Adsorption-Desorption Barrier, Diffusional Exchanges and Surface Instabilities of Longitudinal Waves for Aperiodic Regimes

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Our purpose is to give the physical conditions under which transfer of a surfactant through a fluid interface between two immiscible liquids may induce aperiodic convective motion.

Adsorption-desorption rates are considered together with diffusional exchanges. New kinds of surface instabilities are then predicted.

SCOPE

We studied the convective stability of a fluid interface between two immiscible incompressible fluids when submitted to exchanges of matter. The mass transfer is a two-step process: a diffusion flux between sublayer and bulk phase and an adsorption-desorption kinetic between sublayer and surface.

A linear perturbation analysis restricted to longitudinal waves is performed. For aperiodic regimes we give the complete analysis when there is no accumulation of matter, both in the reference steady state and in the perturbed one. The coupling between surface potential barriers and matter fluxes in the steady state can induce new varieties of instabilities.

We give the general instability conditions involving experimental parameters (diffusion coefficients and profiles, Schmidt numbers, adsorption-desorption coefficients) to extend the Sternling-Scriven criteria for the interfacial convective motion.

CONCLUSIONS AND SIGNIFICANCE

It is experimentally observed that interfacial motion and spontaneous emulsification at liquid surfaces occur during mass transfers together with a decrease of the interfacial resistance.

A pure diffusion kinetics in the bulk phases doesn't always account for this behavior and relaxation mechanisms are then to be considered. England and Berg (1971) gave a comprehensive survey of these last processes. They pointed out the influence of:

- Breaking of formation of hydrogen bonds
- Orientation of molecules
- Dimerization and dissociation reactions in the interface with formation of polymolecular films

All these effects could be responsible for the existence of an additional resistance which may decrease the rate of exchange of molecules between the interface and the adjacent bulk phases. For example, a minimum of dynamic interfacial tension due to a desorption barrier could induce an emulsification. A statistical thermodynamic treatment was also developed a couple years ago in order to show the existence of transitory states of zero interfacial tension (Defay and Sanfeld, 1975).

An interesting hydrodynamic stability analysis was developed by Brian et al. (1971, 1972a,b) for the transfer of a surfactant between water and air. They considered bulk diffusion controlled transfer in the liquid phase and adsorption-desorption in the gaseous phase. They showed the influence of the surface convection and of the Marangoni effect on the mass transfer coefficients in the liquid phase and they predicted numerically the value of the neutral state.

Palmer and Berg (1972) studied the stability of dilute binary solutions bounded on the bottom by a flat solid surface and on the top by an inviscid gas. The shallow liquid pool is heated from below. The numerical analysis put forward by these authors for the marginal state allows them to show the boundary between the regions of oscillatory and stationary instability. The potential barriers of adsorption increase the stability of the system. They played a crucial role in determining the mode of instability and have a major influence on the wavenumber corresponding to the maximum time coefficient.

A Marangoni effect has also been observed in steel-making processes. The slag metal interfacial tensions are one order of magnitude greater than in organic aqueous systems and are highly sensitive to solute concentrations (Davenport et al., 1967; Subramanian and Richardson, 1968). The adsorption of surface active substances such as oxygen or sulfur in such systems reduces the interfacial tension and thus leads to an interfacial flow (Lu and Hamielec, 1973).

McManamey et al. (1975) have investigated molecular diffusion on mass-stirred cells in connection with interfacial stability. Chemical and electrical constraints have also been studied in the frame of surface hydrodynamic stabilities (for example, Miller, 1978; Sanfeld et al., 1979; Van Lamsweerde-Gallez et al., 1979; Bisch et al., 1979; Berg, 1979). Electro and chemical convective coupling terms play a fundamental role for the onset of surface motion.

Our purpose is to give general physical conditions and rules of instability through a linear analysis for aperiodic regimes and longitudinal waves when a two-step process of diffusion and adsorption-desorption occurs (Sanfeld et al., 1979b). Recently we developed the same perturbation formalism for pure diffusional exchanges (Hennenberg et al., 1979; Sørensen et

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al., 1977 and 1979).

The analysis of longitudinal waves related to the Marangoni effect showed that the imposed diffusion profiles modify the elasticity coefficient and may be responsible for the interfacial instability. It leads, among other things, to Lucassen-van den Tempel (1972) results for equilibrium situations and to Sternling-Scriven (1959) stability criteria (Hennenberg et al., 1979, 1980; Sørensen, 1979). For oscillatory regimes, we applied our theory to the influence of a two-step process diffusion and adsorption-desorption in the long wavelength approximation (Hennenberg et al., 1980). The results are summarized in Table 1.

In the next sections, we will recall briefly the model, the linearized hydrodynamical perturbed equations and the surface mass balance. We will then analyze the compatibility cubic relation for aperiodic marginal and unstable states. An exhaustive mathematical analysis leads to physical necessary conditions for the onset of convective surface motion. They relate the diffusion coefficients, the kinematic viscosities, the direction of matter transfer, the adsorption and desorption coefficients.

We compare our results to those obtained by Sternling and Scriven (1959) which are only valid for diffusion-controlled transfer. Their classical theory is valid to some extent for situations which are not diffusion-controlled. Nevertheless, the precise values of the critical wavenumber and of the corresponding maximum time constant are shifted. In addition, out of equilibrium interfacial surface barrier induces new instability criteria. For example, even when matter transfer is directed from the phase with the largest diffusion coefficient towards the other, the steady state might be unstable and convective motion is predicted.

LINEARIZED, PERTURBED HYDRODYNAMICAL EQUATIONS

The reference steady state (superscript o) is supposed to be at rest. Two immiscible, incompressible viscous fluids (subscript γ) are separated by a homogeneous flat interface. We consider the normal to the perturbed interface as directed from the bulk 1 ($z < 0$) towards the bulk 2 ($z > 0$). In the perturbed state, each incompressible volume phase ($\gamma = 1, 2$) is described by the Navier-Stokes equation. There is no slip at the interface which means the continuity of the velocity.

For the sake of simplicity we neglect, in the momentum balance of the interface, the contributions of the intrinsic surface elasticities (Wasan et al., 1979; Maru et al., 1979) and viscosities (Scriven and Sternling, 1964; Sørensen, 1979) as well as the surface acceleration. We want to focus our attention on the role of surface adsorption-desorption processes on interfacial instability.

As mass transfer leads essentially to the variation of surface tension along the interface, we will neglect the coupling with any normal deformation at the surface ($\delta z = 0$). The tangential ($x_j = x, y$) part of the momentum balance depends upon the two-dimensional gradient of surface tension taken along the interface (Sternling and Scriven, 1959; Lucassen et al., 1972; Linde et al., 1979)

$$\eta_2\left(\frac{\partial v_{2j}}{\partial z} + \frac{\partial v_{2z}}{\partial x_j}\right) - \eta_1\left(\frac{\partial v_{1j}}{\partial z} + \frac{\partial v_{1z}}{\partial x_j}\right) = -\frac{\partial \delta\sigma}{\partial x_j} \tag{1}$$

where $\delta\sigma$ is the variation of surface tension due to the transfer of the surfactant, η is the shear bulk viscosity. A compositional dynamic surface elasticity may be defined by an extended Gibbs relation:

$$\epsilon = \frac{\delta\sigma}{\delta \ln A} \tag{2}$$

where A is the surface area and

$$\delta \ln A = -\left.\frac{\partial \delta z}{\partial z}\right|_s \tag{3}$$

There are two kinds of elasticities. The first one (neglected here) characterizes the intrinsic elastic stresses of the surface and may be combined to the surface intrinsic viscous stresses (for example, a single Voigt model, spring and dashpot in parallel). The other one ϵ is directly linked to the dynamic surface tension (Eq. 2) and thus to the exchanges of matter. As shown previously by Hennenberg et al. (1979), this phenomenological coefficient is generally a complex quantity related to the diffusional fluxes, to the adsorption-desorption rates and to the Schmidt numbers.

Using a classical linear development in normal modes, we obtain from the Navier-Stokes equation and the boundary conditions mentioned above, the dispersion relation which links the wavenumber k to the time coefficient ω.

$$\sum_\gamma \eta_\gamma k(Q_\gamma + 1) + \frac{k^2\epsilon}{\omega} = 0 \tag{4}$$

with

$$Q_\gamma = \left(1 + \frac{\omega}{k^2\nu_\gamma}\right)^{1/2} \tag{5}$$

The coefficient ν_γ is the kinematic viscosity of the phase γ and $\mathrm{Re}(Q_\gamma) \geqslant 0$ for the perturbation to vanish far from the interface.

SURFACE MASS BALANCE

The net rate of variation of the adsorbed solute is the difference of the two fluxes reaching the interface. In each phase at rest, the transfer occurs by diffusion from the bulk to the sublayer $J^{o,d}$ and then by an adsorption-desorption process J^{oa-d} from the sublayer to the interface (England and Berg, 1971; Davies, 1972; Defay and Petré, 1979). For each phase γ, we assume:

$$J_\gamma^o = J_\gamma^{od} = J_\gamma^{oa-d} \tag{6}$$

which means no accumulation of matter at the sublayer in the reference state. Each bulk phase is an ideal dilute solution and the steady concentration profile C^o is given by a classical Fick law:

$$C^o = C^{oo} - \beta z \tag{7}$$

This profile is chosen for the sake of simplicity. In fact, significant concentration gradients may be confined in a thinner region near to the interface. This drawback can easily be remedied, however, by allowing for exponential concentration profiles (Sørensen, 1979). In that case, convection appears when a critical penetration depth is reached. Similar conclusions are reached by Berg and Acrivos (1965).

Another interesting model is used by Palmer and Berg (1972). They consider a system in which the bulk phase is uniform in composition up to a layer of a few molecular diameters. The actual concentration of solute in this layer is defined by the ratio of the relative Gibbs adsorption and the thickness of the layer. From a pure thermodynamic point of view, this picture leads to question of the relevance of the Gibbs model (Defay et al., 1966, 1972).

Furthermore, the existence of a large diffusion zone is experimentally shown for monoalcohols (Defay and Petré, 1971).

We suppose that there is no accumulation of matter at the interface (equality of the unperturbed bulk fluxes). This gives for the diffusion fluxes:

$$\beta_1 D_1 = \beta_2 D_2 \tag{8}$$

The coefficient β_γ is positive when transfer is from 1 to 2. We consider that the adsorption-desorption fluxes are proportional to the difference of chemical potentials of the solute between the bulk phase and the interface. The perturbed fluxes at the interface are given by:

$$\delta J_\gamma = -D_\gamma \frac{\partial \delta C_\gamma}{\partial z} = a_\gamma \delta C_\gamma (-1)^{\gamma+1} - b_\gamma \delta\Gamma(-1)^{\gamma+1} \qquad (\gamma = 1, 2) \tag{9}$$

which means no accumulation of matter at the sublayer in the perturbed state (England and Berg, 1971).

For a linear adsorption-desorption kinetic, the quantities a_γ and b_γ are the positive kinetic constants independent of the concentrations. For most of the adsorption-desorption schemes known (i.e., Langmuir or B.E.T. mechanisms), the constants a_γ and b_γ are positive. They, however, depend on the concentrations in the steady state. We assume that there is no net flux at the interface in the perturbed state. Physically, this means that the time during which the molecules of the solute stay in the interface is much smaller than the time they need to cross the interface. Neglecting the surface mass diffusion (Brenner and Leal, 1978), the surface mass balance is given by:

$$\delta J_1 = \delta J_2 \tag{10}$$

This is a generalization of the basic hypothesis of Sternling and Scriven who considered to have equilibrium between the surface and the sublayer. Indeed, they supposed to have bulk diffusion controlled transfer in each phase and no accumulation of matter in the interface. We assumed that the fluctuation of surface tension is only linked to the fluctuation of the surfactant concentration:

$$\delta\sigma = -\alpha\delta\Gamma \tag{11}$$

where

$$\alpha > 0 \tag{12}$$

Expanding into normal modes and introducing the tangential momentum balance (Eq. 1), we obtain the explicit dispersion equation. The formulation of the dynamic surface elasticity is given by comparison of this dispersion equation with Eq. 4. We obtain:

$$\epsilon = \alpha\Gamma^o \frac{\dfrac{\beta_1 D_1}{\omega}\left(\dfrac{R_2 - 1}{R_2 + Q_2}\cdot\dfrac{1}{1 + \dfrac{kD_2R_2}{a_2}} - \dfrac{R_1 - 1}{R_1 + Q_1}\cdot\dfrac{1}{1 + \dfrac{kD_1R_1}{a_1}}\right)}{k\left(\dfrac{b_1D_1R_1}{a_1\omega}\cdot\dfrac{1}{1 + \dfrac{kD_1R_1}{a_1}} + \dfrac{b_2D_2R_2}{a_2\omega}\cdot\dfrac{1}{1 + \dfrac{kD_2R_2}{a_2}}\right)} \tag{13}$$

with

$$R_\gamma = \left(1 + \frac{\omega}{k^2 D_\gamma}\right)^{1/2} \tag{14}$$

and $\mathrm{Re}R_\gamma \geqslant 0$ for the fluctuations to vanish at infinite distance from the interface. The generalization of this relation to systems with surface mass accumulation was previously derived (Hennenberg et al., 1980).

This quantity is, thus, directly linked to the exchanges of matter between the surface and the adjacent phases (D_γ, a_γ, b_γ) to the Gibbs static surface elasticity $\epsilon^o = \alpha\Gamma^o$ and to the viscous effect. Equations 4 and 13 were used to develop the stability analysis of periodic unstable states (Table 1).

NONOSCILLATORY UNSTABLE REGIMES

To study nonoscillatory modes, we will consider that

$$k = k_r = \frac{2\pi}{\lambda}, \quad \omega = \omega_r \quad (\text{sub } r = \text{real}) \tag{15}$$

where λ is the wavelength. When the time coefficient ω is positive (negative), the perturbations are amplified (damped). The marginal state is given by $\omega = 0$. We study the onset of instability at a given position with increasing time.

Taking into account Eqs. 2, 4, 9, 10 and 11 in the development into normal modes of the stability analysis, we obtain the compatibility condition as a parametric cubic equation in the wavenumber k:

$$k^3 + \tilde{a}_2(\xi)k^2 + \tilde{a}_1(\xi)k + \tilde{a}_0(\xi) = 0 \tag{16}$$

with

$$\xi = \frac{\omega}{k^2 D_1} \tag{17}$$

$$\tilde{a}_2(\xi) = \left(\frac{b_1D_1R_1}{a_1} + \frac{b_2D_2R_2}{a_2}\right)\frac{a_1a_2}{(b_1 + b_2)D_1D_2R_1R_2} \tag{18}$$

$$\tilde{a}_1(\xi) = \left(\frac{D_1^2R_1(R_1 + Q_1)\,(R_1 + 1)}{D_2a_1(R_2 + Q_2)\,(R_2 + 1)} - \frac{D_2R_2}{a_2}\right)P \tag{19}$$

$$\tilde{a}_0(\xi) = \left(\frac{D_1(R_1 + 1)\,(R_1 + Q_1)}{D_2(R_2 + 1)\,(R_2 + Q_2)} - 1\right)P \tag{20}$$

$$P = \frac{\alpha\beta_1a_1a_2}{D_1D_2(b_1 + b_2)\,[\eta_1(Q_1 + 1) + \eta_2(Q_2 + 1)]\,[(R_1 + Q_1)\,(R_1 + 1)R_1R_2]} \tag{21}$$

We will first give a detailed mathematical analysis of the compatibility equation (Eq. 16).

After that, we will discuss the physical meaning through instability conditions involving experimental parameters: diffusion profiles and coefficients, adsorption-desorption coefficients, and Schmidt numbers (D_γ/ν_γ).

MATHEMATICAL ANALYSIS

In the absence of adsorption-desorption barrier, the system is diffusion-controlled ($a_\gamma \to \infty$, $b_\gamma \to \infty$, $0 < b_\gamma/a_\gamma < \infty$) and the compatibility equation (Eq. 16) reduces to a second-order relation in the wavenumber k (Sternling-Scriven, 1959). The barrier, thus, increases the number of conditions and new possibilities of instabilities occur.

For unstable and marginal nonoscillating cases, ξ is a nonnegative dimensionless parameter. Henceforward, the analysis will be the study of Eqs. 16-21 for nonnegative values of ξ and thus the search for unstable states. Then, because of Eqs. 5 and

TABLE 1. INFLUENCE OF A TWO-STEP PROCESS

Physical Characteristics	Commentary	Regime
$D_\gamma \to \infty; \quad \delta C_\gamma \to 0$	Adsorption-desorption controlled in both phases	Always stable
$a_\gamma,\ b_\gamma \to \infty$ $0 < \frac{a_\gamma}{b_\gamma} < \infty$	Diffusion controlled in both phases	See Table 1
$\frac{D_1}{D_2} = \left(\frac{a_1}{a_2}\right)^{1/2}$	Both the diffusion and the adsorption-desorption define the instability	
$\beta_1 D_1\left(\frac{D_1}{\nu_1} - \frac{D_2}{\nu_2}\right) < 0$		Stable with respect to oscillations
$\beta_1 D_1\left(\frac{D_1}{\nu_1} - \frac{D_2}{\nu_2}\right) > 0$		Unstable with respect to oscillations
$b_1,\ a_1 \to \infty; \quad 0 < \frac{a_1}{b_1} < \infty$ $D_2 \to \infty; \quad \delta C_2 \to 0$	Diffusion controlled in phase 1 adsorption-desorption controlled in phase 2	
$\Gamma^o b_2 > \lvert\beta_1\rvert D_1$		Stable with respect to oscillations
$\Gamma^o b_2 < \lvert\beta_1\rvert D_1$		Unstable oscillatory zone between two stable ones or Stability with respect to oscillations

14, R_γ and Q_γ are larger or equal to one (neutral stability) and the coefficient $\tilde{a}_2(\xi)$ is always positive. The factor P is positive or negative according to the sign of β_1: P is positive for steady transfer from 1 to 2 and negative for transfer from 2 to 1. Whatever nonnegative ξ considered, P is different from zero.

What are the relations which will promote nonoscillatory instability? According to the Descartes theorem on the sign changes of consecutive coefficients of a polynom:

- If $\tilde{a}_0(\xi)$ and $\tilde{a}_1(\xi)$ are both positive, there is no positive real solution of Eq. 16. Aperiodic, unstable states are thus not allowed.
- If $\tilde{a}_0(\xi)$ is negative, whatever the sign of $\tilde{a}_1(\xi)$, there is one and only one real wavenumber solution of Eq. 16, leading thus to an unstable solution.
- If $\tilde{a}_0(\xi)$ is positive and $\tilde{a}_1(\xi)$ is negative, we have one of the two following possibilities. Either there exists two positive real solutions of Eq. 16 and thus unstable states will be expected, or there is no real solution and no aperiodic instability will occur. A more refined analysis is then required and we will use the classical Sturm method which is a generalization of the Descartes theorem.

When the following inequality is satisfied:

$$\frac{\tilde{a}_2(\xi) - [\tilde{a}_2^2(\xi) - 3\tilde{a}_1(\xi)]^{\frac{1}{2}}}{3} < \frac{\tilde{a}_2(\xi)\tilde{a}_1(\xi) - g\tilde{a}_0(\xi)}{2[\tilde{a}_2^2(\xi) - 3\tilde{a}_1(\xi)]} \tag{22}$$

we obtain two positive wavenumbers. Otherwise, there is no positive roots.

We must search for all the changes of sign of $\tilde{a}_0(\xi)$ and $\tilde{a}_1(\xi)$ for $0 \leqslant \xi \leqslant \infty$. As these coefficients are proportional to P, they depend also on the direction of the transfer of matter. Let us then rather analyze:

$$\frac{\tilde{a}_0(\xi)}{P} = \frac{D_1(R_1 + Q_1)\,(R_1 + 1)}{D_2(R_2 + Q_2)\,(R_2 + 1)} - 1 \tag{23}$$

Sternling and Scriven (1959) have shown that this function has one and only one finite root for $\xi = \xi_o$ provided that:

$$\left(\frac{D_1}{D_2} - 1\right)\left(\sqrt{\frac{D_1}{\nu_1}} - \sqrt{\frac{D_2}{\nu_2}}\right)^{-1} < 0 \tag{24}$$

This criterion is independent of the existence of a potential barrier and was deduced from the limiting behavior of $\tilde{a}_0(\xi)P^{-1}$ for $\xi \to 0$ and $\xi \to \infty$.

The existence of this finite zero ξ_0 implies that $k = 0$ is a solution of Eq. 16. To this value of k corresponds a marginal state ($\omega = 0$) because of the definition (Eq. 17). One should then study the remaining second-order equation:

$$k^2 + \tilde{a}_2(\xi_0)k + (\xi_0) = 0 \tag{25}$$

If $\tilde{a}_1(\xi_0)$ is negative, there exists a positive wavenumber and thus a corresponding amplification factor ω different from zero. If $\tilde{a}_1(\xi_0)$ is positive, the last equation has no real positive solution and Eq. 16 has only one solution for $\xi = \xi_0$, which corresponds to marginal stability.

$$\frac{\tilde{a}_1(\xi)}{P} = \frac{D_1^2R_1(R_1 + Q_1)\,(R_1 + 1)}{D_2a_1(R_2 + Q_2)\,(R_2 + 1)} - \frac{D_2R_2}{a_2} \tag{26}$$

This function has at least one finite zero $\xi = \xi_1$, when $\lim\limits_{\xi \to 0} \tilde{a}_1(\xi)/P$ and $\lim\limits_{\xi \to 0} \tilde{a}_1(\xi)/P$ have opposite signs. More explicitly, this will be in case when:

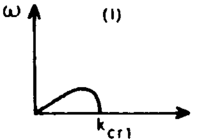
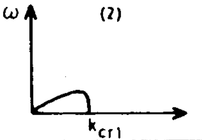
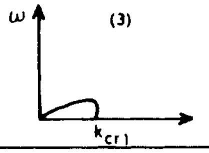
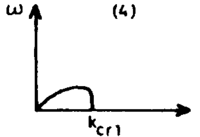
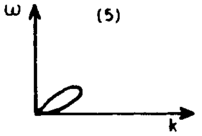
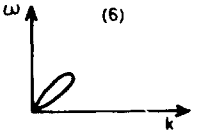
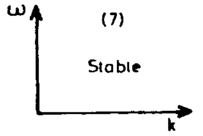
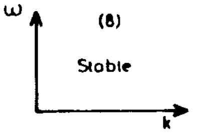
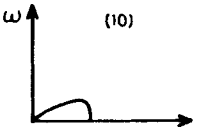
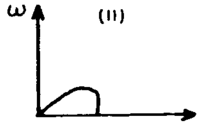
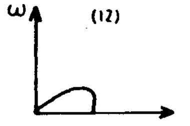
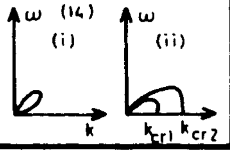
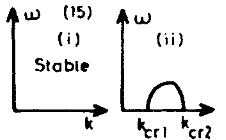
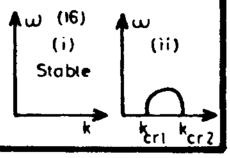
$$\left(\frac{D_1^2}{a_1} - \frac{D_2^2}{a_2}\right) \left(\frac{\sqrt{D_1}}{a_1\left(1 + \sqrt{\frac{D_2}{\nu_2}}\right)} - \frac{\sqrt{D_2}}{a_2\left(1 + \sqrt{\frac{D_1}{\nu_1}}\right)}\right)^{-1} < 0 \tag{27}$$

The barrier plays here an important role. When $\xi \to \infty$, Eq. 16 has a physically meaningful solution provided that:

$$\beta_1\left(\frac{1}{1 + \sqrt{\frac{D_1}{\nu_1}}} - \frac{1}{1 + \sqrt{\frac{D_2}{\nu_2}}}\right) > 0 \tag{28}$$

Then k and ω decrease as ξ^{-1} and we expect a marginal state. The demonstration is similar to the one given by Ruckenstein

TABLE 2. GENERAL REPRESENTATION $\omega = \omega(k)$

$A_1 = (D_1/D_2 - 1)\beta_1$ $A_2 = (D_1^2/D_2^2 - a_1/a_2)\beta_1$ $A_3 = \dfrac{(D_1^2/D_2^2 - a_1/a_2)}{\left(\sqrt{\frac{D_1}{D_2}}\left(1-\sqrt{\frac{D_2}{\nu_2}}\right) - \frac{a_1}{a_2}\left(1-\sqrt{\frac{D_1}{\nu_1}}\right)\right)}$ $A_4 = \left(\frac{D_1}{D_2} - 1\right)\Big/\left(\frac{D_1}{\nu_1} - \frac{D_2}{\nu_2}\right)$		ξ_0 and ξ_1 $\exists$	ξ_0 $\exists$ and ξ_1 $\nexists$	ξ_0 $\nexists$ and ξ_1 $\exists$	ξ_0 and ξ_1 $\nexists$
		$A_3 < 0$ and $A_4 < 0$	$A_3 > 0$ and $A_4 < 0$	$A_3 < 0$ and $A_4 > 0$	$A_3 > 0$ and $A_4 > 0$
$\tilde{a}_0(0) < 0$ and $\tilde{a}_1(0) < 0$	$A_1 < 0$ and $A_2 < 0$				
$\tilde{a}_0(0) > 0$ and $\tilde{a}_1(0) > 0$	$A_1 > 0$ and $A_2 > 0$				
$\tilde{a}_0(0) < 0$ and $\tilde{a}_1(0) > 0$	$A_1 < 0$ and $A_2 > 0$	(9) Inconsistency of the Inequalities (13)			
$\tilde{a}_0(0) > 0$ and $\tilde{a}_1(0) < 0$	$A_1 > 0$ and $A_2 < 0$				

and Berbente (1964).

Let us analyze the compatibility equation (Eq. 16) in terms of the existence or nonexistence of ξ_0 and ξ_1 and the limiting behavior for $\xi \rightarrow \infty$. We will consider that $\tilde{a}_1(\xi)P^{-1}$ has, at most, one zero. Furthermore, we need to know the signs of $\tilde{a}_1(0)$ and $\tilde{a}_0(0)$ which determine the marginal state corresponding to finite k ($k = k_{cr}$) and to $\xi \rightarrow 0$.

Instead of solving numerically the compatibility condition (Eq. 16), the above analysis leads to draw the topological behavior $k = k(\xi)$ and $\omega = \omega(\xi)$. The bi-univocity of these functions gives the general representation $\omega = \omega(k)$ (Table 2).

INSTABILITY CONDITIONS

The above analysis gives 16 different possibilities (Table 2) corresponding to a peculiar set of relationships between the Schmidt numbers $D_\gamma \nu_\gamma^{-1}$, the adsorption-desorption coefficients $a_\gamma b_\gamma^{-1}$ and the ratio of the diffusion coefficients $D_1 D_2^{-1}$. Only 14 cases are consistent. Indeed, when $\tilde{a}_0(0)$ and $\tilde{a}_1(0)$ have opposite signs, the simultaneous existence of ξ_0 and ξ is not allowed.

The results of this analysis are shown in Table 2 for positive values of k and ω. The figures describe the various domains of aperiodic instabilities. The unstable states for $k \rightarrow 0$ and $\omega \rightarrow 0$ depend on the existence of ξ_0 and on the limit $\xi \rightarrow \infty$. The conditions Eqs. 24 and 28 are independent of the barriers of adsorption-desorption. However, the marginal state ($k = k_{cr}$) corresponding to $\xi = 0$ may depend on the adsorption-desorption parameters. In cases 1 to 4 and 10 to 12, $\tilde{a}_0(0)$ is negative and there is only one critical value ($k = k_{cr}$).

For the cases 5 to 8, there is no critical wavenumber different from zero since $\tilde{a}_0(0) > 0$ and $\tilde{a}_1(0) > 0$. For the cases 14 to 16, we have $\tilde{a}_0(0) > 0$ and $\tilde{a}_1(0) < 0$. We have then to consider the following inequality deduced from inequality (Eq. 22) for $\xi = 0$.

$$\frac{1}{3}\left\{\frac{\left(\frac{b_1}{a_1}D_1+\frac{b_2}{a_2}D_2\right)a_1a_2}{D_1D_2(b_1+b_2)} - \left[\frac{a_1a_2\left(\frac{b_1}{a_1}D_1+\frac{b_2}{a_2}D_2\right)}{D_1D_2(b_1+b_2)}\right]^2 + \frac{3a_1a_2\alpha\beta_1\left(\frac{D_1^2}{D_2a_1}-\frac{D_2}{a_2}\right)}{8D_1D_2(b_1+b_2)\,(\eta_1+\eta_2)}\right\}$$
$$< \frac{\left(\frac{b_1}{a_1}D_1+\frac{b_2}{a_2}D_2\right)\frac{a_1a_2\alpha\beta_1}{D_1D_2(b_1+b_2)}\left(\frac{D_1^2}{D_2a_1}-\frac{1}{D_2}\right) - 9\left(\frac{D_1}{D_2}-1\right)\frac{\alpha\beta_1}{\eta_1+\eta_2}}{16\left[\left(\frac{b_1}{a_1}D_1+\frac{b_2}{a_2}D_2\right)^2\frac{a_1a_2}{D_1D_2(b_1+b_2)} - \frac{3\alpha\beta_1}{8(\eta_1+\eta_2)}\left(\frac{D_1^2}{D_2a_1}-\frac{D_2}{a_2}\right)\right]} \tag{29}$$

If it is satisfied, we have two finite wavenumbers k_{cr1} and k_{cr2} (case ii). When not, there is no finite marginal wavenumber (case i). To obtain Table 2, we assume that inequality (Eq. 22) separates two domains on the ξ axis following whether it is satisfied or not. Should there be more domains along the axis with respect to this inequality, the following graphs would be more complicated: cases 1, 2, 5, 7, 14, 15, 16. When the transfer of matter is from the phase with the lowest diffusion coefficient towards the other (cases 1 to 4 and 10 to 12), we recover essentially the same results as those obtained by Sternling and Scriven.

The presence of unstable solutions do not depend on the surface barrier. However, the wavenumber corresponding to the maximum time constant and the precise marginal wavenumber are functions of the adsorption-desorption coefficients.

When the direction of transfer is reversed, the barrier plays an important role. The rate of adsorption-desorption coefficient has to be compared to the square of the rate of the diffusion coefficients. This will distinguish between the cases where the criteria of Sternling-Scriven are recovered for the aperiodic behavior (cases 5 to 8) and those where the inequality (Eq. 29) is required (cases 14 to 16). In other words, when the transfer is from the phase with the largest diffusion coefficient toward the other transfer has also to be from the phase with the large adsorption coefficient to the other phase. This results from the fact that the ratio of the adsorption coefficient has to be larger than the ratio of the square of the diffusion coefficient.

As an illustration of case 16ii, let us examine reasonable experimental data derived from the analysis of England and Berg (1971):

$$\begin{array}{lll} D_1 = 10^{-5}\ \mathrm{cm}^2\ \mathrm{s}^{-1}; & D_2 = 5 \cdot 10^{-7}\ \mathrm{cm}^2\ \mathrm{s}^{-1}; & \eta_1 = 10^{-2}\ p; \\ \eta_2 = 2 \cdot 10^{-1}\ p; & a_1 = 10^{-2}\ \mathrm{cm}\ \mathrm{s}^{-1}; & a_2 = 10^{-5}\ \mathrm{cm}\ \mathrm{s}^{-1}; \\ b_1 = 1\ \mathrm{s}^{-1}; & b_2 = 10\ \mathrm{s}^{-1}; & \alpha\beta_1 = 2 \cdot 10^{-8}\ \mathrm{g}\ \mathrm{cm}^2\ \mathrm{s}^{-1}; \\ \rho_1 = 1\ \mathrm{g}\ \mathrm{cm}^{-3}; & \rho_2 = 0.89\ \mathrm{g}\ \mathrm{cm}^{-3} & \end{array}$$

From the definitions (Eqs. 17 to 21), we get for $\xi = 0$, $\tilde{a}_0(0) = 3.5\ 10^{12}\ \mathrm{cm}^{-3}$; $\tilde{a}_1(0) = -5\ 10^{9}\ \mathrm{cm}^{-2}$; $\tilde{a}_2(0) = 9\ 10^{2}\ \mathrm{cm}^{-2}$, and inequality (Eq. 29) is then satisfied in the vicinity of the marginal state. Parallel roles on the influence of potential barriers were shown by Palmer and Berg (1972), taking also into account the temperature gradient.

CONCLUDING REMARKS

When adsorption-desorption rates are competitive with bulk diffusion fluxes, new kinds of aperiodic instabilities can occur.

Indeed under specific conditions (diffusion profiles and coefficients, Schmidt numbers and adsorption-desorption coefficients an unstable domain separating two stable domains is obtained although the Sternling-Scriven (1959) criteria, valid for diffusion controlled transfers, would predict stable states.

These new situations could play an important role in emulsification (Shah and Schechter, 1977; in surface turbulence (Davies, 1972) in stability and in rupture of thin liquid films (Joosten et al., 1977; Jain et al., 1979b) and in convective processes at biosurfaces (Jain et al., 1979a; Evans and Skalak, 1980). The linear perturbations analysis for longitudinal waves fills up the previous study on periodic instabilities at fluid interfaces (Hennenberg et al., 1980).

All these problems may be viewed as an examplification of the Prigogine-Glansdorff dissipative structures (Glansdorff and Prigogine, 1971; Nicolis and Prigogine, 1977) and their extension to capillary systems (Steinchen and Sanfeld, 1980).

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NOTATION

A = surface area
a_γ = adsorption coefficient
$\tilde{a}(\xi)$ = quantities defined by Eqs. 22-24
b_γ = desorption coefficient
C^o = solute concentration in the bulk phase
C^{oo} = solute concentration at the reference surface
D = diffusion coefficient
J = flux of matter
J^d = diffusion flux
J^{a-d} = adsorption-desorption flux
k = wavenumber
k_r = real part of the wavenumber
k = critical value of the wavenumber
Q_γ = quantity defined by Eq. 5
R_γ = quantity defined by Eq. 14
δ_p = perturbed hydrostatic pressure
P = quantity defined by Eq. 21
v = perturbed velocity
x_j = tangential coordinate
z = normal coordinate

Greek Letters

α = constant of the surface state equation (Eq. 11)
β = coefficient of the diffusion profile
Γ = surface concentration
ϵ = compositional dynamic surface elasticity
λ = wavelength
η = shear viscosity of the bulk phase
ν = kinematic viscosity
ω = time coefficient of the perturbation
ω_r = real part of the time coefficient of the perturbation
ρ = density
σ = surface tension
ξ = quantity defined by Eq. 17

Subscripts and Superscripts

0 = steady state
γ = phase 1, 2

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Model-Based Analysis of Data from Countercurrent Liquid-Liquid Extraction Processes

An efficient iterative method for solving the equations which describe the steady state of a staged countercurrent extraction process is described. The equations include the effects of backmixing, and apply to an arbitrary number of solutes, to nonlinear equilibrium relations, and to variable net phase flow rates (and thus to partially miscible solvents). The solution procedure, based on partial linearization of the equations, is related to and extends the method of Ricker et al. (1980).

This solution procedure has been used, in conjunction with nonlinear regression methods, to investigate problems related to the determination of parameters by analyzing steady state data. The simultaneous determination of several parameters, including mass transfer coefficients, backmixing coefficients, and equilibrium constants, is shown to be possible. The accuracy with which the parameters can be estimated depends, however, on many factors, including the number and location of the sampling points, the intensity of the backmixing, and the extent to which equilibrium is approached in the column.

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SCOPE

In the usual method of scaling-up extraction columns based on transfer unit height estimated from pilot plant data, the separate variation of axial dispersion and mass transfer coefficients with column diameter is not taken into account. In order to develop an improved design procedure, it will be necessary to analyze data from pilot plant or bench scale col-

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