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Interfacial Turbulence at the Surface of a Drop in a Liquid-Liquid Reaction System

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Studies of interfacial phenomena in two phase liquid-liquid reaction systems have indicated an enhancement in the rate of the chemical reaction due to the presence of interfacial turbulence. The nature and the magnitude of interfacial turbulence depends upon the systems under consideration, temperature, and the direction for mass transfer.

For the case of mass transfer without chemical reaction (Bakker et al., 1966, 1967), convection cells are formed on the surface of a suspended drop when the mass transfer of solute is toward the drop. Internal and external circulation is observed when the mass transfer is away from the drop. Treating the problem of interfacial turbulence as one of Marangoni instability, Scriven and Sternling (1959) showed that if the interfacial tension decreases with increasing solute concentration, instability occurs whenever the solute is transferred out of the phase of lower solute diffusivity. Presence of instability in this analysis indicated the presence of interfacial turbulence in real systems.

We attempt here an order of magnitude estimation of the scale and velocity of convection cells due to interfacial turbulence and their contribution to the rate process.

EXPERIMENTAL APPARATUS

The optical system used to observe interfacial turbulence consisted of an optical bench, a prefocused lamp, an adjustable slit, a 10X objective, a corresponding eyepiece and a Bauch and Lomb L photomicrographic camera mounted horizontally. The camera was equipped with a 3¼-in. by 4¼-in. ground glass screen for visual observation and a cut film holder for taking pictures. For most of the photographs, shutter speeds of 1/25 and 1/50 seconds were used.

Reactions were carried out in a 10 × 10 × 80 mm optical cell placed inside a 20 × 30 × 60 mm optical cell on a support grid. The outer cell was provided with an inlet and outlet for circulating water at a predetermined temperature from a water bath. A Gilmont microburet 0.2 ml in capacity and accurate to 0.0002 ml was used to suspend the drops. The tip of the microburet was carefully treated with a dilute solution of Siliclad to make it nonwetting to aqueous solutions and obtain nearly spherical drops.

Before every run, the microburet was taken apart, washed in distilled water, dried, and reassembled. Reactant A was sucked into the buret and the continuous phase reactant B was placed in the inner cell. Water was circulated in the outer cell. About 30 minutes were allowed for achieving steady state in temperature, and then a drop was carefully formed at the tip of the microburet. It was observed on the ground glass screen. Several times during the course of a reaction, the ground glass screen was replaced by a cut-film holder and photographs were taken. Photographs were enlarged to an 8 × 10-in. print size before analysis. Many times the negative was projected on a screen for counting and averaging cell areas. On the print a cell of a 1 micron occupied 0.3 mm-1.0 mm depending on the degree of enlargement. Accuracy of cell size measurement was limited to 0.5 microns. The velocity of the cells was measured by timing movements of individual cell image on the surface of the drop. Points on Figures 1 and 2 represent average values of a number of observations which followed a single cell about 2 cm for about 2 seconds. The accuracy of the velocity was limited to 0.5 microns/sec. Scriven's (1961) criteria was used to determine the direction of the reaction zone movement. In all cases considered here the reaction zone had moved into the dispersed drop phase.

Reactants Used

Two reaction systems were used. In the first pure ethyl acetate constituted the organic continuous phase and dilute NaOH (in the concentration range 0.08 to 0.3N) was the dispersed phase. The second system consisted of a 50% solution of the toluene in DiEthylAmine (DEA) as the continuous organic phase and a dilute solution of acetic acid (25% to 45% by weight) as the dispersed phase.

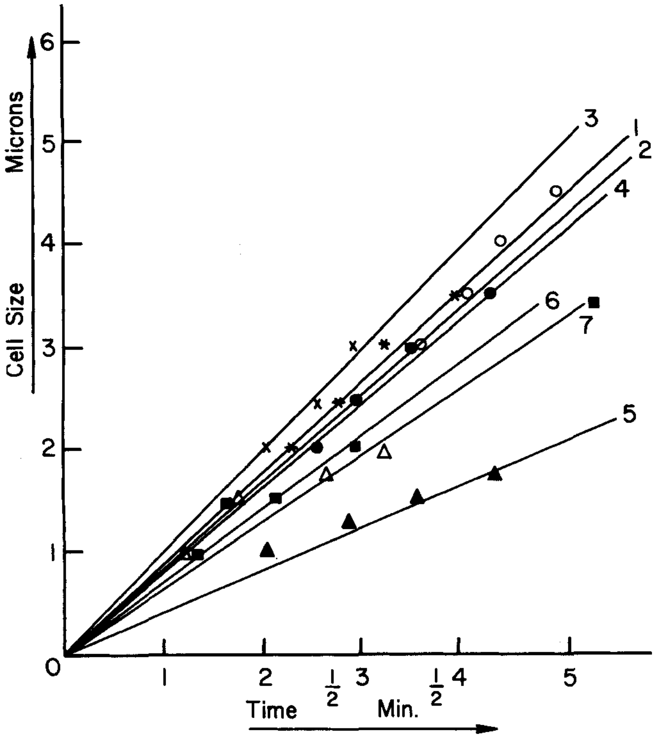

Fig. 1. Growth of cell size with time.
* 0.1092N NaOH-ethyl acetate, 15°C;
⊙ 0.300N NaOH-ethyl acetate, 15°C;
× 0.1092N NaOH-ethyl acetate, 50°C;
● 0.0795N NaOH-ethyl acetate, 30°C;
▲ 30% HAc by weight—50% DEA in toluene, 15°C;
■ 45% HAc by weight—50% DEA in toluene, 15°C;
△ 45% HAc by weight—50% DEA in toluene, 30°C.

OBSERVATIONS

As indicated in Figures 1 and 2, convection cells grew as a linear function of $t^{1/2}$ and their velocity on the surface of the drop (assumed to be of the same order of magnitude as the velocity within an individual cell) was proportional to $t^{-1/2}$. Higher temperatures and higher concentrations, factors which contribute to a greater rate of chemical reaction, increased the rate of growth of these cells as evidenced by higher slopes in the graphs shown. The cell sizes varied from some immeasurable and small value at the beginning of the reaction to about 3 to 4 microns after 15 minutes for a drop of 250 microns. The cellular velocity varied in the range 10 microns/sec to 5 microns/sec. Experimental observations suggest that the convection cells move in a somewhat random fashion within the pattern of cells on the surface of the drop and that the movement of the entire pattern of cells on the surface of the drop is similar to that due to natural convection.

EXPLANATIONS OF OBSERVATIONS

In accordance with the criterion of Scriven and Sternling (1959), it is suggested that the diffusion of the product from the reaction zone across the interface is usually responsible for the presence of interfacial turbulence in reaction systems, that is, whenever a product diffuses into a phase in which its diffusivity is of a larger value. In addition, it is suggested here that the scale λ and velocity V_λ of interfacial turbulence in cases of the type described here are controlled by local fluid mechanics, by convection across cells of scale λ near the phase interface, and by resultant effective diffusion to the interface from the reaction front, a distance which soon becomes larger than λ. Effective diffusivities have been found to be larger than molecular diffusivities by factors of 2 or 3, and the scales λ have been found to be much smaller than the usual size of droplets dispersed in liquids. The product λV_λ was found here to be a time independent constant proportional to D_{pd}, the diffusivity of the product of reaction in the dispersed phase.

Our results are best understood in terms of a nonsophisticated theory that emphasizes limits on complex physico-chemical happenings.

In the observed cell layer near the interface, the viscous stress associated with motion can be equated to the interfacial stress driving the flow

$$\sigma_c \, \Delta C_\lambda/\lambda \simeq \mu \, V_\lambda/\lambda \tag{1}$$

where ΔC_λ is a characteristic concentration difference found in the region λ, σ_c is the change in the interfacial tension per unit change in the concentration of product (a physical property of the system) and μ is dispersed phase viscosity. ΔC_λ, for the pseudo steady process suggested above, is related to the time averaged product concentration profile by

$$\Delta C_\lambda \simeq \lambda (dC_{pd}/dx)_{x=0} \tag{2}$$

if ΔC_λ applies to directions normal as well as parallel to the phase interface. The convective effect of cellular convection can be estimated by a correlation for stagnation flow over half of the interface, that is, by

$$\frac{\lambda (dC_{pd}/dx)_{x=0}}{\Delta C_\lambda} \simeq f(\lambda \, V_\lambda/D_{pd})^{1/2} \tag{3}$$

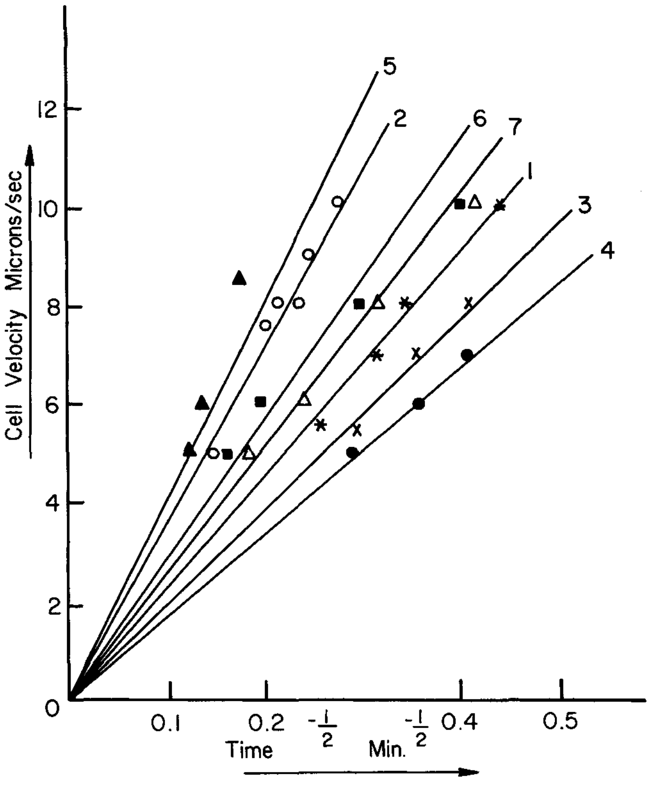

Fig. 2. Variation in cell velocity with time.
* 0.1092N NaOH-ethyl acetate, 15°C;
⊙ 0.300N NaOH-ethyl acetate, 15°C;
× 0.1092N NaOH-ethyl acetate, 50°C;
● 0.0795N NaOH-ethyl acetate, 30°C;
▲ 30% HAc by weight—50% DEA in toluene, 15°C;
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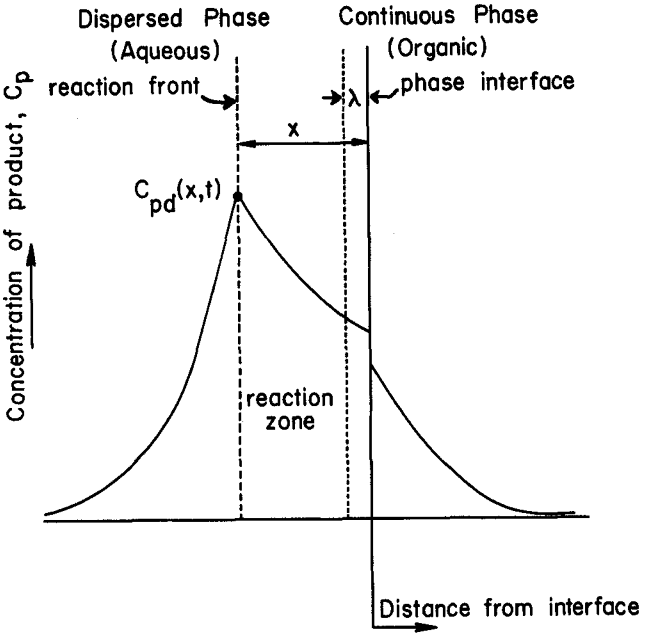

Fig. 3. Product concentration profile for a two phase liquid-liquid reaction system.

where f is a constant, equal approximately to one-half. D_{pd} is the molecular diffusivity of the product. Combination of the last two equations gives

$$\lambda V_\lambda \simeq \frac{1}{f^2} D_{pd} \tag{4}$$

indicating the diffusive restriction on transfer for fully developed interfacial turbulence.

An independent expression for λ, or V_λ, can be developed from the first equation if $(dC_{pd}/dx)_{x=0}$ is predictable on the large scales of reaction zone distance. Assuming that the analysis for molecular diffusion and reaction is a sufficient model (Scriven, 1961) in the case of cellular interfacial turbulence, if all diffusivities are equal to the effective diffusivity $\lambda V_\lambda/2$,

$$(dC_{pd}/dx)_{x=0} \simeq - \overset{\sigma}{\text{♀}}\, C_{B_c}/(\pi\lambda V_\lambda t/2)^{1/2} \tag{5}$$

where $\overset{\sigma}{\text{♀}}$ is a function of initial reactant concentration ratio and the equilibrium concentration distribution constant of reactant and product, C_{B_c} is the reactant concentration in bulk phase and t is the time in seconds of the pseudo steady process of reaction zone movement. Under these circumstances,

$$\lambda \simeq \sqrt{\frac{\mu(\pi D_{pd}^3 t/2)^{1/2}}{f^3 \overset{\sigma}{\text{♀}} \sigma_c C_{B_c}}} \tag{6}$$

A $\sigma_c = 3$ dynes/cm (g/cm^3) was measured for sodium acetate and predicted λV_λ and λ are of the order of those observed experimentally.

ROLE OF INTERFACIAL TURBULENCE IN DISPERSED LIQUID-LIQUID REACTION SYSTEMS

Because interfacial turbulence is a pseudo steady state process soon limited by diffusion controlled convection at the phase interface, it is unlikely that it plays an important role in practical reaction systems.

For an emulsion with a viscosity of 10^{-2} poise and a phase density difference in the range 0.05 to 0.10 g/cm^3 calculations of typical velocities due to gravitational and natural convectional forces showed that the velocities which can be generated by interfacial turbulence are of the same order of magnitude as convection driven velocities for a dispersion smaller than 10 microns average size but are much smaller for larger dispersions.

CONCLUSIONS

In a two-phase liquid-liquid reaction system with a stationary suspended drop of A in a continuum of B, distinct convection cells appear when the mass transfer of B is directed towards the drop surface to reach a reaction zone moving into the drop. The cells grow in size proportional to the square root of time. The appearance of the cells depend upon the concentrations and temperatures of the reaction system or, in general, on the rate of chemical reaction. The product of cell size and its velocity on the surface of the drop is independent of time. It is of the same order of magnitude as the diffusivity of the solute which is responsible for the presence of interfacial turbulence according to the criterion of Scriven and Sternling (1959). The order of magnitude of the scale and intensity of interfacial turbulence is similar to the mixing generated by gravitational and natural convectional driving forces for a dispersion with mean droplet size of about 10 microns. For dispersions with larger mean sizes and in the presence of free and forced convection, for example, in a stirred tank reactor, this kind of interfacial turbulence can be expected to be of little or no consequence.

ACKNOWLEDGMENT

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NOTATIONS

A = dispersed phase reactant
B = continuous phase reactant
P = product of the reaction
f = constant [Equation (3)] dimensionless
$\overset{\sigma}{\text{♀}}$ = function of initial concentration ratio and equilibrium concentration distribution constant of reactant and product (Scriven, 1961)
t = time, s
x = distance from interface, cm
C_{B_c} = concentration of B in continuous phase, g/cm^3
C_{pd} = concentration of P in dispersed phase, g/cm^3
D_{pd} = diffusivity of P in dispersed phase, cm^2/s
ΔC_λ = characteristic concentration difference in region λ [Equation (1)], g/cm^3
λ = characteristic cell size, micron
μ = viscosity, poise
V_λ = characteristic cell velocity, microns/s

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