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Fig. 1

Figure 1: Fig. 1

Abstract

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ON THE MECHANISM OF MASS TRANSFER IN A HETEROGENEOUS LIQUID–LIQUID SYSTEM UNDER STIRRING CONDITIONS

(Presented by Academician P. A. Rebinder, February 11, 1963)

Two basic theories of mass transfer in a liquid–liquid system are known: 1) the two-film theory, based on the presence at the interface of immobile films of both liquids, in which molecular diffusion of the transferred substance occurs ([1]), and 2) the penetration theory, which assumes the transfer of substance from one phase to another by streams of the extracting phase, as if tearing molecules of the transferred substance out of the liquid being extracted ([2–4]). Both theories, as well as their modifications, do not reveal the true mechanism of mass transfer, since they do not take into account surface phenomena at the phase boundary.

Fig. 1. Effect of reagent concentration on the appearance of streams. *I* —crystal violet in dichloroethane, sodium sulfite in water (C_a); *II* —malachite green in dichloroethane, sodium sulfite in water (C_a)

We have observed that, in the case of limitation of the chemical reaction in a liquid–liquid system under stirring conditions by the rate of mass transfer of the substance, two cases may be observed: 1) the reaction proceeds directly at the phase boundary and 2) the substance that has not had time to react at the liquid interface penetrates in streams into the depth of the phase in which the reaction occurs, without spreading throughout its entire volume.

The condition for the appearance of streams of the diffusing substance is that the rate of mass transfer exceed the rate of reaction at the boundary surface

$$\frac{dQ}{dt} \geq \frac{dx}{dt}. \tag{1}$$

As was shown earlier ([5]), the rate of mass transfer complicated by a chemical reaction is expressed by the equation

Fig. 2

Figure 2: Fig. 2

$$\frac{dQ}{dt} = K_m K_p C_b S, \tag{2}$$

where K_m is the mass-transfer coefficient, S is the specific surface area (the interfacial surface area referred to unit volume of the extracted phase), K_p is the distribution coefficient of the diffusing substance, and C_b is its concentration at time t in the extracted phase.

The rate of reaction at the phase boundary can be written as

$$\frac{dx}{dt} = K C_a C_b' S, \tag{3}$$

where C_a and C_b' are the concentrations of the reactants in the reaction zone, and K is the reaction-rate constant.

Let us assume that, in the case of transfer of a surface-active substance, C_b' is equal to the adsorption at the interface according to the Langmuir equation

$$C_b' = \Gamma = \frac{\Gamma_m C_b}{C_b + \alpha}. \tag{4}$$

Then the condition for the appearance of flows will take the following form:

$$K_m K_p C_b S > K C_a \Gamma S. \tag{5}$$

Substituting the value of Γ from (4), we obtain

$$K_m K_p C_b > K C_a \frac{\Gamma_m C_b}{C_b + \alpha}$$

or, after transformation,

$$K_m K_p (C_b + \alpha) > K C_a \Gamma_m. \tag{6}$$

Fig. 2. Dependence between the minimum concentration of sodium sulfite, above which flows appear, and the distribution coefficient of malachite green in the dichloroethane—water system.
$C_b = 0.29 \cdot 10^{-3}$ g-mol/l

We investigated the mass transfer of surface-active dyes—malachite green and crystal violet—from dichloroethane into water. The water contained sodium sulfite, which rapidly reduced the dye to a colorless and practically non-surface-active leuco base. The experiments were carried out in a glass cylinder with an inner diameter of 48.0 mm, with weak stirring of the aqueous solution by a two-bladed stirrer (60 revolutions per minute), i.e., without formation of an emulsion. The experiments were conducted at 15°C (see Fig. 1). The appearance of a dye flow was studied as a function of various parameters. In this connection, the minimum concentration of the aqueous sodium sulfite solution at which no dye flow was observed was determined as a function of the dye concentration in the organic liquid C_b and the distribution coefficient K_p. The latter was varied by adding ether to the dichloroethane, which lowers the solubility of the dye in the nonaqueous phase (see Fig. 2).

Table 1

Mass transfer in the dichloroethane–water system

Transferred reagent (dye)	Reducing reagent in the aqueous phase	C_b, g-mol/l	K_p	K_m, dm/min	K, g-mol/l·min	Γ, mol/cm^2 (from Eq. (7))	Γ_m, g-mol/cm^2 from Eq. (8)	Γ_m, g-mol/cm^2 from Langmuir equation	α from Langmuir equation
Malachite green oxalate	Sodium sulfite	$1.44 \cdot 10^{-4}$ – $7.2 \cdot 10^{-4}$	1.43—1.09	$2.66 \cdot 10^{-4}$	$4 \cdot 10^{4}$	$0.41 \cdot 10^{-10}$	$0.38 \cdot 10^{-10}$	$0.75 \cdot 10^{-10}$	$3.6 \cdot 10^{-6}$
Crystal violet chloride	Sodium sulfite	$1.63 \cdot 10^{-4}$ – $8.2 \cdot 10^{-4}$	0.168	$1.70 \cdot 10^{-3}$	$7.4 \cdot 10^{3}$	$1.69 \cdot 10^{-10}$	$1.7 \cdot 10^{-10}$	$1.1 \cdot 10^{-10}$	$2.47 \cdot 10^{-6}$

For the condition of the minimum concentration of sodium sulfite at which a dye flow first appears, inequalities (5) and (6) may be written as equalities, and from them the values of Γ and Γ_m may be calculated:

$$\Gamma = \frac{K_m K_p C_b}{K C_a}, \tag{7}$$

$$\Gamma_m = \frac{K_m K_p (C_b + \alpha)}{K C_a}. \tag{8}$$

Fig. 3. Dependence of the surface tension at the dichloroethane—water interface on the concentration of the dyes malachite green (I) and crystal violet (II)

Figure 3: Fig. 3. Dependence of the surface tension at the dichloroethane—water interface on the concentration of the dyes malachite green (I) and crystal violet (II)

The experimental data obtained satisfy equation (8), which provides for a linear dependence between the appearance of a dye flow ···

of its distribution coefficient, and also on the concentration of both components; independence from the magnitude of the interfacial surface has been confirmed in experiments with vessels of different diameters.

From the experimental straight lines and the values of K, K_m, and K_p, it is easy to calculate Γ_m from equation (8), by setting up two equations with two unknowns—Γ_m and α. On the other hand, the adsorption of dyes at the liquid interface was calculated by us from the Gibbs equation on the basis of the results of surface-tension measurements (Fig. 3) by the ring-detachment method. The limiting value of the adsorption Γ_m was determined in the usual way from the Langmuir adsorption equation.

Fig. 3. Dependence of the surface tension at the dichloroethane—water interface on the concentration of the dyes malachite green (I) and crystal violet (II).

As can be seen from the data in Table 1, the values of Γ_m found for the dyes agree satisfactorily with the values of Γ_m calculated from equation (8). Analysis of the experimental data shows that the adsorption Γ of the dyes, calculated from equation (7), practically coincides with the values of Γ_m. This is explained by the fact that fluxes are observed at such concentrations of the dye in dichloroethane at which the limiting value of adsorption is reached. It should also be noted that determination of the values of α from our experiments is inaccurate because $C_b \gg \alpha$ (Table 1).

In conclusion, we shall point out that, from the standpoint of the two-film theory, the concentration of the diffusing agent in the reaction zone should be equal to: $C_b' = K_p C_b$. Then the condition for the appearance of fluxes will be $K_m K_p C_b S > K C_a K_p C_b S$, or

$$K_m > K C_a. \tag{9}$$

According to equation (9), the appearance of fluxes should not depend on the concentration of the dye in the extracting phase, which contradicts the experimental data obtained. At the same time, because of the presence at the liquid interface of a saturated adsorption layer, there are no grounds for the usually adopted summation, in mass-transfer processes, of the separate resistances of the two phases and of their interface. This confirms the conclusions we drew earlier (6).

From what has been set forth above there follows the following mechanism of mass transfer in heterogeneous systems under stirring: at the phase interface there exists a barrier in the form of an adsorption layer, from which molecules of the transferred substance are carried away by fluxes of the extracting liquid.

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Note: Figure translations are in progress. See original paper for figures.