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Hydrodynamic Effects in Liquid Membrane Transfer

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Abstract

An experimental apparatus was developed which permitted the thickness of liquid membranes to be measured. The observed values for the thickness were of the order of 0.01 cm which is considerably in excess of those values previously reported in the literature. The experimentally observed data were favorably compared to the thicknesses computed using boundary layer theory. Finally, dimensional analysis was used to develop a correlation of the computed membrane thickness as a function of the droplet diameter and system properties.

INTRODUCTION

The discovery of selective mass transfer across liquid membranes has made available an entirely new separation technique for application in chemical technology. To date only a limited number of studies have been reported which attempt to explain the underlying factors influencing liquid membrane permention rates. Li, when reporting his studies of liquid membrane transport, suggested several mass transfer mechanisms for such systems (*1*). Later work has indicated that some of these proposals might need reconsideration (*2*). In particular, the suggestion that liquid membranes are very thin has been called into serious question.

Steele and Halligan, using a modified liquid membrane diffusion column, measured the thickness of liquid membranes and found them to be of the

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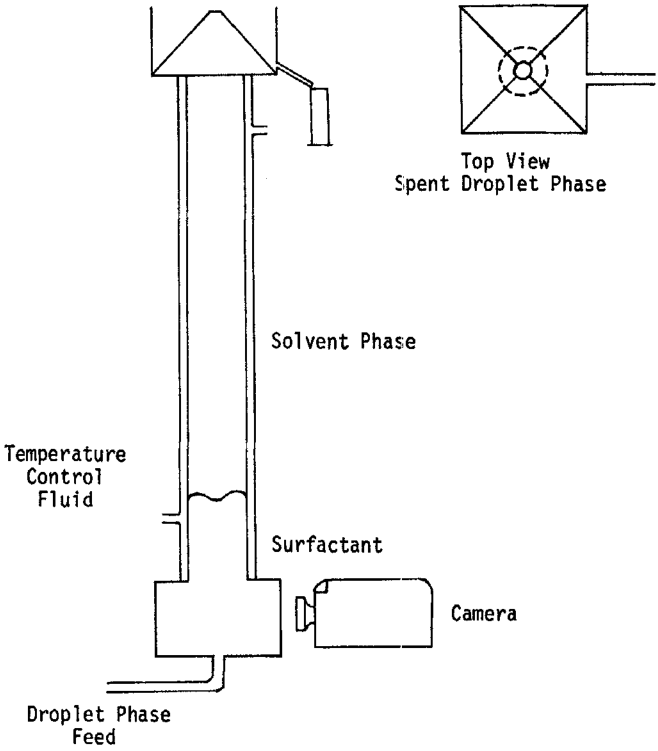

FIG. 1. Liquid membrane diffusion column.

order of 0.005 cm (*2*) while Li in his work has suggested that such films were probably a few molecules thick. However, the studies of Steele and Halligan were limited to a diffusion column, and their results may or may not extend to membranes formed using a different experimental apparatus. The majority of permeation data reported in the literature were obtained using a single-droplet apparatus similar to that shown in Fig. 1. To make informed judgments concerning the mechanism of liquid-membrane transfer, it was deemed necessary to design and carry out experiments in a situation which was hydrodynamically similar to that existing in the single-drop apparatus.

EXPERIMENTAL PROCEDURE AND RESULTS

The experimental technique used to determine the thickness of liquid membranes in the single-droplet experiments involved reversing the normal

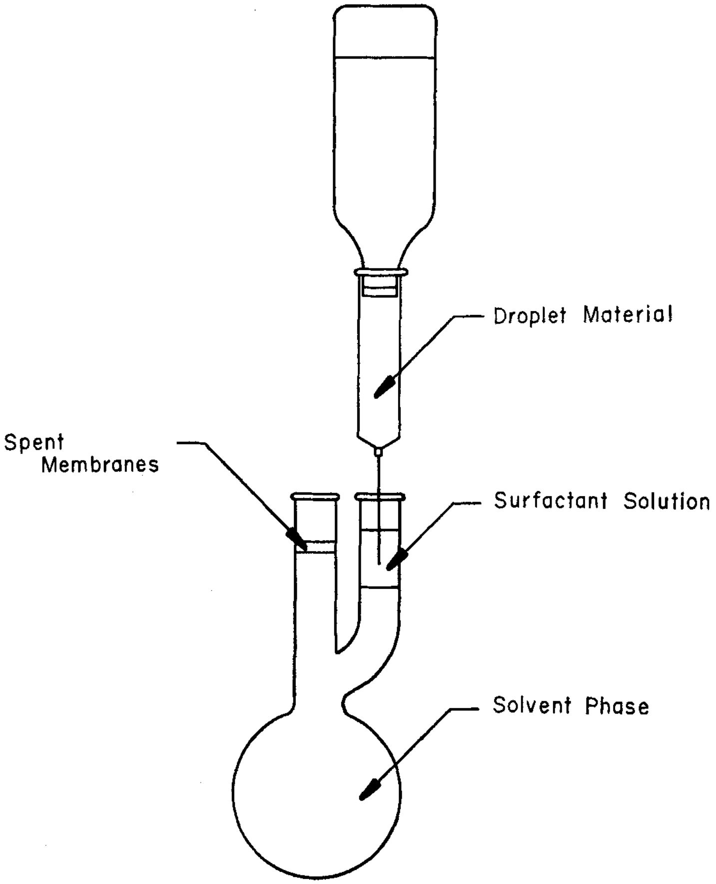

FIG. 2. Device for determination of liquid membrane thickness.

fluid densities found in a diffusion column. A droplet was allowed to fall through an aqueous surfactant solution during which it obtained a membrane coating. Below the surfactant solution was a solvent phase. A droplet, after leaving the surfactant solution and entering the solvent phase, fell through a curved leg into a reservoir. After a sufficient time the droplet broke and the membrane rose through a different leg to the top of the reservoir where it was collected. A drawing of this apparatus is shown in Fig. 2.

The interfacial area of the droplet was calculated by observing its diameter during formation with a cathetometer. If a large number of droplets were injected into the surfactant, a measurable amount of membrane material could be collected at the top of the reservoir and the film thickness calculated.

The injection of a sufficient number of uniformly sized droplets into the solution to obtain a significant amount of membrane material presented a problem. This difficulty was resolved by developing a constant-rate feeding device. The plunger was removed from a 50-ml syringe, and a bottle of droplet material was inverted with its mouth in the syringe. Since the top of the syringe was open to the atmosphere, a pressure head equal to the height of the column of liquid in the syringe was generated. If the level in the syringe fell, air could enter the bottle and allow fluid to flow into the syringe, thereby readjusting the level to a constant height of droplet phase in the syringe. The constant-pressure head on the orifice at the top of the hypodermic needle made possible a constant rate of generation of droplets of known size. This rate could be measured and used to determine the total number of droplets formed in a given time.

The above device was operated with carbon tetrachloride as the droplet phase and a mixture of 1,1,1-trichloroethane and 2,2,4-trimethylpentane having a density of 1.16 g/ml as the solvent phase. Solutions of various surfactants in water were used for the membrane; however, in all cases the density was very near 1 g/ml. The apparatus was operated for about 45 min in this manner at a formation rate of approximately 100 drops/min. Knowing the size of the droplet, the time of operation of the apparatus, and the amount of surfactant collected, it was possible to calculate the mean thickness of an individual liquid membrane. The results of these experiments are summarized in the first three columns of Table 1.

The film thicknesses reported in Table 1 are reasonably consistent with the values of approximately 0.005 cm obtained from diffusion-column data (*2*). The extent of the membranes might lead one to suspect that the hydrodynamic factors suggested with regard to the diffusion-column membranes might also be the controlling influence in the apparatus designed to simulate single-droplet experiments. For an application in which one liquid is in contact with another on a plane surface, Davies and Rideal have suggested that the film thickness might be controlled by the associated hydrodynamic boundary layer (*3*). The size of the film thickness reported in Table 1 would seem at first examination to be consistent with that expected from boundary-layer theory.

The description of a boundary layer around a sphere is discussed by Schlichting in his work *Boundary Layer Theory* (*4*). The velocity profile in a boundary layer is given by a simplified form of the Navier-Stokes equation. One of the boundary conditions used in the solution of this

TABLE 1

Film Thicknesses of Liquid Membranes

Surfactant	Droplet diameter (cm)	Film thickness (cm)	Film thickness from boundary layer theory, the boundary layer extending to the following % of stream velocity				
			70 (cm)	80 (cm)	90 (cm)	95 (cm)	99 (cm)
0.1 % Saponin	0.278	0.0061	0.00496	0.00592	0.00726	0.00836	0.0103
	0.282	0.0048	0.00494	0.00590	0.00724	0.00832	0.0102
	0.295	0.0141	0.00499	0.00596	0.00732	0.00841	0.0104
	0.230	0.0075	0.00474	0.00566	0.00695	0.00799	0.00983
	0.260	0.0010	0.00483	0.00577	0.00709	0.00815	0.0100
	0.248	0.0059	0.00483	0.00577	0.00709	0.00815	0.0100
	0.248	0.0121	0.00483	0.00577	0.00709	0.00815	0.0100
	0.271	0.0102	0.00494	0l00590	0.00725	0.00833	0.0103
	0.258	0.0053	0.00488	0.00583	0.00715	0.00823	0.0101
	0.227	0.0112	0.00482	0.00576	0l00707	0.00813	0.0100
	0.288	0.0039	0.00501	0.00599	0.00736	0.00846	0.0104
	0.302	0.0052	0.00507	0.00606	0.00744	0.00858	0.0105
1 % Saponin	0.225	0.0170	0.00473	0.00565	0.00694	0.00792	0.00982
	0.222	0.0072	0.00474	0.00566	0.00695	0.00799	0.00983
	0.216	0.0079	0.00483	0.00578	0.00709	0.00816	0.0100
0.1 % Deodecyl sodium sulfate	0.161	0.0170	0.00473	0.00566	0.00693	0.00798	0.00982
	0.168	0.0201	0.00471	0.00564	0.00691	0.00796	0.00979
	0.203	0.0081	0.00465	0.00566	0.00683	0.00783	0.00966
	0.168	0.0158	0.00471	0.00564	0.00691	0.00796	0.00979
	0.174	0.0166	0.00471	0.00562	0.00690	0.00794	0.00977
1 % Dodecyl sodium sulfate	0.128	0.0066	0.00492	0.00588	0.00721	0.00830	0.0102
	0.142	0.0089	0.00489	0.00584	0.00716	0.00824	0.0101
	0.152	0.0040	0.00486	0.00581	0.00713	0.00821	0.0101
	0.140	0.0044	0.00489	0.00584	0.00717	0.00852	0.0102
	0.150	0.0033	0.00476	0.00568	0.00697	0.00802	0.00981
1 % Polyvinyl alcohol	0.247	0.0085	0.00483	0.00577	0.00708	0.00814	0.0100

equation matches the velocity obtained at the surface of a sphere from potential flow with the velocity at an infinite distance from the sphere in the boundary layer. This assumption is tantamount to assuming that the boundary layer is small when compared with the diameter of the sphere. The differential equation mentioned above has been solved in series form, giving the velocity in the boundary layer as a function of the velocity of the sphere relative to the surrounding fluid, the position on the surface of the sphere, the radius of the sphere, and the properties of the fluid. The solution and its associated coefficients are tabulated in Schlichting (*4*).

In a previous discussion it was pointed out that the thickness of liquid-membrane films might not be too different from the size expected of a boundary layer (*2*). The thickness of a boundary layer is normally defined as the distance at which the fluid velocity is 99% of the stream velocity at the surface, based on potential flow. Other definitions exist, however, and they might provide an equally good basis for developing correlations for the thickness of liquid membranes.

To examine several possible relations between the predictions obtained from boundary-layer theory and the thickness of liquid membranes, it was decided to examine the boundary layer thicknesses at 70, 80, 90, 95, and 99% of the potential flow velocity. The solution to the boundary-layer problem varies with position; thus the calculations were carried out over the entire surface and an integration was performed to determine the mean value of the thickness. Since the boundary-layer equations are valid only to the point of separation (109.6° from the leading edge of a sphere), the membrane thickness was assumed to be negligible in the wake of the droplet. The velocity of the droplet through the surfactant was assumed to be the terminal velocity of the droplet in the fluid. Relations in Bird, Stewart, and Lightfoot were used to calculate the terminal velocity (*5*).

The boundary-layer thicknesses resulting from the above calculations are tabulated in the last five columns of Table 1. Values calculated for boundary-layer thicknesses were clearly of the same order as those measured for liquid membrane thicknesses. There was, however, a great deal of variation from point to point. This variation could be in large portion due to the amount of the membrane material that was associated with the wake of the droplet. The results tabulated in Table 1 suggest that the experimentally observed liquid-membrane thicknesses are of the same order of magnitude as the values predicted by boundary-layer theory. This observation does not in itself prove that the hydrodynamics of droplet flow controls the size of liquid-membrane films; however, the mechanism is at least given credence. Regardless of the exact mechanism of film formation, this suggests that boundary-layer theory will at least make a reasonable estimation of the thickness of liquid membranes in single-drop experiments.

The calculation of membrane thicknesses from boundary-layer theory is not a simple undertaking. For this reason it was considered desirable to find some means of simplifying this procedure. It was observed that the number of independent variables was such that dimensional analysis might provide a simple graphic solution to the flow equations and the boundary-layer equations (*6*). If the mean boundary-layer thickness is assumed to be a function of droplet diameter, the density of the surfactant, the density difference between the surfactant and the droplet, and the acceleration of gravity, a dimensional analysis may be made. In mathematical terms it is assumed that

$$y = f(d,\rho_s,(\rho_2 - \rho_s),\mu_s,g) \tag{1}$$

Using the Buckingham-Pi method (*6*), proper grouping of the terms in Eq. (1) leads to

$$\frac{y}{d} = f_2\left[\frac{d^3\rho_s{}^2 g}{\mu}, \frac{(\rho_2 - \rho_s)}{\rho_s}\right] \tag{2}$$

Equation (2) implies that it may be possible to plot y/d as a function of $d^3\rho_s{}^2g/\mu$, on lines of constant $(\rho_2 - \rho_s)/\rho_s$. This correlation was tested using data calculated for a wide range of the independent variables. The resulting solution obtained using the calculated data is plotted as Fig. 3.

It was previously noted that the solution of the boundary-layer equations required a relatively thin boundary layer. Since the droplets typical of emulsions are approximately the size which would be represented by the left-hand side of Fig. 3, the application of this relation to emulsion systems should be viewed with suspicion. It should also be noted that the velocity typical of the droplets in emulsions might not be due to free fall but due to mixing effects related to the creation and transfer of the emulsion. Regardless of the difficulties in applying boundary-layer equations to emulsion systems, the data from Fig. 3 still suggest that reasonably thick films could be expected in droplets of emulsion size. Unpublished data obtained by McHaney suggest that film thickness in emulsion systems might not be too different from that indicated in Fig. 3 (*7*).

In summary, the thickness of liquid membranes has been measured experimentally. This thickness was found to be of the order of 0.01 cm, which is considerably larger than the value previously assumed. In addition, membrane thicknesses were estimated using boundary-layer theory. A

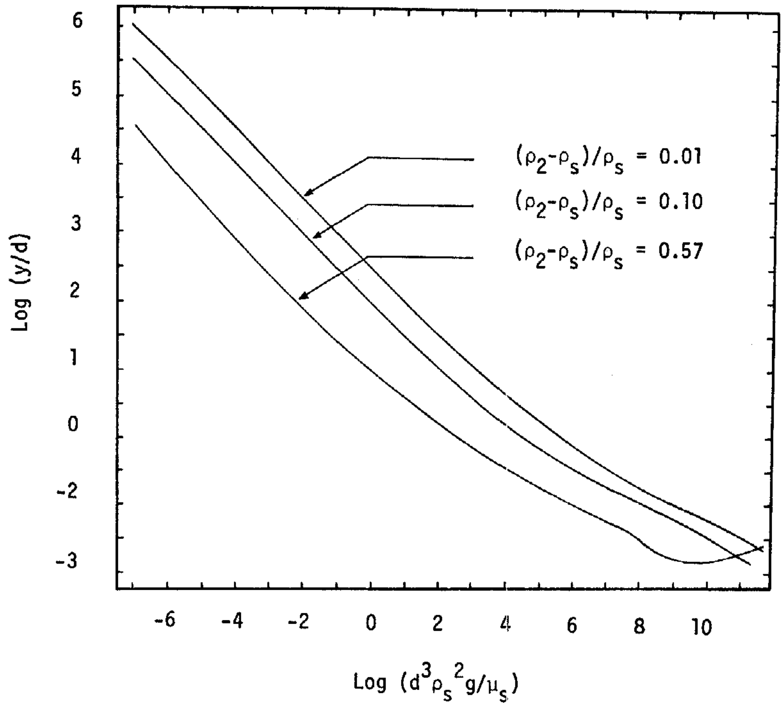

FIG. 3. Correlation for film thickness based on boundary layer extending to .95 of stream velocity.

dimensionless correlation was presented to simplify the estimation of membrane thicknesses.

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SYMBOLS

d	droplet diameter
g	acceleration due to gravity
μ_s	viscosity of the solvent phase
ρ_2	density of droplet
ρ_s	density of the solvent phase

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