), while that of the diffusion-kinetic adsorption is zero (or is finite on a plot of μ vs z). This observation was previously reported by Hansen[4] when he expanded Sutherland's[3] solution for a linear isotherm in series for small times. In the diffusion-controlled case, the subsurface concentration drops from bulk concentration to zero instantaneously at zero time causing the initial fluxes to be infinite. By contrast, in the diffusion-kinetic case, the

adsorption barrier, however, small, inhibits such an abrupt change, thereby maintaining finite initial fluxes. However, this observation is not readily obvious from eqn (17). The first term in eqn (17) is $z^{1/2}$ for both diffusion-controlled and diffusion-kinetic cases. A small z analysis was performed to explain this observation.

Consider the non-dimensionalized form of eqn (10a) for the Frunkin isotherm.

$$\alpha \frac{d\mu}{dz} = (1 - \mu) \left[\hat{C}(o, z) - \frac{\mu}{\psi(1 - \mu)} \exp(-A\mu) \right] \times \exp\left(-\frac{A}{2}\mu^2\right) \quad (26)$$

where $\hat{C}(o, z) = C(o, t)/C_0$ is the dimensionless sub-

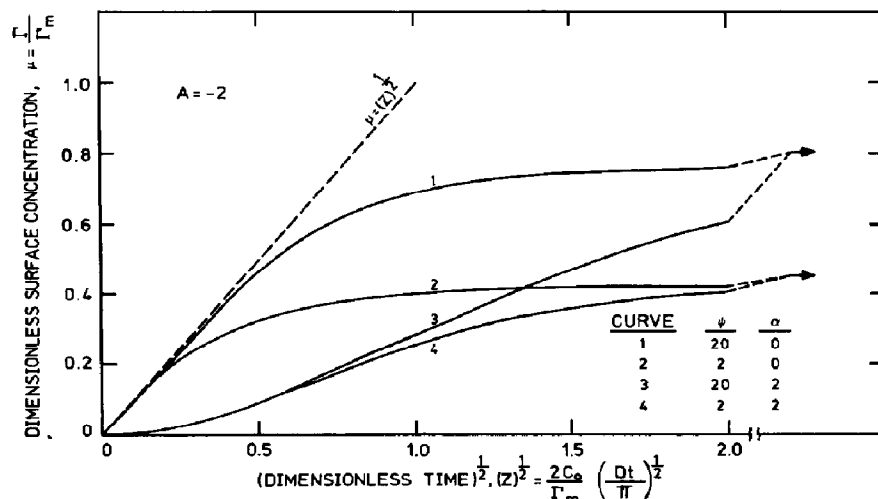


Fig. 4. Dependence of dimensionless surface concentration on square root of dimensionless time for $A = -2$ and various values of ψ and α .

surface concentration as a function of dimensionless time. At small z , the surface is essentially empty and, for the diffusion-kinetic case, the subsurface concentration is equal to the bulk concentration. Thus, at small z , eqn (26) becomes

$$\alpha \frac{d\mu}{dz} \approx 1 \quad (27)$$

and eqn (17) becomes

$$\mu \approx z^{1/2} - \frac{1}{2\psi} \int_0^z \left\{ \psi \alpha \frac{d\mu}{dz} \right\}_\eta \frac{d\eta}{(z-\eta)^{1/2}} \quad (28)$$

Substituting eqn (27) in eqn (28) and integrating,

$$\mu \approx z^{1/2} - z^{1/2} \approx 0. \quad (29)$$

For the diffusion-controlled case, we have

$$\alpha \frac{d\mu}{dz} = 0 \quad z > 0 \quad (30)$$

and from eqn (28)

$$\mu \approx z^{1/2}. \quad (31)$$

At $z = 0$, the quantity $\alpha(d\mu/dz)$ is indeterminate since the subsurface concentration instantaneously drops from the bulk concentration value to zero and, hence, is also indeterminate. This is a consequence of infinite initial flux. For mathematical rigour, therefore, all integral equations for the diffusion-controlled case should have the lower limit 0^+ instead of 0. Thus, the small z analysis has shown that the initial slope of the μ vs $z^{1/2}$ curves for the diffusion-kinetic case is zero, and for the diffusion-controlled case is unity.

A few additional comments evolve from this analysis:

(i) For any non-zero value of α , the term containing

α in eqn (17) exactly cancels the $z^{1/2}$ term outside the integral at small times.

(ii) In the case of diffusion-controlled adsorption, the term $z^{1/2}$ outside the integral corresponds to forward diffusion and the integral corresponds to backward diffusion, whereas, for the diffusion-kinetic case, this term $z^{1/2}$ has no such physical significance.

(iii) The shape of the curve for the diffusion-kinetic case arises as follows:

(a) At first, the $z^{1/2}$ term and the term containing α in the integral exactly cancel each other to give an initial slope of zero.

(b) The $z^{1/2}$ term then increases faster than the term containing α , so that the slope rises continuously from zero.

(c) Finally, the other term in the integral begins to increase rapidly, causing the slope to decrease rapidly.

From the parametric study, it can also be seen that the rates of adsorption for any particular value of α are highest when there is attractive interaction ($A > 0$) between the solute and solvent in the surface, and the rates are lowest when the interaction is repulsive ($A < 0$). This conclusion is intuitively obvious.

Finally, whereas the rate of diffusion-controlled adsorption increases considerably with increasing concentrations, the increase is not so significant in the presence of adsorption barriers. Consequently, the effect of the value of the adsorption rate constant on the adsorption rate is greatest at high concentrations. This observation is important to the correlation of the model to experimental data, and will be discussed in more detail in a later section.

2. Comparison of the exact diffusion-kinetic model to the simplified model

Bogaert and Joos[18] first proposed the use of a diffusion-penetration theory to approximate diffusion in the bulk for the case of diffusion-controlled ad-

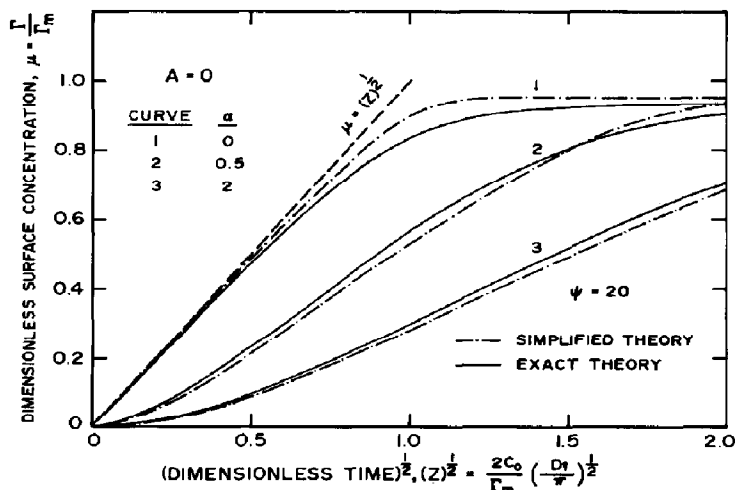


Fig. 5. Comparison between the exact diffusion-kinetic theory and the simplified theory for various values of α ; $A = 0$, $\psi = 20$.

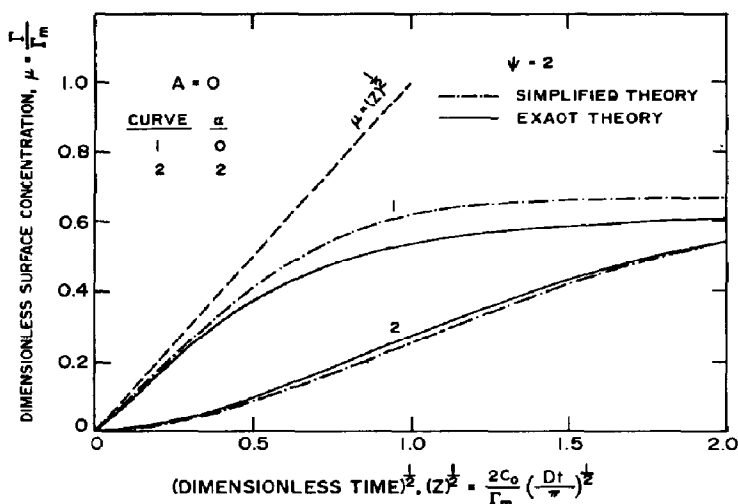


Fig. 6. Comparison between the exact diffusion-kinetic theory and the simplified theory for various values of α ; $A = 0$, $\psi = 2$.

sorption. This method was used here to make a similar approximation for the diffusion-kinetic case. Bogaert and Joos[18] had observed that, for the case of diffusion-controlled adsorption, the approximation overpredicts the rates at higher surface coverage. Since diffusion-kinetic theory involves two resistances, one of which is approximated, the error introduced by such an approximation is expected to decrease with increasing adsorption barriers, tending towards zero as the adsorption-controlled case is approached. Figures 5 and 6 show the comparison between the exact diffusion-kinetic theory and the simplified theory. It can be seen that the error is, indeed, smaller for diffusion-kinetic adsorption than for diffusion-controlled adsorption.

The present results are very encouraging. Since the simplified diffusion-kinetic model permits the use of explicit numerical schemes, considerable computer time and programming effort can be saved. The simplification achieved is not considerable for the gas-liquid case, but can be quite tremendous when extended to the liquid-liquid case[24].

3. Limiting cases

Certain of the limiting cases of the diffusion-kinetic model presented here have been solved previously for specific isotherms only. One of the isotherms considered by Miller[19] for the case of diffusion-controlled adsorption was the Frumkin isotherm. Figures 7 and 8 show typical results of his calculations as a plot of dimensionless surface concentration, μ , vs dimensionless time, z . These figures also show the results of the present calculations for the same set of parameters. The two numerical schemes give results which are in very good agreement.

The results of Miller and Kretzschmar's[9] numerical solution for the Langmuir isotherm have also been compared with the results of the limiting case of the present solution. Their results are plotted as surface tension, σ , vs time, t in Fig. 9, along with the results of the present calculations. Again, the agreement between the two is basically very good, with a slight discrepancy arising probably from the differences in the numerical schemes.

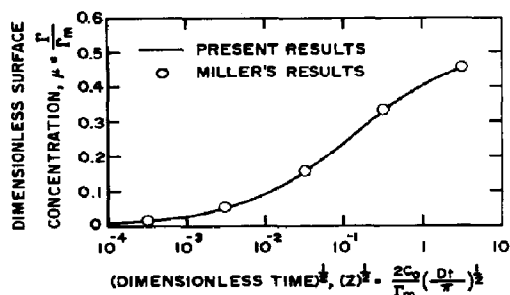


Fig. 7. Comparison of the present results with the results of Miller[19] for $\psi = 0.995$, $A = 0.01$ and $\alpha = 0$.

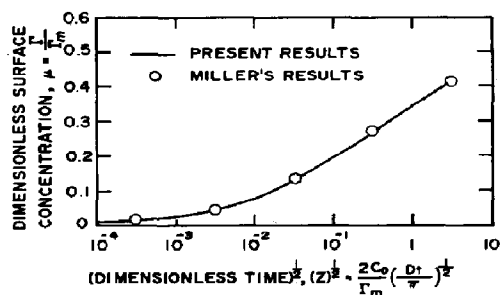


Fig. 8. Comparison of the present results with the results of Miller[19] for $\psi = 0.377$, $A = 1.95$ and $\alpha = 0$.

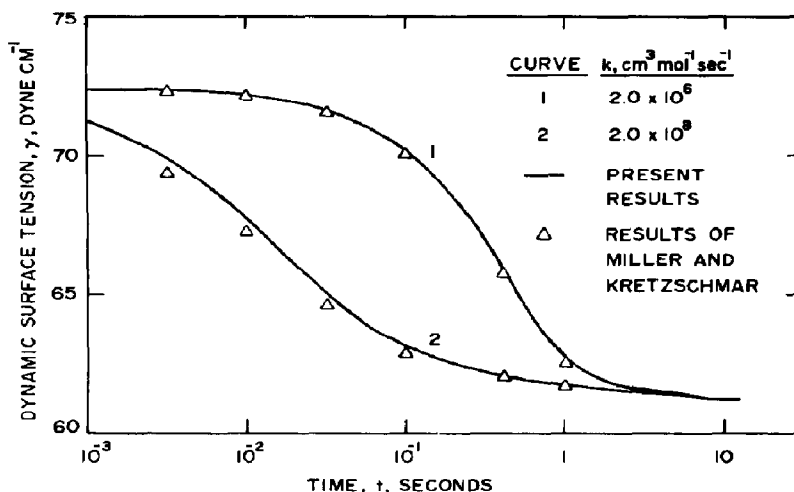


Fig. 9. Comparison of the present results with the results of Miller and Kretzschmar[9] for $\Gamma_{\infty} = 5 \times 10^{-10} \text{ mol cm}^{-2}$, $D = 5 \times 10^{-6} \text{ cm}^2 \text{sec}^{-1}$, $\beta = 1.429 \times 10^6 \text{ cm}^3 \text{mol}^{-1}$, $C_0 = 10^{-6} \text{ mol cm}^{-3}$ for various values of k .

4. Correlation of experimental data

There have been only a few attempts to correlate the models of surfactant transport with experimental dynamic surface tension data. Ward and Tordai[2], and later Lange[26], used experimental data to graphically evaluate the integral in the Ward and Tordai equation (eqn 15), and obtained diffusivity values at various times and for various concentrations. When these calculated diffusivity values were close to those obtained by extraneous means, diffusion-controlled adsorption was considered to be adequate for that system. When these diffusivity values were much lower than those obtained by extraneous means, an adsorption barrier was postulated. Bendure[27] correlated his experimental dynamic data using the approximate solution given by Hansen[28] for the Langmuir isotherm. As pointed out by Tsionopolous *et al.*[5], this method is both indirect and inconclusive. The exact solution of the Ward and Tordai equation has been correlated to experimental data only once, in the work of Bogaert and Joos[18]. In a later paper[20], they derived the theory for rates of diffusion-controlled adsorption for the extended Langmuir isotherm when surfactant mixtures are present, and correlated the theory to their experimental data. As for the diffusion-kinetic case, Tsionopolous *et al.*[5] have correlated data for a single concentration of hexanol in water to the analytical solution for a linear isotherm derived by Sutherland[3]. Although their conclusion seems correct that, for the hexanol/water system, diffusion alone is not the cause of dynamic surface tension, their estimation of the adsorption rate constant from the data for a single concentration is inconclusive.

The model developed herein can be used to predict dynamic surface concentration and, using the equation of state, dynamic surface tension, if the ad-

sorption isotherm, the corresponding kinetic expression, and the value of the kinetic rate constant are known. Since the adsorption isotherm is known from equilibrium considerations, and the kinetic expression is assumed to be known, the correlation of experimental data to the model rests on obtaining the value of the kinetic rate constant which fits the experimental data for all concentrations.

One of the findings of the present parametric study was that the effect of the kinetic rate constant on the dynamic surface concentration (or dynamic surface tension) is greatest at high concentrations. This suggests that the data for the highest concentration studied should be used to obtain a tentative value for the kinetic rate constant, which can then be verified using data for other concentrations. The only limitation to this approach is that the adsorption proceeds very rapidly for high concentration and, therefore, the experimental data for high concentration cannot always be obtained with reliability. The kinetic rate constant obtained from data for high concentrations may therefore have to be subsequently modified to fit data for all concentrations.

Finally, we want to draw attention to the useful comment of Fainerman[7], who pointed out that the experimental verification of diffusion-kinetic model presents difficulties, since the methods used for measuring dynamic surface tension often fail to correspond to the calculated models (e.g. in several of the methods, the convection currents may not be totally eliminated).

We now make use of the formal procedure outlined above to correlate the diffusion-kinetic model with the experimental data.

Decanoic acid/water. Defay and Hommelen[29, 30] have studied dynamic surface tensions for this system. The system obeys the Frumkin isotherm,

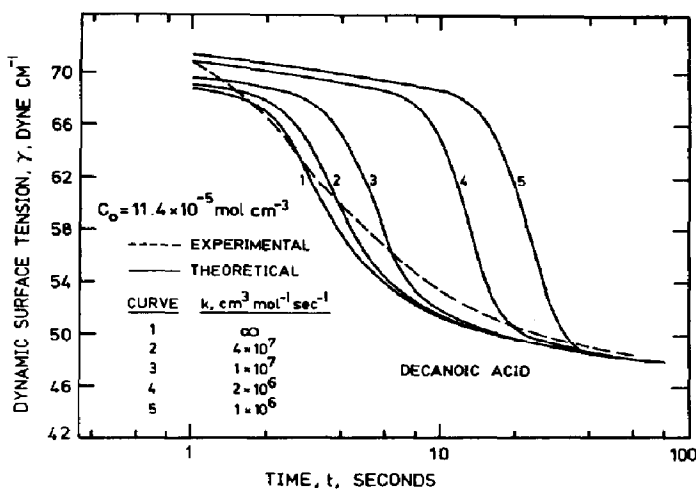


Fig. 10. Comparison of the diffusion kinetic theory with experimental dynamic surface tension data of Defay and Hommelen[29, 30] for Decanoic acid, $C_0 = 11.4 \times 10^{-8} \text{ mol cm}^{-3}$.

and the values of the constants in the isotherm are reported by Thiessen and Scheludko[31] to be $\beta = 1.12 \times 10^7 \text{ cm}^3/\text{mol}$, $A = 3.455$ and $\Gamma_m = 5.36 \times 10^{-10} \text{ mols/cm}^2$. The data for the highest concentration reported was used to obtain the value of the kinetic rate constant. The diffusion coefficient was calculated from the Wilke-Chang correlation. It can be seen from Fig. 10 that $k = 4 \times 10^7 \text{ cm}^3/(\text{mol-sec})$ fits the data fairly well for the concentration $11.4 \times 10^{-8} \text{ mols/cm}^3$. This value was checked against data at two other concentrations. Figure 11 and 12 show that the value $4 \times 10^7 \text{ cm}^3/(\text{mol-sec})$ does fit the data for these concentrations. It can thus be concluded that a weak adsorption barrier exists for the decanoic acid/water system, in disagreement with Defay and Hommelen[32] who had concluded that the data is

explicable using a diffusion-controlled model, and that the rate constant is about $4 \times 10^7 \text{ cm}^3/(\text{mol-sec})$. Any further refinement of this value is not justified given that the data available are limited.

Dodecanol + 7 (ethylene-oxide)/water

Lange[26, 33] has studied both equilibrium and dynamic surface tensions of this system. The system obeys the Langmuir isotherm, and the values of the constants in the isotherm as reported by Lange are $\beta = 4.95 \times 10^9 \text{ cm}^3/\text{mol}$ and $\Gamma_m = 2.498 \times 10^{-10} \text{ mol/cm}^2$. Lange[26, 33] used the data to calculate diffusion coefficients from the Ward and Tordai equation by graphically evaluating the integral in the equation. He concluded that diffusion-controlled adsorption adequately accounts

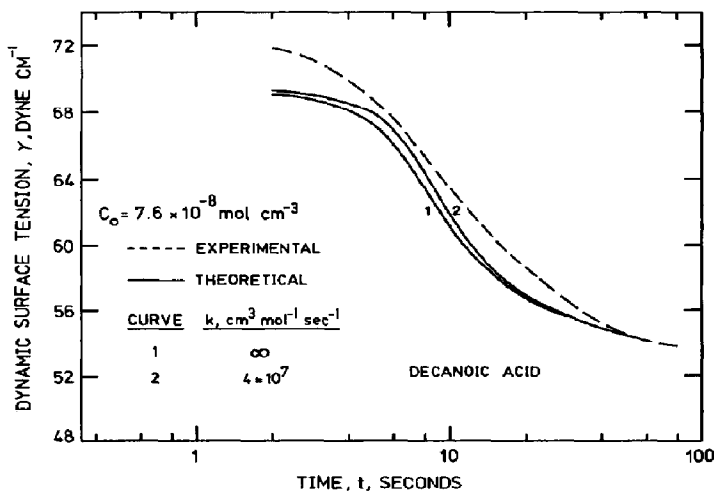


Fig. 11. Comparison of the diffusion-kinetic theory with experimental dynamic surface tension data of Defay and Hommelen[29, 30] for Decanoic acid, $C_0 = 7.6 \times 10^{-8} \text{ mol cm}^{-3}$.

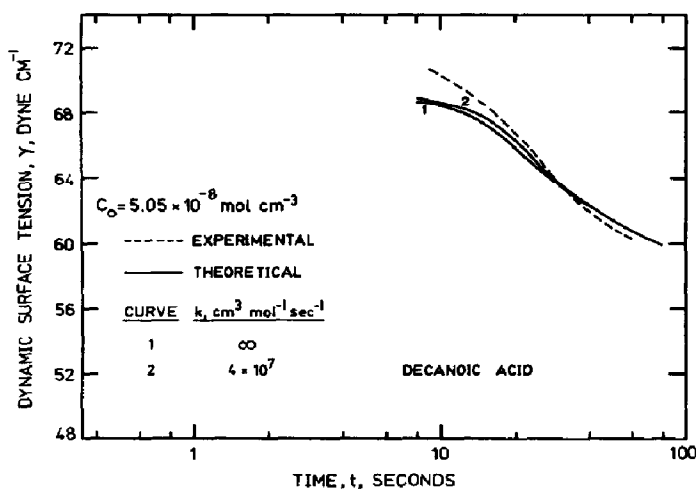


Fig. 12. Comparison of the diffusion kinetic theory with experimental dynamic surface tension data of Defay and Hommelen[29, 30] for Decanoic acid, $C_0 = 5.05 \times 10^{-8} \text{ mol cm}^{-3}$.

for the data for this system. With the diffusivity value calculated from the Wilke-Chang correlation, theoretical predictions of the dynamic surface tension for the diffusion-controlled case can be made. Figures 13–15 show the comparison of experimental data with the theoretical predictions for this case. It can be seen that diffusion-controlled adsorption is in good accord with experimental data for high concentrations (Figs. 13, 14). The agreement is not so good, however, at low times for low concentrations (Fig. 15). Since the experimental data falls below the theoretical curves, the possibility that an adsorption barrier exists is excluded. The discrepancy may be explained as follows:

It is not possible to obtain highly accurate values of β from data for high concentrations. Since the equilibrium constants for this system were obtained from data for concentrations of $5 \times 10^{-9} \text{ mol/cm}^3$ and higher[33], the inaccuracy of the β values may cause considerable deviations in surface tension val-

ues at lower concentrations, particularly since surface tension values are extremely sensitive to β in the lower concentration range. On the other hand, equilibrium data cannot be obtained from measurements at lower concentrations, because of the prolongation of dynamic effects at these concentrations. Thus, constants obtained from measurements at higher concentrations, may cause considerable deviation when they are used to evaluate dynamic surface tension at low dynamic concentrations. These deviations will be most prominent for low concentrations at small times. An alternative explanation of this discrepancy between theory and experiments has been suggested by Fainerman[8].

CONCLUSIONS

A general model of adsorption of surfactants at a gas-liquid surface has been developed, which accounts for both the diffusion in the bulk and the

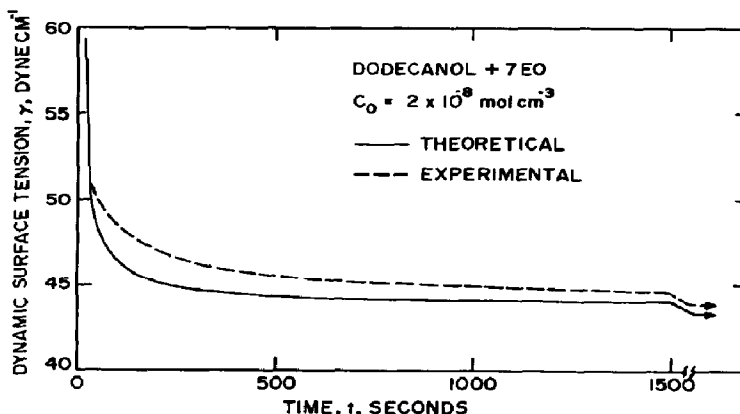


Fig. 13. Comparison of the diffusion-controlled limiting case of the diffusion-kinetic theory with experimental dynamic surface tension data of Lange[26] for Dodecanol + 7EO, $C_0 = 2 \times 10^{-8} \text{ mol cm}^{-3}$.

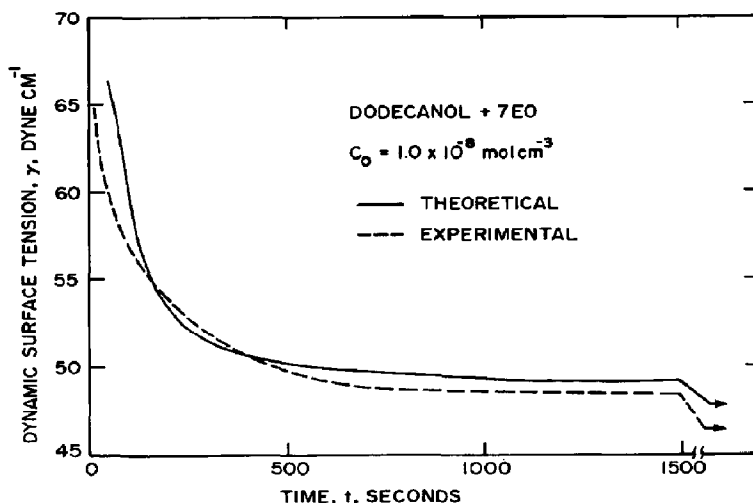


Fig. 14. Comparison of the diffusion-controlled limiting case of the diffusion-kinetic theory with experimental dynamic surface tension data of Lange[26] for Dodecanol + 7EO, $C_0 = 1.0 \times 10^{-8} \text{ mol cm}^{-3}$.

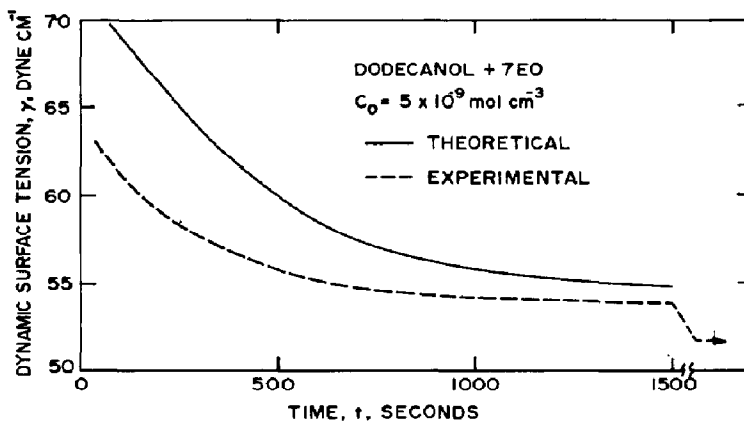


Fig. 15. Comparison of the diffusion-controlled limiting case of the diffusion-kinetic theory with experimental dynamic surface tension data of Lange[26] for Dodecanol + 7EO, $C_0 = 5.0 \times 10^{-9} \text{ mol cm}^{-3}$.

barrier to adsorption. The theory accounts for this activation energy barrier to surface entry by means of a kinetic expression. A numerical solution based on the trapezoidal rule is illustrated for the case of the Frumkin isotherm.

A simplification of the diffusion-kinetic model is proposed. This simplified model accounts for diffusion in the bulk using the diffusion-penetration theory. The simplified model compares very well with the exact model, especially for high barrier resistances.

A parametric study was conducted to study the effect of several parameters involved in the diffusion-kinetic model. The study reveals that the adsorption rate is maximized when there is attraction between adsorbed molecules, and is minimized when there is repulsion. Furthermore, the effect of the adsorption rate constant on the rate of adsorption is found to be greatest at the highest concentrations.

This fact has been used in correlating the diffusion-kinetic model with the limited experimental data available.

A precise experimental verification of the diffusion-kinetic model depends on finding the single value of the kinetic rate constant, k , which best fits the data for all concentrations. Exact quantitative verification of the model, therefore, requires accurate measurements of both the equilibrium and dynamic surface tensions over a wide range of concentrations. The importance of dynamic surface tension data cannot be overemphasized, since from these data the extent of barrier to adsorption can be estimated using the diffusion-kinetic model presented here. Knowledge of the kinetic rate constant is essential whenever a mathematical model involving surfactant transport to and from the surface is to be applied to experimental data.

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