THEORY OF NONSTATIONARY DIFFUSION FROM A MOVING DROPLET

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The equations which describe the convective diffusion in droplets (or bubbles) moving in a liquid medium at large Peclet numbers are usually solved on the assumption [1, 2] that the rate of mass transfer is limited by the resistance of the external medium, and that the diffusion is stationary. The time required for establishment of the stationary state has not been calculated so far. Higbie's so-called penetration model is often used in the literature dealing with extraction and absorption; according to this model, mass transfer from droplets or bubbles, being limited by the resistance of the external phase, is described by a one-dimensional equation of nonstationary diffusion into a stagnant semiinfinite medium, and the time of phase contact, which corresponds to the average time of propagation of the diffusion front, is taken equal to the droplet (or bubble) diameter divided by the velocity of the droplet (bubble). This model completely ignores the hydrodynamic conditions which accompany the mass transfer and determine the transfer rate; consequently, this model does not at all describe the actual mechanism of the process. As the experimental data show [4], the effect of nonstationary diffusion on the total resistance to mass transfer becomes ever more essential when the fraction of the disperse phase is increased. The nonstationary character of the diffusion, which is one of the causes of the so-called end effect, is particularly noticeable in the initial and final stages of the process. The existing theories of nonstationary convective diffusion inside a droplet [5, 6] are based on the assumption that the concentration is constant along the hydrodynamic flow lines. This assumption, as is well-known, does not hold for what happens inside the diffusion boundary layer and, hence, cannot be used for describing the processes taking place at large Peclet numbers. In the present paper the problem of nonstationary diffusion from a moving droplet is solved for the case that the resistances of the continuous and the disperse phase are of the same order of magnitude, and that the distribution of the hydrodynamic velocities in these phases are given by the formulas proposed by Hadamard [7] and Rybczinski [8].

We shall consider a spherical droplet of radius R moving in a liquid medium at a constant velocity U determined by Hadamard-Rybczinski's formula. If the Peclet numbers $\mathrm{Pe}_1 = \mathrm{UP}/\mathrm{D}_1$ and $\mathrm{Pe}_2 = \mathrm{UP}/\mathrm{D}_2$ (D_1 and D_2 are the diffusion coefficient to be extracted inside and outside the droplet, respectively) are sufficiently large, the equation of convective diffusion in the zero approximation with respect to the parameters $f_1 = \sqrt{(1+\mu^*)/\mathrm{Pe}_1}$ and $f_2 = \sqrt{(1+\mu^*)/\mathrm{Pe}_2}$ ($\mu^* = \mu_1/\mu_2$ is the ratio of the dynamic viscosities of the internal and external media) reads:

$$\frac{R(1+\mu^*)}{U}\frac{\partial c_i}{\partial t} + y\nu\frac{\partial c_i}{\partial y} + \frac{1-\nu^2}{2}\frac{\partial c_i}{\partial \nu} = \frac{\partial^2 c_i}{\partial y^2} \quad (i = 1, 2), \cdot \tag{1}$$

where the independent variables r, ν are replaced by the independent variables y, ν, which are defined as follows:

$$r = 1 + f_i y \quad (i = 1, 2), \quad \vartheta = \arccos \nu. \tag{2}$$

In addition to the initial conditions, which we write as

$$c_i(y, \nu, t = 0) = c_i^* = \mathrm{const} \quad (i = 1, 2), \tag{3}$$

the boundary condition far from the droplet

$$c_2(\infty, \nu, t) = c_2^* \tag{4}$$

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and the condition of current continuity at the droplet surface

$$\frac{\partial c_1}{\partial y}(0, \nu, t) = \sqrt{\frac{D_2}{D_1}}\frac{\partial c_2}{\partial y}(0, \nu, t), \tag{5}$$

two further boundary conditions for the concentrations near the droplet surface and inside the droplet far away from the surface, must be fixed before we can solve the set (1). We shall assume that the rate of physical dissolution is so much higher than the rate of mass transfer that the interphase equilibrium at the boundary surface establishes almost instantaneously. If the concentrations of the substance to be extracted are low enough, the latter conditions is described by Henry's law

$$c_1(0, \nu, t) = \alpha c_2(0, \nu, t), \tag{6}$$

where α is a constant coefficient. We shall further suppose, that the relaxation time of the diffusive boundary layer is much shorter than the time in which the droplet is noticeably depleted of (or enriched with) the soluble substance, so that the concentration of the substance in the droplet core can be considered as constant during the time intervals considered:

$$c_1(-\infty, \nu, t) = c_1^*. \tag{7}$$

The correctness of this assumption will be confirmed by the results obtained.

Equation (1) is solved by means of the Laplace transformation

$$\tilde{c}_i(y, \nu, p) = \int_0^\infty c_i(y, \nu, t)\, e^{-pt} dt \tag{8}$$

and replacement of $\tilde{c}_i$ by the new unknown functions

$$\tilde{C}_i(y, \nu, p) = \left(\frac{1-\nu}{1+\nu}\right)^{-Rp\,(1+\mu^*)/U} [p\tilde{c}_i(y, \nu, p) - c_i^*], \tag{9}$$

which, as is easily verified, should satisfy the set of equations

$$y\nu\frac{\partial \tilde{C}_i}{\partial y} + \frac{1-\nu^2}{2}\frac{\partial \tilde{C}_i}{\partial \nu} = \frac{\partial^2 \tilde{C}_i}{\partial y^2} \tag{10}$$

with the following boundary conditions:

$$\begin{gathered}\tilde{C}_i(\pm\infty, \nu, p) = 0; \quad \tilde{C}_i(y, -1, p) = 0; \; \frac{\partial \tilde{C}_1}{\partial y}(0, \nu, p) = \sqrt{\frac{D_2}{D_1}}\frac{\partial \tilde{C}_2}{\partial y}(0, \nu, p); \\ \tilde{C}_1(0, \nu, p) = \alpha\tilde{C}_2(0, \nu, p) - (c_1^* - \alpha c_2^*)\left(\frac{1-\nu}{1+\nu}\right)^{-\quad 1+\mu^*)/U}\end{gathered} \tag{11}$$

Any Eq. (10) can be transformed to an equation of the heat-conductivity type by means of the following replacement of the independent variables:

$$y \to \psi = y(1-\nu^2); \quad \nu \to \tau = {}^2/_3(2-\nu)(1+\nu)^2.$$

From the solutions $\tilde{C}_i$ (ψ, τ, ρ) thus obtained we can derive the equation for the local substance current near the droplet surface:

$$j(\nu, t) = -\frac{D_i}{Rf_i}\frac{\partial C_i}{\partial y}(0, \nu, t) = -\frac{D_i}{Rf_i}(1-\nu^2)\frac{\partial c_i}{\partial \psi}(0, \nu, t). \tag{12}$$

This is achieved by applying the reverse Laplace transformation to any of the functions

$$\frac{1}{p}\left(\frac{1-\nu}{1+\nu}\right)^{Rp\,(1-\mu^*)/U}\frac{\partial \tilde{C}_i}{\partial \psi} \quad (\psi = 0, \tau, p).$$

The resulting equation for the current reads

$$j(\nu, t) = -\frac{iD_2\sqrt{(1+\mu^*)\,\mathrm{Pe}_2}\,(c_1^* - \alpha c_2^*)}{2\pi^{3/2}U(\alpha + \sqrt{D_2/D_1})}\int\limits_{\sigma - i\infty}^{\sigma + i\infty}\int\limits_{0}^{\tau(\nu)} \times \left[\frac{(1-\nu)(1+k(\xi))}{(1+\nu)(1-k(\xi))}\right]^{Rp(1+\mu^*)/U} \frac{\exp(pt)\,d\xi\,dp}{[1-k^2(\xi)]^2\sqrt{\tau(\nu)-\xi}},$$

where $\tau(\nu) = 2(2-\nu)(1+\nu)^2/3$, and the function $k(\xi)$ is defined by $\xi = 2(2-k)(1+k)^2/3$. Calculation of the integrals yields the expression

$$j(\nu, t) = \frac{c_1^* - \alpha c_2^*}{\alpha + \sqrt{D_2/D_1}}\frac{D_2}{R}\sqrt{\frac{3\mathrm{Pe}_2}{2\pi(1+\mu^*)}} \times \frac{1-\nu^2}{\sqrt{(2-\nu)(1+\nu)^2 - [2-\eta(\nu,t)][1+\eta(\nu,t)]^2}}, \tag{13}$$

where

$$\eta(\nu, t) = -\frac{(1-\nu) - (1+\nu)\exp\{-Ut/[(1+\mu^*)R]\}}{(1-\nu) + (1+\nu)\exp\{-Ut/[(1+\mu^*)R]\}}. \tag{14}$$

From formulas (13) - (14) it follows that the relaxation time of the diffusive boundary layer, i.e., the time in which the ratio $[j(\nu, t) - j(\nu, \infty)] / j(\nu, \infty)$ drops by a factor e, equals $\tau_r = R(1 + \mu^*) / 2U$. Since, as was shown in paper [5], the time τ_d required for noticeable depletion of the droplet has the lower bound $0.022R^2/D_1$, the inequality $\tau_r \ll \tau_d$ holds at sufficiently large values of the Peclet number Pe_1. This inequality was already used previously in formulating the boundary conditions.

The average current

$$\bar{j}(T) = \frac{1}{2T}\int\limits_{0}^{T}\int\limits_{-1}^{1} j(\nu, t)\,d\nu\,dt, \tag{15}$$

where T is the contact time of the phase, is of practical interest. Substituting formulas (13), (14), into (15), and carrying out the integration, we find:

$$\bar{j}(T) = \frac{D_2(c_1^* - \alpha c_2^*)}{TU(\alpha + \sqrt{D_2/D_1})}\sqrt{\frac{2\mathrm{Pe}_2(1+\mu^*)}{3\pi}}\,Y(\omega_T), \tag{16}$$

where

$$Y(\omega_T) = \sqrt{\frac{1-\omega_T}{(1+\omega_T)^3}}\int\limits_{-1}^{1}[2(1+4\omega_T+\omega_T^2) + 3\eta(1-\omega_T^2) + \eta^2(1-\omega_T)^2]^{1/2}\left[1 + \frac{1-\omega_T}{1+\omega_T}\eta\right]^{-3/2} d\eta, \tag{17}$$

$$\omega_T = \exp\{-UT/[(1+\mu^*)R]\}. \tag{18}$$

The function $Y(\omega_T)$ cannot be expressed by finite combinations of elementary functions. However, its value can be easily computed by expanding Y into a series of powers of the parameter ω_T or the ratio $(1-\omega_T)/(1+\omega_T)$, if the parameter or the ratio are small compared with unity. Thus, for example, to an accuracy of the first-order terms of the $(1-\omega_T)/(1+\omega_T)$ ratio (which yields correct results if $T \ll \tau_r$), we find:

$$\bar{j}(T) = \frac{c_1^* - \alpha c_2^*}{\alpha + \sqrt{D_2/D_1}}\sqrt{\frac{4D_2}{\pi T}}. \tag{19}$$

To an accuracy of the zero-order terms of ωT (which yields correct results if $T \gg \tau_r$), formula (16) transforms into:

$$\bar{j}(T) = \frac{c_1^* - \alpha c_2^*}{\alpha + \sqrt{D_2/D_1}} \frac{D_2}{R} \sqrt{\frac{2\mathrm{Pe}_2}{3\pi(1+\mu^*)}}. \tag{20}$$

In case the total mass transfer is limited by the external medium, formal substitution of $D_1 \to \infty$, $\alpha \to 1$ in formulas (19) and (20) yields Higbie's [3] and Levich' formulas [9], respectively. Hence, it follows in particular that application of Higbie's formula to time intervals $T \sim R/U$, as is usual practice in the analysis of experimental data, has no foundation at all.

LITERATURE CITED

1. V. G. Levich, Physicochemical Hydrodynamics [in Russian], Moscow (1959).
2. C. W. Bowman and D. M. Ward et al., Canad. J. Chem. Eng., 39, No. 1, 9 (1961); D. M. Ward, O. Trass, A. L Johnson, Canad. J. Chem. Eng., 40, No. 4, 164 (1962).
3. R. Higbie, Trans. Am. Inst. Chem. Eng., 31, 365 (1935).
4. B. I. Brounshtein and L. R. Ritman, Collection: Liquid Extraction Processes [in Russian], Leningrad (1963), pp. 17-38.
5. R. Kroning and J. C. Brink, Appl. Sci. Res., A2, No. 2, 142 (1950).
6. A. F. Handlos and F. Baron, Am. Inst. Chem. Eng. J., 3, 127 (1957).
7. J. Hadamard, C. R., 152, 1735 (1911).
8. Rybczinski, Bull. de Cracovie, A, 40 (1911).
9. V. G. Levich, ZhFKh, 22, 721 (1948).

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