

The Permeability of Soap Films to Gases^{1,2}

II. A Simple Mechanism of Monolayer Permeability

H. M. PRINCEN,³ J. TH. G. OVERBEEK AND S. G. MASON

Van 't Hoff Laboratory, State University, Utrecht, Netherlands and Chemistry Department, McGill University, Montreal, Canada

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It is generally assumed that permeation through insoluble monolayers is best described in terms of the energy-barrier theory. In this paper evidence is provided that transport of gases through soluble monolayers is governed by a different mechanism, namely, simple Fickian diffusion. Moreover, there are strong indications that diffusion actually takes place through aqueous pores between the surfactant molecules. These conclusions follow from an improved analysis of previously reported data on the permeability of extremely thin soap films to various gases.

INTRODUCTION

In a previous study (1) the permeability of thin equilibrated soap films to gases was measured from the rate of shrinkage of single gas bubbles at gas-water interfaces. It was concluded that the results obtained for monatomic and diatomic gases agreed rather well with the "energy-barrier theory" which assumes that the monolayer acts as a single energy barrier. More recent work (2), however, shows that this conclusion is not justified; the results can be better interpreted on the basis of Fickian diffusion through the monolayer, especially if one assumes that diffusion takes place through water channels taking up a considerable fraction of the monolayer area.

THEORY

In reference 1 we derived the following relation between the monolayer permeability

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³ Present address: Research and Development Division, Lever Brothers Company, Edgewater, N. J.

(k_{ML}) and that of the complete film (k):

$$k = \frac{DH}{h + 2D/k_{ML}}, \quad [1]$$

where h is the thickness of the central liquid layer in the soap film, and D and H are the diffusion coefficient and the Ostwald coefficient of solubility of the gas in the liquid (i.e., in the aqueous bulk solution). In [1] k_{ML} is defined by

$$\frac{dN}{dt} = k_{ML}A(\bar{C} - C'), \quad [2]$$

where N is the number of moles of gas diffusing through the monolayer separating a gas phase of concentration C and a liquid phase of concentration C' ; A is the area of the monolayer; and \bar{C} is the equilibrium concentration of gas in the liquid corresponding to C , so that

$$\bar{C} = HC. \quad [3]$$

The parameter k_{ML} is identical with the transmission coefficient T_s defined by Hawke and co-workers (3, 4).

Alternatively, the monolayer permeability can be defined by

$$\frac{dN}{dt} = k'_{ML}A(C - \underline{C}), \quad [4]$$

where \bar{C} is the concentration in the gas phase with which C' would be in equilibrium. The two permeabilities are related through

$$k'_{ML} = Hk_{ML}. \quad [5]$$

For extremely thin films [1] reduces to

$$k = \frac{Hk_{ML}}{2} = \frac{k'_{ML}}{2}. \quad [6]$$

Since such a film lacks a central liquid layer, its permeability should no longer depend on H , indicating that k'_{ML} rather than k_{ML} is the proper measure of monolayer permeability.

The mechanism of monolayer permeation can be treated in two different ways: (a) the monolayer can be treated as a homogeneous phase with Fickian diffusion; (b) it can be assumed that permeating gas molecules must strike the monolayer with sufficient kinetic energy to form a hole through which they can pass; this is the energy-barrier theory.

1. *Fickian Diffusion.* The concentration in the monolayer varies between C_m and C'_m (Fig. 1). It is assumed that each surface of the monolayer offers no resistance to permeation, so that C_m and C'_m are always in equilibrium with \bar{C} and C' , i.e.,

$$C_m/\bar{C} = H_m \quad [7]$$

and

$$C'/C'_m = H'_m, \quad [8]$$

where H_m and H'_m are the partition coefficients of the gas across the gas-monolayer and liquid-monolayer interface, respectively; they are related through

$$H = H_m H'_m, \quad [9]$$

where, as before, $H = \bar{C}/C$.

The flux is given by

$$\frac{dN}{dt} = D_m A \frac{C_m - C'_m}{\delta}, \quad [10]$$

where D_m is the diffusion coefficient in the monolayer, and δ is the thickness of the monolayer. By substitution of [7] to [9], [10] yields

$$\frac{dN}{dt} = \frac{D_m}{\delta H'_m} A (\bar{C} - C'). \quad [11]$$

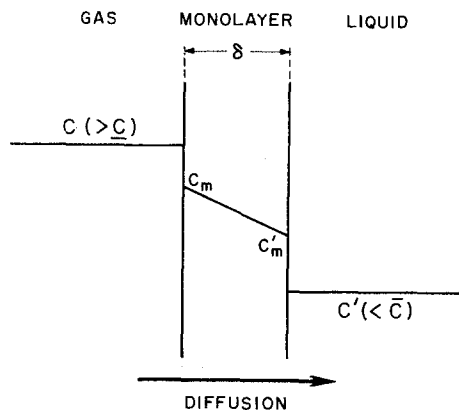


FIG. 1. Fickian diffusion of gas through a monolayer.

Comparing [2] and [11] shows that

$$k_{ML} = \frac{D_m}{\delta H'_m} = \frac{D_m H_m}{\delta H}, \quad [12]$$

or

$$k'_{ML} = \frac{D_m H_m}{\delta}. \quad [13]$$

Since k'_{ML} is proportional to $D_m H_m$, no direct relation with the molecular size of the gas is expected.

The previously introduced quantity h^* , which is the thickness of a water layer of the same permeability as the monolayer (1), is given by

$$h^* = \frac{D}{k_{ML}} = \frac{DH}{k'_{ML}}, \quad [14]$$

or, by substitution for k'_{ML} ,

$$h^* = \frac{DH}{D_m H_m} \delta. \quad [15]$$

Within the framework of this mechanism are the following two possibilities.

a) The monolayer is considered as a homogeneous organic phase, e.g., hexadecane. In this case one would find roughly the same value of h^* for different gases through the same monolayer, because both D/D_m and H/H_m will not vary appreciably. For D/D_m this follows from the Stokes-Einstein relation; for H/H_m from "Just's law" (5, 6). There are notable irregularities in Just's law, however, especially the relatively low

solubility of CO_2 and, to a lesser extent, N_2O in organic solvents as compared to that in water. For example, in water $H(\text{CO}_2) = 28 H(\text{O}_2)$ and $H(\text{N}_2\text{O}) = 20 H(\text{O}_2)$, whereas in hexadecane (7) $H_m(\text{CO}_2) = 5.5 H_m(\text{O}_2)$ and $H_m(\text{N}_2\text{O}) = 8.5 H_m(\text{O}_2)$. This would lead to values of h^* for CO_2 and N_2O which are several times that of oxygen.

b) The monolayer may be "wet," i.e., there is a substantial amount of water present between the hydrocarbon chains of the surfactant molecules. Diffusion could then take place through these aqueous pores with the same values of D and H as in water. In this case h^* would even be more constant, although one might expect a systematic increase in h^* with increasing size of the permeating molecule owing to a decrease in the effective diameter of the pores.

As Fick's law is strictly applicable only in macroscopic systems, objections can be raised against treating a monolayer on this basis (7, 8). Thus it has been found that the permeability of insoluble monolayers to water is not inversely proportional to the monolayer thickness, i.e., to the length of the spread molecules (9). Therefore, the energy-barrier theory is generally preferred to describe the transport of water and gases through insoluble monolayers. We have nevertheless given the above treatment, since it will be shown below that it adequately accounts for the permeability of *soluble* monolayers to various gases, as measured before (1).

2. *Energy-Barrier Theory of Monolayer Permeation.* The monolayer is bombarded by gas molecules from both sides, and a certain fraction of these molecules actually permeate.

For small concentrations the number of moles of gas permeating from the gas side can be written

$$(dN/dt)_g = k_g A C, \quad [16]$$

and from the water side

$$(dN/dt)_w = k_w A C'. \quad [17]$$

This results in a net flux

$$\begin{aligned} dN/dt &= (dN/dt)_g - (dN/dt)_w \\ &= A(k_g C - k_w C'). \quad [18] \end{aligned}$$

When the system is in equilibrium, i.e., when $C' = \bar{C}$, the net flux is zero, which requires that

$$k_g/k_w = \bar{C}/C = H. \quad [19]$$

Therefore, [18] can be written

$$\begin{aligned} \frac{dN}{dt} &= k_w A \left(\frac{k_g}{k_w} C - C' \right) \\ &= k_w A (\bar{C} - C'), \end{aligned} \quad [20]$$

or, alternatively,

$$\begin{aligned} \frac{dN}{dt} &= k_g A \left(C - \frac{k_w}{k_g} C' \right) \\ &= k_g A (C - \bar{C}). \end{aligned} \quad [21]$$

Comparison of [20] and [2] and of [21] and [4] indicates that k_{ML} and k'_{ML} are identical with k_w and k_g , respectively.

In general, one can write for a uni-directional flux, e.g., from the gas into the liquid:

$$\left(\frac{dN}{dt} \right)_g = \frac{n_c}{N_{Av}} A W, \quad [22]$$

where n_c is the number of molecules that strike 1 square cm. of the monolayer from the gas side per unit time, N_{Av} is Avogadro's number, and W is the fraction of molecules that enter the liquid after striking the monolayer.

From the kinetic theory of gases it follows that

$$n_c = CN_{Av} \sqrt{\frac{RT}{2\pi M}}, \quad [23]$$

where R is the gas constant, T is the absolute temperature, and M is the molecular weight of the gas.

Permeation requires in the first place that the molecule pass through a hole in the monolayer. This hole may originate from the kinetic energy of the striking molecule, from fluctuations in the molecular density in the monolayer, or from both (10). Upon reaching the end of a hole, however, the molecule does not necessarily enter the liquid, but may be reflected from the exposed water surface (10). This leads to

$$W = \alpha_c \exp(-E/kT), \quad [24]$$

where k is Boltzmann's constant, and α_c is

assumed to be equal to the condensation coefficient at a pure water surface. Here E is the free energy of hole formation, and will increase with the size of the gas molecule. A reasonable estimate is $E = \pi_s a_0$, where π_s is the surface pressure, and a_0 is the cross-sectional area of the gas molecule.

Substituting for n_c and W in [22] yields

$$\left(\frac{dN}{dt}\right)_g = \alpha_c AC \cdot \sqrt{\frac{RT}{2\pi M}} \exp(-E/kT). \quad [25]$$

From [16] and [25] one obtains

$$k'_{ML} = k_g = \alpha_c \sqrt{\frac{RT}{2\pi M}} \exp(-E/kT). \quad [26]$$

Thus the energy-barrier theory predicts that $k'_{ML}\sqrt{M}$ decreases with increasing size of the gas molecule, provided that α_c is approximately the same for all gases.⁴

It is now clear that our previous conclusion as to the mechanism of monolayer permeation is invalid (1), because the pre-exponential term F of [44] in reference 1 is not a constant. It still depends on the kind of gas according to

$$F = \frac{\alpha_c}{H} \sqrt{\frac{RT}{2\pi M}}.$$

REINTERPRETATION OF RESULTS

Experimental data have been given in reference 1 for 4% hexadecyltrimethylammonium bromide (HDTAB), 4% HDTAB + 1% NaBr, and 4% HDTAB + 10% NaBr. In all cases it was assumed that the equilibrium film was a Perrin first-order film,

⁴ This assumption is open to question; experimental values could only be found for the condensation coefficient of some vapors at the surface of their own condensates (11-13). For nonpolar molecules (Hg, C₆H₆, CCl₄, etc.) α_c appears to be equal or close to unity. For polar molecules it may be considerably smaller, e.g., for H₂O: 0.036; glycerine: 0.052; CH₃OH: 0.045; C₂H₅OH: 0.020; CHCl₃: 0.16. Littlewood and Rideal (14), however, have thrown serious doubt on these low values. They suggest that in all cases α_c is equal or very close to unity.

i.e., a bimolecular leaflet of surfactant molecules and possibly a few hydration layers, so that [6] could be applied. Although circumstantial evidence supported this assumption, more direct evidence has been obtained only recently, at least for the salt-containing systems. Using the same surfactant, van der Waarde measured the reflection coefficients of these films and thus found thicknesses of 57 and 52 Å in 4% HDTAB + 1% NaBr, and 4% HDTAB + 10% NaBr, respectively; hence, these films may undoubtedly be classified as Perrin first-order films. Since the length of an HDTAB molecule is about 20 Å, each monolayer still contains a hydration layer which is approximately 7 Å thick. In 4% HDTAB without salt the situation is less clear. Van der Waarde measured thicknesses ranging from 113 to 86 Å, depending on the hydrostatic pressure in the film. The maximum between the primary and secondary minima in the free energy versus thickness curve (15) was apparently too high to be overcome by local fluctuations. The chance that a Perrin film is formed owing to such fluctuations is obviously proportional to the surface area of the film which in our experiments was several times larger than in van der Waarde's. The kind of film one obtains may also depend on the manner in which it is prepared. Therefore, the assumption that we were also dealing with Perrin films in the saltless system is not necessarily at variance with van der Waarde's results, and is strongly supported by the data in Table V of reference 1, which show that the film permeability is virtually unaffected by adding salt, although this might also result from a simultaneous decrease in h and k'_{ML} upon adding 1% NaBr.

To avoid this uncertainty we shall concentrate on the data obtained with 4% HDTAB + 1% NaBr (Table IV of reference 1), given in a slightly different form in Table I. The film permeabilities for Ne and CO₂ were not actually measured in this system. They were assumed to be 4% higher than in the saltless system (Table III of reference 1), as this was the average difference for all other gases considered.

There appears to be no relation whatso-

TABLE I
DIFFUSION OF VARIOUS GASES THROUGH A 4% HDTAB + 1% NaBr FILM

Gas	$H \times 10^2$ (est.)	$D \times 10^5$ (cm. ² /sec.)	σ (Å)	k (cm./sec.)	k'_{ML} (cm./sec.)	$k'_{ML}\sqrt{M}$	k_{ML} (cm./sec.)	h^* (Å)
He	0.90	5.8	2.16	0.398	0.796	1.59	88.5	65
(Ne)	1.07	2.8	2.58	0.211	0.422	1.90	39.5	70
A	3.43	2.0	3.62	0.322	0.644	4.06	18.8	105
H ₂	1.86	5	2.71	0.577	1.154	1.63	62.0	80
O ₂	3.14	2.1	3.58	0.321	0.642	3.62	20.5	105
N ₂	1.58	2.0	3.72	0.131	0.262	1.38	16.6	120
(CO ₂)	88.0	1.8	4.54	7.85	15.7	104.	17.8	100
N ₂ O	63.5	2.0	4.59	4.31	8.62	57.1	13.6	145

ever between $k'_{ML}\sqrt{M}$ and the molecular diameter σ . Especially the high values of $k'_{ML}\sqrt{M}$ for CO₂ and N₂O are striking, and our results appear to disprove, rather than confirm, the energy-barrier theory. The inverse relationship between k_{ML} and σ cannot be interpreted as a confirmation of the energy-barrier theory, as was done in reference 1.

On the other hand, the equivalent thickness h^* does not vary appreciably, indicating that Fickian diffusion is very probable. Moreover, the observation that h^* for CO₂ and N₂O are not much larger than for the other gases strongly suggests that diffusion actually takes place through aqueous pores. This is further supported by the increase of h^* with σ (owing to a decrease in the effective diameter of the pores), although the values of h^* are not very accurate because of possible errors in D (16).

DISCUSSION

The proposed mechanism of permeation, though extremely simple, adequately explains the relative permeabilities of the soluble monolayer to the various gases. Apart from the objection that application of Fick's law to the submicroscopic pores may be questionable, the model is still rather crude for other reasons.

In the first place, the water in the pores probably differs structurally from bulk water, especially around the ionic heads of the surfactant molecules, resulting in different values of D and H ; little is known about this at present.

Secondly, the length of the aqueous pores

is uncertain. If they extend all the way to the ends of the hydrocarbon chains, i.e., if their length is δ , the fraction of the surface taken up by the pores is given by $\delta/h^* \approx 0.3$. This fraction becomes proportionally smaller if one assumes that only part of the surfactant molecules is "submerged," which is more likely. In any case there is hardly any doubt that in *soluble* monolayers there is enough room for these pores, considering the large area per molecule ($\sim 50 \text{ \AA}^2$). In *insoluble* condensed monolayers, where the area per molecule may be as small as 20 \AA^2 , hardly any interstitial water can be present, and the mechanism of permeation must be essentially different. Here the energy-barrier theory is probably the better approach. In this connection it is important to note that soluble monolayers are several orders of magnitude more permeable than insoluble ones. For example, Hawke and Parts (3) measured for CO₂ through an octadecanol monolayer a value of k_{ML} of 1.3×10^{-3} cm./sec., which compares with $k_{ML} = 17.8$ cm./sec. for the HDTAB monolayer. Consequently, the techniques used by Blank and Roughton (17, 18) and Hawke and Parts (3) are not useful in the study of soluble monolayers, since the effect of the monolayer on the over-all rate of mass transport would be immeasurably small owing to the large resistance of the underlying liquid phase.

Finally, with our technique one measures the permeability of a monolayer as it is present in a thin soap film. Its structure, and thus its permeability, may differ from that of a monolayer at a free bulk surface.

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REFERENCES

1. PRINCEN, H. M., AND MASON, S. G., *J. Colloid Sci.* **20**, 353 (1965).
2. PRINCEN, H. M., "Shape of Fluid Drops at Fluid-Liquid Interfaces and Permeability of Soap Films to Gases." Ph.D. Thesis, Utrecht, 1965.
3. HAWKE, J. G., AND PARTS, A. G., *J. Colloid Sci.* **19**, 448 (1964).
4. HAWKE, J. G., AND ALEXANDER, A. E., In V. K. La Mer, ed., "Retardation of Evaporation by Monolayers: Transport Processes," p. 67. Academic Press, New York, 1962.
5. JUST, G., *Z. Phys. Chem.* **37**, 342 (1901).
6. HILDEBRAND, J. H., "Solubility of Non-electrolytes," p. 136. Reinhold, New York, 1936.
7. BLANK, M., *J. Phys. Chem.* **66**, 1911 (1962).
8. BARNES, G. T., AND LAMER, V. K., in V. K. LaMer, ed., "Retardation of Evaporation by Monolayers: Transport Processes," p. 19. Academic Press, New York, 1962.
9. ARCHER, R. J., AND LAMER, V. K., *J. Phys. Chem.* **59**, 200 (1955).
10. BLANK, M., *J. Phys. Chem.* **68**, 2793 (1964).
11. WYLLIE, G., *Proc. Roy. Soc. (London)* **A197**, 383 (1949).
12. ALTY, T., *Nature*, **139**, 374 (1937).
13. BARANAEV, M., *J. Phys. Chem. U.S.S.R.* **13**, 1635 (1939).
14. LITTLEWOOD, R., AND RIDEAL, E., *Trans. Faraday Soc.*, **52**, 1598 (1956).
15. PRINCEN, H. M., AND MASON, S. G., *J. Colloid Sci.* **20**, 156 (1965).
16. HIMMELBLAU, D. M., *Chem. Rev.* **64**, 527 (1964).
17. BLANK, M., AND ROUGHTON, F. J. W., *Trans. Faraday Soc.* **56**, 1832 (1960).
18. BLANK, M., In V. K. LaMer, ed., "Retardation of Evaporation by Monolayers: Transport Processes," p. 75. Academic Press, New York, 1962.