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Abstract

Full Text

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ON DIFFUSIONAL EXTRACTION FROM POROUS MATERIALS IN THE PROCESS OF CAPILLARY IMPREGNATION

The extraction of various substances from porous materials, especially when the substance to be extracted is present in small amounts, is expediently carried out by leaching ([1,4]). Processes of desorption by solvents ([2]) and intensification of oil recovery with the aid of solutions of surface-active substances ([3]) are close to leaching.

The extraction process is accompanied by capillary impregnation, and the rate of extraction is in a definite way related to the rate and depth of capillary impregnation. The diffusion theory of extraction calculates the kinetics of extraction without taking capillary phenomena into account ([4]). This simplification is undoubtedly justified when extraction occurs from materials whose pores are formed in the course of leaching. However, in processes of extraction from pores in which the substance being extracted occupies only an insignificant part of the volume, while the other part of the volume is filled with gas, it is useful to take capillary impregnation into account. Below an attempt is made to describe the kinetics of extraction by solvents from capillaries in the process of capillary impregnation.

Let us consider diffusion from a capillary on whose inner walls the substance subject to extraction is uniformly distributed in a thin layer. We shall assume that the substance sorbed (or deposited) on the walls dissolves immediately as the inner surface of the capillary is wetted by the solvents, and that transverse mixing occurs instantaneously. This makes it possible to consider a one-dimensional problem.

The pores in disperse bodies may be through pores and dead-end pores, and the fraction of the latter may be quite considerable ([5]). Capillary impregnation of dead-end pores is described by the equation ([6])

$$t = \frac{4\alpha\eta l_0^2}{r\sigma\cos\theta}\left\{\frac{1}{2}\varphi^2 + (1-\alpha)\left[-\alpha\ln\frac{\alpha-\varphi}{\alpha} - \varphi\right]\right\}, \tag{1}$$

whereas the initial stage of capillary impregnation of dead-end and through pores is described by the equation

$$l^2 = \frac{r\sigma\cos\theta}{2\eta}\,t = \beta^2 t, \tag{2}$$

where t is the duration of impregnation; l is the depth of impregnation; l_0 is the total length of a dead-end capillary; $\varphi = l/l_0$ is the dimensionless degree of impregnation; r is the pore radius; σ is the surface tension; η is the viscosity of the liquid; θ is the wetting angle; $\alpha = \dfrac{2\sigma\cos\theta}{rP_a + 2\sigma\cos\theta}$; P_a is atmospheric pressure.

Molecular diffusion of the dissolved substance from the meniscus to the mouth of the capillary will be complicated by convective transport of the dissolved substance in the opposite direction, which is described by the equation of convective diffusion

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x_1^2} + v_{x_1}\frac{\partial C}{\partial x_1}. \tag{3}$$

From considerations of continuity of the jet it follows that the mean velocity of the liquid in the capillary v_{x_1} is equal to the velocity of motion of the meniscus $dl/dt = v_{\mathrm{m}}$.

Let us now pass to a coordinate system moving with velocity dl/dt, with the origin at the meniscus. Then, in the right-hand side of equation (3), the second term becomes equal to zero, and it can be written in the simpler form

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}. \tag{4}$$

We shall now formulate the boundary conditions. At the mouth of the capillary, i.e., for $x = l = \int_0^t v_{\mathrm{m}}\,dt$, the concentration is constant and equal to the concentration C_0 of the liquid flowing around the porous body,

$$x = l = \int_0^t v_{\mathrm{m}}\,dt, \qquad C_{(x,t)} = C_0. \tag{5}$$

All the substance dissolving at the meniscus diffuses in the direction of the mouth of the capillary. Let during the time dt the meniscus move through a segment dl. In this case, $2\delta\pi r\,dl = \pi r^2 C_s dl$ of substance will pass into solution in the neighborhood of the meniscus, which diffuses toward the mouth; hence it follows that

$$C_s\frac{dl}{dt} = -D\frac{\partial C}{\partial x}, \tag{6}$$

Fig. 1. Scheme of the transition from the coordinate system associated with the meniscus to the coordinate system associated with the mouth of the pore

Figure 1: Fig. 1. Scheme of the transition from the coordinate system associated with the meniscus to the coordinate system associated with the mouth of the pore

where C_s is the volume concentration of the dissolved substance in the absence of diffusion; δ is the thickness of the precipitated (adsorbed) layer.

Fig. 1. Scheme of the transition from the coordinate system associated with the meniscus to the coordinate system associated with the mouth of the pore

Let us now write the boundary conditions taking into account that in the initial stage of capillary impregnation law (2) holds, which facilitates the solution of equation (4).

At the meniscus:

$$x = 0, \qquad D\frac{\partial C}{\partial x} = -C_s\frac{dl}{dt} = -\frac{\beta C_s}{2\sqrt{t}}; \tag{7}$$

at the mouth:

$$x = -\beta\sqrt{t}, \qquad C_{(x,t)} = C_0. \tag{8}$$

In this form the problem is analogous to the problem of freezing (7). We seek the solution of the problem in the form

$$C_{(x,t)} = A + B\,\mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right), \tag{9}$$

where $\mathrm{erf}\,x = \frac{2}{\sqrt{\pi}}\int_0^x e^{-y^2}\,dy$ is the probability integral. Using the boundary conditions (7) and (8), we find the values of the constants

$$A = C_0 + \frac{\beta C_s\sqrt{\pi}}{2\sqrt{D}}\,\mathrm{erf}\left(\frac{\beta}{2\sqrt{D}}\right), \qquad B = -\frac{\beta C_s\sqrt{\pi}}{2\sqrt{D}}. \tag{10}$$

The solution obtained,

$$C_{(x,t)} = C_0 + \frac{\beta C_s\sqrt{\pi}}{2\sqrt{D}}\left[\mathrm{erf}\left(\frac{\beta}{2\sqrt{D}}\right) + \mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)\right] \tag{11}$$

satisfies equation (4) and the boundary conditions (7) and (8).

The concentration of the extracted substance at the meniscus is constant and equal to

$$C_{0,t} = C_0 + \frac{\beta C_s \sqrt{\pi}}{2\sqrt{D}} \operatorname{erf}\left(\frac{\beta}{2\sqrt{D}}\right). \tag{12}$$

Let us now return to a coordinate system fixed relative to the walls and with the origin at the mouth of the capillary, by means of the transformation (see Fig. 1)

$$x_1 = x + \beta\sqrt{t}. \tag{13}$$

The concentration distribution in this system is

$$C_{(x_1,t)} = C_0 + \frac{\beta C_s \sqrt{\pi}}{2\sqrt{D}} \left[\operatorname{erf}\left(\frac{\beta}{2\sqrt{D}}\right) + \operatorname{erf}\left(\frac{x_1 - \beta\sqrt{t}}{2\sqrt{Dt}}\right)\right]. \tag{14}$$

The extraction rate is

$$j = -D\left(\frac{\partial C}{\partial x_1}\right)_{x_1=0} + C_0 v_{\mathrm{m}} = \frac{\beta C_s}{2\sqrt{t}}\left(e^{-\beta^2/4D} + \frac{C_0}{C_s}\right), \tag{15}$$

whence we find

$$\beta_{\mathrm{cr}}^2 = 4D \ln \frac{C_s}{C_0}. \tag{16}$$

It can be seen from (15) that, in the initial stage of impregnation, when expression (2) is satisfied, extraction occurs only if the condition $\beta < \beta_{\mathrm{cr}}$ is fulfilled. From (2) and (16) one can find the critical value of the radius of the pores from which, under the given experimental conditions, extraction will proceed:

$$r < r_{\mathrm{cr}} = \frac{8\eta D}{\sigma \cos\theta} \ln \frac{C_s}{C_0}. \tag{17}$$

We see that, under conditions of convective diffusion arising as a result of the transport of the dissolved substance into the depth of the capillaries together with the absorbed liquid, the rate of impregnation, along with diffusion, plays a determining role. As is evident from (2), the rate of impregnation depends on the pore radius, and consequently the rate of convective transport of the substance dissolved in the liquid also depends on it.

Since in dead-end pores the rate of capillary impregnation deviates from law (2) because of the counteraction of the gas trapped in the pores, extraction, other conditions being equal, will also begin earlier.

Let us also note that extraction can occur only for a definite ratio C_s/C_0, created by the value of $\beta^2/4D$, whereas the usual requirement for the course of a diffusion process, $C_s > C_0$, proves insufficient (the exception is the value $C_0 = 0$, when extraction proceeds for any $C_s > 0$).

The considerations set out above make it possible to regard, as one of the possible explanations of the anomalous form of the desorption curves in the work$^{(2)}$, the polydispersity of silica gels$^{(8)}$. Indeed, as is clear from expression (17), extraction will begin immediately after wetting from pores of a certain radius, while from other pores extraction will begin only as the law of capillary impregnation deviates from the quadratic one.

The obtained expression (15) is also of interest from the point of view of separating mixtures of substances. Let us consider, for example, the case in which two substances contained in a porous body in equal amounts are subject to extraction, and the liquid flowing around the body contains none of the extracted substances, i.e. $C_{1s} = C_{2s} > 0$ and $C_{01} = C_{02} = 0$. Then the ratio of the fluxes of the two substances does not depend on the extraction time (provided the quadratic law is obeyed) and is equal to

$$\frac{j_1}{j_2} = e^{\frac{\beta^2}{4}\frac{D_1 - D_2}{D_1 D_2}}. \tag{18}$$

Thus, when extracting from capillaries with $r = 10^{-6}$ cm, by water, a mixture of two substances whose diffusion coefficients are $D_1 = 1.1 \cdot 10^{-5}$ cm^2/s and $D_2 = 1.0 \cdot 10^{-5}$ cm^2/s, $j_1/j_2 = e^{8.2}$, i.e., in the first stage an almost completely pure substance with the larger value of the diffusion coefficient will be extracted.

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

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