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Dissipative Structures in Ligand-Accelerated Metal Extraction Systems

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Abstract

Interfacial turbulence created by the addition of a ligand during the extraction of metal ions by an organic extractant can considerably enhance the speed of extraction. In the extraction of nickel with di-2-ethylhexyl phosphoric acid, interfacial turbulence in the oil phase was observed at the oil–water interface, accompanied by spontaneous emulsification, in the presence of acetate ligand. The dissipative structures were studied by Schlieren photography and found to consist of two distinct patterns of roll cells in addition to rapid twitching and fluctuation of the interface. 1) Small roll cells originating at the interface, moving rapidly along the interface and dissipating at the interface. 2) Large roll cells originating in the bulk aqueous phase, traveling toward the interface while gaining momentum, bouncing back from the interface, and dissipating as they receded. Both flow patterns were confined to the oil phase, the aqueous phase being virtually quiescent. The turbulence lasted for a minute, and rapid extraction of Ni ions was observed during this time period. The turbulence was completely damped out when surfactants were added to the system, and no turbulence was observed in the absence of ligand. The observations were interpreted in terms of interfacial instability theories. They are important for liquid membrane technologies because they suggest that systems with high extraction efficiencies can be engineered, even when the dispersed phase lifetimes are short.

INTRODUCTION

Metal extraction from wastewater effluents, using liquid membrane technology with a variety of extracting solvents, has been extensively studied (*1–9*). High extraction efficiencies are achieved by the large increase in

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interfacial area obtained by dispersing the extracting phase in effluent streams. The dispersed phase is usually an emulsion of the stripping phase encapsulated in the extractant and stabilized by surfactants (see Fig. 1). The encapsulated phase area is usually extremely large compared to the interfacial area of the extracting phase due to the difference in drop sizes of the encapsulated and dispersed phases. The extraction efficiency is therefore controlled by the rate at which metal ions are removed from the outer aqueous phase to the dispersed extracting phase. Increased external phase mass transfer rates have been obtained by the addition of ligands, such as acetate, to the outer aqueous phase through enhanced transport mechanisms (*10*). In this work we show that the ligand causes interfacial turbulence at a range of concentrations that considerably enhances mass transfer rates.

The turbulence patterns are created by interfacial tension gradients that occur during ligand-enhanced transport across the interface. The turbulence prevails for about a minute, during which time the surfaces are constantly renewed, and this results in rapid mass transfer of the metal ions. The presence of surfactants completely destroys the turbulence patterns because the highly interfacially active surfactant molecules rapidly adsorb on the interface and dampen any interfacial tension gradients.

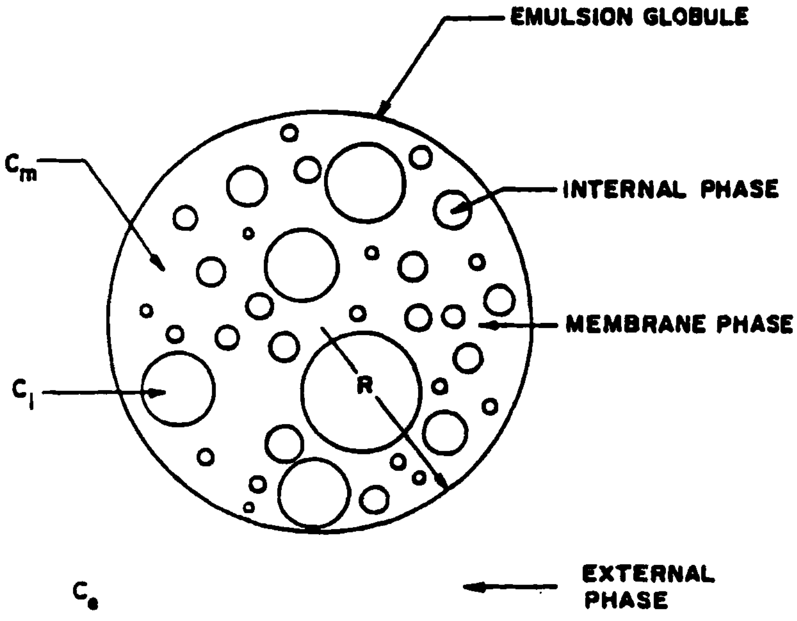


FIG. 1. Model liquid membrane system.

The significance of this work lies in showing unique features of the turbulence patterns that are inexplicable in terms of present interfacial instability theories. The turbulence patterns were studied using Schlieren optics, and the observations were compared to theoretical models of interfacial instability. These data indicate that, within a range of ligand concentrations, complete metal extraction may be rapidly achieved by invoking interfacial turbulence-enhanced mass transfer mechanisms. The extraction process is completed during the short lifetimes of the dispersions (about a minute), which makes the addition of surfactant to stabilize emulsions unnecessary.

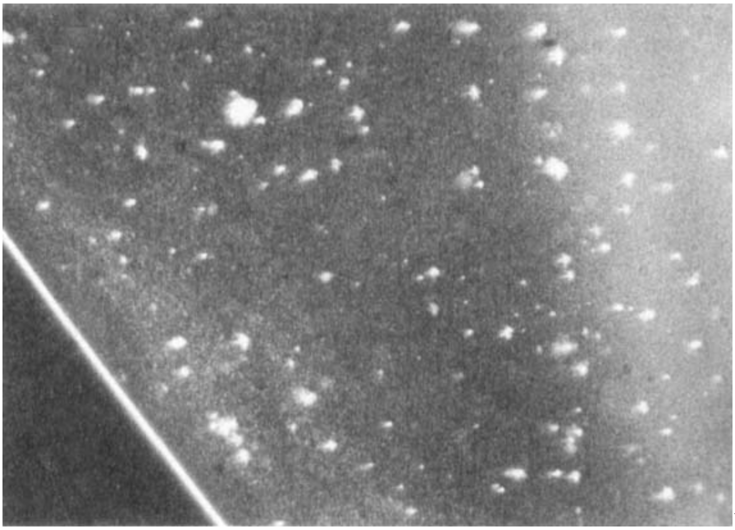
EXPERIMENTAL

Solvent extraction of metal ions from an aqueous solution to a nonpolar organic phase involves three principal steps: 1) adsorption of extractant molecules from the organic phase to the liquid/liquid interface, 2) interfacial chemical reactions between such molecules and the metal ions to form an interfacial species capable of dissolving in the organic phase, and 3) their desorption into the organic phase. Thus the liquid/liquid interface plays an important role in the solvent extraction process. Due to their amphipathic nature, solvent extracting reagents tend to adsorb at the liquid/liquid interface and reduce interfacial tension (γ). The extent of lowering of γ is related to the interfacial activity of the extractant. The particular system used for our study was an oil phase composed of Alkylac (containing 10% petroleum distillates) as solvent (viscosity, 1.23 cP), D2EHPA (di-2-ethylhexyl phosphoric acid) as extractant, and acetate as ligand. The external aqueous phase was a solution of $NiSO_4 \cdot 6H_2O$ containing 1000 ppm Ni ions.

Static interfacial tension measurements were made for various concentrations of D2EHPA both in the presence and absence of acetate (ligand). The interfacial tension decreased to 10.6 from the base value of 34.9 dyn/cm with D2EHPA present, a clear indication of extractant interfacial activity. Acetate, though a weak surfactant, also showed a drop in interfacial tension when added to the aqueous phase. When both acetate and D2EHPA were present, the interfacial tension rose, suggesting depletion of D2EHPA at the interface due to increased rates of complex formation with the nickel ion. The ligand, therefore, serves to increase metal ion concentration at the interface.

The liquid–liquid interface was directly observed by introducing various aqueous phases to the recesses of a microscope and then placing a drop of the organic phase on top. There seemed to be a rapid emergence of structure in the oil phase accompanied by massive interfacial turbulence. Both the structure and turbulence were strongest on contact and dissipated

Low ligand concentration (0.02M Ac^{-})



High ligand concentration (0.1M Ac^{-})

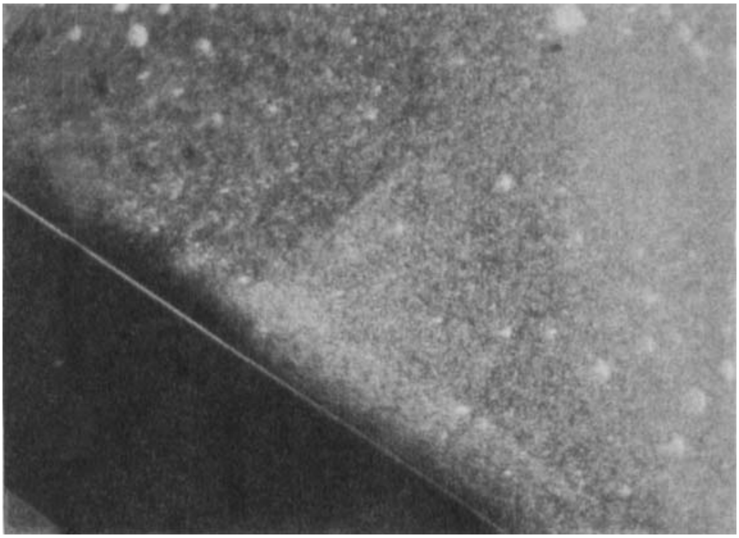


FIG. 2. Turbulence in the presence of low (0.02 M) and high (0.10 M) ligand concentrations.

after a while. The interfacial turbulence was further investigated by Schlieren optics. A drop of oil phase was created on a sintered glass surface immersed in the aqueous phase so that the liquid–liquid interface could be observed from the instant of contact of the two phases. The interface was observed for a period of several minutes from the moment of contact of the two phases, and the observations were recorded with a 16mm movie camera. The frames from the movie are shown in Figs. 2–5. The white dots represent spontaneously emulsified drops of water in the oil phase, and they served as natural tracers in visualizing the turbulence patterns. Figure 2 shows the turbulence patterns in the presence of low and high concentrations of ligand. The turbulence is more intense and of greater duration at the higher ligand concentrations. For ligand concentrations greater than 0.1 *M*, no change in turbulence patterns or intensity could be observed. Figure 3 shows the persistence of spontaneous emulsification even in the absence of metal ions. The accompanying turbulence was less intense and of shorter duration, and it was probably driven by water molecules penetrating the oil phase. Figure 4 shows a quiescent interface in the absence of ligand in the aqueous phase. Clearly, ligand is the important

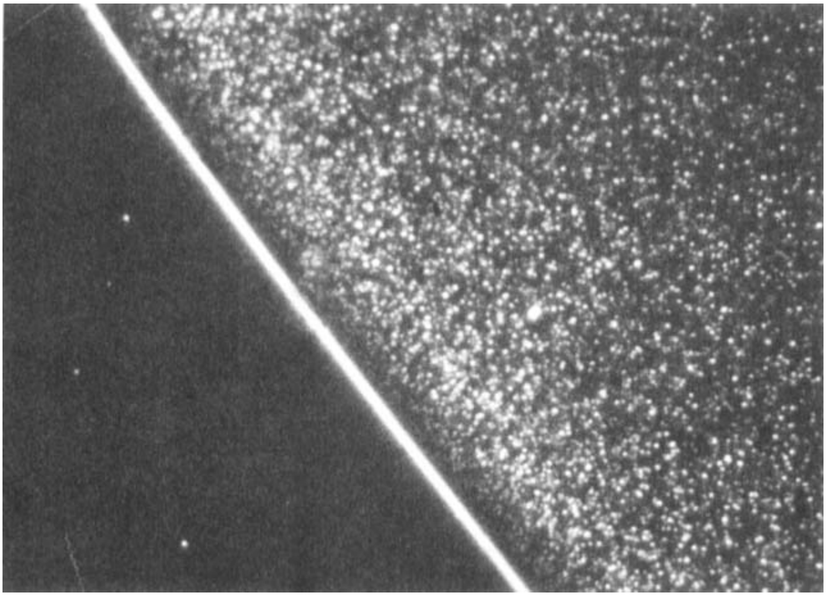


FIG. 3. Persistence of turbulence in the presence of 0.1 *M* ligand even in the absence of metal ions.

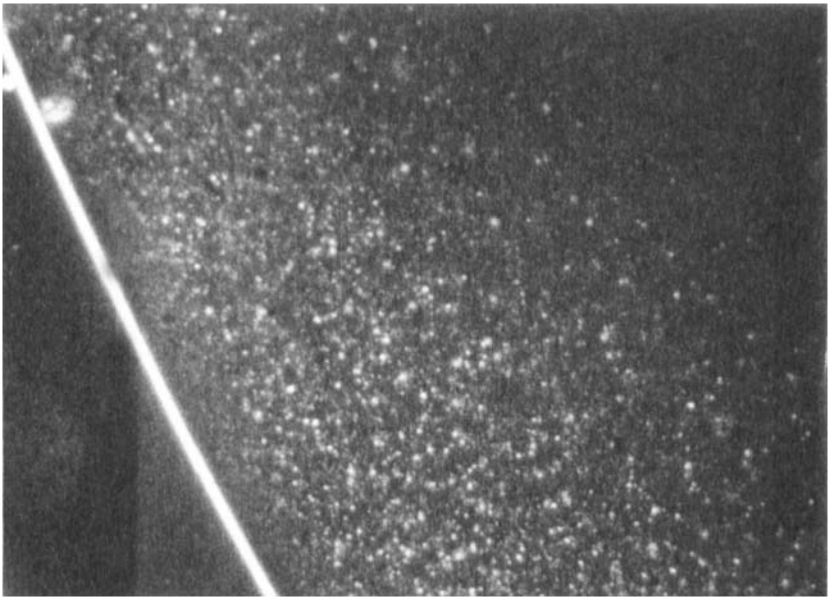


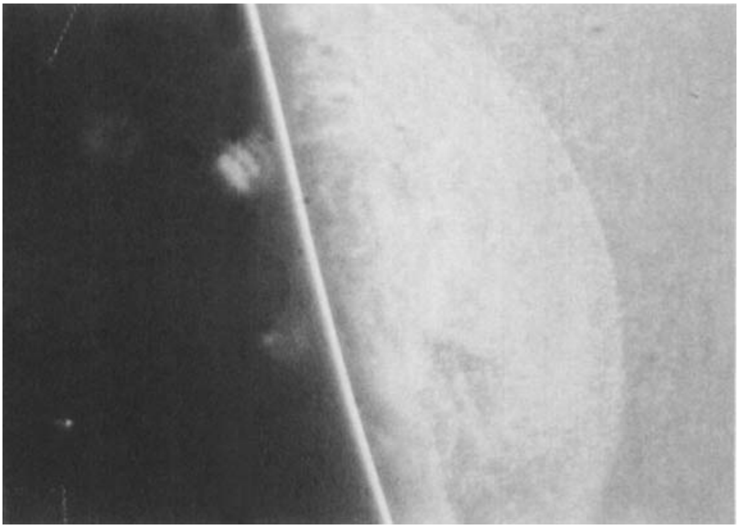
FIG. 4. Quiescent interface in the absence of ligand.

constituent in determining the presence or absence of interfacial instability. Surfactants (Exxon 164), when added to a system that gave a high degree of turbulence without it, completely destroyed the turbulence patterns. Figure 5 shows the turbulent and quiescent interfaces for system with and without surfactant.

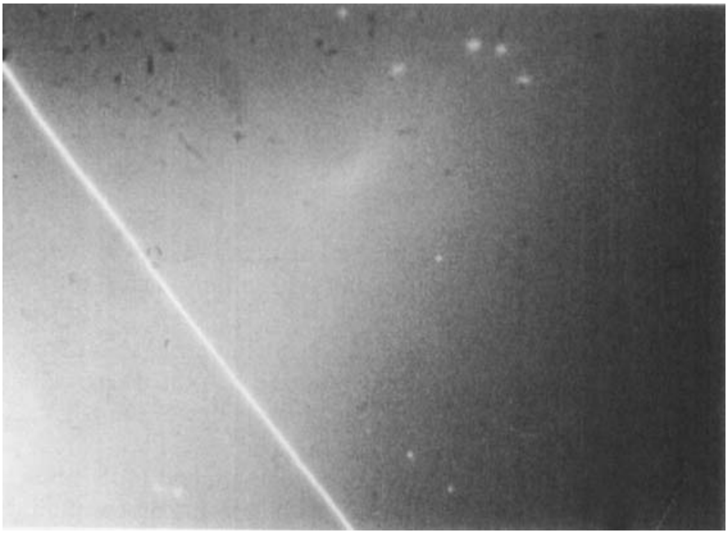
The turbulence and spontaneous emulsification were greatest for systems containing both ligand and extractant. The turbulence, characteristics of which are shown schematically in Fig. 6, occurred exclusively in the oil phase accompanied by spontaneous emulsification. The discernible features of the instability included the following.

(a) Spontaneous emulsification of water into the oil phase. The emulsions were generated continuously from the moment of contact for a period of 1 min and had an average drop size of 1 μm. Figure 7 shows the spontaneously generated emulsions. The emulsions were stable for a period of several minutes during the interfacial instability and eventually disappeared after all the action had subsided. The emulsions served as natural markers in outlining the turbulent stream lines.

(b) Rapid twitching and fluctuation of the interface. Figure 8 is a photograph showing this phenomena. No roll cells were seen while the interface



System without surfactant



System containing 0.1M surfactant (Exxon 164)

FIG. 5. Turbulence in identical systems in the presence and absence of surfactants.

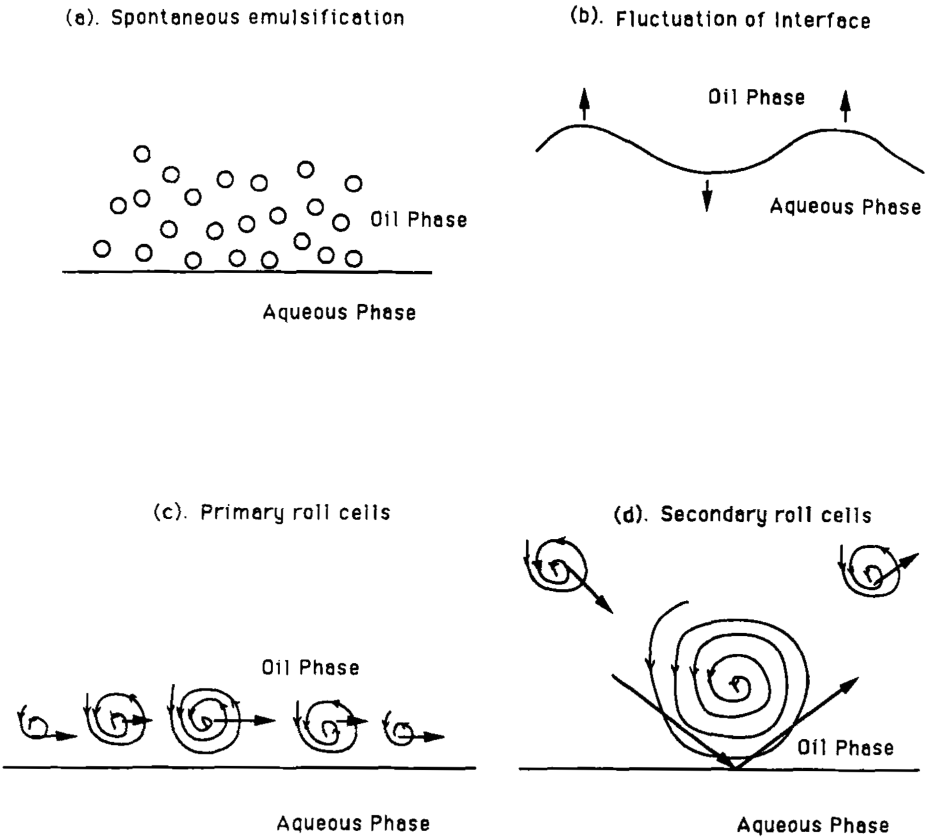


FIG. 6. Schematic diagram of turbulence characteristics.

was fluctuating, suggesting that this is a distinct mode of instability. While it lasted, the fluctuations were regular with a periodicity of 0.2 s and an amplitude of 10 μm.

(c) Primary roll cells. These roll cells, shown in Fig. 9, originated at the interface, gained in intensity as they moved along the interface, and eventually dissipated at the interface. The average size of the roll cells was of the order of 100 μm.

(d) Secondary roll cells. These roll cells originated in the bulk aqueous phase and moved toward the interface while gaining momentum, bounced away from the interface, and dissipated as it receded to the bulk phase. The roll cells were larger in size (of the order of 1000 μm) and were less frequent than the interfacial roll cells. They are shown in Fig. 10.

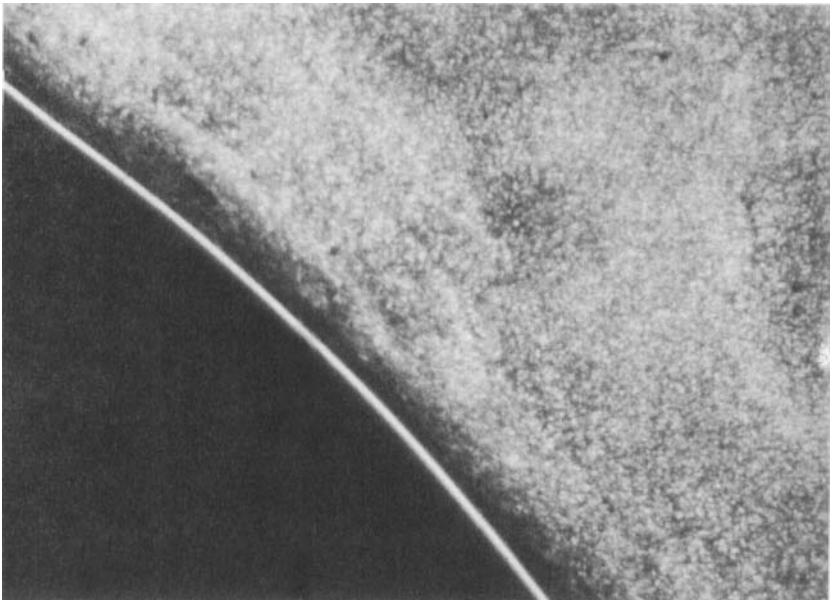


FIG. 7. Photograph of spontaneously generated emulsions during interfacial instability.

The primary roll cells at the interface arise from self-amplification of fluctuations created by interfacial tension gradients (Marangoni instability). The secondary roll cells that emerge are caused by rapid depletion of the chemical species close to the interface and the consequent density differences between the interfacial region and bulk phase (Raleigh instability). The mechanisms for the incipience of the interfacial instabilities are examined below.

Dissipative Structures: Thermodynamic Considerations

Following Prigogine's approach, a liquid–liquid interface will be unstable when the excess entropy production term is negative (*11*). Based on this consideration, it can be shown that the basic thermodynamic conditions for the instability of a liquid–liquid interface are

$$\epsilon = \frac{1}{A}\frac{\partial \sigma}{\partial A} < 0 \qquad \text{(interfacial elasticity induced instability)}$$

$$\sigma < 0 \qquad \text{(low interfacial tension instabilities)}$$

where ϵ is the interfacial elasticity, σ is the interfacial tension, and A is the interfacial area.

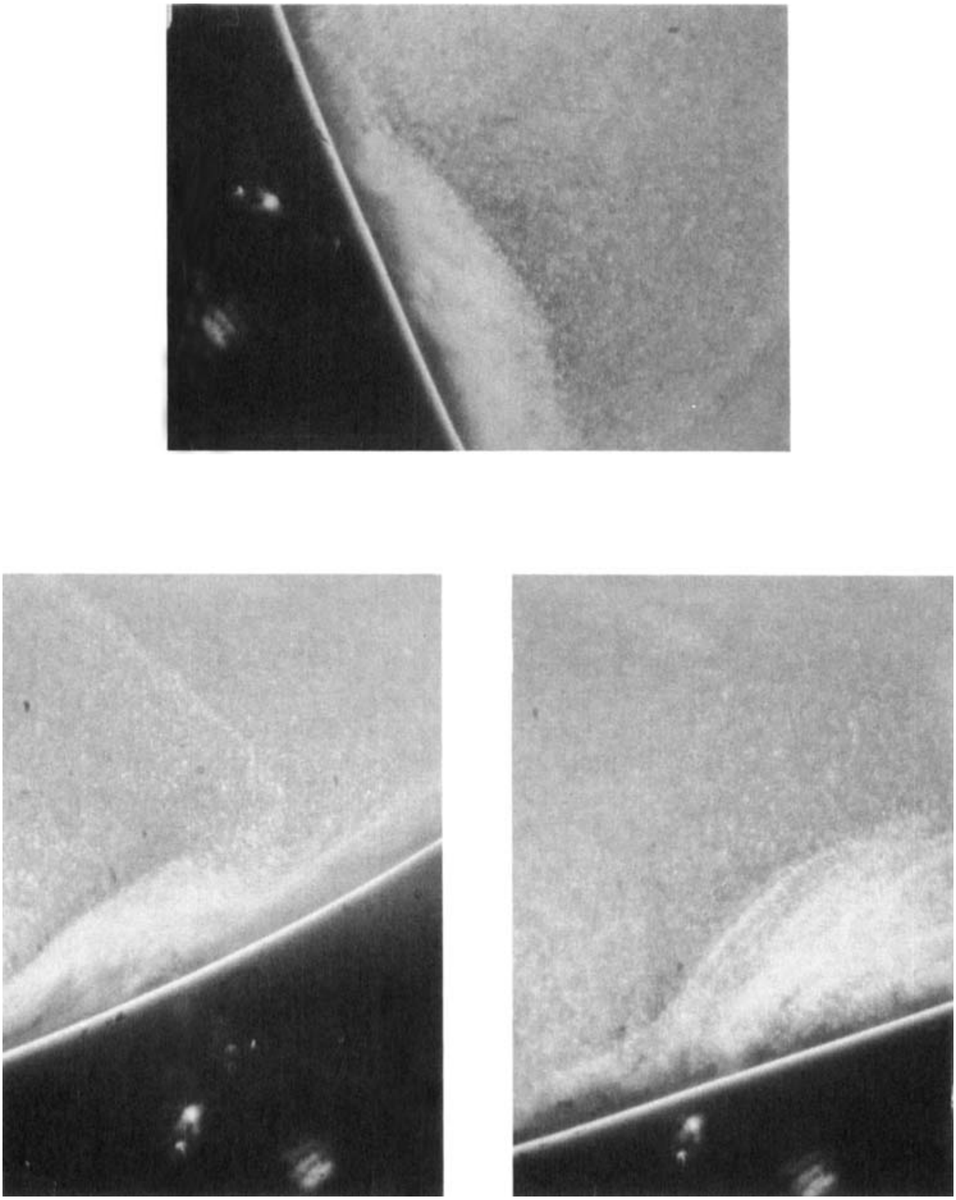


FIG. 8. Selection of photographs showing twitching and fluctuation of the interface.

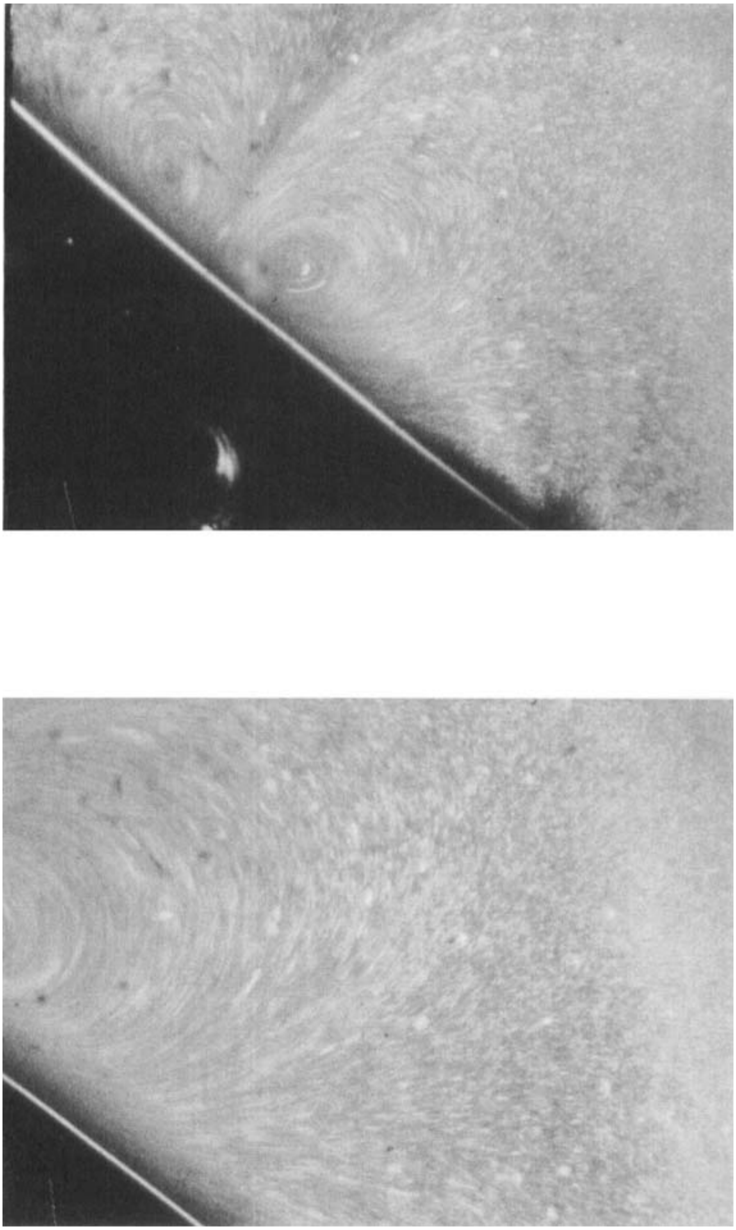


FIG. 9. Primary roll cells that emerge, traverse, and dissipate at the interface.

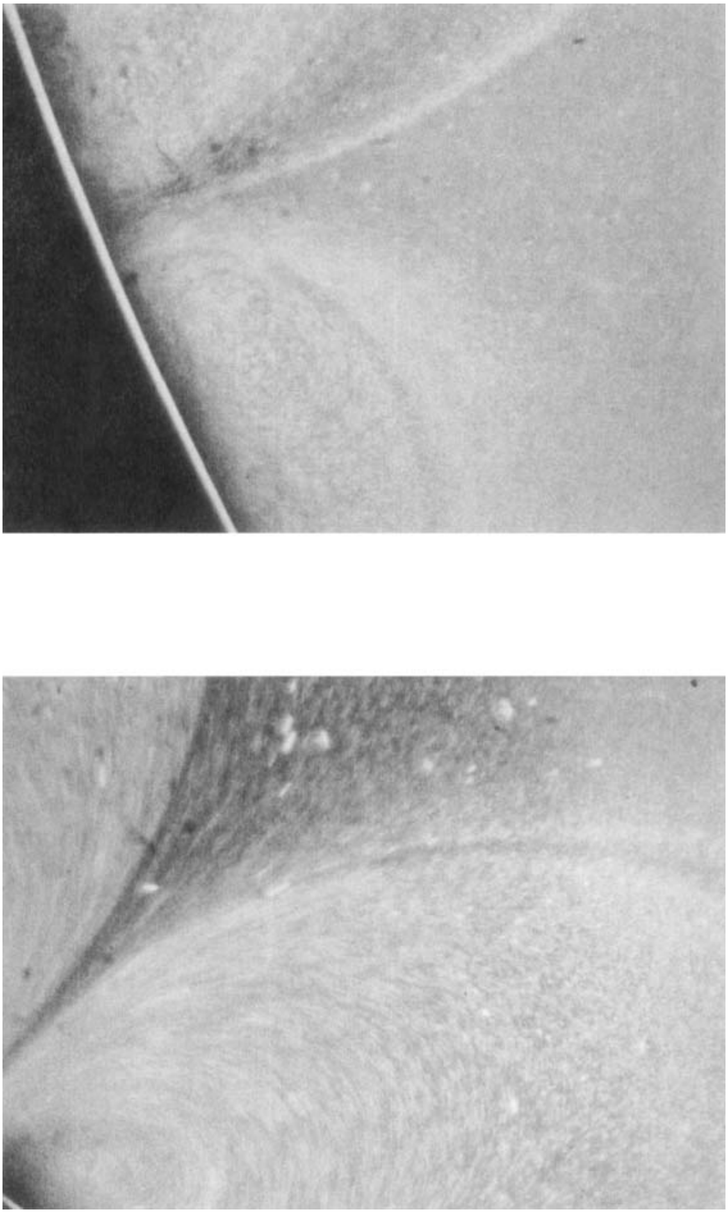


FIG. 10. Secondary roll cells that emerge in the bulk phase, bounce off the interface, and dissipate in the bulk phase.

When the excess entropy production is negative, the system becomes unstable in the far from equilibrium range. This can occur under conditions of (a) solute transport and (b) interfacial reactions. In extraction systems there is both reaction and transport, and the instabilities most likely arise from a coupling of these effects. The limiting cases, when both solute transport and reactions are rate determining, are examined and compared with our experimental observations.

Hydrodynamic Instability of Interfaces under Conditions of Solute Transport

Sterling and Scriven (*13*) analyzed the problem of interfacial instability under conditions of solute transport, when tension gradients arise due to concentration fluctuations at the interface, and obtained a set of criteria for predicting when Marangoni instability would occur. A qualitative understanding of interfacial instability is possible by equating the shear stress due to bulk flow at the interface to interfacial tension gradients (*12*). Consider the situation shown in Fig. 11, where solute diffuses from Phase A to Phase B. Now further suppose that interfacial tension decreases with increasing solute concentration. If a small disturbance at Point P of the interface brings some solute-rich liquid from the interior of Phase A to the interface, the resulting interfacial tension gradient generates a flow which draws more liquid in A to the interface as shown, thus promoting instability. But the flow also brings solute-lean fluid from B to the interface, which acts to increase interfacial tension at P and oppose the instability. Thus, whether instability develops depends on the relative magnitudes of these opposing effects. The key results derived from the analysis of Sterling and Scriven (*13*) are: 1) If one phase has higher viscosity and lower diffusivity than the other phase, then the system will be unstable if solute is being transferred from the phase with the higher viscosity provided that the interfacial tension decreases with increasing concentration of the solute at the interface. 2) If the interfacial tension increases with increasing solute

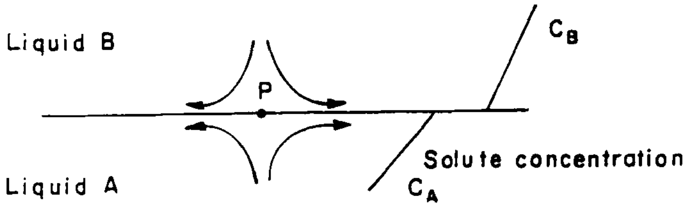


FIG. 11. Interfacial tension gradients generated during solute transport.

concentrations, then the system will be unstable if the solute is being transferred from the phase with lower viscosity. 3) If the viscosity and diffusivity are both higher in one phase than in the other, then the system will be unstable no matter what direction the solute transfer is.

Our system conforms to the second criteria. The viscosity of the aqueous phase is lower than that of the oil phase (2.5 versus 1.5 cP). The diffusivity of the nickel ion is clearly greater in the aqueous phase than in the oil phase because the nickel ions exist in a free state in the aqueous phase but exist as a complex with D2EHPA in the oil phase. The size of the Ni-D2EHPA complex is much larger than the size of the ions in solution and, consequently, have a lower diffusivity. Increasing the concentration of the solute by displacing the more surface-active ligand can be expected to increase the interfacial tension. In fact, it was observed that there was a measurable increase in the interfacial tension when ligand and extractant were both present. Since the solute transfer was occurring from the phase with lower viscosity (water), conditions are indeed ripe for interfacial turbulence. Increasing the interfacial concentration of the nickel ions should not affect interfacial tension values when no ligand molecules are present. Consequently, no interfacial turbulence is expected under these conditions, and the experimental observation of no turbulence in the absence of ligand (see Fig. 4) is consistent with this argument. The underlying assumption in this analysis is that the reaction rates at the interface occur so fast that the extraction process is controlled by the rate-limiting step of slow diffusion of the nickel ions to the interface.

The absence of turbulence in the surfactant system, as seen in Fig. 5, is due to the increase in interfacial viscoelastic properties (*14*). The interfacial shear viscosity, which was 2.2×10^{-4} surface poise in the absence of surfactants, and measured by us using a viscous traction deep channel viscometer, rose by two orders of magnitude to 3.4×10^{-2} surface poise when surfactants were present.

Several features of turbulence observed in the present study are not in accord with the theory of solute-transport-induced turbulence. The turbulence lasted for only a minute even though mass transfer of nickel to the oil phase lasted for almost 30 min. This suggests that, in contrast to theory, *the rate of mass transfer* of the solute between the phases is important in determining interfacial turbulence. Further, for a process governed by diffusion, the roll cell width is expected to increase as the square root of elapsed time. Our observations, however, did not show the roll cells dissipating in this manner. The roll cell patterns lead us to believe that the instabilities were sustained by other mechanisms in conjunction with the solute transport mechanism.

Instability Due to Reaction Kinetics

It is a well-known result that instabilities can be caused by chemical reaction schemes involving autocatalytic reactions (*11*). The known extraction reaction of metals with an organic extractant does not involve any autocatalytic steps (see Fig. 12) and, therefore, instabilities due to intrinsic kinetics may be ruled out. Instabilities can be generated by interfacial tension gradients that arise due to surface temperature variations that occur when large heats of reaction are involved. This type of instability is relevant only when the heat of reaction is large, as in liquid–vapor transitions (*15*). In the liquid–liquid extraction of metal ions, the heats of reaction are very low, and this type of instability is not expected to be a factor.

Veldove and Sanfeld showed that the coupling between surface chemical reactions and hydrodynamics can induce interfacial turbulence, under nonequilibrium conditions (*16*), when the interfacial reaction rates are the rate-determining step. Their analysis differs from most previous theories of the Marangoni effect in that thermal and concentration gradients in the bulk phases are not the destabilizing factors but, rather, it is the combined effects of surface chemical reactions and convective flow that are destabilizing. The nonequilibrium surface elasticity coefficient ϵ, defined in terms of the surface relaxation processes, has to be negative for instabilities to occur. This will happen when, within the time scale of convective fluctuation of interface, reactions deplete the interface of metal ions so that surface-active ligands are instantaneously adsorbed and result in a lowering of interfacial tension with surface expansion.

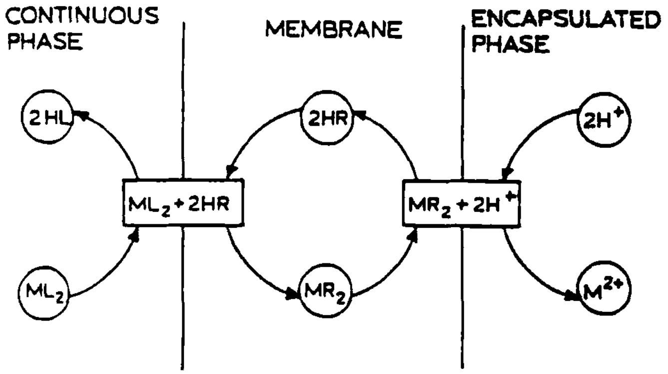


FIG. 12. Reaction mechanisms during ligand-enhanced extraction of metal ions by organic extractant (*10*).

The coupling between the convective and the chemical kinetic processes induces a feedback loop responsible for the onset of surface motion. Mechanochemical instabilities can occur only when more than one fluctuating species is present. The ligand is considered to be the second fluctuating species at the interface that creates turbulence. The fact that no turbulence was observed in the absence of ligand (see Fig. 4) supports this hypothesis. The addition of ligand, therefore, makes it possible for mechanochemical turbulence to occur by providing a second fluctuating species, in addition to the nickel ion, at the interface. The viscosities in the bulk phases and in the surface play a different role in mechanochemical stability. Viscous effects cannot stabilize the interface when the surface kinetics are unstable. However, for intrinsically stable kinetics, as in the ligand-enhanced metal extraction systems, large viscous effects completely stabilize the interface and, hence, there is an absence of turbulence in systems containing surfactants.

A unique feature of the presently observed turbulence is the complete absence of turbulence in the organic phase (see Figs. 1–5, 7–10). This is a feature that is inexplicable in terms of the known models of interfacial instability. The absence of turbulence at high surfactant concentrations has been attributed to the rigidity of the film, and the observation of no turbulence in our system is consistent with the absence of momentum transfer across interfaces in surfactant systems (*12*). The complete absence of turbulence in the organic phase, but its persistence in the aqueous phase for a long period of time, leads us to believe that the interface is actually a liquid membrane, one interface being highly dilational and the other interface being rigid. This would account for the observed flow patterns. Clearly, what this implies is that the interface may not, in all cases, be regarded as a surface of discontinuity where density, composition, etc. change abruptly, but, instead, a region of finite thickness where properties changes continuously. To be sure, this thickness is, except near the critical point, only a few molecular diameters. Nevertheless, it is an integral feature of interfacial structure. Attempts to include intermolecular forces and thus predict density profiles and interfacial tensions go back at least as far as van der Waals, who used his equation of state in a calculation of density profiles. Davis and Scriven (*17*) recently summarized work in this area very clearly, including some of their own significant contributions of recent years. Among the topics they discussed are the use of density and composition profiles to calculate the stress distribution within the interfacial region. The observed fluid flow patterns clearly show that a fluid–fluid interface may be elastic on one side of the interface and rigid on the other.

In addition to the important role the acetate ligand plays in creating conditions ripe for interfacial turbulence, it also serves to enhance metal extraction rates by increasing the metal ion concentrations at the interface. The ligand, being more surface active than the nickel ions, exists primarily at the interface, and the negatively charged ligand increases the interfacial concentration of nickel ions by coulombic attraction. The D2EHPA molecules then have a greater probability of colliding with the nickel ions held at the interface, and this results in nickel extraction from the aqueous phase.

Mass transfer and dynamic interfacial tension measurements indicate that most of the extraction takes place within 1 minute of contact of the aqueous and organic phases (*18*). Figure 13 shows the concentration of nickel ion in the aqueous phase as a function of time under conditions of interfacial turbulence. It can be seen that for the period during which turbulence lasted, about 1 minute, there was an exponential rate of metal extraction. This was followed by a much slower linear rate of nickel removal when the turbulence subsided. Dispersion lives of about a minute may therefore suffice for metal extraction. These observations have the important implication that efficient liquid membrane technologies can be successfully developed without the addition of surfactants to prolong dispersion lives, and that the exclusion of surfactants will also reduce mass transfer resistance at the interface and facilitate eventual phase separation of the organic and aqueous phases.

SUMMARY

Interfacial trubulence created during the extraction of metals by organic extractants can considerably enhance the speed of extraction. Dissipative structures created during Ni extraction with D2EHPA and acetate ligand were investigated by Schlieren photography and were shown to possess two distinct roll cells in addition to rapid twitching and fluctuation of the interface. Smaller and more frequent roll cells developed at the interface, traveled parallel to it, and eventually dissipated there. Larger roll cells, which had their incipience in the bulk aqueous phase, traveled toward the interface and dissipated while receding from the interface after collision. The primary roll cells arise from self-amplification of fluctuations created by interfacial tension gradients (Marangoni instability). The secondary roll cells are caused by rapid depletion of the chemical species close to the interface and the consequent density differences between the interfacial region and bulk phase (Raleigh instability). Schlieren photographic studies showed that there are several novel features of the turbulence patterns, such as its occurrence exclusively in the oil phase and the multiplicity of roll cell types, not accountable in terms of existing models, and that turbulence is completely eliminated by the addition of surfactants.

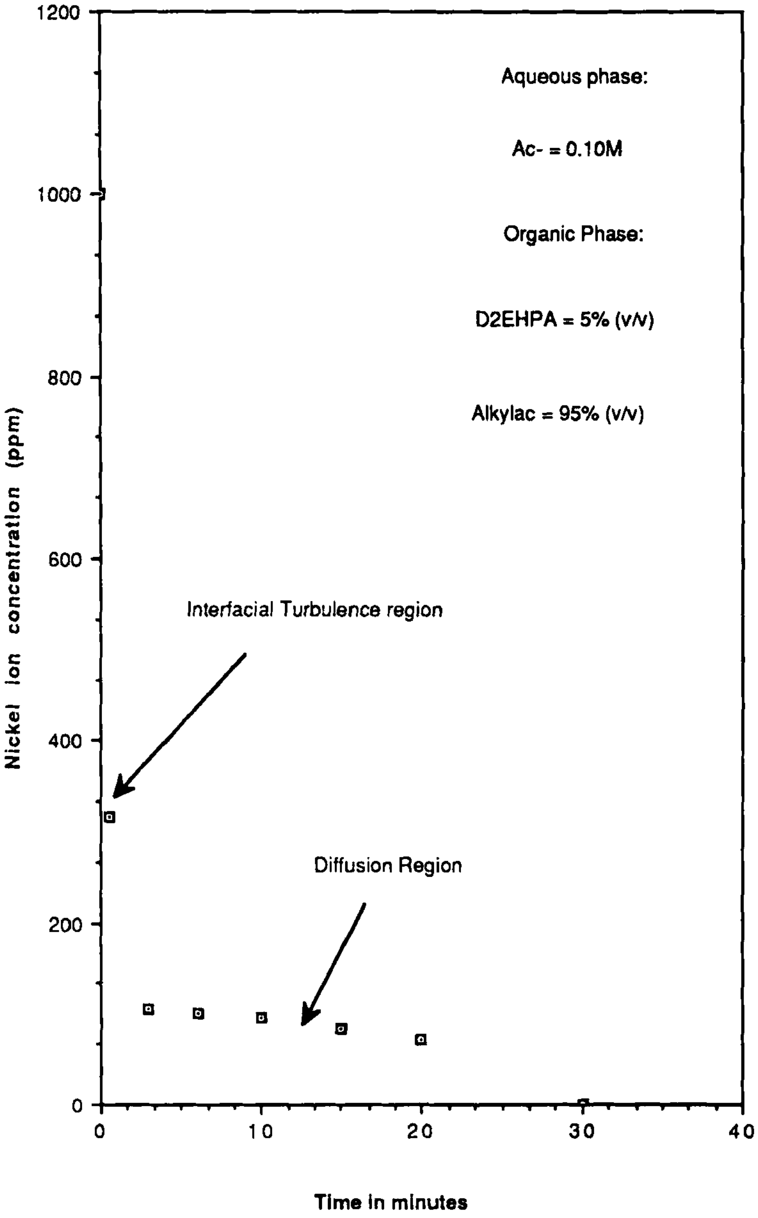


FIG. 13. Nickel ion concentration in the aqueous phase during the time scale of turbulence and beyond.

Acknowledgments

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REFERENCES

1. N. N. Li, "Separation of Hydrocarbons with Liquid Membranes," U.S. Patent 3,410,794 (1968).
2. E. L. Cussler and D. F. Evans, *J. Membr. Sci.*, *6*, 113–121 (1980).
3. R. M. Izatt, M. P. Biehl, J. D. Lamb, and J. J. Christensen, *Sep. Sci. Technol.*, *17*, 1351–1360 (1982).
4. J. W. Frankenfeld, R. P. Cahn, and N. N. Li, *Ibid.*, *16*, 385 (1981).
5. T. Kitagawa, Y. Nichikawa, J. W. Frankenfeld, and N. N. Li, *Environ. Sci. Technol.*, *11*, 602 (1977).
6. J. Strezelbicki and W. Charewicz, *Sep. Sci. Technol.*, *13*, 141 (1978).
7. M. Teramoto, T. Sakai, K. Yanagawa, M. Ohsuga, and Y. Mikaye, *Ibid.*, *18*, 397 (1983).
8. D. T. Wasan, Z. M. Gu, and N. N. Li, *Faraday Discuss. Chem. Soc.*, *77*, Paper 6 (1984).
9. Z. M. Gu, D. T. Wasan, and N. N. Li, *Sep. Sci. Technol.*, *20*, 599 (1985).
10. Z. M. Gu, D. T. Wasan, and N. N. Li, *J. Membr. Sci.*, *26*, 129–142 (1986).
11. P. Glansdorff and I. Prigogine, *Thermodynamic Theory of Structure, Stability and Fluctuations*, Wiley, New York, 1971.
12. C. A. Miller and P. Neogi, *Interfacial Phenomena, Equilibrium and Dynamic Effects*, Dekker, New York, 1985.
13. C. V. Sterling and L. E. Scriven, *AIChE J.*, *5*, 514, (1959).
14. L. E. Scriven and C. V. Sterling, *J. Fluid Mech.*, *19*, 321 (1964).
15. J. R. A. Pearson, *J. Fluid 4,Mech.*, *4*, 489 (1958).
16. W. D. Veldoe and A. Sanfeld, *J. Colloid Interface Sci.*, *84*, 318 (1981).
17. H. T. Davis and L. E. Scriven, *Adv. Chem. Phys.*, *49*, 357 (1981).
18. C. Thomas, PhD thesis, Illinois Institute of Technology, May 1990.

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