ϵ = eddy viscosity, L^2/T
μ = viscosity, M/LT or length dimension, micron
ν = μ/ρ, L^2/T
ρ = density M/L^3
$\bar{\tau}_0$ = average wall shear stress, ML/T^2L^2
θ = time, T
θ_c = total time for which a fluid mass had been in contact with the wall, T

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Transport of Gases Through Insoluble Monolayers

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The reduction in gas desorption through surface active monolayers on a water substrate has been investigated for five compounds (1-hexadecanol, 1-octadecanol, 1-docosanol, 1-eicosanoic acid, and 1-docosanoic acid) and four gases (oxygen, nitrogen, methane and carbon dioxide) at 25°C. Gas transport was retarded significantly at high surface coverage and decreased nonlinearly with change in surface coverage past the point equivalent to zero surface pressure.

Interphase mass transfer coefficients for transport through the films were calculated, but no simple correlation could be discovered which could be used to predict film coefficients or the reduction as a function of surface coverage.

Insoluble monolayers which occur naturally on bodies of water, and which are introduced occasionally by man to retard evaporation, also may suppress the transport of respiratory and toxic gases through gas-liquid interfaces. Diffrences have been noted between the permeability of monolayers to gases such as carbon dioxide, oxygen, and nitrogen, and the permeability to water vapor. LaMer (9) has summarized some of the interesting properties of monolayers in the retardation of evaporation and its importance in water conservation. It has been demonstrated that transport of water through compressed monolayers is not solely a diffusion process but must be treated as a combined process of diffusion and reaction (or adsorption) at the monolayer.

Some of the earliest work in the field dealing with a dissolved substance in water was by Langmuir and Langmuir (*10*), who reported on the evaporation of ethyl ether from water through oleic acid monolayers, but the effect noted was that the ether primarily prevented enhanced transport in the liquid by reducing convection in the liquid. Sebba and Rideal (*14*) studied the effect of monolayers on the evaporation of ethanol and ammonia.

More recently Blank and Roughton (3) reported on the results of their work in the absorption of oxygen and carbon dioxide through monolayers into reacting solutions. Blank (*2*) also has investigated the transfer of oxygen, carbon dioxide, nitrous oxide, and sulfur dioxide with and without monolayers from the gas to the liquid phase as a

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function of time. He included the effect of the solvent used to dissolve the monolayer in his work. His results supported the idea of the existence of a diffusion barrier. Hawke and Alexander examined the desorption of hydrogen sulfide and carbon dioxide from water for various films in terms of a resistance concept (7).

Richardson (*12*) studied the evaporation of two components with different relative volatilities by the Winkelmann method. He found the diffusion rate was so high in the gas phase that the air flow rate and tube diameter were not significant variables. However, density differences in the liquid were found to cause mixing. Grassman and Anderes (*6*) found for oxygen and nitrogen that a higher mass transfer rate constant existed for transfer in the direaction in which surface tension was increased by mass exchange. Other related work is by Goodridge and Robb (*5*) and Whitaker and Pigford (*18*).

New data on the effect of acid and alcohol monolayers on the interphase desorption of oxygen, nitrogen, methane, and carbon dioxide are reported.

ANALYSIS OF THE INTERPHASE TRANSPORT OF GASES

The representation of interphase transport of gases through monolayers quantitatively by transport phenomena types of models is exceptionally difficult. The experimental conditions must truely agree with the assumptions in the mathematical description, or at the best only qualitative results can be obtained. One can think of the transport process of desorption as consisting of the following steps: diffusion through the liquid phase, passage from the liquid phase to the surface of the monolayer, adsorption and/or diffusion through the monolayer, passage from the monolayer to the gas phase, and diffusion in the gas phase. In a quiescent or laminar system, for the monolayer to have a noticeable effect, the monolayer permeability must be quite low because the diffusion coefficient in the liquid phase is only of the order of 10^{-5} sq.cm./sec.; that is, there is considerable resistance to transport in the liquid phase. On the other hand, in the gas phase the diffusion coefficient is 10^4 times as large as the liquid diffusivity, and the resistance is quite small; in fact, it is usually negligible in comparison with that of the liquid in a two-phase system with a dilute solute.

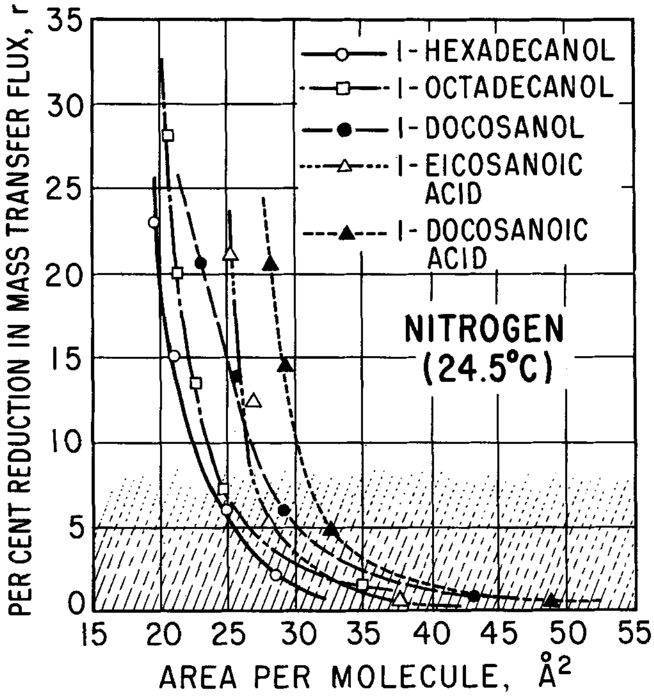

Fig. 1*a*. Percent reduction in interphase mass transfer flux vs. area per molecule.

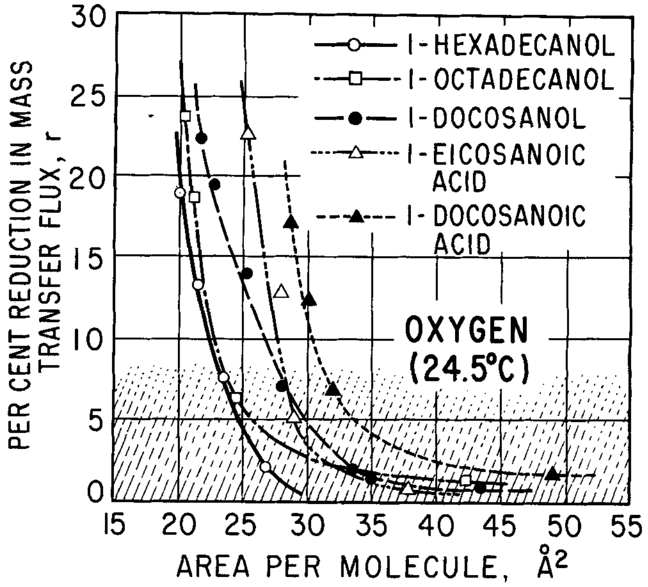

Fig. 1*b*. Percent reduction in interphase mass transfer flux vs. area per molecule.

With isothermal gas absorption into the liquid phase, for even modest contact times of the order of 1 min., instability can arise; that is, adverse density gradients of solute gas cause uncontrollable mixing in the liquid phase and destroy the assumed velocity field. For gas desorption without surface layers, stability is assured. With films of surface active agents present the possibility of surface tension driven convection may exist, but long chain compounds exert a damping effect, and, most importantly, if the liquid is saturated with gas, mixing will not significantly affect initial interphase transfer as will be the case for gas absorption into a gas free solution. In this investigation the transport was measured from a saturated liquid into the gas phase (desorption) from an interface with and without monolayers with the aid of a special probe. The gas phase resistance essentially controlled the rate of transport, but the velocity field in the gas phase was unknown; hence only simple rate types of boundary conditions could be postulated.

The three-film model is nothing more than an extension of the classical two-film model of interphase transfer; the added film is the monolayer. While it can be argued that film models are too simple to represent a very realistic picture of the actual transport process, it is also true that no simple model can do this anyway, while at the same time there are significant advantages in working with a simple model for which an analytical solution can be obtained.

The usual expressions for the overall mass transfer coefficient (*1, 4, 15, 16*) with and without the monolayer present are

Without monolayer:

$$\frac{1}{K^o} = \frac{1}{k_L} + \frac{1}{h}\left(\frac{1}{k_G}\right) \qquad (1)$$

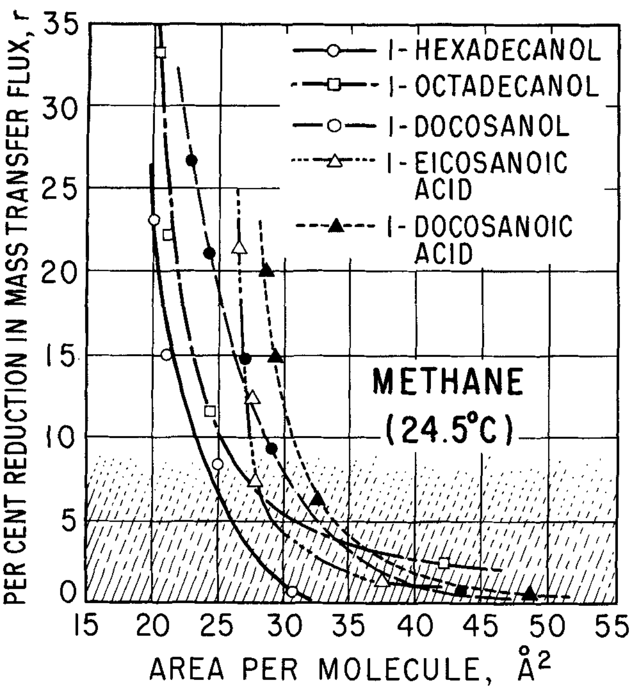

Fig. 1c. Percent reduction in interphase mass transfer flux vs. area per molecule.

With monolayer:

$$\frac{1}{K} = \frac{1}{k_L} + \frac{1}{h}\left(\frac{1}{k_F} + \frac{1}{k_G}\right) \tag{2}$$

where K (or K^o) is defined by the measured quantities N (or N^o), c_o, and c^*:

$$N = K\,(c_o - c^*)$$

$$N^o = K^o\,(c_o - c^*) \tag{3}$$

and

$$p_i = h_i\, c_i$$
$$k_L = D_L/z_L$$
$$k_F = D_F/RTz_F$$
$$k_G = D_G\, p/RTz_G\,(p_G)_{lm}$$

These equations can be rearranged to give an expression for k_F solely in terms of the measured experimental quantities:

$$k_F = \frac{1}{h\,(c_o - c^*)\left(\dfrac{1}{N} - \dfrac{1}{N^o}\right)} \tag{4}$$

In the experimental work described below c^* was zero. k_F is directly proportional to the film permeability of other authors and inversely proportional to the film resistance. If a thickness is assumed for the monolayer film, such as $z_F = 30$ Å. (3.0×10^{-7} cm.), the effective diffusion coefficient D_F through the film can be calculated from the definition of k_F.

EXPERIMENTAL APPARATUS AND PROCEDURE

The apparatus used in this work was essentially the same as that developed by Walker (*17*) for measuring the evaporation of water. It provided for a simple type of gas analysis and fairly rapid experimentation. Gas transported through the interface was carried into a probe by a flowing helium stream, and the flowing desorbed gas was monitored by a thermal conductivity cell. The cylindrical probe was placed 0.72 mm. above the surface of the water. As helium passed through an outer annulus, one-sixth of the helium passed into the inner core of the probe, at the same time sweeping up the gas of interest being transported through the interface. The residual helium flowed outward from the probe forming a barrier which prevented external air and any other gas from entering the core of the probe.

To collect the experimental data, a Petri dish was filled with doubly distilled water saturated with the selected gas at 1 atm. For each run the water was saturated by bubbling and absorbing the desired gas in a separate system at 25°C. and a pressure somewhat above atmospheric. At periodic intervals the bubbling rate was set high enough to cause foam to overflow and carry away some of the residual surface materials. After saturation the pressure was reduced to atmospheric and the saturated gas stirred vigorously until bubbles no longer left the solution. After the air in the Petri dish had been displaced by a blanket of the same gas as in the saturated solution, the proper quantity of solution for a mass transfer experiment was allowed to flow from the middle of the reservoir into the Petri dish by gravity.

Next, the probe cover (which was also 0.72 mm. from the probe) was withdrawn and the probe dropped to its fixed position above the water surface as indicated by a needle reference point. Measurements of the interphase transfer of gas were made for periods up to 5 min., a time long enough to achieve a new steady state flow (value of N) through the chromatograph, but short enough to prevent any substantial transfer of dissolved gas as required by the mathematical model. For any run, the variation of N was less than the variation in the mean values of N among different runs. Tests of the probe in evaporating water (without a surface film) at the same

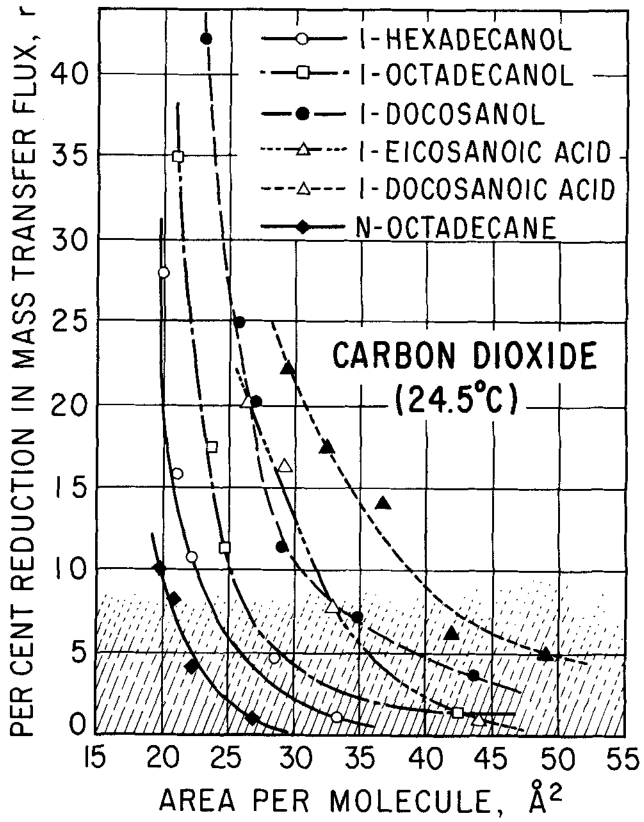

Fig. 1d. Percent reduction in interphase mass transfer flux vs. area per molecule.

Table 1. Surface Active Agents Studied

Compound	Chem. formula	Source
1-Hexadecanol (cetyl alcohol)	$C_{16}H_{33}OH$	K&K Laboratories
1-Octadecanol	$C_{18}H_{37}OH$	Eastman Kodak
1-Docosanol	$C_{22}H_{45}OH$	K&K Laboratories
1-Eicosanoic acid	$C_{19}H_{39}COOH$	K&K Laboratories
1-Docosanoic acid	$C_{21}H_{43}COOH$	K&K Laboratories

operating conditions as used by Walker yielded essentially the same results, namely, 0.93 × 10^{-5} g./(sq.cm.)(sec.) at 25°C.

Because it was possible to obtain reproducible values of N^o (± 4%) for the gas transfer from the saturated solutions under the same operating conditions (temperature, helium flow rate, etc.), the transfer with most monolayers was carried out in a separate series of runs. As soon as a fixed quantity of surface active agent (in hexane solution) was spread on the gas-saturated water substrate, the probe was lowered. Most of the hexane had evaporated by the time the probe was in position, but the chromatograph did detect some brief initial disturbance caused by the remaining hexane. The area per molecule was calculated from the known surface area of the substrate and the known number of moles placed on the substrate.

The long chain films were spread by displacing from a microsyringe the appropriate volume of hydrocarbon dissolved to approximately 0.1% (by weight) in hexane. The liquid volumes were reproducible to ± 2%, and to all visible appearances the long chain compounds were spread successfully.

Attempts were made to check the character of the film by measuring the surface pressure of the spread monolayers in situ with a Wilhemy plate, without success. Techniques which worked for soluble monolayers proved to yield nonreproducible results for the insoluble films used in this study. The plate and film interacted erratically when the plate was either pulled or dipped through the film. Separate surface pressure measurements of hexadecanol and octadecanol were obtained in a Cenco version of the Langmuir trough, and they corresponded roughly to those reported in the literature for these two compounds. However, the measurements in the Cenco trough were by no means as accurate as those reported in the literature.

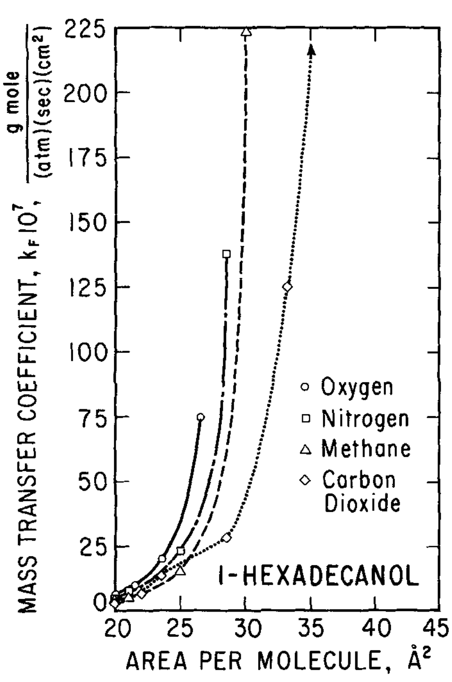

Fig. 2a. Mass transfer coefficient as a function of the surface coverage.

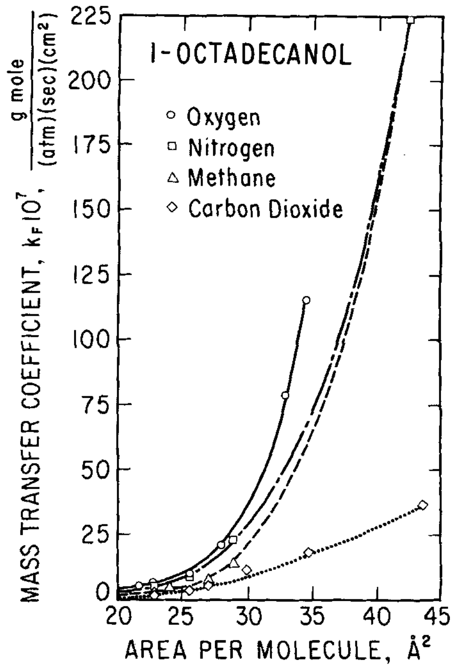

Fig. 2b. Mass transfer coefficient as a function of the surface coverage.

As a result of these measurements, it was assumed the films in the mass transfer apparatus were spread properly. It would be possible for the helium flow to influence the monolayer at surface concentrations corresponding to zero surface pressure. However, movement of the probe across the interface did not yield significantly different values of N. Presumably the probe measured such a large area of the interface that any local discontinuities were averaged out. Tests (by radioactive tracer) to see if the film evaporated were negative.

EXPERIMENTAL RESULTS AND DISCUSSION

Table 1 lists the chemical compounds studied; they were all long chain saturated hydrocarbon derivatives.

Table 2 indicates in a qualitative way for a typical set of operating conditions how the interphase transport was governed by the gas phase diffusion process rather than by the liquid phase diffusion. The relative diffusivities, D_L and D_G in helium, of each gas to those of carbon dioxide (without surface films being present) are compared with the relative transport fluxes, and the ordering agrees more closely with the gas diffusivities listing.

Table 2. Diffusivities and Interphase Transport Fluxes (without Surface Monolayers) Relative to Carbon Dioxide

	$D_L/D_{L,CO_2}$	$D_G/D_{G,CO_2}$	$N^o/N^o_{CO_2}$
O_2	1.02	1.55	1.13
N_2	0.84	1.60	1.05
CH_4	0.66	1.32	1.01
CO_2	1.00	1.00	1.00

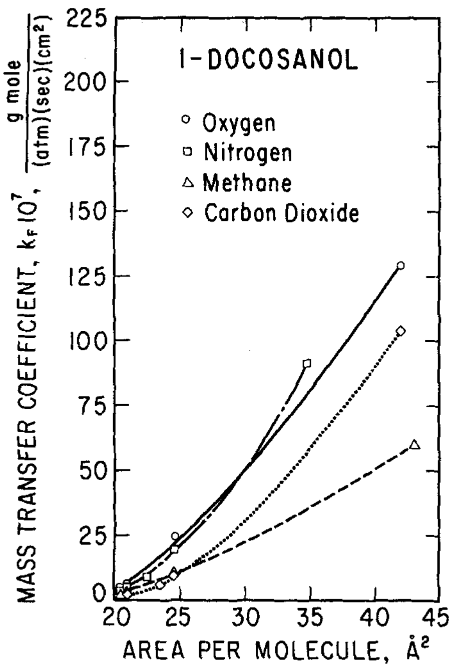

Fig. 2c. Mass transfer coefficient as a function of the surface coverage.

The percent reduction in interphase transport

$$r = \frac{N^o - N}{N^o}(100) \tag{5}$$

is shown in Figures 1*a* through 1*d* as a function of the area per molecule for each gas. Some special measurements for carbon dioxide through *n*-octadecane are also shown in Figure 2*d*. The error in the percent reduction *r* unfortunately grows as $N \rightarrow N^o$; hence the values for the reduction under 7% are somewhat uncertain, as indicated in the figures by light shading. The indicated curves are not statistical fits but simply representative lines and are shown asymptotically approaching the origin on the principle that at zero surface coverage no interference with mass transfer should occur.

It is well known that for the long chain compounds used in this work the limiting range of area per molecule in which a measurable surface pressure exists lies roughly between a dense packing of 20 Å.²/molecule, which borders on the collapse and folding of monolayers, on one hand and the limiting value of 25 Å.²/molecule for zero film pressure on the other hand. No films were spread to an area per molecule of less than 19.5 Å.², while many films were spread to a molecular coverage as low as 50 Å.²/molecule. It is believed that the reduction in interphase transfer does not terminate at the limiting value of approximately 25 Å.², but as the film breaks up *r* gradually declines from some low value. Even though no surface film pressure can be measured at an area per molecule of greater than 25 Å.², the monolayer remnants still exist as individual molecules or islands and cover part of the surface. Electron micrographs of films of stearic acid spread to 25 Å./molecule and then removed from water have indicated that roughly 50% of the surface is still uniformly covered with irregularly shaped lumps of apparently continuous material (*13*). The portion of the surface covered by such islands presumably has a slight effect on the interphase gas transfer, but the experimental accuracy in this work was not adequate to verify such an hypothesis.

Figure 2 presents the values of k_F calculated from Equation (4). The behavior of carbon dioxide is somewhat anomalous, for unknown reasons. All the curves are drawn by eye since they were quite nonlinear. As a rule the highest values of k_F at any given surface coverage was

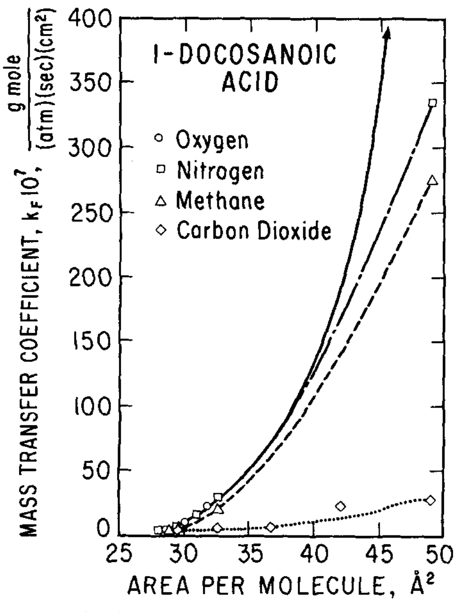

Fig. 2*d*. Mass transfer coefficient as a function of the surface coverage.

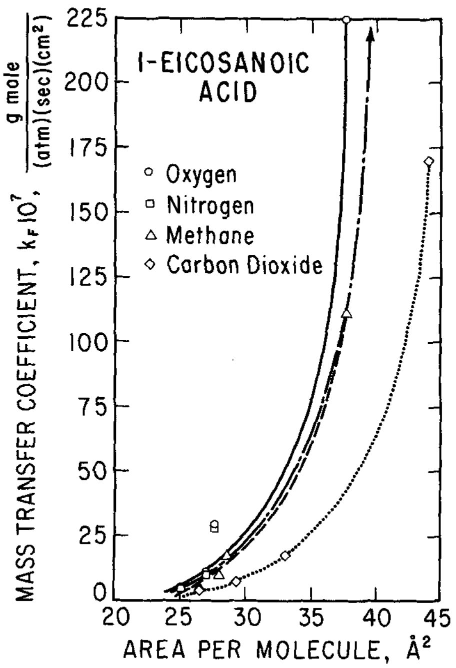

Fig. 2e. Mass transfer coefficient as a function of the surface coverage.

for oxygen, followed by nitrogen, methane, and carbon dioxide in that order.

Of special interest is the limiting value of k_F at the collapsing point of the film which can be compared with the results of previous investigations. These values (some extrapolated) ranged from 3.6 to 6.9 $\times 10^{-7}$ for hexadecanol, 0.1 to 4.0 for octadecanol, and 1.9 to 4.2 for docosanol; estimated values for the acids were from 0.1 to 3 $\times 10^{-7}$. Plevan (*11*), for a very dense surface coverage, reported for sulfur dioxide absorption through hexadecanol at 25°C. values of $(hk_F)^{-1}$ = surface resistance of 170 to 215 which corresponds to k_F values of 1.6 to 2.0 $\times 10^{-7}$. A value of 3.6 $\times 10^{-7}$ was obtained for carbon dioxide in this work, a surprisingly close agreement in view of quite different techniques and gases used and the diametrically opposite directions of transfer in the two experiments. Plevan's value of k_F for octadecanol was 4 $\times 10^{-7}$ compared with an extrapolated value in this work of 0.5 $\times 10^{-7}$.

In the series of experiments by Blank and Roughton (*3*) for absorption of carbon dioxide through hexadecanol into basic solutions, k_F was 4.2 $\times 10^{-7}$, while for octadecanol the range was from 0.8 to 1.5 $\times 10^{-7}$. The values of Hawke and Parts (*8*) for desorption of carbon dioxide through various compounds at 25°C. and a surface pressure of 35 dynes/cm., which corresponded probably to a area per molecule lower than the collapsing point of the film, were

	$k_F h \times 10^3$	
Compound	Reference 8	This work
Hexadecanol	>5	6 to 9
Octadecanol	1.3	3 to 5
Docosanol	0.6	1.2 to 2.4

While these values do not agree exactly, they are essentially the same order of magnitude and are a measure of the reduction in interphase mass transfer by a surface completely covered with a monolayer.

CONCLUSIONS

No doubt exists that monolayers reduce the transfer of gases from water, and presumably in the reverse direction, particularly at high surface concentrations in static gas-liquid systems. The reported interphase gas transport coefficients have not appeared amenable to simple correlations as a function of the surface coverage but are related nonlinearly to surface coverage. Some evidence of reduction exists when the film only partially covers the surface.

ACKNOWLEDGMENT

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NOTATION

A = area per molecule, Å.²/molecule
c = concentration of diffusing gas, g.-mole/cc.
c^* = concentration (as given by the equilibrium relationship) corresponding to bulk phase partial pressure of diffusing gas, g.-mole/cc.
D_F = moleclular diffusion coefficient of gas in surface film, sq.cm./sec.
D_G = molecular diffusion coefficient of gas in gas phase, sq.cm./sec.
D_L = molecular diffusion coefficient of dissolved gas in liquid, sq.cm./sec.
h = Henry's law constant, (g.-mole^{-1}) (atm.) (cc.)
k_G = interphase mass transfer coefficient in gas phase, model I, g.-mole/(atm.) (sq.cm.) (sec.)
k_F = interphase mass transfer coefficient in monolayer, model I, g.-mole/(atm.) (sq.cm.) (sec.)
k_L = interphase mass transter coefficient in liquid phase, cm./sec.
K = overall mass transfer coefficient with monolayer, g.-mole/(atm.) (sq.cm.) (sec.)
K^o = overall mass transfer coefficient without monolayer, g.-mole/(atm.) (sq.cm.) (sec.)
N = interphase mass transfer flux with monolayer, g.-mole/(sq.cm.) (sec.)
N^o = interphase mass transfer flux without monolayer, g.-mole/(sq.cm.) (sec.)
p = partial pressure of diffusing component
r = fractional reduction in interphase mass transfer flux
R = gas constant, (cc.) (atm.)/(g.-mole) (°K.)
T = temperature, °K.
z = coordinate perpendicular to interface, cm.
z_F = monolayer film thickness, cm.
z_G = gas film thickness, cm.
z_L = liquid film thickness, cm.

Subscripts

F = monolayer film
G = gas phase
L = liquid
o = saturated solution

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