Physical Chemistry

Corresponding Member of the Academy of Sciences of the USSR B. V. DERYAGIN, M. A. AL’ TSHULER

1963

SovietRxiv

Abstract

Full Text

Physical Chemistry

Corresponding Member of the Academy of Sciences of the USSR B. V. DERYAGIN, M. A. AL’ TSHULER

ON THE QUESTION OF CAPILLARY IMPREGNATION OF SPHERICAL GRANULES AND DIFFUSIONAL EXTRACTION DURING THE STAGE OF CAPILLARY IMPREGNATION

In work (1), the processes of extraction by solvents from porous materials of substances completely filling the pores were studied in detail. Extraction from granules in which the soluble substance occupies only part of the pore volume is, naturally, subject to other regularities. An essential feature of such an extraction process is that it proceeds during the impregnation of the granules under the action of capillary forces.

As was noted earlier (2), capillary impregnation of a piece of porous body completely immersed in a liquid is similar to the impregnation of a system of blind pores, since the gas present in the pores is trapped and undergoes compression, thereby determining the rate and depth of capillary impregnation. The extraction rate is limited by the rate of capillary impregnation of the granules, since dissolution and diffusion of the dissolved substance occur only in the impregnated part of the grain.

The kinetics of capillary impregnation of a spherical granule is considered, as is customary (3), in the quasi-stationary approximation. In addition, the calculations do not take into account the possible presence in the granules of blind, or too narrow, or too tortuous pores. In this case, no bubbles of trapped air will remain behind the impregnation front.

Let us write Darcy’ s law in differential form:

$$Q = kS\partial P/\partial x, \tag{1}$$

where Q is the volumetric filtration rate; k is the filtration coefficient; $\partial P/\partial x$ is the pressure gradient; $S = 4\pi x^2 n$ is the filtration surface; n is the porosity; x is the distance from the center of the granule to the surface of the impregnation front.

Separating the variables and integrating (1) over the thickness of the impregnated layer, we obtain

$$Q = \frac{4\pi k n \Delta P}{1/(R-h) - 1/R}, \tag{2}$$

where R is the radius of the granule; $h = R - x$ is the depth of impregnation; ΔP is the difference between the pressure P_a of the liquid surrounding the granule and the pressure of the gas trapped in the granule. On the other hand, by definition:

$$Q = 4\pi(R-h)^2 n\, dh/dt, \tag{3}$$

where dh/dt is the filtration rate measured at the spherical front of impregnation of the spherical granule.

Using (2) and (3) and taking into account that for a sphere

$$\Delta P = P_k + P_a - P_a \left(\frac{R}{R-h}\right)^3,$$

where

$$P_k = \frac{2\sigma}{r} \cos\theta$$

is the capillary pressure, and r is the hydraulic pore size, equal to the ratio of the pore volume to their surface, we obtain an expression for the capillary impregnation rate in the form

$$\frac{dh}{dt} = \frac{kRP_a\left[\alpha - (R/(R-h))^3\right]}{R^2\varphi(1-\varphi)}, \tag{4}$$

where $\alpha = (P_\mathrm{k} + P_\mathrm{a})/P_\mathrm{a}$, or, denoting $h/R = \varphi$, in the form

$$\frac{d\varphi}{dt} = \frac{kP_\mathrm{a}\left[\alpha - (1/(1-\varphi))^3\right]}{R^2\varphi(1-\varphi)}. \tag{5}$$

Taking into account the condition for cessation of capillary impregnation,

$$\alpha - \left(\frac{1}{1-\varphi_\infty}\right)^3 = 0, \tag{6}$$

where φ_∞ is the limiting degree of capillary impregnation, the expression for the rate of capillary impregnation can be written as

$$\frac{d\varphi}{dt} = \frac{kP_{\mathrm{a}}}{R^2\varphi(1-\varphi)}\left[\left(\frac{1}{1-\varphi_\infty}\right)^3 - \left(\frac{1}{1-\varphi}\right)^3\right]. \tag{7}$$

Separating the variables in (5), after integration we obtain the dependence between the duration and the degree of capillary impregnation

$$Mt = \frac{\psi^3}{3\alpha} - \frac{\psi^2}{2\alpha} - \frac{1}{3\alpha^2}\ln|\alpha\psi^3 - 1| - \frac{\alpha^{-5/3}}{6}\ln\left|\frac{(\psi-\alpha^{-1/3})^2}{\alpha^{-2/3}+\alpha^{-1/3}\psi+\psi^2}\right| +$$

$$+\frac{1}{\alpha\sqrt{3}}\operatorname{arc\,tg}\frac{2\psi+\alpha^{-1/3}}{\sqrt{3}\alpha^{-1/3}}, \tag{8}$$

where $\psi = 1-\varphi;\ M = kP_{\mathrm{a}}/R^2$.

As is seen from (4), in the initial stage of impregnation, when the term $(R/(R-h))^3$ may be neglected in comparison with α, and h in comparison with R, the impregnation rate $dh/dt \simeq kP_{\mathrm{a}}\alpha/h$, which leads to the generally known parabolic law of impregnation

$$h^2 \simeq 2kP_{\mathrm{a}}\alpha t. \tag{9}$$

Let us note that, using (6), one can estimate the mean pore radius of silica gels by measuring the limiting depth of capillary impregnation. These measurements are conveniently made by observing impregnation under a microscope at low magnification. The impregnated part of the grain becomes transparent, and inside it the nonimpregnated core with trapped air is visible:

$$r \simeq \frac{2\sigma}{P_{\mathrm{a}}\left[1/(1-\varphi_\infty)-1\right]}. \tag{10}$$

Experiments on capillary impregnation of granules may also be used to study the nature of the surface of modified sorbents. Usually the surface of modified sorbents (^{6}) is characterized by adsorption isotherms of vapors of polar and nonpolar substances. On the other hand, for smooth surfaces one convenient characteristic is the value of the wetting angle. By studying the character of impregnation of the initial and then the modified sorbent, one can judge the change in the properties of its surface from the change in the wetting angle. A hydrophobized silica gel will behave, with water that does not wet it, like materials not wetted by mercury in porometric studies (^{7}), and water will enter the pores of such a silica gel only under excess pressure.

By placing granules of hydrophobized silica gel in a bomb with water and measuring the depth of impregnation and the pressure at which this impregnation has reached a given value, one can determine the wetting angle from the formula

$$\cos\theta \simeq \frac{r-\Delta r}{2\sigma}\left[\frac{P_{\mathrm{a}}}{(1-\varphi_2)^3}-P\ \right], \tag{11}$$

where φ_2 is the limiting depth of impregnation by a nonwetting liquid, attained under the pressure P ; Δr is the thickness of the layer of modifying substance.

Let us now turn to the analysis of extraction during the stage of capillary impregnation. The equation of convective diffusion for a spherical granule is

$$\frac{\partial c}{\partial t} = D\left(\frac{\partial^2 c}{\partial x^2}+\frac{2}{x}\frac{\partial c}{\partial x}\right)+V_x\frac{\partial c}{\partial x}, \tag{12}$$

where

$$R-h \le x \le R; \qquad V_R \le V_x \le V_{R-h}.$$

Boundary conditions:

$$X=R, \quad c=c_0; \qquad x=R-h, \quad c_s V_x = -D\,\partial c/\partial x, \tag{13}$$

where c_s is the volume concentration of the extracted substance in the pores in the absence of diffusion; c_0 is the concentration of the same substance in the surrounding liquid.

From equation (4) and the condition of continuity of the liquid, the velocity of motion in any cross section is

$$V_{(x,R-h)} = V_{(x=R-h,h)}\frac{S_{(R-h)}}{S_x} =$$

$$= \frac{kRP_a(R-h)}{hx^2}\left[\alpha-\left(\frac{R}{R-h}\right)^3\right] = \frac{A}{x^2}. \tag{14}$$

In the initial stage, the rate of capillary impregnation may, with a small error, be considered independent of x, and one may put

$$dh/dt \approx kRP_a\alpha/h. \tag{15}$$

Earlier [4], a solution was obtained for the convective-diffusion equation from capillaries, describing extraction under a parabolic law of impregnation. Since the initial stage of impregnation of granules is likewise described by a parabolic law, and the term $(2/x)(\partial c/\partial x)$ in expression (12), as we shall see below, is small in comparison with $\partial^2 c/\partial x^2$, we use this solution. The solution in the "meniscus" system, i.e., in a system stationary relative to the spherical impregnation front, is

$$c_{(x_1,t)} = c_0 + \frac{\beta c_s\sqrt{\pi}}{2\sqrt{D}}\left[\operatorname{erf}\left(\frac{\beta}{2\sqrt{D}}\right) - \operatorname{erf}\left(\frac{x_1}{2\sqrt{Dt}}\right)\right], \tag{16}$$

where $\beta = \sqrt{2kRP_a\alpha}$. Let us pass to the "granule" system by means of the transformation $x_1 = x - R + \beta\sqrt{t}$:

$$c_{(x,t)} = c_0 + \frac{\beta c_s\sqrt{\pi}}{2\sqrt{D}}\left[\operatorname{erf}\left(\frac{\beta}{2\sqrt{D}}\right) - \operatorname{erf}\left(\frac{x - R + \beta\sqrt{t}}{2\sqrt{Dt}}\right)\right], \tag{17}$$

where

$$\operatorname{erf} y = \frac{2}{\sqrt{\pi}}\int_0^y e^{-t^2}\,dt$$

is the probability integral.

Expression (17) is an exact solution of the equation

$$\partial c/\partial t = D\,\partial^2 c/\partial x^2 + V_x\,\partial c/\partial x \tag{18}$$

with the same boundary conditions as in our problem. Comparing $\partial^2 c/\partial x^2$ and $(2/x)(\partial c/\partial x)$ as $x \to R$, we find that $\partial^2 c/\partial x^2 \gg (2/x)(\partial c/\partial x)$, and therefore equation (12) may be regarded as identical with (18), the solution of which is known.

The rate of extraction from the granule in the initial stage is

$$j = -S\left[D\frac{\partial c}{\partial x} + V_x c_x\right]_{x=R} = \frac{4\pi R^2 \beta c_s n}{2\sqrt{t}}\left[e^{-\beta^2/4D} - \frac{c_0}{c_s}\right], \tag{19}$$

and is described analogously to the rate of extraction from a single capillary; therefore all conclusions concerning the character of extraction from capillaries, obtained in [4], may be carried over to the initial stage of extraction from their spherical granule.

In particular, setting in (19) $e^{-\beta^2/4D} - c_0/c_s = 0$, one can find the critical values $\beta^2_{\text{cr}} = 4D\ln(c_s/c_0)$, which determine whether extraction will occur during the initial stage of capillary impregnation, when the liquid moves according to a parabolic law.

It should be noted that, for normal values of the viscosity and diffusion coefficients, extraction can proceed practically only in a medium that does not contain the substance being extracted. This agrees with the experiments of M.

V. Tovbin and V. P. Musienko[5], in which no extraction at all was observed in the initial stage of impregnation.

When the condition $t > h^2/D$ is fulfilled, the extraction process becomes quasi-stationary[8] and is described by the equation

$$j = -S\left[D\,\partial c/\partial x + V_{x,h}c_x\right] \tag{20}$$

with boundary conditions (13).

Using (13) and (14), we solve (20):

$$c_{(x,h)} = c_0 + c_s\,\frac{e^{A/Dx} - e^{A/DR}}{e^{A/D(R-h)}}, \tag{21}$$

$$j = 4\pi A h\left[c_s e^{A/DR - A/D(R-h)} - c_0\right]. \tag{22}$$

Setting the term in square brackets in expression (22) equal to zero, we find the corresponding critical values of the parameters that determine the possibility of the process occurring in its quasi-stationary stage:

$$D \ln\frac{c_s}{c_0} = kP_a\left[\alpha - \left(\frac{R}{R-h}\right)^3\right]. \tag{23}$$

As was to be expected, in the final stage of impregnation, when the role of convective transport is weakened owing to the decrease in the rate of capillary impregnation, extraction becomes possible even at smaller values of the concentration difference than are required in the initial stage of impregnation.

From this same equation one can find the depth of impregnation starting from which, for a given ratio of concentrations in the porous body and in the solvent surrounding it, the molecular flux will exceed the convective flux and the extraction process will begin:

$$h = R\left(1 - \frac{1}{\sqrt[3]{\alpha - \dfrac{D}{kP_a}\ln\dfrac{c_s}{c_0}}}\right). \tag{24}$$

Since, at large concentration differences, the extraction process may begin outside the quasi-stationary stage as well, expression (24) is only of an approximate character.

The expressions obtained make it possible to describe the initial and final portions of the extraction process during capillary impregnation. The problem of mass exchange at a moving boundary, when the law of motion deviates appreciably from quadratic and the process itself has not yet become quasi-stationary, is more complicated and will be considered by us subsequently.

Institute of Physical Chemistry
Academy of Sciences of the USSR

Received
11 V 1963

CITED LITERATURE

1. G. A. Aksel' rud, *Theory of Diffusional Extraction from Porous Bodies*, L' vov, 1959.
2. M. A. Al' tshuler, *Koll. zhurn.*, No. 6 (1961).
3. V. G. Levich, *Physicochemical Hydrodynamics*, Moscow, 1959.
4. B. V. Deryagin, M. A. Al' tshuler, *DAN*, **146**, No. 1, 139 (1962).
5. V. P. Musienko, M. V. Tovbin, *Ukr. khim. zhurn.*, **28**, No. 3 (1962).
6. I. E. Neimark, I. B. Slinyakova, *Ukr. khim. zhurn.*, **27**, No. 2 (1961).
7. T. G. Plachenov, V. A. Aleksandrov, G. M. Belotserkovskii, *Collection: Methods for Studying the Structure of Highly Disperse and Porous Bodies*, Publishing House of the Academy of Sciences of the USSR, 1953.
8. A. N. Tikhonov, A. A. Zhukhovitskii, Ya. L. Zabezhinskii, *ZhFKh*, No. 10, 1113 (1946).

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.