

## 單分子層内の 表面擴散(Ⅱ)

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## Surface Diffusion in Monomolecular Films(Ⅱ)

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### Abstract

The theories for diffusive transport in bulk liquids are extended to surface diffusion in liquid-expanded monolayers which approximate liquids in regard to both thermodynamic behavior and momentum transfer. The apparent failure of the extended theories is noted and its implications are discussed. A new model is proposed and developed on the postulate that the film molecules diffuse as a two-dimensional gas in the loosely adsorbed state rather than in the regular monolayer state.

### Introduction

Experimental data on surface diffusion coefficients of several long chain fatty acids in their monolayers were reported in the previous paper.<sup>5)</sup> It would be desirable to develop a theory which explains consistently the behavior of surface diffusion in all of the film phases in terms of the monolayer properties. It is difficult at this point, however, to develop a completely general theory, because the experimental results are not sufficient, particularly for the condensed and gaseous phases. Furthermore, the temperature dependence of the phenomenon has not been elucidated. This study concerns primarily surface diffusion in the liquid-expanded phase and contemplates the nature of surface diffusion in other film phases in the light of the model developed for this phase.

The history of theoretical studies is meager. Crisp<sup>4)</sup> in 1946 assumed for estimation of an upper limit of

$D$ , for gaseous monolayers that the discontinuity at a liquid surface is very sharp, that an approximately spherical polar group of a surfactant molecule is at least half "submerged" in the liquid substrate, while the nonpolar hydrophobic portion lies above, and that the drag exerted by the film molecules on one another is negligible. The hydrodynamical theory<sup>2)</sup> of diffusion in liquids then leads to the expression

$$D_s = \frac{kT}{3\pi r\mu_0} \quad (1)$$

where  $k$  is the Boltzman constant,  $T$  the absolute temperature,  $\mu_0$  the viscosity of the pure substrate, and  $r$  the radius of the polar group. Equation (1) typically yields values of the order of  $10^{-5}$  cm<sup>2</sup>/sec for  $D_s$ . As noted above, however, Crisp's treatment must be far from exact when applied to monolayers in other states. The drag acting on the diffusing molecule therein is highly asymmetrical and arises not only from the substrate but also from the neighboring film molecules. It is also questionable to assume that the polar group of a surfactant molecule is totally submerged or even one-half submerged, as Crisp did. The actual configuration of the molecule on the

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surface should be determined solely by whichever configuration yields the minimum total surface free energy, although no one succeeded in making an exact calculation of it.

Blank and Britten<sup>3)</sup> in 1965 made a thorough-going theoretical treatment of surface transport properties (surface self-diffusivity, surface shear viscosity and surface conductivity) of a condensed monolayer on the basis of equilibrium fluctuations in monolayer density. Their theory predicts  $\sim 10^{-8}$  cm<sup>2</sup>/sec for  $D_s$  at a surface pressure of 20 dynes/cm for a stearic acid monolayer. The resulting value is noted to be slightly lower than diffusion coefficients in bulk surfactant liquids, but not nearly as low as values for solids. However, the same theory predicts values for surface viscosity ( $\sim 10^{-11}$  g/sec) in condensed films several orders of magnitude smaller than those obtained experimentally (cf. Table 1). Such disagreement is too large to permit even tentative acceptance of the theory for the prediction of the transport properties of even condensed monolayers.

Recently Whitaker<sup>13)</sup> attempted a continuum mechanical approach, extending Truesdell's mechanical theory of diffusion<sup>12)</sup> to the ideal surface gas diffusion. His treatment, however, leads to a screeching halt with the expression

$$\frac{\Gamma_{(1)} u_{(1)}^2}{\Gamma} = \left\{ 2 G_{12} a^{\alpha\beta} \frac{\partial \sigma_{(1)}}{\partial \Gamma_{(1)}} \right\} \frac{\partial \Gamma_{(1)}}{\partial x} \quad (2)$$

for a flat interface. Here

- $u_{(1)}^2$  = Surface diffusion velocity for species 1
- $a^{\alpha\beta}$  = Surface metric tensor (the surface Kronecker delta for a flat interface)
- $G_{12}$  = A positive number
- $\sigma_{(1)}$  = The "partial surface tension" for component 1
- $\Gamma_{(1)}$  = The surface density of species of 1
- $\Gamma$  = Total surface density

The result given here indicates that species 1 diffuses in the direction of increasing species 1 concentration. This analysis would seem to suggest the idea that the mass and momentum transport mechanisms are quite different.

### Extension of Bulk Diffusion Theories

Two approximate theories (Eyring rate theory<sup>7)</sup>

and hydrodynamical theory<sup>2)</sup>] appear worthy of extension in order to correlate surface diffusivity ( $D_s$ ) with surface shear viscosity ( $\mu_s$ ). In bulk liquids the final expressions for  $D$  are given, respectively,

$$D = \frac{kT}{4 \pi r \mu} \quad (3)$$

and

$$D = \frac{kT}{2 r \mu} \quad (4)$$

If  $D_s$  is related to  $\mu_s$  in some manner as in bulk liquids, such an attempt would be fruitful for two reasons. First, these theories, especially the activation theory, could help elucidate the basic mechanism of surface diffusion. Second, rough quantitative estimation of  $D_s$  could be made from the surface viscosity data which are available at present and readily obtainable when desired. Within their own contexts, the extension of the theories leads to the following expression for a two-dimensional case:

$$D_s = \frac{kT}{\mu_s} \quad (5)$$

and

$$D_s = \frac{kT}{2 \pi \mu_s} \quad (6)$$

In the derivation of Equations (5) and (6), a liquid-expanded monolayer is treated as matter in the liquid-like state of aggregation, as was done by Moore and Eyring<sup>11)</sup> in their theoretical treatment of viscous flow in the monolayer. The inherent difference in molecular environment between the interface and the interior of bulk matter is then reflected in the surface viscosity coefficient. The parent theories for three-dimensional fluid phases, especially the hydrodynamical theory, correlate the self-diffusivity with the viscosity within about  $\pm 20\%$  for a number of liquids including polar substances, associated substances, liquid metals and molten sulfur.<sup>2)</sup> It might therefore be expected that the relationship between  $D_s$  and  $\mu_s$  for monolayers as given by Equations (5) and (6) would be valid in order of magnitude. The magnitude of  $D_s$  could then be roughly estimated for long chain acids by the use of experimental data on  $\mu_s$  (Table 1). This results in resounding failure. The Eyring theory predicts values

for  $D_s$  of  $10^{-9}$ – $10^{-10}$  cm<sup>2</sup>/sec, while the hydrodynamical theory yields  $10^{-10}$ – $10^{-11}$  cm<sup>2</sup>/sec. These values, when compared with the experimental data on  $D_s$ , are about five orders of magnitude too small!

At this stage one must entertain at least two types of explanations for the observed discrepancy. One is that such a discrepancy results from inaccurate or inappropriately interpreted measurements of  $\mu_s$  and  $D_s$ , as well as the inherent weakness of the theories. The second is that surface diffusion in monomolecular films takes place by an essentially different mechanism from that by which surface momentum is transported. As discussed by Joly,<sup>10</sup> the absolute determinations of  $\mu_s$ , by the best presently available techniques, are reasonably reliable. In the acquisition of the data on  $D_s$ , there are some possible errors which may result in larger apparent values of  $D_s$  than the true values but definitely not in excess of an order of magnitude. In addition, the extended three-dimensional theories are inherently approximate, but should be valid within an order of magnitude. Combining all the above uncertainties in the least favorable manner still falls far short of explaining the discrepancy of five orders of magnitude. We then look for alternate transport mechanism. The development of a new viewpoint of transport phenomena in monolayers is also appealing in that it might provide some explanation for the "abnormally high" surface shear viscosities which they exhibit.

Table 1. Surface Viscosity of Long-Chain Fatty Acids on 0.01N HCl Substrates<sup>9)</sup>

Substances (Film state)	T °C	A Å <sup>2</sup> /molecule	$\mu_s$ g./sec
Myristic Acid (Liquid-expanded)	22	29.6	$1.7 \times 10^{-5}$
		31.8	$6.5 \times 10^{-5}$
		34.5	$9.0 \times 10^{-5}$
		39	$11.8 \times 10^{-5}$
		43.9	$15.2 \times 10^{-5}$
Palmitic Acid (Condensed)	22	23.1	$2.6 \times 10^{-4}$
		24.1	$2.8 \times 10^{-4}$
		25.2	$1.5 \times 10^{-4}$
		26.8	$2.3 \times 10^{-4}$
Stearic Acid (Condensed)	20	19.8	$7.4 \times 10^{-4}$
		21.3	$3.9 \times 10^{-4}$
		23	$2.3 \times 10^{-4}$
Oleic Acid (Vapor-expanded)	17	38.1	$1.0 \times 10^{-4}$
		43.1	$1.5 \times 10^{-4}$

If the monolayer molecules are confined to motion

of the type implied by extensions of three-dimensional diffusion theories, they would indeed be diffusing very slowly because they must experience the same large frictional resistance to their migration implied by the measured values of  $\mu_s$ . Since the drag between the film molecules in their viscous flow is evidenced to be significantly greater than in bulk liquids,  $D_s$  would have to be as small as  $10^{-10}$  cm<sup>2</sup>/sec, being smaller than the diffusivity in bulk liquids ( $10^{-8}$  cm<sup>2</sup>/sec). The experimental values for  $D_s$  are, however, apparently much greater than such expected values, even if generous allowances for possible errors in the measurements are made. If the true values of  $D_s$  were of such small magnitudes, no surface migration would have been observed by the present experimental technique. What is considered below, then, is a possible alternate path that the film molecules can take in randomizing their distribution on the liquid surface.

### Proposed Model

We now postulate that the film molecules may escape from their regular monolayer environment to some loosely adsorbed state where they can migrate with great mobility until they are recaptured by the monolayer (cf. Fig. 1). In catalysis, the concept of the loosely adsorbed state is quite acceptable today and is known as a Rideal intermediate.<sup>8)</sup>

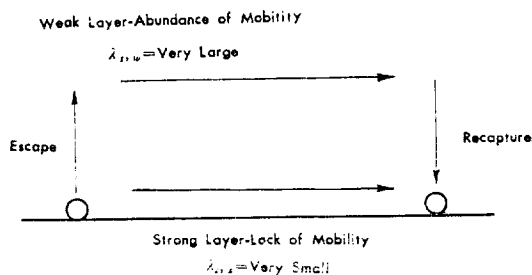


Fig. 1. Schematic representation of an alternate path to surface diffusion

As the loosely adsorbed state of interest, consider the intermediate binding state on the surface of the hydrocarbon portion in the monolayer. The preferred orientation of the hydrocarbon chains in concentrated

monolayers leads to the duplex film structure in which the upper hydrocarbon surface behaves as a liquid-like or a solid-like surface depending on the monolayer state. Apparently the film molecules adsorbed on top of such a surface can migrate much more rapidly (perhaps as a two-dimensional gas) than in the regular monolayer state. The rate of the escaping process need not be very great for the film molecules to attain a virtually instantaneous equilibrium between the regular monolayer state and this "loosely adsorbed" state. It can be assumed, therefore, that there is an equilibrium population at any instant, however small, in the loosely adsorbed state because of the statistical distribution of the kinetic energies normal to the surface among the molecules in the monolayer. Since the population will be much smaller than in the monolayer itself, there will be no change in the film state and hence in the film structure. The adsorption energy of the partially escaped molecules, which presumably amounts to some fraction of the full heat of vaporization of the molecules from the surface, is great enough to retain them on the surface for an appreciable time. Since the energy profile of the surface fluctuates, sometimes increasing the variation in the adsorption potential far beyond the average thermal energy of the film molecules, they will readsorb into the regular monolayer state when they encounter, occasionally, a large energy barrier during their migration.

In the present model that postulates the real existence of such an alternate path for the migration of monolayer molecules on liquids, the effective surface flux is given as the contribution due to the weakly (or loosely) adsorbed layer, that is,

$$J_{s,l} \approx J_{s,w} \quad (7)$$

because the concomitant transport in the regular monolayer is negligibly small, as predicted by the extended three-dimensional theories. Each flux is given by the product of its diffusivity and the driving force by Fick's law:

$$J_{s,l} = -D_{s,l} \frac{d\Gamma_l}{dx} \quad (8a)$$

and

$$J_{s,w} = -D_{s,w} \frac{d\Gamma_w}{dx} \quad (8b)$$

The two concentrations can be related through an equilibrium distribution constant defined by

$$\Gamma_w(x) = \phi \Gamma_l(x) \quad (9)$$

It should be noted that  $\phi$  is the same at all values of  $x$  because the entire surface is covered with a uniform concentration of one chemical compound with only the ratio of radioactive molecules to ordinary molecules varying. From Equations (7) through (9), it follows that

$$D_{s,l} = D_{s,w} \phi \quad (10)$$

This equation represents the basic expression for the effective surface diffusion coefficient which is to be measured in the experiment.

In the light of the present model  $D_{s,w}$  depends on the energetical profile of the upper hydrocarbon surface which is in turn prescribed by the state of configuration of the hydrocarbon chains in the monomolecular film. For the case of a liquid-expanded monolayer, it has been inferred from the analysis of the thermodynamic properties of the film that the hydrophobic portion of the monolayer behaves like a thin hydrocarbon liquid. In such a case, the adsorption of the escaped molecules is non-localized. Since the population thereon is very small,  $D_{s,w}$  can then be calculated approximately by the following equation for two-dimensional gaseous diffusion<sup>6)</sup>.

$$D_{s,w} = \frac{1}{4} \frac{1}{d_m \Gamma_w} \sqrt{\frac{\pi RT}{2M}} \quad (11)$$

This oversimplified description, in general, does not give an adequate representation of surface migration on the real surface. It can be used, however, for the rough estimation of the surface diffusivity in an ideal case where the adsorption is completely non-localized.

Inserting Equation (11) into Equation (10), it follows that

$$D_{s,l} = \frac{1}{4} \frac{1}{d_m \Gamma_l} \sqrt{\frac{\pi RT}{2M}} \quad (12)$$

It is noticed that the term  $\phi$  in Equation (10) drops out, replacing  $\Gamma_w$  in Equation (11) with  $\Gamma_l$ . In the derivation of Equation (12), a local equilibrium between the two states was assumed and a simple

treatment for  $D_{s,w}$  was given. The final predictive equation, Equation (12), then takes a very simple form.

Based on the present model, the experimental data on  $D_s$  can all be explained consistently. The calculated magnitude about ten times greater than the experimental values. This relatively small discrepancy can be readily ascribed to some inadequacy of Equation (11) for calculation of  $D_{s,w}$ . It may also be possible to explain the discrepancy by considering that the process of partial escape is not high enough to justify the assumption of an instantaneous equilibrium between the regular monolayer state and the loosely adsorbed state. Although Equation (12) cannot be an exact expression for  $D_s$ , it explains the experimental observations that  $D_s$  is nearly independent of monolayer concentration and that  $D_s$  varies only slightly with the molecular size (the chain length). Equation (12) also predicts a weak dependence of  $D_s$  on temperature. Such a behavior is within expectations from the observed surface isotherms of liquid-expanded monolayers that are nearly overlapped. The effect of monolayer state on  $D_s$  is reflected in the term  $D_{s,w}$ . As pointed out previously, the behavior of the molecules on the upper surface of the hydrocarbon layer is dictated by the physical structure of the hydrocarbon layer. In the condensed state the upper surface is certainly energetically heterogeneous, so that the real value for  $D_{s,w}$  and hence  $D_s$  will be much smaller than calculated by Equation (12). In the intermediate state, where the micells are formed in the sea of the molecules in the liquid-expanded state, the real value for  $D_{s,w}$  will be smaller than that in the liquid-expanded state. It will, however, not be smaller than in the condensed state. In the transition state (of palmitic and stearic acid) the monolayer is very concentrated and has a hydrocarbon layer possessing all the natural freedom of motion of liquid.  $D_s$  in such a state will be on the same order of magnitude as that in the liquid-expanded state.

### Conclusions

1. Theoretical correlation of the monolayer diffusivities could not be accomplished through modification

of the hydrodynamical or Eyring theories for three-dimensional fluids. Use of parameters in these theories evaluated from surface viscosity data generally led to surface diffusivities five orders of magnitude smaller than those obtained experimentally. This suggested that molecular diffusion in monolayers occurred by a mechanism essentially different from that of surface momentum transport.

2. A new theoretical model for surface diffusion in liquid expanded monolayers has been developed in which the existence of a small equilibrium population of weakly adsorbed monolayer molecules was populated. Surface migration was assumed to occur primarily through two dimensional gas-like diffusion of the weakly adsorbed molecules leading to the final predictive equation for surface diffusivity:

$$D_s = \frac{1}{4 d_m \Gamma} \sqrt{\frac{\pi R T}{2 M}}$$

Where  $d_m$  is the effective molecular diameter,  $\Gamma$  is the surface concentration of monolayer molecules,  $T$  is the absolute temperature,  $M$  is the molecular weight and  $R$  is the gas constant. This predicted values for  $D_s$  of the same order of magnitude as those obtained experimentally and displayed the weak dependence upon chain length and concentration also observed experimentally. Further experiments on the temperature dependence of  $D_s$  should be made. Finally, the model did not produce inconsistencies with measured surface viscosity data.

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