LBL-30935
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EARTH SCIENCES DIVISION

Presented at the Sixth IFP Exploration and Production Research Conference, Saint-Raphael, France, September 4–6, 1991, and published in Proceedings, H. Toulhoat and J. Necourtier, Eds. (Edition Technenip, Paris, 1992)

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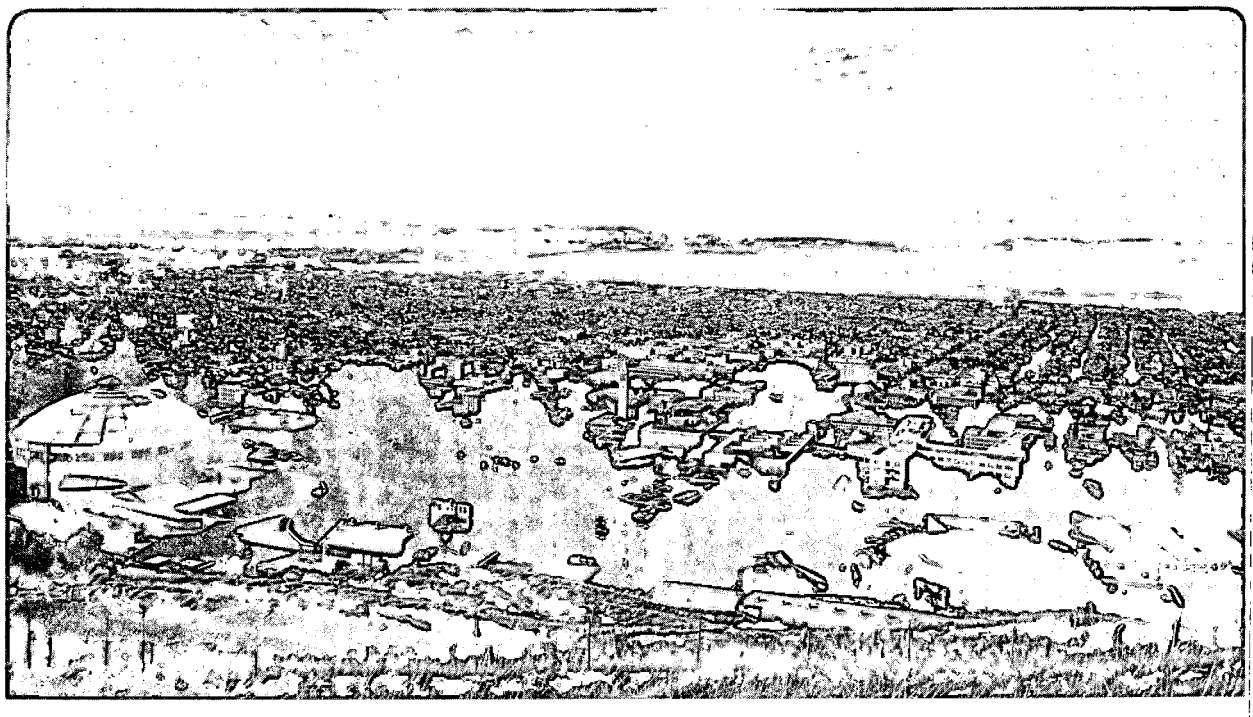

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Prepared for the U.S. Department of Energy under Contract Number DE-AC03-76SF00098

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V. Bergeron and C. J. Radke

Department of Chemical Engineering
University of California

and

Earth Sciences Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

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This work was supported by the Assistant Secretary for Fossil Energy, Office of Oil, Gas and Shale Technologies, under U.S. Department of Energy Contract No. DE-AC03-76SF00098.

Thin-Film Forces in Pseudoemulsion Films

Vance Bergeron and C.J. Radke

Chemical Engineering Department and Earth Science Division,
Lawrence Berkeley Laboratory
University of California, Berkeley, Ca. 94720

INTRODUCTION

Use of foam for enhanced oil recovery (EOR) has shown recent success in steam-flooding field applications (1-3). Foam can also provide an effective barrier against gas coning in thin oil zones (4). Both of these applications stem from the unique mobility-control properties a stable foam possesses when it exists in porous media. Unfortunately, oil has a major destabilizing effect on foam (5-9). Therefore, it is important for EOR applications to understand how oil destroys foam.

Recent work on oil destabilization mechanisms has focused on spreading and entering coefficients (7-10). These ideas are descendants of the work done by Ross (11) and Robinson and Woods (12) on mechanisms for the rupture of liquid films by antifoaming agents. For oil at a gas-water interface the spreading and entering coefficients are defined from the thermodynamic conditions for the minimization of the surface free energy (13) :

Spreading Coefficient :

$$S_{ow} = \sigma_{wg} - \sigma_{ow} - \sigma_{og},$$

Entering Coefficient :

$$E_{ow} = \sigma_{wg} + \sigma_{ow} - \sigma_{og},$$

where σ_{ij} corresponds to the surface or interfacial tension and the subscripts o,w, and g signify oil, water, and gas respectively. These relationships indicate that for a positive S_{ow} oil spreads on a gas-water interface, while a positive E_{ow} corresponds to oil penetrating the gas-water interface from the aqueous side. As pointed out by Ross (14) the entering and spreading coefficients are related in the following way, $-E_{ow} = S_{wo}$. That is, a non-entering oil is thermodynamically equivalent to, water spreading on the gas-oil interface.

To date a definitive correlation between oil spreading and foam stability in porous media has not emerged. There is, however, evidence for oil tolerant foams in systems which have negative entering coefficients (8,10,12). Clearly foam destruction by oil requires the penetration of oil into the gas water interface as a first step (5,15). Manlowe and Radke (6) have demonstrated this by observing pore-level events of foam flowing in the presence of oil. Their conclusion was that foam stability in contact with oil in a porous-medium micromodel is controlled by the stability of the aqueous films separating oil and gas. These three-phase (oil/water/gas) surfactant-laden films are called "pseudoemulsion" or "asymmetrical" films (5,16).

Previously, Kruglyakov (16) showed that the stability of bulk foams exposed to organic fluids also relies on the longevity of these asymmetrical films. Moreover, Kruglyakov maintains that water

spreading on oil (ie. $S_{wo} = -E_{ow} > 0$) is a necessary but not sufficient condition for asymmetrical film stability. This assertion is consistent with the oil tolerance demonstrated by negative entering coefficient systems. These studies all indicate that stabilization of the pseudoemulsion film is critical to maintain foam stability in the presence of oil. Hence, to aid in design of surfactant formulations for foam insensitivity to oil we pursue direct measurement of the thin-film or disjoining forces (17) that stabilize pseudoemulsion films.

EXPERIMENTAL INVESTIGATION

Film thickness measurements and dynamic thinning observations of microscopic pseudoemulsion films were made with the apparatus pictured in Fig. 1. A specially equipped reflected-light microscope permits film thickness measurements according to the thin-film interference technique developed by Scheludko (18), with appropriate modifications to the optical equations. To provide independent verification of the thickness two different wavelengths (i.e. 546 nm and 665 nm) are monitored simultaneously with two photomultiplier tubes (PMT).

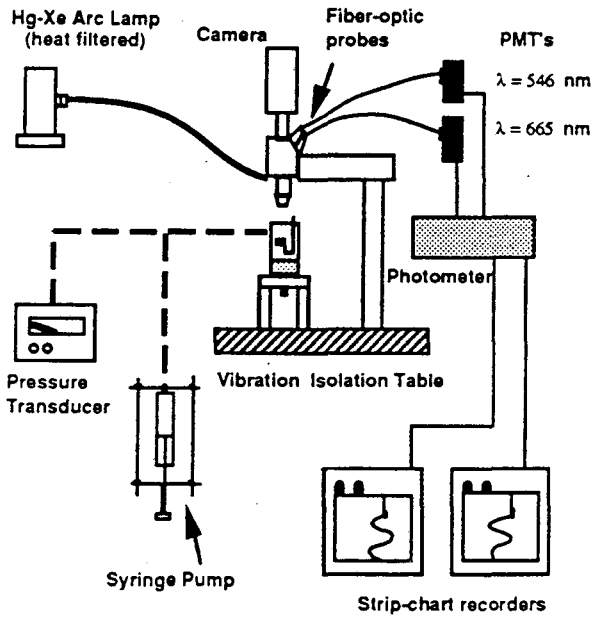

Fig. 1. Experimental apparatus.

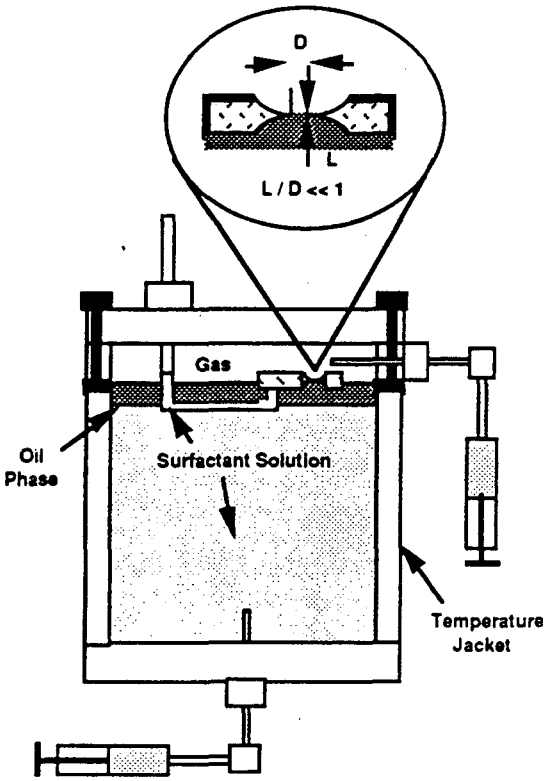

FIG. 2. Expanded view of the pseudoemulsion-film cell.

The experimental cell used is depicted in more detail in Fig. 2. It is a variant on the porous plate method of Mysels (19) and others (20,21,22). The film holder, made from a porous glass frit, is machined so that the hole diameter is much larger than the hole depth (see the inset in Fig. 2). This particular hole geometry allows us to acheive extremely low capillary pressures without gravity deformation of the film. The capillary pressure, $P_C = P_G - P_L$, which equals the disjoining pressure at equilibrium, is measured directly with a sensitive pressure transducer. Experimental details are available elsewhere (23).

PRELIMINARY RESULTS

Thinning Measurements

A typical photocurrent versus time interferogram for a pseudoemulsion film, stabilized with surfac-

tant at concentrations above the critical micelle concentration (CMC), is presented in Fig. 3. Since photocurrent is an indirect measure of the thickness, this curve represents the thinning behavior of the film. The pronounced horizontal portions of the interferogram clearly show that pseudoemulsion films undergo the same step-wise layer thinning previously observed in foam and emulsion films containing surfactant above the CMC (5,24,25). Although the interferogram shows only two distinct transitions, simultaneous video observations from the camera attached to the microscope confirm that two layers passed the optical probe after 2.5 minutes of thinning. Therefore the transition from 51.9 nm to 26.3 nm actually corresponds to two layer transitions and we find a total of three transitions for this system. It can also be noted that the photocurrent for a pseudoemulsion film rises as the film thins instead of declining as in symmetrical films (foam or emulsion). This simply arises from the differences in optical phase changes that take place upon reflection at the interfaces. Consequently pseudoemulsion films below 50 nm appear white while symmetrical films of comparable thickness appear black.

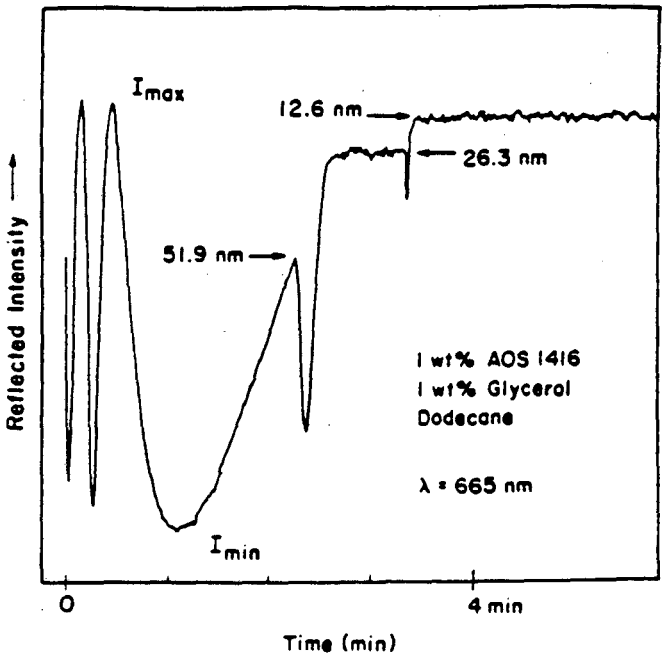

FIG. 3. Typical interferogram of pseudoemulsion film thinning at surfactant concentrations above CMC.

Table 1 demonstrates the effect increased surfactant concentration has on the time required for pseudoemulsion films, made from dodecane and solutions of an alpha olefin sulfonate of chain length 14 to 16 (Enordet AOS 1416 form Shell), to reach their metastable equilibrium thicknesses. For an imposed capillary pressure of approximately 50 Pa, both the number of stratified layers and the thinning time increase with added surfactant. Note however that the bulk viscosity changes very little. This suggests that increased surfactant concentration increases the disjoining forces within the film.

Table 1
Pseudoemulsion film thinning times *,†

Surfactant (wt %)	Viscosity (mPa• s)	# Layers	Thinning Time (s)
0.05	0.98	1	39
0.5	1.01	2	38
1.0	---	3	131
1.0 + 1.0 wt% glycerol	1.08	3	210
5.0	1.33	6	305

* surfactant : AOS 1416; organic phase : dodecane
† for an applied Pc ~ 50 Pa

Disjoining Pressure Measurements

At surfactant concentrations above the CMC we find that pseudoemulsion films exhibit stratified layering phenomena. The disjoining pressure measurements on these stratifing systems reveal an equilibrium oscillatory component which is reproducible in both the expansion and thinning directions (23). The layers observed likely originate from surfactant structuring within the film. The magnitudes of the structural forces are low (< 100 Pa.) but the length scale of the oscillations is large (> 10 nm) and rather far reaching (~ 50 nm) in the present case.

Of the surfactants studied, the most interesting observations centered around the behavior demonstrated by a fluorocarbon surfactant, a perfluoroalkyl betaine from Dupont, Zonyl™ FSK. Pseudoemulsion films made from dodecane and Zonyl FSK solutions were significantly more stable than hydrocarbon surfactants at similar concentrations. This stability derives from the highly repulsive (i.e. positive) character of the disjoining pressure isotherm for this system.

Another distinctive characteristic of the Zonyl FSK solutions is that they exhibit negative entering coefficients. Recall that negative entering coefficients correspond to stable wetting films of water on oil. From this we argue that a negative entering coefficient reflects a purely repulsive pseudoemulsion film disjoining pressure. This therefore explains the observed pseudoemulsion film stability for negative entering systems. For systems with a positive entering coefficient, pseudoemulsion film disjoining forces can still prevent oil from entering depending on the level of the capillary pressure imposed on the film.

Measurements of the disjoining pressure and thinning observations indicate that pseudoemulsion films are in general, significantly less stable than foam films formed from the same surfactant solution. This indicates that, when exposed to the same capillary pressure the asymmetric pseudoemulsion film is much more likely to rupture. If however the pseudoemulsion film disjoining forces are large, as demonstrated by certain fluorosurfactant systems, then the rate of foam destruction due to oil interactions will diminish. This hypothesis finds support in some instances (8,10).

SUMMARY

Because of its unique mobility control properties foam has application for enhanced oil recovery. These applications require foam to be stable in the presence of oil. This stability depends on the stability of the pseudoemulsion films developed. We are investigating the stability of pseudoemulsion films by studying their thinning characteristics and by directly measuring disjoining pressure isotherms.

Our measurements show that when surfactant is present above the CMC pseudoemulsion films undergo the same stepwise layer thinning observed in foam and emulsion films. Furthermore, increasing the surfactant concentration generates more layers and significantly slows the thinning of the film, without a substantial effect on bulk viscosity. The decrease in thinning rate arises from increased disjoining forces in the pseudoemulsion films.

Disjoining pressure measurements on systems stabilized above the CMC reveal an equilibrium oscillatory structural component. Moreover, we find that capillary pressures required to rupture pseudoemulsion films are much lower than the rupture pressures for foam films. This finding is in agreement with the deleterious effect oil has on foam stability in porous medium.

Finally, we note the correspondence between entering coefficients and thin film forces. Negative entering coefficient systems predict highly stable pseudoemulsion films and hence oil tolerant foams. However, disjoining forces can also provide protection against pseudoemulsion film rupture in positive entering coefficient systems. The conclusion we draw is that surfactant design criteria for foam insensitivity to oil should focus on stabilizing pseudoemulsion films.

Acknowledgement

This work was supported by the United States Department of Energy under Grant DE AC03-76SF00098 to Lawrence Berkeley Laboratories of the University of California. Thanks also to Jan Erik Hanssen for his help in the preparation of this manuscript.

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LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
TECHNICAL INFORMATION DEPARTMENT
BERKELEY, CALIFORNIA 94720