Experiments on the Stability of Surfactant Solution Pools Heated From Below

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It is well known that the presence of even trace amounts of surface active material can have profound effects on the behavior of many multiphase fluid systems and that accurate knowledge of the hydrodynamic effects of surface forces in such systems is vital if their overall behavior is to be anticipated. Theoretical models describing the hydrodynamics of interfaces have been formulated by Scriven (1960), Levich (1962), and others, but thorough experimental corroboration of them has been limited because many systems in which surface phenomena are important are too complex to permit both an explicit theoretical analysis and a straightforward quantitative experimental investigation. To examine the equations of interfacial hydrodynamics, it is desirable to employ an experimental system for which the descriptive equations can be solved despite the inclusion of all pertinent surface properties, as well as one whose behavior is very sensitive to changes in these properties. The hydrodynamic stability of a shallow, dilute, surfactant solution pool heated from below is well suited to this purpose. The system has been analyzed theoretically (Palmer and Berg, 1972) without the introduction of assumptions which might severely restrict its applicability as an investigative tool, and the results of the analysis indicate that the stability limit is extremely sensitive not only to the amount of surface active material present and to the magnitude of its effect on surface tension but also to the rate and mechanism of the solute's lateral transport. Finally, the system has proven amenable to experimental examination. Using an adaptation of the Schmidt-Milverton technique, Palmer and Berg (1971) have measured stability limits in shallow pools of pure liquids heated from below and thus provided an experimental corroboration of Nield's (1964) linear stability analysis which takes surface tension forces into account. In this paper, this experimental technique is used to measure stability limits for shallow pools of certain surfactant solutions heated from below, and the results are interpreted in terms of theoretical predictions.

EXPERIMENT

The experimental method, as described earlier (Palmer and Berg, 1971), employs a liquid pool and thin air gap confined between a pair of horizontal metal plates. The liquid pool is heated from below and cooled from above yielding a sequence of steady temperature drops across the layer. When the heat flux across the liquid pool is plotted against the temperature drop through the liquid, a straight line of slope k/d is obtained for the quiescent regime, but when the stability of the pool collapses, heat is transferred by convection as well as conduction, yielding a rather sharp increase in slope which identifies the stability limit.

In the present investigation, experiments are performed on dilute solutions of *n*-butanol in a glycerol-water (82.5 wt. % glycerol) solvent and *n*-octanol in ethylene glycol. The solutes are mildly surface active in these systems ($-\partial\sigma/\partial c < 10^5$ dynes-cm^2/mole), and their rate of adsorption is expected to be large compared with the rate of bulk diffusion to and from the interface. The solvents were chosen for their high surface tension and viscosity, the former permitting greater flexibility in the choice of surface-active solutes and the latter ensuring that the solution pools have large enough stability limits to make precise measurements of the critical temperature gradients possible. Stability limits were measured for pool depths ranging from 3.78 to 8.51 mm and solute concentrations ranging from 0.0222 to 0.126 mol/liter. In each experiment all materials were meticulously purified to guard against spurious contamination. The organic compounds were doubly distilled under vacuum using a 30-stage spinning band column, and the water was triply distilled.

To interpret the experimental results, the various physical properties of the systems must be accurately determined. The bulk fluid properties of the glycerol-water mixture and of ethylene glycol were obtained from the literature (compare Palmer, 1971), but surface tension data were measured (by the drop-weight method) in the authors' laboratory, and solute diffusivities were estimated by the Wilke-Chang correlation.

RESULTS AND DISCUSSION

The conditions of each experiment and the experimental results are summarized in Table 1. The stability criteria for the liquid pools are presented in terms of the critical Marangoni number Ma_c and the critical Rayleigh number R_c. All results were interpreted under the assumption that solute adsorption and desorption rates at the surface were much more rapid than its rate of bulk diffusion to the surface. For such systems the theory of Palmer and Berg (1972) predicts that the stability criterion, in terms of Ma and R, depends only upon the elasticity number N_{EL} and the Biot number Bi. The values of these dimensionless groups together with the theoretically predicted values of Ma^* and R^* are also given in Table 1 for each experi-

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TABLE 1. STABILITY RESULTS

Experiment no.	Solvent	Solute	Solute conc., mole/liter	Liquid depth, mm	N_{EL}	Bi	Ma^*	R^*	ΔT_L (°C)	Ma_c	R_c
1	Glycerol	Water	11.80	5.18	0.014	0.28	90	705	2.2	200	400
2	Glycerol	Water	11.80	5.18	0.014	0.29	90	705	2.2	210	410
3	Glycerol-water	Butanol	0.0270	8.51	110	0.44	4,380	1,330	2.5	270	1,400
4	Glycol	None	0.000	3.78	0.000	0.25	91	707	1.0	210	270
5	Glycol	None	0.000	3.94	0.000	0.30	93	717	1.0	240	320
6	Glycol	Octanol	0.0222	5.46	48	0.30	1,860	1,300	1.7	530	1,400
7	Glycol	Octanol	0.0509	4.34	96	0.25	3,550	1,320	2.0	560	930
8	Glycol	Octanol	0.0733	5.11	120	0.32	4,700	1,330	1.7	540	1,200
9	Glycol	Octanol	0.126	5.99	170	0.35	6,540	1,330	1.0	300	990

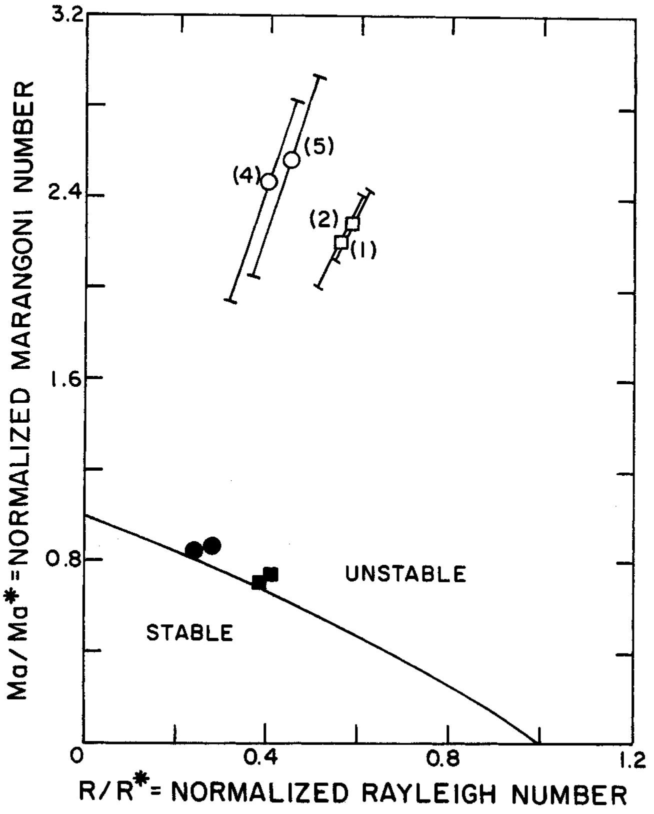

Fig. 1. Stability diagram together with the experimental stability data for pools of pure ethylene glycol (○) and the mixture glycerol—water (□). The solid lines represent the theoretical predictions.

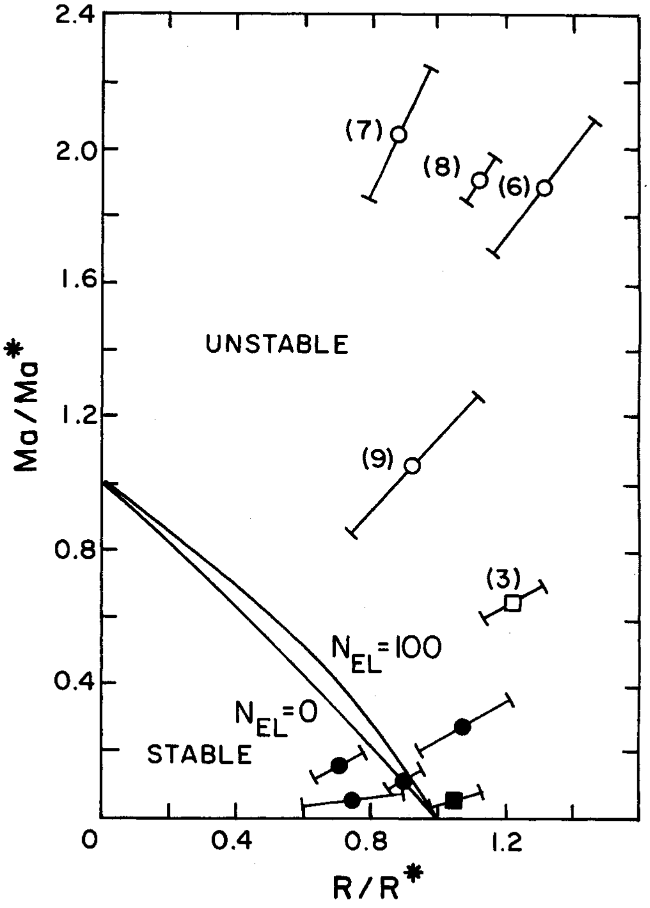

Fig. 2. Stability diagram together with the experimental stability data for pools of *n*-octanol in ethylene glycol (○) and *n*-butanol in glycerol—water (□). The solid lines represent the theoretical stability predictions.

ment. Ma^* is the expected stationary critical Marangoni number in the absence of buoyancy forces and R^* is the expected critical Rayleigh number in the absence of destabilizing surface tension forces. The values of Ma^* and R^* varied from one experiment to the next because of their dependence on N_{EL} and Bi.

The experimental results are best compared with the theoretical predictions by plotting a normalized critical Marangoni number Ma_c/Ma^* versus a normalized Rayleigh number R_c/R^* as in Figures 1 and 2. The theoretical predictions are represented by the solid curves in these figures. Curves for various values of the Biot number are not presented since, for the range of Bi considered in the experiments, the theoretical curve of Ma_c/Ma^* versus R_c/R^* remains virtually unchanged.

In all, ten experiments were conducted, five with the solvents alone and five with the surfactant solutions. The results for the solvents alone, shown in Figure 1, were first normalized with the values of Ma^* and R^* expected if the solvents had been completely pure. In such a case, for the ethylene glycol $N_{EL} = 0$ and for the glycerol-water mixture $N_{EL} = 0.014$. (Water is the solute in this mixture.) These results are shown as open points in the figure, and it is seen that pool stability was significantly in excess of prediction, suggesting that the liquids were not entirely free of surface contamination despite their high degree of purification. Such behavior for these pure solvents was not unexpected. The problem of obtaining a clean water surface has long been recognized (Hickman, 1952), and the present results indicate the equal difficulty of purifying other high surface tension liquids to yield clean surfaces.

The back-calculated value of the apparent elasticity number required to bring the stability data for the solvents into line with theory is approximately 5 in all cases. For contaminant equivalent in surface activity to either *n*-butanol in glycerol-water or *n*-octanol in ethylene glycol, an N_{EL} of 5 corresponds to a concentration of well under 100 ppm. The solid points on Figure 1 represent these data correlated using $N_{EL} = 5$.

The inability to obtain an absolutely clean solvent surface should not prevent the achievement of quantitative agreement between experiment and theory for systems with relatively larger amounts of measured surfactant addition. Indeed such agreement was obtained for both the solution of *n*-butanol in the glycerol-water solvent and for the solution of *n*-octanol in ethylene glycol. The results are presented in Figure 2 in two ways. First the stability results, in the form of critical Marangoni and Rayleigh numbers, were normalized by the values of Ma^* and R^* expected if the liquid pools had been the purified solvents alone, that is, the elasticity number was set equal to 5. These normalized stability limits are shown as open points on the graph, and it is seen that these pools were much more stable than would be expected if the solutes had not been added to the fluids. Secondly, each stability limit was properly normalized with theoretically predicted Ma^* and R^* based on the elasticity number calculated from the known concentration of solute in the solution, that is, using the values of N_{EL} in Table 1. These results are shown on Figure 2 as solid points, and it is seen that the use of the elasticity number calculated from the actual solute concentration, shows the data to be in reasonable qualitative agreement with the theory of Palmer and Berg.

The precision with which Ma_c and R_c could be determined depended in each case upon the distinctness of the break in the plot of heat flux versus ΔT_L. Error analysis indicated that while individual temperature differences were accurate to within $\pm$ 0.02°C, the derived critical values of ΔT_L could be determined only to within $\pm$ 0.10°C. Precise knowledge of Ma^* and R^* was also imperative in the presentation of results and depended upon accurate determination of the elasticity number. The chief source of uncertainty in its independent evaluation is the estimated solute diffusivity, which might be in error by as much as 20%. Due to such an error, Ma^* could be confidently determined to within only $\pm$ 15% while R^* was determined to within $\pm$ 1%. The relatively high accuracy in R^* was obtainable because, for the degree of contamination studied here, the upper surface was rendered hydrodynamically fixed with R^* at its upper limit. Under these conditions, any change in N_{EL} has little effect on R^*. The total extent of uncertainty in the reported results, that is, the uncertainty in both the measured critical ΔT_L and in the calculated normalizing parameters Ma^* and R^*, is shown graphically using error flags in Figures 1 and 2.

Comparison of the experimental results with theory must be made with caution. The test of the theory rests on data presented in Figure 2, data for which, unfortunately, buoyancy effects play a major role, as can be noted by the large values of R/R^*. The stabilizing effect of the solute represented by N_{EL} in the theory has a relatively weak influence on R^* compared with its enormous effect on Ma^*. It would thus have been desirable to perform experiments for which Ma/Ma^* was large, that is, nearer the upper left corner of Figure 2. Unfortunately, on the solutes used this would have required pool depths smaller than could be accommodated by the experimental method, that is, critical temperature drops would have been too small to be determined with precision.

Despite the precautions noted above, the results presented here for pools of surfactant solution do represent a first step in an attempt to provide an experimental verification of the analysis of Palmer and Berg. In particular they demonstrate the ability of the theory to predict qualitatively the stability of surfactant solution pools in which surface tension forces play a nonnegligible but not large role in inducing convection. Furthermore, the data obtained using multiply distilled solvents indicate the degree of difficulty involved in the purification of any liquid of high surface tension to obtain a hydrodynamically clean surface.

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NOTATION

Bi = hd/k = Biot number
c = molar concentration of solute in solution
d = depth of liquid pool
$\mathcal{D}$ = molecular diffusivity of solute in liquid
g = gravitational acceleration
h = heat transfer coefficient of vapor near the interface
k = thermal conductivity of liquid
k_1 = rate constant for adsorption of solute into the surface
Ma = $(\partial\sigma/\partial T)\Delta T_L d/\mu\kappa$ = Marangoni number
N_{AD} = $\mathcal{D}/k_1 d$ = adsorption number
N_{EL} = $(\partial\sigma/\partial c)^2\, c/R_G T\mu\mathcal{D}$ = elasticity number
R = $\alpha g d^3 \Delta T_L/\kappa\nu$ = Rayleigh number
R_G = gas constant
T = absolute temperature of the surface
ΔT_L = critical temperature drop across the liquid pool below which the pool remained stagnant

Greek Letters

α = thermal expansivity
$(\partial\sigma/\partial c)$ = concentration coefficient of surface tension
$(\partial\sigma/\partial T)$ = temperature coefficient of surface tension
κ = thermal diffusivity
μ = dynamic viscosity
ν = kinematic viscosity
σ = surface tension

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