

## 物質移動中の界面現象

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## Interfacial Phenomena During Mass Transfer

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## Abstract

Unusually high mass transfer rates are often observed in fluid-fluid contacting operations. This may, in part, be attributed to the turbulent motions in the bulk phases which are expected to bombard the interface. In many systems, however, the interface itself may become active as mass transfer proceeds and the induced convection activities will undoubtedly enhance significantly the interphase mass transport. The general aspects of this problem are discussed briefly.

## Introduction

The contacting of unequilibrated fluid phases with the object of exchanging matter between them constitutes the heart of such processes as distillation, absorption, and extraction. The overall mass transfer efficiency depends on many interrelated factors, including the mass transfer rates in both phases, the interfacial resistance, if any, the contact time between the phases, and the interfacial area. Mass transfer rates, in turn, depend on flow geometry, flow characteristics and boundary conditions. Several models have been proposed to correlate the experimental data on mass transfer coefficients and to understand the underlying physical process. Predictions of transport behavior at high mass-transfer rates from the conditions of turbulent flow, for example, have been attempted, and a knowledge of mass transfer has progressively been refined.

The effects are strange, however, when quiescent but unequilibrated liquid layers are carefully brought into contact. They exhibit spontaneous rippling, twitching, emulsification, and other exotic forms of visible motion at the interface. Such convection acti-

vities accompanying transfer of solute across the interface, in any of its bizarre forms, unquestionably assist in the interphase mass transport and often lead to mass transfer rates considerably greater than those predicted by molecular diffusion alone.

The proper interpretation of interphase mass transfer experiments and the rational scale up of bench and pilot plant equipment thus require the answer to the questions: (1) What is the mechanism of interfacial convection activities? (2) How can one recognize beforehand the situation in which they will arise? (3) How can one predict their forms and magnitude from first principles? Limited primarily to the first query, this paper attempts to introduce the reader to this rapidly growing subject.

## Models for Turbulent Transfer Coefficients

It may be useful but not necessary to make first a brief discussion on some of the models and developments that have come to light to provide a link between the observed mass transfer coefficients and the state of the turbulent field.

We should start by mentioning the two-film model developed by Lewis and Whitman<sup>1)</sup> in the early

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1920's. In the film model, whatever chaos may be going on in the bulk phases, all resistance to transfer is concentrated in a film of finite thickness on each side of the interface and solute is transferred through this film by steady-state diffusion, as depicted in Fig. 1. This classic theory is patently inadequate for describing the real mechanism of interphase mass transfer in its prediction of a first power dependence of the mass transfer coefficient on the diffusion coefficient. In addition, the "fictitious" film thickness cannot be measured or predicted directly.

In 1935 Higbie<sup>2)</sup> abandoned the assumption of a "stagnant film" liquid at the interface, and instead proposed a penetration model in which mass is transferred in the liquid by unsteady-state molecular transport. This model as sketched in Fig. 2 is also certainly oversimplified, but it does predict a square root dependence of mass transfer coefficient on diffusion coefficient which is much closer to experiment than the Lewis-Whitman model. This striking success of the theory has led more recent workers to propose various elaborate models<sup>3-6)</sup>. Some of them are shown in Fig. 3. Particularly noteworthy of them is the well-known surface renewal model of Danckwerts<sup>3)</sup>. The results of other models are similar to Danckwerts' result. He postulated that small chunks of fluid in the turbulent core migrate to the interface, are each subjected to transfer by diffusion for some identical eddy residence time, and then return to the bulk. The mean rate of production of fresh surface, called the surface renewal factor, is constant for a given degree of turbulence in the bulk phase. The mathematical treatment of the model results in the square root dependence of mass transfer coefficient

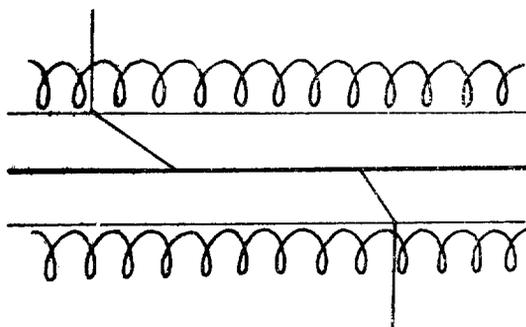


Fig. 1. Lewis-Whitman Two-Film Model.

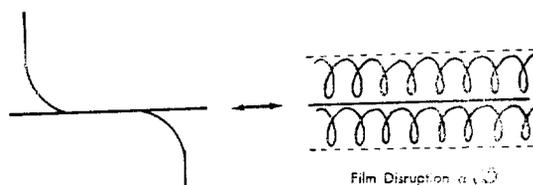


Fig. 2. Higbie Penetration Model.

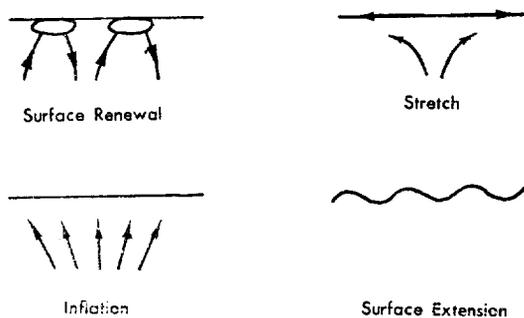


Fig. 3. Mass Transfer Models.

on the surface renewal factor as well as diffusion coefficient.

Predictions of transport behavior thus require a means for evaluating the surface renewal factor based on a physically realistic (but undoubtedly idealized) model of the velocity field near the interface. Several aspects of this problem are considered in recent papers<sup>7-11)</sup>, but no satisfactory quantitative link between mass transfer rates and the turbulent motions has emerged. This area of fluid mechanics needs a much improved understanding. As Fortescue and Pearson<sup>12)</sup> indicate, however, progressively improved agreement with observation has only been achieved at the expense of increasing complexity (and at times the incorporation of more adjustable arbitrary parameters).

## Interfacial Convections

We now discuss various interfacial convections that are thought to be induced by unbalanced buoyant

forces and/or unbalanced interfacial tension forces or build-up of energy barriers in the interfacial region, all of which may be sustained by the mass transfer process itself. Since the driving force for convection originates at the interface, the situation concerned is different from that when the interface is bombarded or disrupted by the large-scale convection currents or any other gross upset originating at distance from the interface.

### Interfacial Turbulence

Consider the situation depicted in Fig. 4 where diffusion is allowed to proceed between the unequilibrated phases A and B. Even in the quiescent system there may be ever-present or momentarily occurring small disturbances about the interface. Such disturbances, in the form of roll cells, sweep fluid radially outward from a particular location 1 at the interface and in some cases may increase the interfacial concentration at that point. Because of symmetry and the necessary conservation of solute the change in solute concentration is the opposite at point 2. Thus, if interfacial tension decreases with increasing solute concentration, such variations in concentration along the interface induce "spontaneously" interfacial tension-driven flows from 1 toward 2. The resulting dilation of the interface at 1 then brings up more undeposited liquid to that point, and thereby the original small disturbance is reinforced and self-amplified as mass transfer proceeds.

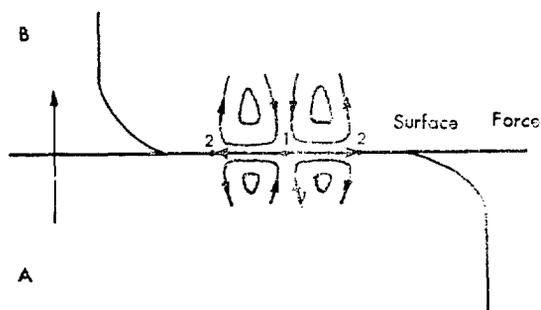


Fig. 4. Generation of Interfacial Turbulence.

Interfacial tension instability was first analyzed theoretically by Sternling and Scriven<sup>13)</sup> in 1959 and the following conditions favorable to it were predicted

based on their quite idealized models: (1) solute transfer out of the phase of higher viscosity, (2) solute transfer out of the phase in which its diffusivity is lower, (3) large differences in kinematic viscosity and solute diffusivity between the two phases, (4) steep concentration gradients near the interface, (5) interfacial tension highly sensitive to solute concentration, [and] (6) low viscosities and diffusivities in both phases. The establishment of these stability criteria is an important step in the understanding of interfacial turbulence, but it has yet furnished neither fundamental information concerning the nature of the developed flows nor design information to be used by the engineer. A great deal of experimental data based on direct observation of "interfacial turbulence" are needed, both to elucidate the nature of the developed flows under various conditions and to construct correlation suitable for design calculations.

Another interesting feature of interfacial tension-driven flows is their ability to be suppressed by small amounts of surface active agents, a fact that has long been known experimentally<sup>14)</sup> and has recently been analyzed theoretically<sup>15,16,17)</sup>. The anticipated stabilizing effect of surface active agents is elaborated with the aid of an example. The system selected is that of nitric acid transferring across the iso-butanol-water interface. This system is particularly interesting for two reasons: First, its properties are such that the Sternling-Scriven criteria for interfacial turbulence due to interfacial tension forces are satisfied when the nitric acid diffuses from the isobutanol into the water, but not when transfer is in the opposite direction; second, a thorough study yielding mass transfer data for this system was published by Olander and Reddy in 1964<sup>18)</sup>. The mass transfer rates obtained in their study were comparable to those predicted from molecular diffusion for transfer from water to isobutanol, but approximately four times greater for transfer in the opposite direction, as might be expected from the theory. If surfactant molecules are present at the interface in this system, they will be swept outward with the movement of the adjoining liquids, as shown in Fig. 5. Since a local drop in surfactant concentration increases the surface tension, surface forces will be established which oppose the outward flow of

the liquid. Such behavior simulates "elasticity." A drop of oleic acid (a traditional surfactant for aqueous systems) injected into the surface was found to damp out virtually all of the convection in its path of spreading over the surface<sup>19)</sup>.

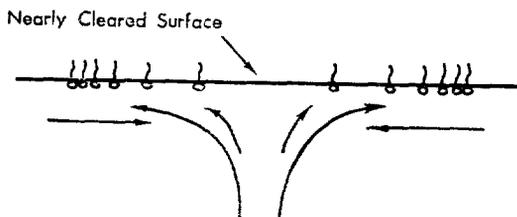


Fig. 5. Illustration of Surface Elasticity.

### Macro-Interfacial Convection

Another important type of interfacial tension-driven convection may arise even when no interfacial turbulence occurs at the planar interface<sup>20)</sup>. This convection is distinct from the former in that it occurs solely by the inherent asymmetric behavior of interphase mass transfer along the curved meniscus near the wall. As shown in Fig. 6, since the rates of mass transfer are always greater near the wall than in the adjoining less curved areas of the interface, these unequal mass transfer rates generate upward surface forces which tend to cause convection currents in the neighborhood of the wall. Meniscus convection activities are so vigorous that Sternling Scriven type of turbulence at the planar interface often plays a minor role in enhancing the total interphase mass transport.

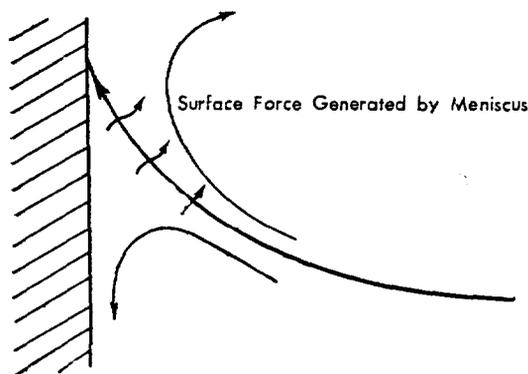


Fig. 6. Generation of Macro-Interfacial Convection.

### Spontaneous Emulsification

Spontaneous emulsification is of wide occurrence in liquid extraction. It will clearly affect the rate of transfer in a stirred system. The mechanisms of spontaneous emulsification are now well understood and need not be discussed here. Yet, another important mechanism has recently been proposed by England and Berg<sup>21)</sup>. They obtained analytical solution for the transfer of an adsorbing solute across a liquid-liquid interface, taking into account the effects of molecular diffusion in both bulk phases, adsorptive accumulation at the interface, and energy barriers to adsorption and/or desorption. These solutions made possible the examination of the nature and relative importance of the above factors as they influence the mass transfer process. The calculations show that the effect of adsorptive accumulation alone on the overall mass transfer rate is small, generally yielding effective interfacial resistances of less than 10 sec/cm for contact times in excess of 1 msec. On the other hand, adsorption and/or desorption barrier, depending on their magnitude, can produce large interfacial resistance persisting for long periods of time. Finally the presence of a desorption barrier could cause the dynamic interfacial tension to pass through a minimum below the steady state value, as shown in Fig. 7. This was evidenced in the exceptional data on the transfer of normal and isobutyric acids from Marcol-70 white oil to water which were obtained using a laminar contracting jet. Under the right conditions, it may be possible for this dynamic interfacial tension to a fall

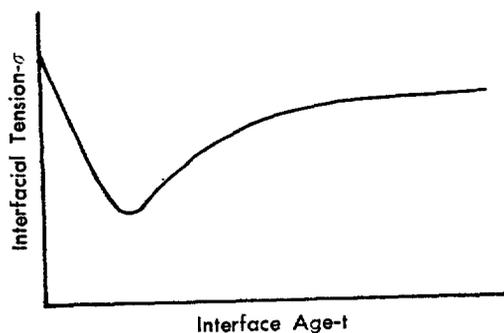


Fig. 7. Generation of Spontaneous Emulsification.

below enough so that a slight agitation could result in so-called spontaneous emulsification.

### Density Convection

Consider again the situation depicted in Fig. 4. With the depletion of the solute from the lower layers of phase A and its enrichment in the upper layers of phase B, several types of density inversion as shown in Fig. 8 may occur near the interface: phase A may become denser in its lower, depleted layers; phase B may become lighter in its upper, enriched layers; or the enriched phase B may become heavier than the depleted phase A beneath. Any of these types of density inversion may lead to an unstable stratification of some of the fluid near the interface and, upon the introduction of a small disturbance, to spontaneous bulk motion. Note that in the last case, the interface itself may be shaken by the density inversion. The occurrence of density convection adds the effect of density streamering to the usual interfacial turbulence, propagating it into the interior of the bulk phase or confining it to the region only directly adjacent to the interface, as shown in Fig. 9. A good example may be taken from the system of benzene transferring across the interface of chlorobenzene-water. This system satisfies the Sternling-Scriven criteria in both phases, so that interfacial turbulence should occur in both phases. As benzene (s.g., 0.879) transfers from the oil (s.g., 1.106) to the water phase (cf. Fig. 10), the resulting density inversion

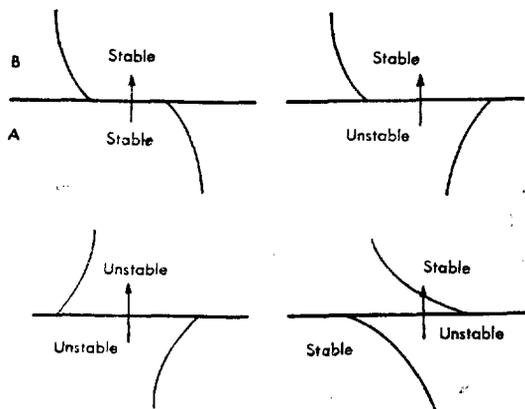


Fig. 8. Generation of Density Convection.

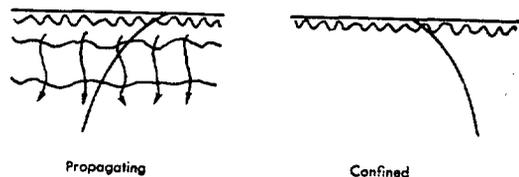


Fig. 9. Density Effects Superimposed on Interfacial Turbulence.

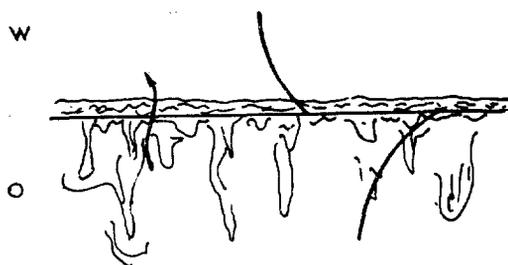


Fig. 10. Convection Pattern Formed During Transfer of Benzene from Chlorobenzene Phase to Water Phase.

in the oil phase will propagate the interfacial turbulence way down the phase. On the other hand, the density inversion in the water phase will confine the interfacial turbulence to the very near region of the interface.

### Experimental Technique

Interfacial convection, unfortunately, is perhaps more often invisible to the naked eye. This is sometimes true because the scale of the flow is very small, being confined to regions within a few microns of the interface. More often, however, it eludes detection because it occurs without distorting or "twitching" the interface.

The injection of dye or suspended solid particles has sometimes been used to render these flows in the bulk phases near the interface visible, but such "contaminants" are often capable themselves of altering the interfacial properties and flow conditions. The schlieren technique is generally used for the direct observation and study of interfacial convection.

The schlieren method of observation is purely optical technique that takes advantage of the variations in refractive index accompanying the mass transfer, so rendering the flows visible without disturbing them. The principle is schematically shown in Fig. 11 (a). The schlieren method is subject to a great many variations. The equipment designed at the University of Washington is shown in Fig. 11 (b).

Light from a 105-w tungsten ribbon-filament lamp is folded with a prism and collimated by a 24-in.  $f/6.0$  Aero Tessar lens. The beam is directed through the capillary slit by means of a mirror with an optically flat front surface,  $M_1$ , and redirected through the medium by a second plane mirror,  $M_2$ . Passing the light beam through the medium twice doubles the sensitivity of the system and allows the same lens to serve as both the collimator and the schlieren

lens. It also makes the system considerably more compact. A knife-edge diaphragm, a blackened razor blade mounted to the movement of a microscope stage, serves to block deflected rays; and a third plane mirror,  $M_3$ , directs the schlieren image into a ground glass screen or onto the film plate of a Graflex (Series B) single-lens reflex camera. The position of  $M_2$  determines the size of the image on the screen. Top views of convection patterns in horizontal fluid layers can be obtained by removing mirror  $M_1$  and replacing it with a horizontal dish, the bottom of which is a plane mirror. The system which proved to be both efficient and versatile was constructed at a total cost of less than \$100.00 (not including the camera). Other versions of the schlieren technique have also been used in the investigation of mass transfer and heat transfer phenomena in fluids<sup>22,23,24</sup>.

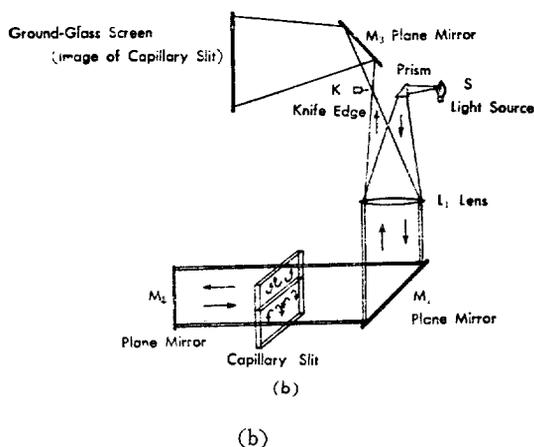
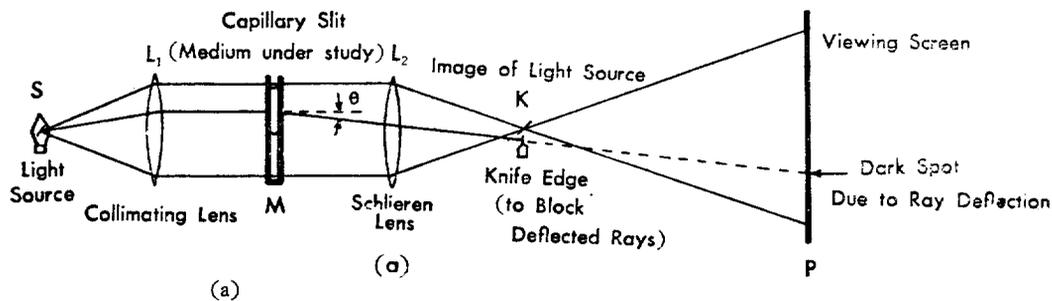


Fig. 11. Schlieren System Construction for the Study of Interfacial Turbulence.

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