Interfacial Cellular Mixing and a Conjecture on Global Deposit Morphology

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We report the development of cellular mixing at a vertical interface between miscible solutions with a single diffusing species. For the binary systems studied, this patterned convection occurs only when the interface is driven. Experimental results support the interpretation of this hydrodynamic instability as a surface-tension effect. We relate this convective instability, and viscous fingering between fluids with small relative viscosities, to the macroscopic morphology of electrodeposits and precipitates.

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We report here on cellular mixing at the interface between miscible solutions with different solute concentrations. The simplest system described is a binary one with cellular convective mixing occurring when aqueous solution is driven into water or vice versa (see Fig. 1). For the solutions used, cellular convection does not occur if the interface is stationary. This suggests a previously unreported driven-interface surface-tension instability. The experiment is performed in a horizontal quasi-two-dimensional geometry so that only concentration diffusion occurs; the temperature and gravitational gradients of "salt-fingering" and more complex ternary or double-diffusive systems[1] are not present. For this reason, our experiment may be the simplest diffusive system in which convective cells develop. Our purpose is to (1) describe this cellular mixing, (2) distinguish it from viscous fingering[2] at low interfacial velocity and small relative viscosities, (3) provide evidence that it is a Marangoni (i.e., surface-tension) effect[3,4] with horizontal convective cells, and (4) conjecture on the effect on deposit morphology of hydrodynamic patterning at the fluid-fluid interface which develops during diffusion-controlled growth.

Our investigations were motivated by the nature of deposit growth from solution.[5] When a solid interface grows by a diffusion-controlled mechanism, a gradient is maintained across a diffusion layer lying between depleted solution at the solid interface and the bulk liquid. Examples of a concentration gradient arise during precipitation from supersaturated solution[6] and electrochemical deposition;[7–10] during solidification from the melt the gradient is in the temperature field.[11] As the interface advances, the diffusion layer precedes it into the bulk solution. Our hypothesis is that the liquid-liquid interface between the diffusion-layer region and the bulk solution is a principal determinant of *global morphology* in diffusion-controlled growth. If the gradient is across a narrow region, the viscosity and surface-tension differences between the depleted region liquid and the bulk fluid define the stability of the envelope surrounding the growth. This theoretical picture provides a means to treat, for example, the disconnected branching structures observed during quasi-two-dimensional electrodeposition.[9] The liquid-liquid "interface" is continuous, and encompasses the branching growth; its hydrodynamic stability can be critical in determining the morphology of observed deposits.[12]

Motivated by the above, we studied the interface between fluids with closely matched viscosities, and small relative interfacial tensions. Our cell consists of two

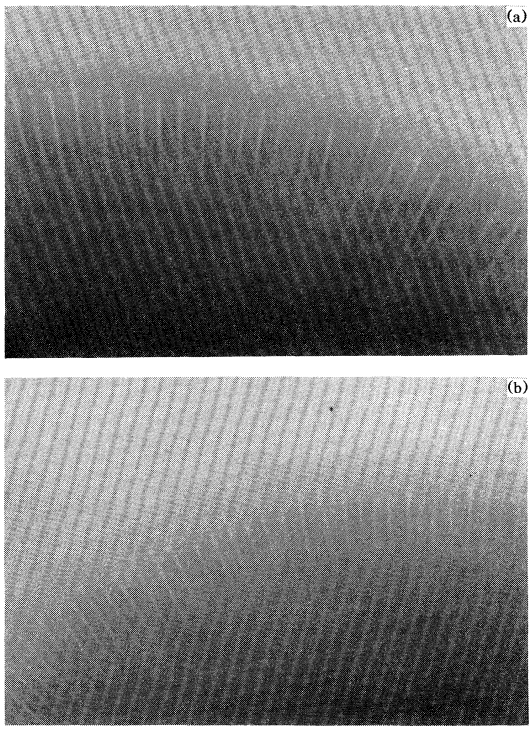

FIG. 1. (a) Cellular interfacial convection pattern for water with food color (20:1 ratio) driven into 0.1M $CuSO_4$ solution at constant-flow rate of 36.6 μl/sec at a radius of 3.43 cm and plate spacing of 290 μm (interfacial velocity of 0.88 mm/sec). (b) The reverse flow case of more viscous into less viscous fluid, 0.1M $CuSO_4$ with food color driven into water at 21.2 μl/sec at a radius of 2.66 cm (interfacial velocity of 0.66 mm/sec). The true width of the picture is ≈ 2 cm.

square pieces of acrylic sheet separated by 290 μm (two cover slips). Thickness variation of the plastic results in a spacing variation of up to 30 μm. The cell is first filled with solution. A second solution is then injected at the center of the cell at a constant-flow rate with a syringe pump. Flow rates used varied from 5.0 to 36.6 μl/sec ($\pm 5\%$).

Green food color, added to either solution, is used to make visible the mixing as depleted (or enriched) regions are left behind the advancing interface. These regions appear to decay diffusively. For an undriven interface, only diffusive spreading occurs. The dye (1 part Durkee brand to 20 parts water) is passive in the experiment. If an aqueous solution of this concentration is injected into water (or vice versa), only diffusive dispersion is observed. Moreover, without dye the cell pattern is faintly visible presumably due to variation in the fluid index of refraction. These observations rule out double-diffusion-induced convection.

We observed the cellular mixing in other restricted geometries. When cupric-sulfate solution is injected near the bottom of a Petrie dish of water with food color, a cellular pattern is visible at the interface as it moves along the bottom. The pattern also emerges for cupric-sulfate solution driven from a pipette close to the surface of a puddle of water. The free surface in these experiments demonstrates that the convection cells are horizontal, and not determined by the presence of plates. These results also confirm that in the quasi-two-dimensional cell the pattern is not due to wetting of the plates.

Depending on the flow rate, it takes 60–300 sec for the dyed region to move 4 cm. Diffusion constants for the solutes and green food color are on the order of 10^{-6}–10^{-5} cm^2/sec suggesting that the diffusional spread of the interface is ≈ 500 μm over 2 min. Visually the interface color fades over a few millimeters, and in photographic enlargements cellular patterning extends beyond the dye front. This can be accounted for in part by the velocity profile. For volume flow rate I, plate spacing $2b$, and vertical coordinate $z=0$ at the midplane as a function of radius r the interfacial velocity is $v(r,z)=(3I/8\pi br)(1-z^2/b^2)$. Since the center of the interface moves fastest, the forward tongue of injected fluid becomes progressively thinner, and the vertical depth of dye decreases, until no longer visible. (At a spacing of 290 μm, a ratio of food color to water of $\approx 1{:}320$ is visually undetectable.) Interfacial mixing also reduces the dye concentration.

Figures 1(a) and 1(b) distinguish cellular mixing from the pattern-forming mechanism of viscous fingering. In Fig. 1(a) dyed water is injected into 0.1M $CuSO_4$ solution at a flow rate of 36.6 ± 0.65 μl/sec; in Fig. 1(b) 0.1M $CuSO_4$ solution (with green food color) is injected into water at a flow rate of 21.2 ± 1.6 μl/sec. Viscous fingers do not develop when a more viscous fluid is driven into a less viscous one. Here the pattern emerges with either fluid the injected one.

Figure 2 is a plot of cell wavelength versus interface velocity for the injection of colored water into different molarity solutions of $CuSO_4$. The selected wavelength appears in bands corresponding to the molarity, decreases with viscosity, and is independent of interface velocity over our range of flow rates. At 0.1M, 0.2M, 0.3M, and 0.4M $CuSO_4$ the average wavelengths are 885, 642, 575, and 503 μm, respectively. Tabulated viscosities[13] relative to water are 1.04, 1.07, 1.13, and 1.18 at 30°C. Our measured viscosities at 22°C of 1.063 ± 0.009 and 1.175 ± 0.012 for 0.1M and 0.4M solutions are in good agreement. Data points for a specific interface velocity in Fig. 2 may be measured at different flow rates and radii since at the tip $v \sim I/R$.

We conjecture that the cellular mixing arises from surface-tension gradients inducing tangential interfacial flow, i.e., a Marangoni effect.[3] This is consistent with the wavelength dependence on viscosity: The larger the viscosity difference between the fluids, the larger the surface-tension gradient which can be maintained, and so the smaller the distance between cells. The Marangoni effect is usually associated with spontaneous mixing at the interface between two stationary solutions when one has a surfactant solute. In our experiment convective mixing only develops if the fluid interface is externally driven. Presumably fluctuations of solute concentration give rise to a tangential surface-tension gradient at the driven interface, and hence cellular mixing.[14]

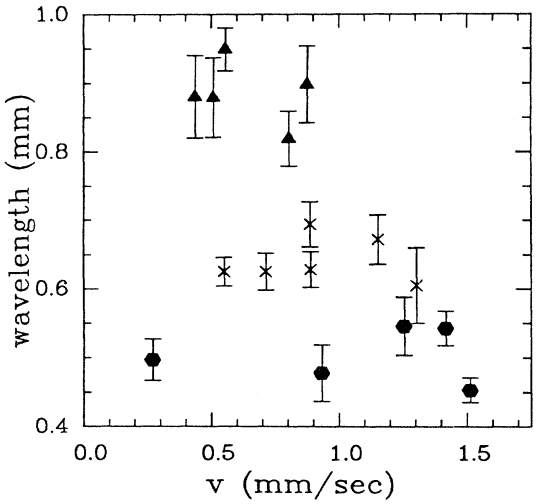

FIG. 2. Cellular wavelength as a function of interface velocity for water injected into an aqueous $CuSO_4$ solution: ▲, 0.1M; ×, 0.2M; and ●, 0.4M. Data for 0.3M solution, for which the average wavelength is 575 μm, are omitted here. The velocity is computed for the interface at the midplane. The wavelength was measured by counting the number of depletion regions per radian. The error in wavelength is due to ambiguity in identifying depleted regions, error in locating the interface, and error in scaling to the picture. The error in velocity, $\approx 8\%$, also has uncertainty in flow from the syringe pump.

The cellular wavelength was determined by counting the "needles' eyes" (color-enriched or -depleted regions) in an arc of the interface on photographs. For a specific run this might only be possible over a radius change of 5 mm. Frequently, for only one radius could a count be made; when distinct cells were maintained over a centimeter distance, the wavelength was constant within our accuracy. Ambiguity in counting occurred due to cell splitting. Streaks appear in regions where an "eye" seems "missing," or between otherwise regularly spaced cells. Counts were usually possible only over a limited arc (typically 90°). These difficulties are in part attributable to nonuniformity of the cell plates and spacing. As the interface advances, the fine resolution of the cellular pattern decays, and the interface appears fringed. The disintegration of the interface may have a chaotic aspect to it, beginning with regular cell splitting.

Cellular interfacial mixing occurs for nonelectrolytic solutes (sucrose and glycerine), as well as for salts ($CuSO_4$ and $ZnSO_4$), and ternary combinations. Limiting conditions are the following:

(i) A minimum solution concentration must be exceeded. For our range of flows, convection cells were not observed for $CuSO_4$ with concentrations of $0.05M$ and smaller.

(ii) A minimum plate spacing is necessary. Cellular mixing was not observed for a plate spacing of 145 μm. This may be a viscous effect of the wetting layer and the no-slip boundary conditions of laminar flow.

(iii) The radius at which cellular mixing begins is a function of both flow rate and concentration. At 5 μl/sec cells appear at about 1.0 cm, as compared to 2.0 cm at 36.6 μl/sec. At lower concentrations the pattern appears later, and fades earlier. Since $v \sim I/R$, the $0.1M$ data points are bunched at low velocity in Fig. 2. As the solution advances, diffusion and convection diminish the gradient, eventually destroying the pattern.

(iv) A cellular interface does not develop for $0.1M$ $CuSO_4$ driven into equal concentrations of sucrose or $ZnSO_4$ but does emerge for a sufficient mismatch in the solute concentrations, e.g., $0.4M$ $CuSO_4$ and $0.1M$ sucrose solution. The relative viscosity of $0.1M$ sucrose to water is 1.13 ± 0.04 while that of $0.1M$ $CuSO_4$ to water is 1.06. The viscosity difference of 0.07 between these solutions is greater than that between $0.1M$ $CuSO_4$ and water, where convection cells develop. This suggests that at equal concentrations of cupric-sulfate and sucrose solutions the surface-tension gradient necessary for cellular mixing cannot be established.

Viscous fingering is also a surface-tension- and viscosity-dependent effect. However, the fingering instability is normal to the interface, as opposed to the tangential driving force of the Marangoni effect. To contrast the two, we used glycerine solution. For pure glycerine the relative viscosity η to water is ≈ 1400, while for a water and glycerine mixture 7:10 by volume, $\eta = 11.15 \pm 0.03$. At low concentrations only cellular mixing occurs, independent of whether aqueous glycerine solution is driven into water or vice versa. However, above a critical concentration ($\eta \approx 10$), the interface develops viscous fingers *when water is driven into the more viscous glycerine solution,* but only cellular mixing occurs when the glycerine solution is injected into water. The combination of viscous fingers and convection cells is shown in Fig. 3.

Adopting the fastest-growing-mode hypothesis,[5,12,15-17] and using linear stability analysis for the mode number and parameters of Fig. 3, the dimensionless parameter[18] $\mu I/b^2\sigma$ can be fitted to provide a rough estimate of the dynamical surface tension[12,19,20] between the miscible fluids of this experiment as $\sigma \approx 0.09$ dyn/cm. (μ is the bulk fluid viscosity.) In this experiment, σ is time dependent because of both mixing and diffusion. For the lower σ and I expected in electrodeposition, stability analysis predicts viscous fingering can occur consistent with observed branching.[12,21-23]

On the basis of the above experimental results, we hypothesize that the global morphology of depositional growth, i.e., the number of branches, the stability of the branch tips, and the way it fills space (its "dimension"), is determined by the hydrodynamic stability of the interface between the depleted fluid near the growth and the bulk fluid *provided* the gradient is *sufficiently sharp* to provide an effective liquid-liquid interface. Since leading edges grow fastest, hydrodynamic modulation of the liquid-liquid interface *à la* Hele-Shaw would determine branch position, just as cellular mixing will.

In electrodeposition the existence of a sharp gradient sustained by the growing deposit is experimentally supported.[21,22] The analogy to directional solidification, where a constant temperature gradient is imposed,[11] and the cellular mixing described above, leads us to describe the electrodeposit in Fig. 4 as cellular growth. By contrast, for deposits which have the dense-branching morphology[12] (DBM), the branch tips regularly split. For

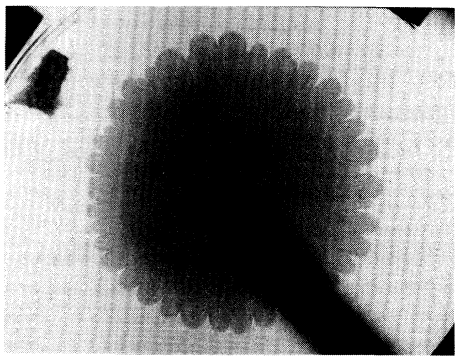

FIG. 3. Viscous fingering with cellular interfacial convection. Water with food color is injected into glycerine solution (10 parts glycerine to 7 parts water) at a flow rate of 15.2 μl/sec. The solution viscosity relative to water is 11.15 ± 0.03. The pattern's radius is ≈ 2.5 cm.

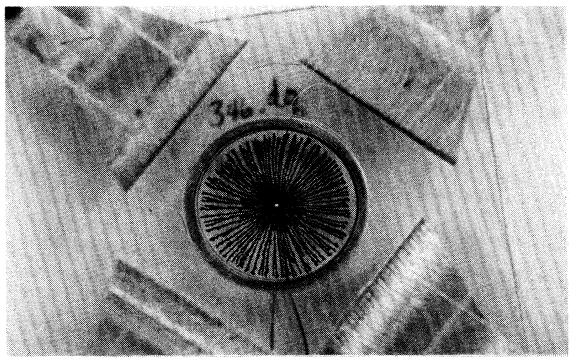

FIG. 4. Copper electrodeposit grown from 0.1M aqueous $CuSO_4$ solution with an applied potential of 15 V. The radius of the cell is 10 mm, and the plate spacing is 290 μm. The cellular character of the branches suggests they are fed by cellular convection at the interface.

such a DBM electrodeposit, branches would extend from the center of Fig. 3 to the convectively enriched regions in the forward portions of the viscous fingers. Electrodeposits with a long-wavelength modulation to bunched branches occur experimentally.[23] When fine structure is lost, only the "viscous finger" structure may remain.[9] Absence of this modulation in Fig. 4 suggests that the interfacial viscosity difference is insufficient for viscous fingering. Finally, for zinc's long isolated dendrites,[5] the above suggests a hydrodynamic selection corresponding to a low-mode-number perturbation of the liquid-liquid interface. This has very recently been confirmed experimentally.[22] Cellular hydrodynamic patterning may also explain the long-range ordering observed during precipitation from supersaturated solutions.[24]

To conclude, we have reported on the stability of the interface between two miscible fluids of closely matching viscosities when one is driven into the other. For the case where the fluids differ only in solute concentration, we find that spontaneous cellular convective mixing can develop. We suggest that this interfacial patterning is a surface-tension effect distinct from viscous fingering; the latter can occur simultaneously. Finally, we have conjectured on the effect of hydrodynamic patterning at a fluid-fluid interface on the transport of material during depositional growth, and so to the determination of deposit morphology.

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Note added.—We recently obtained preprints from Joseph.[20,25] Reference 20, since published, provides an excellent review of prior research on miscible fluid interfaces; it and subsequent papers[25] provide a discussion of the nature of the dynamic, or transient, surface tension between miscible fluids.

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[1]J. S. Turner, *Buoyancy Effects in Fluids* (Cambridge Univ. Press, Cambridge, 1973).

[2]D. Kessler, J. Koplik, and H. Levine, Adv. Phys. **37**, 255 (1988), and references therein.

[3]C. V. Sternling and L. E. Scriven, Am. Inst. Chem. Eng. J. **5**, 514 (1959).

[4]S. M. Troian, X. L. Wu, and S. A. Safran, Phys. Rev. Lett. **62**, 1496 (1989).

[5]E. Ben-Jacob and P. Garik, Nature (London) **343**, 523 (1990), and references therein.

[6]W. W. Mullins and R. F. Sekerka, J. Appl. Phys. **34**, 323 (1963).

[7]Y. Sawada, A. Dougherty, and J. P. Gollub, Phys. Rev. Lett. **56**, 1260 (1986).

[8]D. Grier, E. Ben-Jacob, R. Clarke, and L. M. Sander, Phys. Rev. Lett. **56**, 1264 (1986).

[9]P. Garik, D. Barkey, E. Ben-Jacob, N. Broxholm, B. Miller, B. Orr, and R. Zamir, Phys. Rev. Lett. **62**, 2703 (1989).

[10]A. J. Bard and L. R. Faulkner, *Electrochemical Methods* (Wiley, New York, 1980).

[11]J. Langer, Rev. Mod. Phys. **52**, 1 (1980), and references therein.

[12]E. Ben-Jacob, G. Deutscher, P. Garik, N. D. Goldenfeld, and Y. Lareah, Phys. Rev. Lett. **57**, 1903 (1986).

[13]R. H. Stokes and R. Mills, *Viscosity of Electrolytes and Related Properties* (Pergamon, New York, 1965).

[14]P. Garik (to be published).

[15]P. G. Drazin and W. H. Reid, *Hydrodynamic Instability* (Cambridge Univ. Press, Cambridge, 1981).

[16]E. Ben-Jacob, P. Garik, and D. Grier, Superlattices Microstruct. **3**, 599 (1987).

[17]L. Schwartz, Phys. Fluids **29**, 3086 (1986).

[18]S. N. Rauseo, P. D. Barnes, and J. V. Maher, Phys. Rev. A **35**, 1245 (1987).

[19]S. E. May and J. V. Maher (to be published); M. W. DiFrancesco, Ph.D. thesis, University of Pittsburgh (unpublished).

[20]D. D. Joseph, Eur. J. Mech. B/Fluids **9**, 565 (1990), and references therein.

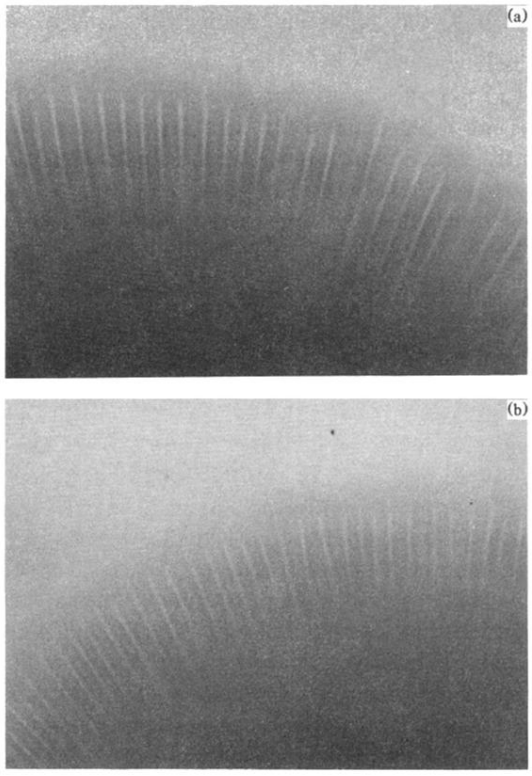
[21]D. P. Barkey and P. D. Laporte, J. Electrochem. Soc. **137**, 1655 (1990).

[22]D. Barkey (to be published).

[23]P. Garik, D. Barkey, E. Ben-Jacob, E. Bochner, N. Broxholm, B. Miller, B. Orr, and R. Zamir (to be published).

[24]E. Raz, S. G. Lipson, and E. Ben-Jacob (to be published).

[25]P. Galdi, D. D. Joseph, L. Preziosi, and S. Rionero (to be published); D. D. Joseph and H. H. Hu (to be published).



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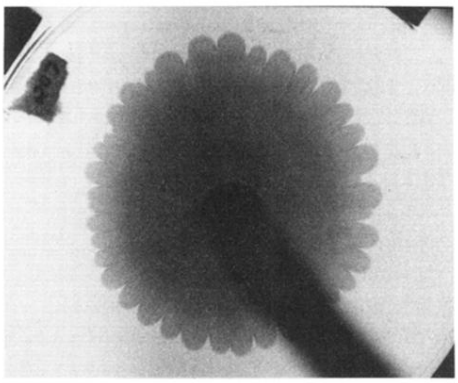

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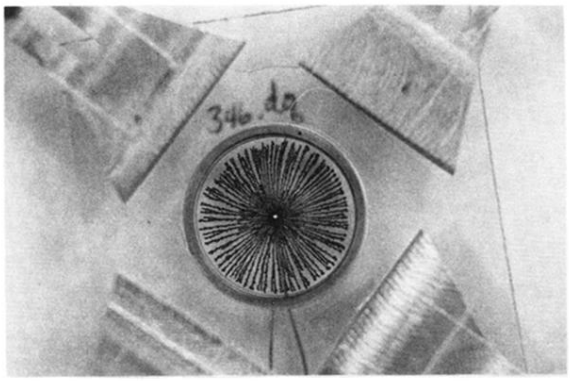

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