

Some Experiments on the Marangoni Effect

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An experimental study of the spreading and dissolving of thin liquid films under the action of surface forces is presented. The method consists of the continuous feeding of a liquid over the surface of another liquid into which it dissolves; the steady film thus obtained covers only a part of the supporting liquid surface, dependent on the flow rate of the liquid fed. The dependence of the radius of the film contour on flow rate and concentration driving force is obtained for various film forming liquids dissolving into water. By using a Schlieren technique the film contour and the flow pattern outside the film contour are studied, several structures being evidenced.

Experiment and theory (3 to 7, 10, 12 to 14, 16 to 18) show that when the Marangoni effect controls the hydrodynamics of the fluid-fluid interfaces the mass transfer is particularly enhanced. The hydrodynamic phenomena which are triggered by the Marangoni effect are complex (3, 5, 6, 11, 14) owing to the interfacial turbulence it may produce, and their detailed examination is difficult. We have examined a less involved manifestation of the Marangoni effect related to dissolving of thin liquid films, and the aim of this paper is to present our observations.

The starting point was our observation that during the reciprocal dissolving of two pure partially miscible liquids (for example, isobutanol and water), conditions for the occurrence of the Marangoni effect may appear. In an open dish a layer of *i*-butanol was placed above a layer of water. If the lighter *i*-butanol is present only in amounts sufficient to form a thin continuous film over the water surface, its thickness decreases continuously as a result of the combined effects of evaporation and dissolving. At a certain moment, the continuous film breaks down and regions of the supporting liquid surface become free of *i*-butanol; thus zones, across which surface tension gradients are present, appear. The rapid movements due to the Marangoni effect now taking place in the plane of the free surface of the supporting liquid lead to an intense agitation, similar to that of a boiling liquid. The agitation ceases suddenly when all the *i*-butanol film has dissolved. Somewhat similar observations have been reported in references 1, 2, 4, 8, 15.

We have "purified" this experiment by controlling the proportion between the covered and free surfaces of the film supporting liquid. This was achieved by feeding continuously one liquid over the surface of another one into which it dissolves; the steady film thus formed covers only a determined fraction of the supporting liquid surface dependent on the flow rate of the liquid fed.

THE EXPERIMENTAL ARRANGEMENT (FIGURE 1)

In all experiments the film supporting liquid (tap water*) was contained in a prismatical transparent, open dish 300 mm. by 300 mm. by 80 mm. The liquid to be dissolved is allowed to flow over the supporting liquid surface from a glass capillary ($D = 1.2$ mm.; I.D. = 0.6 mm.) placed immediately above

the water surface and connected flexibly to a constant flow graduated burette.

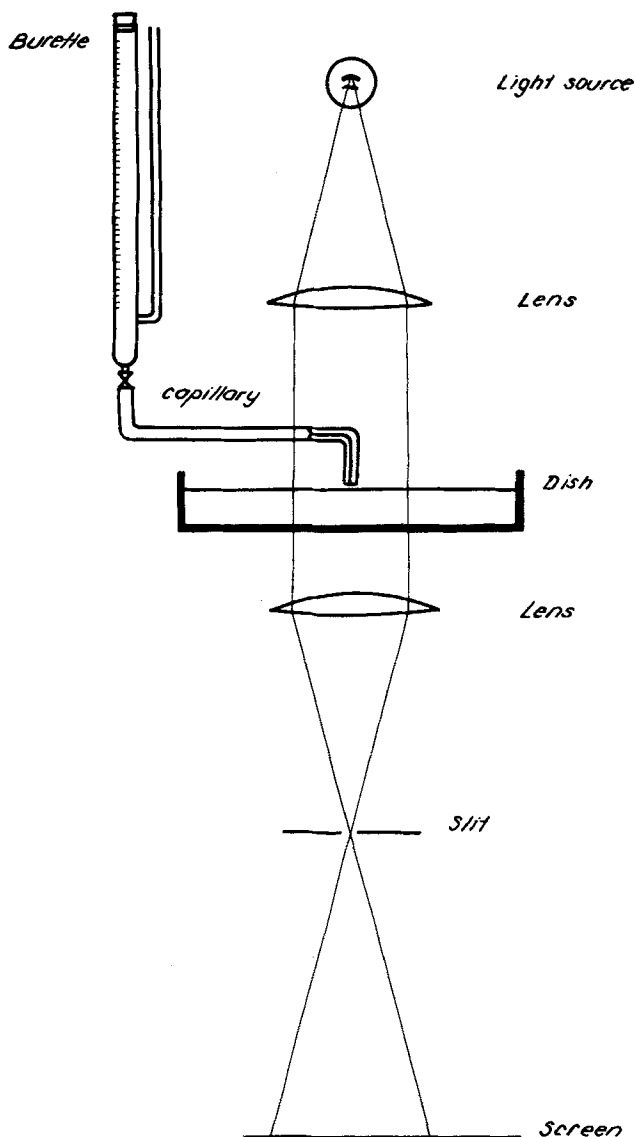


Fig. 1. Scheme of the experimental arrangement.

* No differences have been observed by using water distilled from alkaline-potassium permanganate solutions.

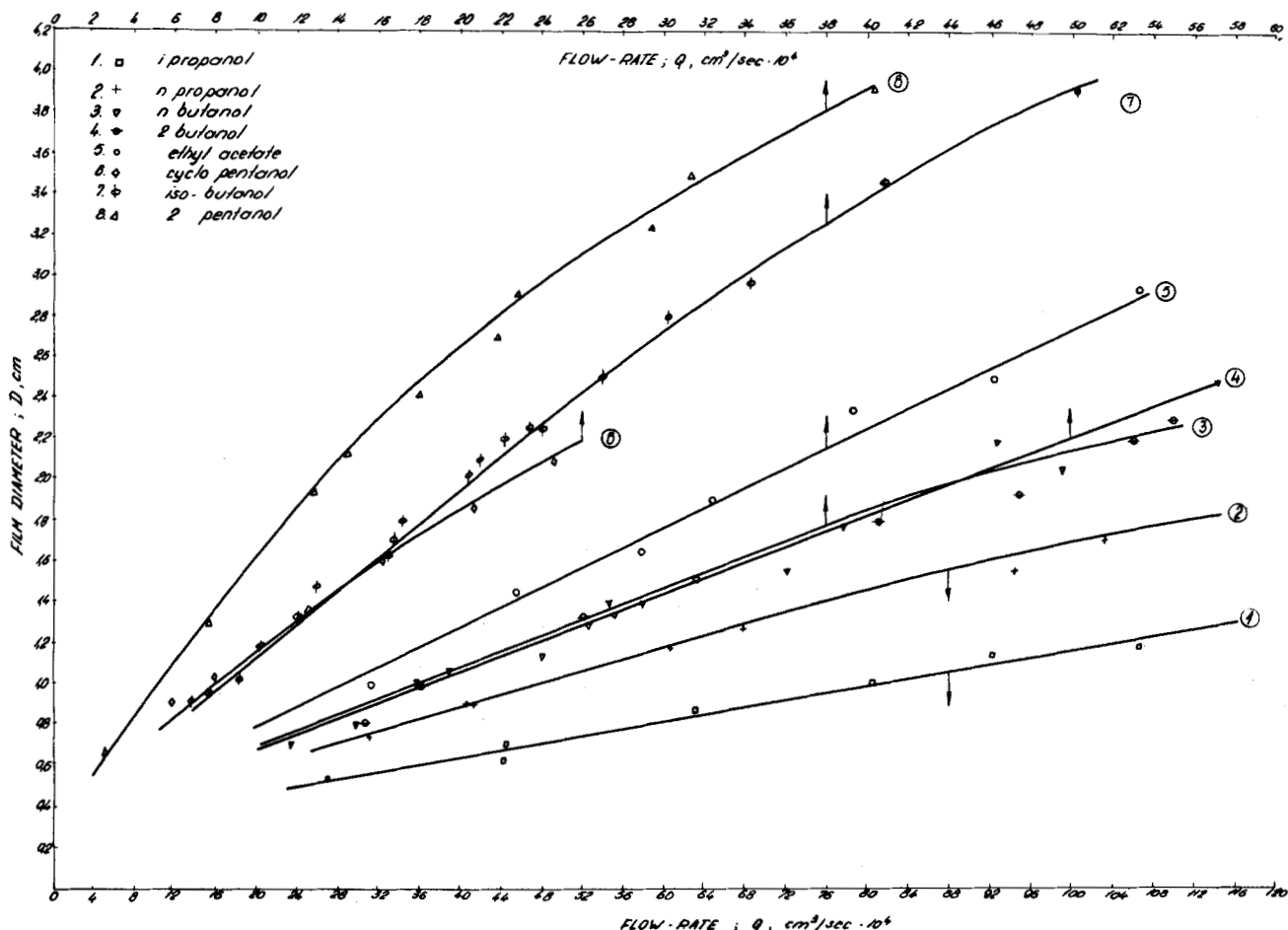


Fig. 2. Dependence of film diameter on flow rate.

The dish and glass capillary were placed in the optical field of a vertically mounted Schlieren device. During the experiments the dish was open and the concentration in water of the organic liquids used did not vary by more than 0.1%. For this reason the dissolution may be considered as proceeding under quasi stationary conditions.

EXPERIMENTAL RESULTS

All liquids partially miscible with water (as well as some of those completely miscible) spread over its surface and form a film having a defined contour, which, in certain conditions, is practically circular. This contour of the film is the origin of radial motions of the free water surface, which, in the absence of surface active agents, are extending over relatively long distances.†

The Dissolving Film

The film contour is circular for small flow rates, its diameter D having a linear dependence on the flow rate Q (Figure 2).

This dependence shows that the dissolving process takes place mainly along the film contour. For sufficiently large values of the flow rate, the circle becomes unstable and the contour of the film oscillates between a circular and an elliptical shape. At still higher flow rates the contour becomes quite irregular (Figure 3).* In the gulfs of

this contour, waves may appear, which at times may be rising more than 1 mm. above the water surface. When high flow rates are used, deep gulfs appearing in various parts of the contour may unite, thus separating "islands" from the main film area which dissolve independently and die out.

The slope β of the lines Q vs. the film contour length P , called in the following the specific dissolving rate, is constant as long as the contour is circular. If the contour ceases to be circular, β increases with increasing flow rate.

The specific dissolving rate depends on the difference ΔC between the saturation concentration of the film forming liquid in the supporting liquid and its actual concentrations in the bulk of the supporting liquid.† This is shown in Figure 4 for an *i*-butanol film dissolving in *i*-butanol aqueous solutions of various concentrations.

The sudden change in slope is probably the consequence of a qualitative change observed to occur in the aspect of the film contour at about the same value of the driving force. Indeed, for driving forces smaller than a certain value, the film contour loses its smoothness and presents along its whole length a multitude of minute indentations pulsating continuously (Figure 5). These small "gulfs" appear at all flow rates, even with film contours having a macroscopically circular form.*

† The size of the dish is important, since for small dish areas the liquid streams generated by the radial motions and reflected by the dish walls and bottom may upset the form of the film. Bottom effects are negligible for water layers deeper than about 15 mm.

* The photographs are taken by placing photographic paper directly over the screen. The white band is the image of the capillary and the small white circle is the image of the meniscus formed around the capillary tip.

† It is to be noted that the ratio $\beta/\Delta C$ has the significance of a mass transfer coefficient along the film contour.

* The nonlinear dependence of diameter on flow rate (the variation of the specific dissolving rate) for cyclopentanol and 2-pentanol (Figure 2) may be put in connection with the indentations appearing at all flow rates along the film contour of these substances.

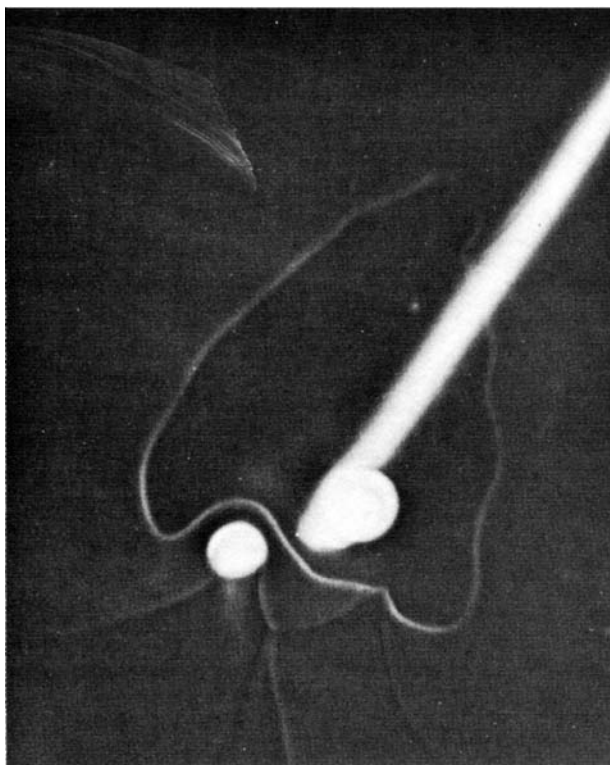


Fig. 3. Iso-butanol film on water. Flow rate, 32.10^{-4} cc/sec.; driving force, 11.1×10^{-4} mole/cc. Magnification ca. 1.8 times. The white circle outside the film contour is given by a wave rising above the water surface.

When the concentration driving force is lowered further, the form of the liquid film becomes more involved; streams are generated in a pulsating manner at or near the film contour and move under the film radially toward the capillary tip or approximately parallel to the contour.

Table 1 gives qualitatively the aspect of the film contour as a function of the concentration driving force. It may be noticed that the contour aspect seems to depend strongly on the driving force and less on the nature of the substance forming the film.

Movements of the Free Surface

Motions of the free (not covered by the film) surface of the supporting liquid take place (when this is not contaminated) from the film contour radially up to the dish walls. After a certain time has elapsed from the beginning of the experiment, a second outer contour, at which all radial motions stop abruptly, is seen to form. This second contour is circular provided the film contour is also circular. The diameter of this contour is decreasing in time. Impurities existing in the water, in the film forming liquid as well as in the atmosphere (since the dish is not covered), accumulate at the air-water interface resulting in a stagnant film probably similar to that described by Merson and Quinn (9). As the amount of surface contaminants increases, the surface covered by the stagnant film becomes larger. Tracer particles spread over the film, move radially toward the film contour at relatively low velocities (estimated to be of the order of millimeters per second), pass across it, and then with much higher velocities (estimated to be of the order of tens of cm./sec.) continue moving radially up to the outer contour. After having crossed the outer contour they move slower and less regularly; once outside the area comprised between the two contours no tracer recrosses the outer contour to enter this area again. The outer contour seems to represent a front along which the spreading forces of the

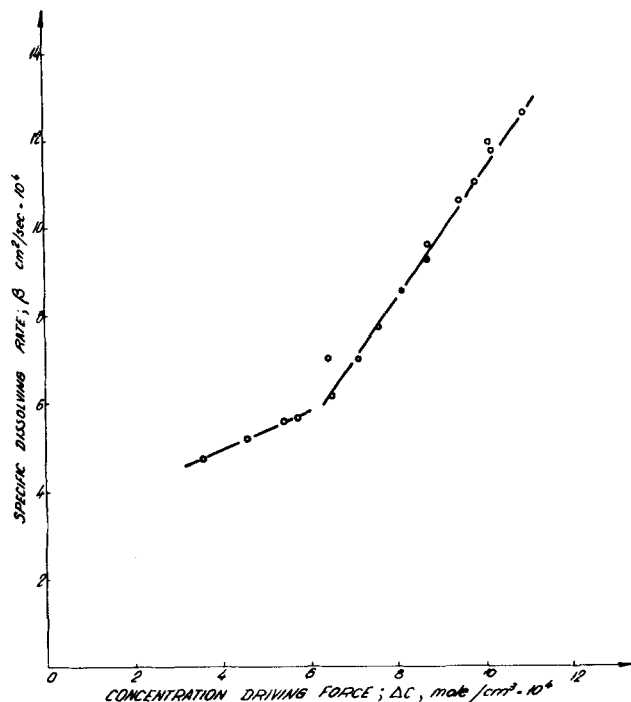


Fig. 4. Dependence of specific dissolving rate on concentration driving force.

stagnant film are in equilibrium with the forces generated by the surface tension gradient existing between the two contours. Indeed, when feeding of the film forming liquid is stopped, the peripheric stagnant film extends over the whole supporting liquid surface in the dish. Resuming the feeding makes the stagnant film to be pushed back outside the outer contour.

The formation of the outer contour may be caused at will by using surface active agents (Figure 6); traces of them markedly diminish the diameter of the outer con-

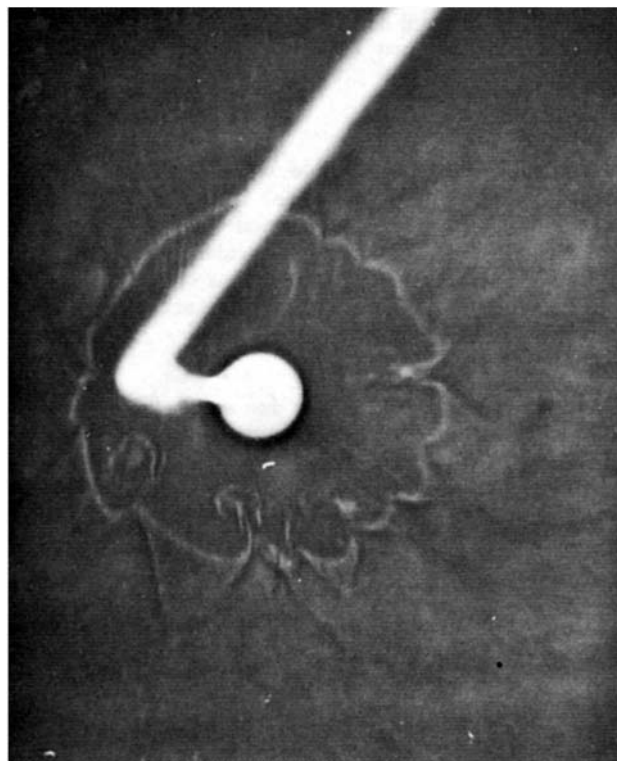


Fig. 5. Iso-butanol film on water. Flow rate, 11.8×10^{-4} cc/sec.; driving force, 6.5×10^{-4} mole/cc. Magnification ca. 2.2 times.

TABLE 1. FILM CONTOUR ASPECT IN RELATION TO THE CONCENTRATION DRIVING FORCE

Concentration driving force,* moles/cc. $\times 10^4$	Substances fed over the water surface	Film Formation	Aspect of the film contour at low flow rates	Observation
	Methanol, ethanol, acetone acetic acid, propionic acid dioxan, ethylene glycol, etc.	No		completely miscible
	<i>i</i> -Propanol, <i>n</i> -propanol, butiric acid, etc.	Yes	Circular, relatively diffuse, microscopically agitated	completely miscible
23.4	2-Butanol	Yes	Circular, well-defined, smooth. (as in Figure 6.)	Partially miscible
11.1	<i>i</i> -Butanol	Yes	Same as above	Same as above
9.9	<i>n</i> -Butanol	Yes	Similar to 2-pentanol	Same as above
8.44	Ethyl acetate	Yes	Circular, well-defined smooth	Same as above
ca. 6.0	<i>i</i> -Butanol†	Yes	"macroscopically" circular; with indentations (Figure 5.)	Same as above
5.02	2-Pentanol	Yes	Same as above	Same as above
3.56	Cyclopentanol	Yes	Same as above	Same as above
3.3	<i>i</i> -Butanol†,‡	Yes	The film breaks down and forms islands which dis- solve separately	
3.18	<i>i</i> -Pentanol	Yes	Same as above	Same as above
2.49	<i>n</i> -Pentanol	Yes	Same as above	Same as above
0.16	<i>n</i> -Hexanol	Yes	Same as above	Same as above
0.045	<i>n</i> -Octanol	Yes	Monomolecular film spread- ing over the entire water surface; drops rest on the film without dissolving	Same as above

* Pure substance dissolving into tap water. The concentration driving force equals the saturation concentration. Working temperature 25°C.

† Pure iso-butanol dissolving into tap water partially saturated with iso-butanol.

‡ Same film aspect was obtained by dissolving pure iso-butanol into saturated sodium chloride aqueous solution.

tour. With increasing amounts of surfactants the outer contour moves nearer the film contour until they almost coincide (but without doing this completely).

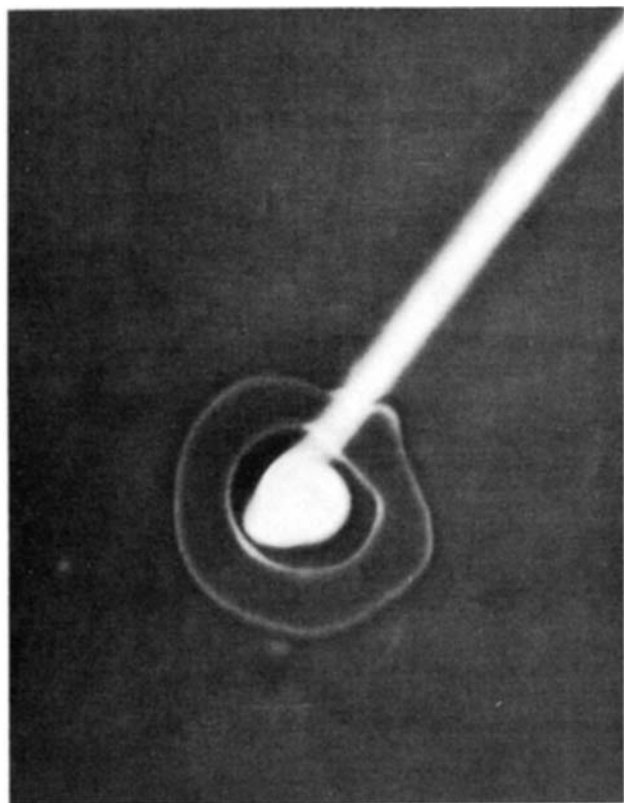


Fig. 6. Iso-butanol film on water, in presence of cetyltrimethylammonium bromide. Flow rate, 11.6×10^{-4} cc/sec.; driving force, 11.1×10^{-4} mole/cc. Magnification ca. 1.8 times.

Noteworthy is the fact that the dimensions of the outer contour have no influence on those of the film. In other words, the specific dissolving rate for a given flow rate is not influenced by the amount of the surface active agent present. Nevertheless, very high concentrations, especially of insoluble surface active agents, upset the circular form of the film apparently by mechanical action.

For liquids completely miscible with water, such as methanol, ethanol, acetone, dioxan, ethylene glycol, acetic acid, etc., no film could be detected over a water surface (for feed rates up to 10 cu.mm./sec.) The outer contour was the only one formed. The same is true for aqueous solutions of completely or partially miscible organic substances. This is due to the fact that they mix with water practically the very moment they are brought into contact with it.

Of the above liquids, dioxan, ethylene-glycol, etc., although heavier than water, do not move directly downward into the water phase (as they do if the capillary tip is submerged) but spread over the water surface, up to the outer contour, behaving exactly as liquids lighter than water. Obviously the surface forces exceed in these cases the gravity forces. Glycerine has an intermediate behavior; part of it dissolves at the surface, behaving as the above liquids, while the rest forms drops which move downward through the water. It is to be noted that some liquids, such as iso-propanol, *n*-propanol, *n*-butiric acid, etc., although completely miscible with water at the working temperatures, nevertheless form a film over the water surface (see also Table 1).

Movements Within the Water Layer

The drag exerted by the rapidly moving free surface results in convection currents in the bulk of the water layer. The water layers swept along with the moving free surface acquire, with increasing radial distance from the capillary tip, a downward motion. This motion may

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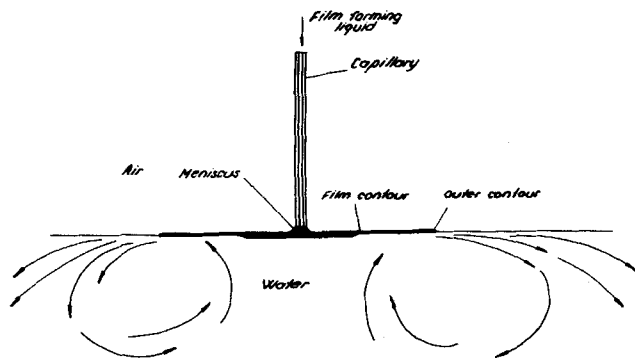


Fig. 7. Flow pattern formed during the dissolving process of a film under the action of surface forces.

be assisted by the influence of the walls and bottom of the dish. On the other hand, near the film contour a certain suction is exerted on the bulk liquid (by the rapid moving free surface), so that the bulk liquid moves upward below the film, to be eventually swept along by the surface layer. After a certain time, a steady toroidal motion pattern is developed (Figure 7). If the free surface is contaminated by surface active agents, this toroidal motion becomes more evident, since the moment the moving surface reaches the outer contour, it is deflected below the stagnant film. The movement continues beneath this stagnant film but the horizontal velocity components are reduced more quickly, resulting in a more marked downward motion.

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An Improved Version of the Rate Equation for Molecular Diffusion in a Dispersed Phase

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A frequency domain analysis of reversible molecular diffusion in a granule or relatively stagnant drop of fluid reveals that for the larger values of time the rate equation reduces to

$$\frac{dW}{dt} = \frac{15D}{R^2} (W^* - W)$$

Compared with an earlier time domain result

$$\frac{dW}{dt} = \frac{\pi^2 D}{R^2} (W^* - W)$$

the rate predicted is $15/\pi^2 = 1.516$ greater and this has been confirmed by results of experiment. An analysis of time constants shows that the dimensionless group relation

$$\frac{Dt}{R^2} \geq 0.101$$

defines mathematically that which is meant by the larger value of time limitation.

Some time ago it was observed that clarification appeared to be desirable for the rate equation for reversible molecular diffusion within a dispersed phase such as a granular solid or a relatively stagnant drop of fluid (2). This was based on the fact that in the periodical literature one frequently finds the assumption that

$$\text{rate} = \text{constant} (W^* - W) \quad (1)$$

At that time it was shown that the governing differential equation for diffusion in an equivalent sphere of dispersed phase, which is

$$\frac{\partial C_s}{\partial t} = D \left[\frac{\partial^2 C_s}{\partial r^2} + \frac{2}{r} \frac{\partial C_s}{\partial r} \right] \quad (2)$$

could be solved subject to the limiting conditions