MASS TRANSFER IN CAPILLARIES WITH ABSORBENT WALLS

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We considered the problem of the transfer of a substance for a liquid to the absorbent surface of a circular capillary. We conducted a general analysis. Using the method of two-time formalism, we found the solution of the problem in one special case.

In addition to technologies in which a substantial role is played by mass-transfer phenomena complicated by heat transfer [1, 2], industry also makes use of apparatuses in which mass transfer is carried out under quasiisothermal conditions without any phase transitions. These include devices for the extraction of various substances from porous materials, the dyeing of textile products made of natural and synthetic fibers, all sorts of bathing and soaking processes carried out for the purpose of imparting necessary properties to substances, and others. The course of these processes is determined in large measure by the capillary-porous structure of the material. This explains the interest in mass transfer in a single capillary.

Suppose that into a liquid solution of concentration C_0 we introduce (at $t = 0$) a straight circular capillary (of length l and radius R, where $l \gg R$), whose inner surface sorbs the substance dissolved in the liquid. It is clear that the diffusion-sorption phenomena will be preceded by the hydrodynamic ones: the formation of a capillary meniscus and of the velocity profile of Poisuille flow of the liquid under the influence of the capillary pressure and the pressure drop Δp.

It is natural to expect that the characteristic time τ_1 of the establishment of a capillary meniscus (and the creation of a pressure drop leading to the motion of the liquid along the capillary) is independent of the viscosity and depends only on the surface-tension coefficient σ, the density ρ of the medium, and the capillary diameter d. From an analysis of the dimensionality of $\tau_1 = \text{const}\ \rho^{1/2}\sigma^{-1/2}d^{3/2}$, we can take the constant factor equal to unity; then $\tau_1 \backsim \rho^{1/2}\sigma^{-1/2}d^{3/2}$. In a similar manner, we can find $\tau_2 = \text{const}\ d^2\nu^{-1}$.

In monotonic relaxation processes the constant factor in the dimensional formulas is usually much less than unity. However, if we set it equal to unity (i.e., greatly exaggerate it), the time required for establishing the profile is nevertheless found to be extremely small, owing to the smallness of the capillary diameter: $\tau_2 \backsim d^2\nu^{-1}$.

In estimating the times τ_3 and τ_4, we start from the assumption that each of them is much longer than τ_1 and τ_2. This condition enables us to consider the motion of the liquid at any instant of time to be Poiseuille motion. The time required for the solution to penetrate to a distance h into the capillary under the influence of capillary forces can obviously be obtained as the ratio of h to the average velocity of the motion: $\tau_3 \backsim h\langle v\rangle^{-1}$ (the true velocity v is determined from the equations of hydrodynamics, $0 = -\frac{\partial p}{\partial x_i} + \eta\Delta v_i,\ \frac{\partial v_i}{\partial x_i} = 0$). If the pressure drop Δp is due to the action of capillary forces, it will be proportional to the ratio σ/d. Thus, we find for τ_3 that $\tau_3 \backsim \eta h^2\sigma^{-1}d^{-1}$.

The time τ_4 can be estimated in a manner similar to τ_3. However, here Δp should be determined by Bernoulli's formula $\Delta p \backsim \rho v^2$, $\tau_4 \backsim h^2\eta d^{-2}\rho^{-1}v^{-2}$.

We reduce the results so obtained to a table and proceed to estimate them for the case of the motion of aqueous solutions, setting $\rho = 10^3$ kg/m^3, $\sigma = 10^{-1}$ N/m, $\nu = 10^{-6}$ m^2/sec, the capillary diameter $d = 10^{-8}$ m, the height of the rise in the capillary $h = 10^{-3}$ m, and the velocity of the flow going past is $v = 1$ m/sec.

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TABLE 1. Estimate of the Characteristic Times

Hydrodynamic processes			Diffusion processes		
I	II	III	I	II	III
τ_1	$\rho^{1/2}\sigma^{-1/2}d^{3/2}$	10^{-10}	τ_5	$\delta^2 D_{\mathrm{m}}^{-1}$	1
τ_2	$d^2\nu^{-1}$	10^{-10}	τ_6	$h^2 D_{\mathrm{m}}^{-1}$	10^8
τ_3	$h^2\eta\sigma^{-1}d^{-1}$	1	τ_7	$h^2 D_{\mathrm{liq}}^{-1}$	10^4
τ_4	$h^2\eta d^{-2}\rho^{-1}v^{-2}$	10^4			

Remark. I) times; II) calculation formula; III) order of magnitude of time, sec.

From Table 1 it follows that if the capillary surface is well wetted by the solution, then the meniscus and the stationary motion of the liquid will be established practically instantaneously. But the time required to move the solution a distance of 0.001 m is of the order of 1 sec. If the walls are not wetted by the solution, then the time required to move the liquid the same distance along the capillary is 10^4 times as long. Thus, the "capillary transport" of the dissolved substance to the surface (its delivery as a result of flow under the influence of capillary pressure) takes place many times faster than the hydrodynamic transport resulting from the pressure proportional to the square of the velocity. From this we can draw a conclusion of great importance for the organization of technological processes: we must make sure by some method or other that the surface of the material is wettable, but if it is impossible for some reason, we can bring about the delivery of the solution by the hydrodynamic method if we create a pressure drop by considerably increasing the velocity of the liquid (dynamic head) or by vacuuming.

Now let us consider diffusion-sorption phenomena. The following processes may be distinguished: "transverse" diffusion of the dissolved substance from the surface to the depths of the material, "longitudinal" diffusion in the material along a capillary, and lastly, "longitudinal" diffusion in the solution along a capillary. The characteristic times for these processes [3] are equal, respectively, to $\tau_5 \sim \delta^2 D_{\mathrm{m}}^{-1}$, $\tau_6 \sim h^2 D_{\mathrm{m}}^{-1}$, $\tau_7 \sim h^2 D_{\mathrm{liq}}^{-1}$. As applied to the dyeing of textile materials, we can take [4]: $\delta = 10^{-7}$ m, $D_{\mathrm{m}} = 10^{-14}$ m^2/sec, $D_{\mathrm{liq}} = 10^{-10}$ m^2/sec, $h = 10^{-3}$ m. The estimates obtained for the times are shown in Table 1. It can be seen from the table that $\tau_6 \gg \tau_7$. This means that in organizing a technological process, we may disregard the phenomenon of diffusion along the material.

Since the diffusion coefficient in solids is smaller by many orders of magnitude than the diffusion coefficient in liquids, it has conventionally been assumed that the limiting stage of the mass-exchange processes between a solid and a liquid is the transfer of mass in the solid. However, this is not always so, and there exist various possibilities, which are classified below. We begin by considering the case in which, owing to the smallness of the fiber diameters, the time for "capillary transport" of the dissolved particles, τ_3, and the time for transverse diffusion, τ_5, have the same order of magnitude: $\tau_3 \infty \tau_5$. In this case, during an interval of time τ_3 the pores of the material are filled with the solution, and there are two possible situations: either the mass of the arriving substance arriving by "capillary transport" is sufficient to give the material the necessary properties (color, crease-resistance, fireproofness, purity, etc.) or this quantity is insufficient.

In the first case the technology may be organized according to the following scheme: leaving the material in the solution for a short time (equal to τ_3), making sure that the pores are filled with the liquid by the capillary method, and thereafter placing the material in an apparatus which accelerates the transverse diffusion in the material (time τ_5). This may be called a capillary-diffusion technology, on the basis of the method by which the processes take place.

In the second case the mass of dissolved substance entering the pores of the material through capillary absorption is insufficient to give the material the necessary properties. This means that the material must be kept in the solution longer, for a period of time greatly exceeding τ_3. The necessary residence time of the porous solid in the solution depends on the transport paths of the dissolved substance into the solution-filled material. We can organize the delivery of the substance to the surface of the material by hydrodynamically forcing the solution through the pores of the material, with subsequent "transverse" diffusion from the pores into the "skeleton" of the material. This scheme may be referred to as a hydrodynamic-diffusion (HD) scheme. On the other hand, the dissolved substance may enter the material in a process of "longitudinal" diffusion of the liquid along the capillary, with subsequent "transverse" diffusion into the depths of the material. This scheme may be given the name of capillary-diffusion-diffusion scheme (CDD).

It may happen, in turn, that the process of diffusion into the material by the CDD scheme takes place much faster than sorption by the surface but more slowly than the delivery of the dissolved substance by "longitudinal" diffusion along the capillary. We shall call this an adsorption-diffusion (AD) process. It is observed, for example, in the case when the requirements imposed on the properties of the material are satisfied as soon as the dissolved substance is localized on the surface of the material (in our model, on the capillary walls, without penetrating into the interior); in the case of slow adsorption (low chemical affinity between the dissolved substance and the wall material); in the case when there is rapid adsorption (high chemical affinity for the material) and the mass of the dissolved substance that enters the capillary in the capillary-hydrodynamic transport stage is insufficient for obtaining the necessary properties of the material after treatment, which makes it necessary to deliver new batches of the substance into the capillary by "longitudinal" diffusion.

For a mathematical description of the problem according to the AD scheme, we shall make use of the equation, reduced to dimensionless form, that describes the law of conversion of mass of the dissolved substance in a one-dimensional capillary [5]:

$$\frac{\partial\beta}{\partial t}=\frac{D_{\text{liq}}}{l^2}\frac{\partial^2\beta}{\partial z^2}-\frac{\partial n}{\partial t}. \tag{1}$$

The equation for n(z, t) is obtained by the usual scheme of nonequilibrium thermodynamics:

$$\frac{\partial n}{\partial t}=-\gamma(n-\alpha\beta). \tag{2}$$

Combining (2) with (1) and giving the initial and boundary conditions, we finally have

$$\frac{\partial\beta}{\partial t}=\frac{D_{\text{liq}}}{l^2}\frac{\partial^2\beta}{\partial z^2}-\frac{\partial n}{\partial t},\quad \frac{\partial n}{\partial t}=-\gamma(n-\alpha\beta), \tag{3}$$
$$z=0,\ z=l{:}\ \beta=1;\ t=0{:}\ \beta=1,\ n=0.$$

In the problem (3) there are two characteristic times: the time of "longitudinal" diffusion $\tau_7=l^2/D_{\text{liq}}$, during which a Brownian particle suceeds in diffusing along the capillary, and the characteristic adsorption time, $\tau_8 = 1/\gamma$. Let us consider the case of "rapid" diffusion ($s \equiv \tau_7/\tau_8 \ll 1$). It is clear that as a result of the "rapid" diffusion of the dissolved substance from the solution volume outside the capillary to the interior and along the capillary, the concentration inside the capillary during the process is kept constant and equal to the concentration in the volume outside the capillary, i.e., $\beta(z, t) = 1$. The problem for n(z, t) takes the form $dn/dt = -\gamma(n - \alpha)$, $n|_{t=0} = 0$, from which it follows that

$$n=\alpha\,[1-\exp(-\gamma t)]. \tag{4}$$

We shall give a formal argument to justify the result (4), using two-time formalism. To do this, we introduce two new (dimensionless) times: $t_1 = t/\tau_7$ and $t_2 = t/\tau_8$. Since in the case under consideration $s \equiv \tau_7/\tau_8 \ll 1$, time t_1 is "fast," and t_2 is "slow." Rewriting the system (3) in the new time variables, we obtain

$$\frac{\partial\beta}{\partial t_1}+s\frac{\partial\beta}{\partial t_2}=\frac{\partial^2\beta}{\partial z^2}-\frac{\partial n}{\partial t_1}-s\frac{\partial n}{\partial t_2},\quad \frac{\partial n}{\partial t_1}+s\frac{\partial n}{\partial t_2}=-s(n-\alpha\beta), \tag{5}$$
$$t_1=t_2=0{:}\ \beta=1,\ n=0;\ z=0,\ z=1{:}\ \beta=1.$$

We shall try to find a solution of the system (5) in the form of an expansion in the parameter s, which in the case under consideration is small: $\beta = \beta_0 + s\beta_1 + s^2\beta_2 + \ldots$; $n = n_0 + sn_1 + s^2n_2 + \ldots$.

Substituting these expansions into (5), we obtain the following equations for the zeroth and first approximations:

$$\frac{\partial\beta_0}{\partial t_1}=\frac{\partial^2\beta_0}{\partial z^2}-\frac{\partial n_0}{\partial t_1},\quad \frac{\partial n_0}{\partial t_1}=0;$$

$$t_1 = 0\colon \beta_0 = 1,\ n = 0;\ z = 0,\ z = 1\colon \beta_0 = 1;$$

$$\frac{\partial \beta_1}{\partial t_1} - \frac{\partial^2 \beta_1}{\partial z^2} + \frac{\partial n_1}{\partial t_1} = -\frac{\partial \beta_0}{\partial t_2} - \frac{\partial n_0}{\partial t_2}, \tag{6}$$

$$\frac{\partial n_1}{\partial t_1} = -\frac{\partial n_0}{\partial t_2} - (n_0 - \alpha\beta_0). \tag{7}$$

Substituting the solution of the problem (6), $n_0 = n_0(t_2, z)$, $\beta_0 = 1$, into the second equation of the system (7), we find

$$\frac{\partial n_1}{\partial t_1} = -\frac{\partial n_0}{\partial t_2} - (n_0 - \alpha). \tag{8}$$

Assuming that $n_0 = n_0(t_2, z)$, we find, after integrating Eq. (8), that

$$n_1 = -\left[\frac{\partial n_0}{\partial t_2} + (n_0 - \alpha)\right] t_1 + A(t_2, z). \tag{9}$$

The two-time method requires that there be no secular terms. In accordance with this requirement, in (9) we must set the expression $\partial n_0/\partial t_2 + (n_0 - \alpha)$ equal to zero. Thus:

$$\frac{\partial n_0}{\partial t_2} + (n_0 - \alpha) = 0,\ n_0|_{t_2=0} = 0. \tag{10}$$

Integrating (10), we finally obtain

$$n_0 = \alpha[1 - \exp(-t_2)] = \alpha[1 - \exp(-\gamma t)]$$

in complete agreement with the result (4) obtained from qualitative considerations.

In a similar manner, using the scheme of two-time formalism, we can consider the case of slow diffusion ($s \equiv \tau_7/\tau_8 \gg 1$). However, in this case the expansion must be in the small parameter s^{-1}.

Thus, an analysis of the process of transfer of the dissolved substance from the volume of solution outside the capillary to the surface of the absorbing capillary enables us to make a classification of the technologies and, on the basis of that classification, to indicate the technical methods for realizing and intensifying them, as well as to obtain exact solutions in limiting cases.

NOTATION

C_0, concentration of the dissolved substance in the solution outside the capillary; l, R, length and radius of the circular capillary; σ, ρ, surface tension and density of the solution; τ_1, time for establishment of the capillary meniscus; τ_2, time for establishment of the velocity profile; τ_3, τ_4, times for penetration of the liquid to a distance h into the interior of the capillary under the influence of capillary and hydrodynamic forces, respectively; Δp, pressure drop; ν, kinematic viscosity of the solution; η, dynamic viscosity of the solution; v, velocity of flow; D_{liq}, D_m, coefficients of diffusion of the dissolved substance in the liquid and the wall material; τ_5, time for the diffusion of particles of the dissolved substance from the surface into the interior of the material; τ_6, τ_7, times for the diffusion of particles of the dissolved substance along the capillary for the material and the liquid, respectively; z, dimensionless longitudinal coordinate; β, dimensionless concentration of the solution ($\beta \equiv C/C_0$); n, dimensionless concentration of the substance on the surface; $n = 2aR^{-1}C_0^{-1}$; a, surface concentration of the sorbed substance; t, time; α and γ, constants.

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