II. Effect of Monomolecular Films on Natural Convection in Water

The reduction in evaporation from a water substrate and the accompanying change in heat transport through the water induced by monolayers of cetyl alcohol and stearic acid are investigated. Evaporation resistance of the monolayer and Nusselt number in the water are determined at 2° to 22°C. The evaporation resistance increases with increasing surface pressure of the monolayer. In the presence of natural convection in the water, the Nusselt number decreases during monolayer compression. This reduction is larger than could be expected just from the lowered evaporative heat flux and the resulting reduction in the Rayleigh number. It may be due to a change in the surface hydrodynamic characteristics caused by the monolayer.

The inhibiting effect that certain insoluble monolayers can have on the evaporation of water has been the subject of intensive research since Rideal's experiments in 1925 (*1*). Notable among the investigations are those by Langmuir and Schaefer (*2*) and by La Mer and co-workers (*3, 4*). Yet the mechanism of the inhibition and the reasons for differences in effectiveness between different monolayers are not entirely clear. The only available theory, first suggested by Langmuir and Schaefer and later developed by La Mer et al., explains the monolayer resistance in terms of an activation energy barrier to diffusion through the monolayer. Experimental tests of this theory have been carried out only with long-chain alcohols in the limited surface pressure range, of about 15 to 30 dynes/cm., and over a relatively narrow temperature range from 15° to 30°C. Although the few available results are reasonably consistent with the theoretical model, it cannot be said that the theory is either complete or well established. There continues to be scientific interest in the mechanism. There is also the possible practical importance of monolayers in evaporation control. A further study of the problem might therefore elucidate further the inhibition mechanism.

Evaporation from a liquid surface is governed by three rate processes: the transfer of liquid molecules across the surface into the vapor phase, the removal of newly formed vapor from the interface, and the supply of heat to the surface. The rate of each of these processes is determined by a driving force and can be expressed in terms of a process resistance. The evaporation rate will generally depend upon the sum of these resistances. In particular situations any one of them may be dominating. If, for instance, the heat transfer to the surface is insufficient to maintain the evaporation rate permitted by the surface resistance or the gas-phase diffusional resistance, the surface temperature and the evaporation rate will decrease until a balance occurs again between the heat transfer rate and the evaporation rate. Conversely, when evaporation rate is suppressed by a monolayer, the surface temperature rises, as was experimentally demonstrated by Jarvis and co-workers (*5* to *7*). In a case where some of the heat of evaporation is supplied to the surface through the water by means of convective transfer, a monolayer at the surface, in addition to being a barrier to passage of water molecules, might conceivably affect the hydrodynamic behavior of water near the surface. In other words, it might alter not only the surface resistance to evaporation but also the liquid resistance to heat transfer. It is interesting that very little effort has been made to investigate the possibility of a relation between the evaporation-inhibiting properties of monolayers and a change in the diffusional resistance of the gas or heat transfer resistance of the water caused by the presence of the monolayer.

Some indication of the effect of surface films on convection in water was reported by Ewing and McAllister (*8*). They used a radiometric technique to measure surface temperature, but their tests were not done with pure monolayers under well-defined surface conditions. Berg et al. (*9*) found, by means of Schlieren techniques, that when surface tension rather than buoyancy was important, surface-active material had a strong effect on the convection. Also in their work the monolayer state was not well defined during the experiments. An observation of a different nature was reported by Nakagawa (*10*). In his experiments with convective heat transfer in mercury he found that surface contamination, which is difficult to avoid on mercury, did inhibit buoyancy-driven convection at least at the surface region. An entirely different possibility was pointed out in two recent communications by MacRitchie (*11, 12*), who suggested that the thickness of the diffusion boundary layer in a gas flowing over a water surface was increased in the presence of cetyl alcohol monolayers. This increase, according to the author, was responsible for the evaporation-retarding properties of cetyl alcohol!

The difficulty in measuring directly the effect of monolayer on natural convection lies in the interdependence between the evaporation rate and the thermal driving force. A monolayer which suppresses evaporation of water by whatever mechanism also reduces the temperature difference between the bulk liquid and the surface and hence the driving force for heat transfer to the surface. It becomes clear then that any attempt to describe completely the effect of monolayers on evaporative heat transfer in the water must distinguish explicitly between the resistance provided by the monolayer to transfer of water molecules from the surface and possible resistance resulting from direct inhibition of heat transfer in the water.

EXPERIMENTAL PROCEDURE

In the present work the rate of evaporation from a given water surface area into a flowing inert gas was measured both in the absence and presence of monolayers. The difference between the resistances to evaporation with and without mono-

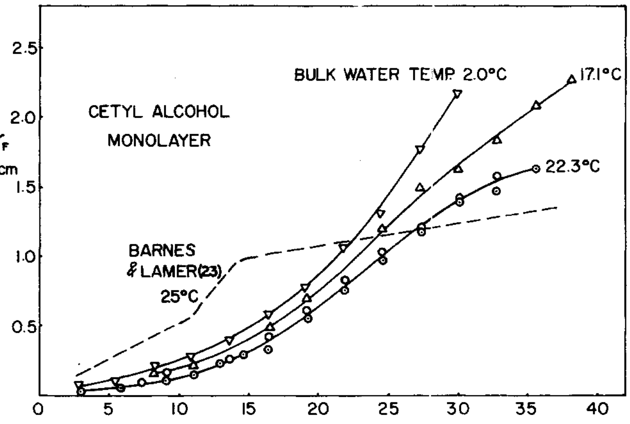

Fig. 1. Evaporation resistance of cetyl alcohol monolayer at several water temperatures.

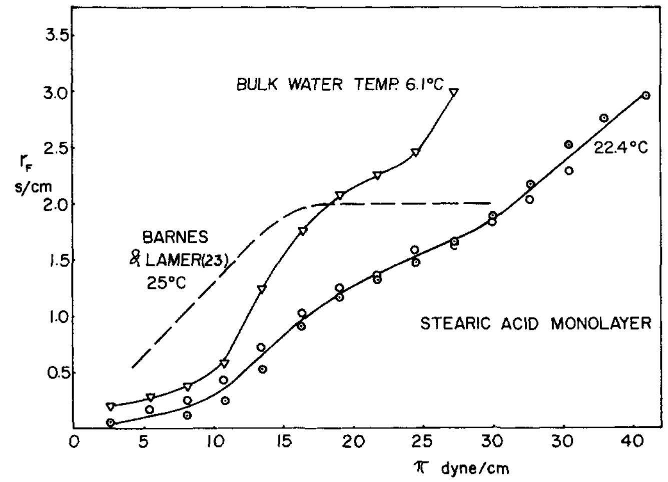

Fig. 2. Evaporation resistance of stearic acid monolayer at water temperatures of 6.1° and 22.4°C.

layers under otherwise identical conditions yielded the monolayer resistance to evaporation. If the mole fractions of water vapor in the gas entering and leaving the evaporating area A are x_1 and x_2, respectively, the equilibrium water concentration at the surface is x_s, and the evaporation rate is W, the overall diffusional mass transfer coefficient is defined by

$$k_x = \frac{W(1 - x_s)}{A \Delta x_{ln}} \tag{1}$$

The overall resistance to evaporation, which is defined as $r = c/k_x$, can be written in terms of measurable quantities by expressing W from Equation (1) in terms of the rise in water concentration and using the conventional definition of ΔX_{ln}. The resulting expression is

$$r = \frac{A}{V} \; \frac{1}{(1 - x_s) \ln \dfrac{x_s - x_1}{x_s - x_2}} \tag{2}$$

and the average monolayer resistance r_F is then

$$r_F = r_{\text{with film}} - r_{\text{without film}} \tag{3}$$

Evaporation rate was measured by a probe similar to that used by Sebba and Briscoe (*13*) and by Walker (*14*). The version used in the present work has been described in detail and analyzed in a companion paper (*15*). The probe, which was comprised of two concentric cylinders with a narrow annular space between them, was placed near the water surface, and dry nitrogen was introduced through the annulus toward the surface. A small part of the gas was withdrawn through a central passage after sweeping the water surface and then analyzed continuously by a coulometric moisture monitor (CEC Model 26-303). The rest of the gas flowed outward from the probe, forming a barrier to diffusion of external moist gas. The advantages of this probe include a relatively low gas-phase resistance to vapor diffusion together with a fast and continuous monitoring of water content in the withdrawn gas. Thus evaporation rates were determined very rapidly.

In addition to the evaporation probe, the apparatus included a surface balance and an array of thermocouples for measuring the temperature profile in the water. The surface balance consisted of Teflon-coated tray 50 cm. × 14 cm. by 2 cm. deep. The surface pressure of the monolayer could be measured by either a Wilhelmy plate or a Langmuir-Adam float connected to a torsion balance. The monolayer materials used were cetyl alcohol $C_{16}H_{33}OH$ (Eastman) and stearic acid $C_{17}H_{35}COOH$ 99%+ (Nutritional Biochemicals). *n*-Hexane (Fisher spectranalyzed) was used as a spreading solvent. The entire apparatus was contained in a thermostatically controlled enclosure which provided a constant and uniform temperature at any desired level.

To obtain the data after the system reached the desired temperature, the evaporation measuring system was flushed with dry nitrogen until a steady low moisture level (usually 15 to 20 p.p.m.) was indicated by the moisture monitor. The water surface was then swept several times with a Teflon bar and the evaporation probe was placed about 2 mm. from the surface with dry nitrogen passing through the probe and initiating evaporation. The flow rate through the probe, the water vapor concentration in the gas, and the temperature profile in the water were recorded. The Wilhelmy plate was then dipped in the water and the monolayer, dissolved in *n*-hexane at a concentration of 2 mg./cu.cm., spread at the surface. After the *n*-hexane was allowed to evaporate, the remaining monolayer was compressed in steps of about 3 dynes/cm. At each surface pressure the film area was measured in addition to evaporation rate and water temperatures. Changes in the flow rate of dry nitrogen into the probe had no effect on the data, indicating that the monolayer was not swept away or disrupted because of the flow shear at the surface.

RESULTS AND DISCUSSION

Evaporation Resistance

Evaporation resistance-surface pressure isotherms are shown for monolayers of cetyl alcohol in Figure 1 and for stearic acid monolayers in Figures 2 and 3. The ordinate values are the film resistance as defined in Equation (3). The results show that the evaporation resistance of stearic acid is higher than that of cetyl alcohol. This result is consistent with previous investigations. It is attributed to the longer chain of the acid and the higher activation energy associated with the polar group. The results reported by Barnes and La Mer (*16*) and shown in dashed curves indicate a higher resistance than the present data at low surface pressure but a lower resistance at high surface pressure. The reason for these differences is not clear, but it should be pointed out that because of the rapid response of the evaporation probe it was much easier in the present work to associate a particular rate with a given surface pressure.

The dependence of evaporation resistance on surface pressure at water temperatures below 15°C. is reported here for the first time. The lower temperatures result in higher evaporation resistance, particularly at high monolayer compression. A marked difference is seen between the alcohol and the acid. While the resistance curves of 1-hexadecanol remain smooth at temperatures as low as 2°C., the stearic acid curves exhibit bends which become sharp kinks near the freezing point of water. There is not an obvious explanation for this behavior, and it is noteworthy that no corresponding discontinuities are observed

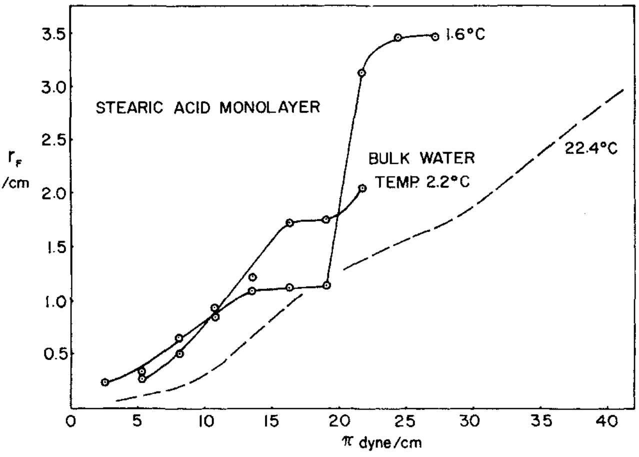

Fig. 3. Evaporation resistance of stearic acid monolayer at water temperatures of 1.6° and 22.4°C.

on the surface pressure area isotherm for a stearic acid monolayer. Consequently it would seem difficult to relate the abrupt changes of film resistance to first-order phase transition. One might invoke the possibility of higher order phase changes. A more likely explanation would be the "squeezing out" of residual impurities in the monolayer. As observed by La Mer (*4*), such impurities can have a marked effect on film resistance.

Effect of Monolayers on Heat Transfer Through the Water

In the case of a clean water surface both the conductive and convective modes of heat transfer to the evaporating surface were investigated in the present apparatus and the results reported in the companion paper (*15*). The heat flux was calculated from the known evaporation rate and the heat of vaporization at the surface temperature T_s. Heat transfer was expressed in terms of Nusselt number calculated from the equation

$$N_{Nu} = \frac{qH}{(T_b - T_s)k} \; \frac{1}{5.15} \tag{4}$$

As defined here, N_{Nu} represents the ratio of the actual heat transfer to that which could be accounted for by conduction only.

In the presence of a monolayer at the surface the reduced evaporation rate resulted in a lower heat flux and a different temperature distribution in the water. Figure 4 shows how the vertical temperature profile at the center of the evaporating area is changed when a monolayer of cetyl alcohol under high surface pressure is present at the surface. The curves are shown for water temperatures of 2° and 17.1°C., that is, in the absence and presence of natural convection. Both the temperature difference across the layer and the temperature gradient near the surface decrease as a result of the lowered heat flux.

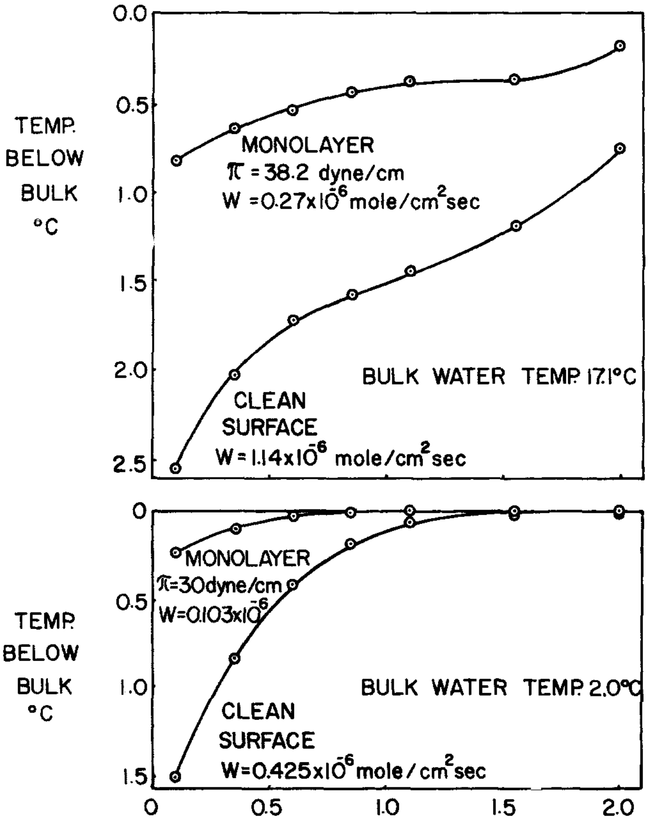

Fig. 4. Effect of cetyl alcohol monolayers on the water temperature profile in the absence and presence of natural convection.

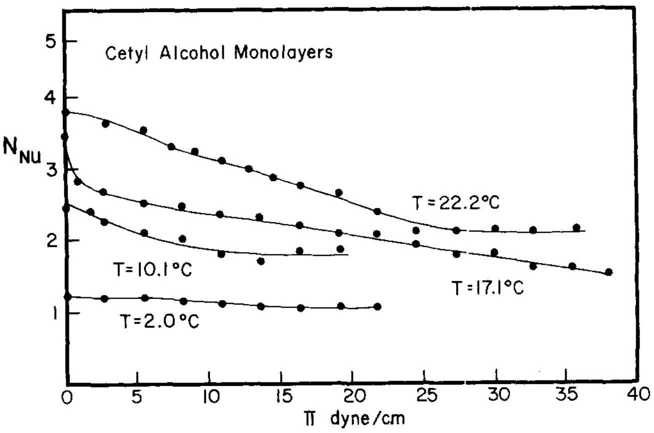

Fig. 5. Effect of compression of cetyl alcohol monolayers on N_{Nu}.

The effect of the surface pressure of hexadecanol monolayers on heat transfer through the water for several water temperatures is shown in Figure 5. The curves were derived from the data corresponding to Figure 1. Each represents a typical example chosen from three to four runs which were reproducible within about 5%. All the curves, except the one at 2°C., show a decreasing N_{Nu} with rising surface pressure, which indicates the reduction of natural convection in the water in the presence of a compressed surface film. Whether this reduction is merely a manifestation of the overall reduction in the evaporative heat flux or involves also a direct inhibition of natural convection can be determined by comparison with measurements obtained in the present apparatus with clean water surfaces (*15*). That there is indeed an effect on convection is demonstrated clearly by comparing the solid and the dashed curves in Figure 6. The dashed curves represent the lowering of N_{Nu} that would be expected had it been due solely to the diminishing N_{Ra} as the evaporation rate decreases with monolayer compression. The fact that in the presence of hexadecanol monolayers N_{Nu} drops more rapidly means that the monolayer affects the convection directly.

The reduction in the convective heat transfer can be explained, at least qualitatively, by a change in the hydrodynamic boundary condition at the surface due to the presence of a condensed monolayer. A monolayer of this kind has a rather low surface compressibility and a high

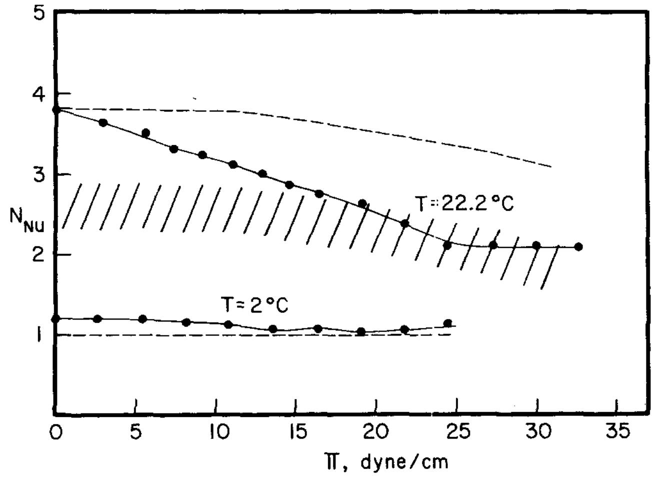

Fig. 6. Comparison between N_{Nu} obtained with cetyl alcohol monolayers and N_{Nu} for a clean water surface but at the same values of N_{Ra}. Shaded area marks expected approximate range of N_{Nu} with the water layer in the present system bounded by two rigid surfaces.

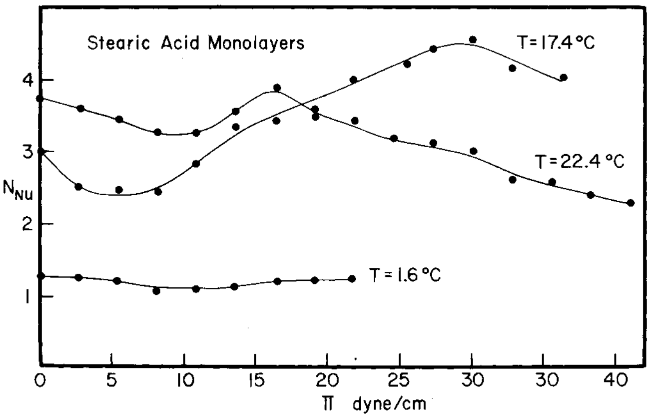

Fig. 7. Effect of compression of stearic acid monolayers on N_{Nu}.

surface viscosity. If it behaves like a solid no-slip boundary, it could have a profound effect on buoyancy-driven convection in the water. That N_{Nu} depends strongly on whether the boundary conditions relate to free or rigid-bound surfaces has been shown in an analysis of the nonlinear heat transfer problem (*17*). For two bound surfaces N_{Nu} is approximately one-half its value for the case of two free surfaces at any particular supercritical N_{Ra}. It might be expected that a system with one free boundary would be intermediate in its behavior between layers with two rigid boundaries and those with none. On this basis the shaded region in Figure 6 represents a crude approximation of what might be expected for two rigid boundaries in the present system. It is tempting to explain the decrease in N_{Nu} with increasing surface pressure as a transition from a free to a rigid boundary at the surface. In any event it seems abundantly clear that compressed monolayers can have a direct influence on natural convection. At least part of their ability to inhibit evaporation of water stems from this effect.

The results for stearic acid monolayers are not as easily interpreted. In Figure 7 it appears that sometimes the N_{Nu} actually increases with increasing surface pressure. In fact at 17.4°C. it rises above the value for a clean surface. We cannot readily understand this behavior. One plausible explanation is that a local convection cell near the thermocouples might cause a distortion in the temperature profile. Indeed, there is a marked change in the subsurface temperature distribution that accompanies the increase in surface temperature. It is not clear, however, why this behavior should occur with stearic acid and not with cetyl alcohol.

There are other differences between the behavior of stearic acid and cetyl alcohol monolayers. The sharp changes in resistance of stearic acid monolayers shown in Figure 3 which occur below 4°C. cannot be explained by convection effects. As indicated above, these may be related to the expression of impurities in the film. It is also inviting to speculate that there may be some sort of polarization or orientation of the molecules forming soft ice or some such structuring in the substrate water. There is much evidence for cybotactic groups in liquids, especially near the freezing point. In this connection we recall the suggestion by Claussen (*18*) that the average distance between OH groups is about the same in compressed monolayers as it is in ice. It would not be surprising if the compressed monolayer might form a pattern or matrix which enhances the structuring of adjacent liquid. Such anomalous semicrystalline water may offer some resistance to escape of water molecules into the gas phase. Any contribution of this type to the surface resistance is included in the measured resistance values. Near the freezing point of water such a layer of soft ice might very well cause a sudden increase of the resistance at a particular state of compression of the monolayer. If this speculation is at all meaningful, the differences in the behavior of stearic acid and cetyl alcohol at low temperatures might well be related to the structural differences in their hydrophilic groups.

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NOTATION

A = effective evaporation area, sq.cm.
c = molar concentration of water vapor, g.-mole/cu.cm.
H = height of water layer, cm.
k = thermal conductivity of water, cal./(sec.)(cm.)(°C.)
k_x = mass transfer coefficient, g.-mole/(sq.cm.)(sec.)
N_{Nu} = Nusselt number as defined in Equation (7), dimensionless
N_{Ra} = Rayleigh number, dimensionless
q = heat flux to the water surface, cal./(sq.cm.)(sec.)
r = resistance to evaporation, sec./cm.
r_F = resistance of film to evaporation, sec./cm.
T_b = temperature at bottom of water layer, °C.
T_s = temperature at the water surface, °C.
V = rate of withdrawal from the probe, cu.cm./sec.
x_s = mole fraction of water vapor at the water surface
x_1 = mole fraction of water vapor at entrance to evaporation area
x_2 = mole fraction of water vapor at exit from evaporation area

LITERATURE CITED

1. Rideal, E. K., *J. Phys. Chem.*, **29**, 1585 (1925).
2. Langmuir, I., and V. J. Schaefer, *J. Franklin Inst.*, **235**, 119 (1943).
3. La Mer, V. K., ed., "Retardation of Evaporation by Monolayers: Transport Processes," Academic Press, New York (1962).
4. ———, T. W. Healy, and L. A. G. Aylmore, *J. Colloid Sci.*, **19**, 673 (1964).
5. Jarvis, N. L., C. O. Timmons, and W. A. Zisman, in "Retardation of Evaporation by Monolayers: Transport Properties," V. K. La Mer, ed., pp. 41-58, Academic Press, New York (1962).
6. Jarvis, N. L., and R. E. Kagarise, *J. Colloid Sci.*, **17**, 501 (1962).
7. Jarvis, N. L., *ibid.*, **17**, 512 (1962).
8. Ewing, G., and E. D. McAllister, *Science*, **131**, 1374 (1960).
9. Berg, J. C., M. Boudart, and A. Acrivos, *J. Fluid. Mech.*, **24**, 721 (1966).
10. Nagakawa, Y., *Proc. Roy. Soc.*, **A249**, 138 (1959).
11. MacRitchie, F., *Nature*, **218**, 669 (1968).
12. ———, *Science*, **163**, 929 (1969).
13. Sebba, F., and H. W. A. Briscoe, *J. Chem. Soc. London*, **106** (1940,I).
14. Walker, D., *Rev. Sci. Instr.*, **34**, 1006 (1963).
15. Navon, Uri, and J. B. Fenn, *AIChE J.*, see this issue.
16. Barnes, G. T., and V. K. La Mer, in "Retardation of Evaporation by Monolayers: Transport Properties," V. K. La Mer, ed., p. 9, Academic Press, New York (1962).
17. Fromm, J. E., *Phys. Fluids*, **8**, 1757 (1965).
18. Claussen, W. F., *Science*, **156**, 1226 (1967).

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