KINETICS OF ION EXCHANGE

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The simplest mathematical model is considered for explaining the mechanism of the kinetics of ion exchange by cationites. The effect of pulsed motion of the liquid on the rate of exchange is investigated.

The purpose of this investigation is to construct an approximate mathematical model of the ion exchange process and its experimental verification. It was established earlier [1-3] that the rate of exchange is determined by the diffusion of ions within the bounds of particles of the exchanger and beyond these bounds. The absorbed ions, having reached the interior of the exchanger grains are distributed between two phases. Part of the ions fill the pore spaces forming a solution of concentration C_2 and the other part C_a is concentrated on the surface of the pores. The appearance of concentration gradients leads to migration of the ions both in solution and at the inside surfaces. In accordance with this, two fields of concentration are formed which interact with one another because of exchange with ions.

The mathematical model which describes each of these fields must include the concept of sinks and sources of the substance. Thus, the concentration field C_2 is changing not only because of the diffusion of ions but also because of drainage of the substance to the surface. There is a relation between the concentrations C_2 and C_a which is determined by an equilibrium curve (Fig. 1). The differential equations for the transfer of ions within the exchanger grains have the form

$$m\frac{\partial c_2}{\partial t} = -\operatorname{div} j_c - w_{ca},$$

$$m\frac{\partial c_a}{\partial t} = -\operatorname{div} j_a - w_{ac}. \tag{2}$$

Combining Eq. (1) and (2) and taking into account that $w_{ac} = -w_{ca}$, we obtain

$$m\frac{\partial (c_2 + c_a)}{\partial t} = -\operatorname{div}(j_c + j_a). \tag{3}$$

The flow densities of the substance are proportional to the concentration gradients in corresponding phases:

$$j_c = -D_{1c}\operatorname{grad} c_2, \tag{4}$$

$$j_a = -D_{1a}\operatorname{grad} c_a. \tag{5}$$

Substitution of Eq. (4) and (5) in Eq. (1) and (2) leads to the equation

$$\frac{\partial (c_2 + c_a)}{\partial t} = D_c\nabla^2 c_2 + D_a\nabla^2 c_a. \tag{6}$$

The initial and boundary conditions must be added to this equation. At the instant t = 0 the required concentrations C_2 and C_a are constant or equal to 0,

$$c_2(x,\ y,\ z,\ 0) = c_0;\quad c_a(x,\ y,\ z,\ 0) = c_{a0}. \tag{7}$$

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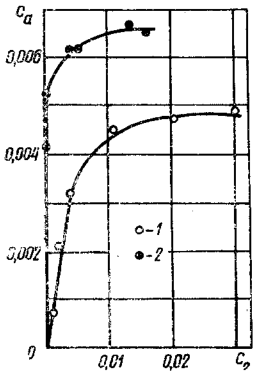

Fig. 1

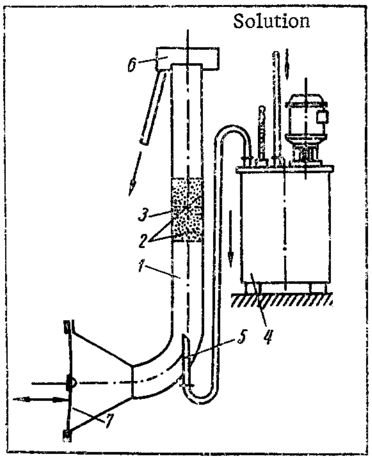

Fig. 2

Fig. 1. Equilibrium curves on cationite KU-2 at 298°K: 1) for potassium ions; 2) for mercury ions, c_a, g·equiv./g; c_2, g·equiv./litre.

Fig. 2. Diagram of experimental apparatus: 1) column; 2) rings; 3) "short" layer of cationite; 4) thermostat; 5) inlet tube; 6) receiver; 7) diaphragm pulsator.

We now establish the boundary conditions. The total flow of ions reaching the outer surface of a grain of exchanger by the external diffusion mechanism is divided into two flows, in the solution and at the pore walls respectively. Consequently the boundary conditions can be written in the form

$$D_{1c}\left(\frac{\partial c_2}{\partial n}\right)_s + D_{1a}\left(\frac{\partial c_a}{\partial n}\right)_s = k(c_1 - c_{2s}). \tag{8}$$

The solution of Eq. (6) with conditions (7) and (8) presents specific difficulties in view of the nonlinear relation between the quantities C_2 and C_a (equilibrium curve). A considerable simplification is achieved for a linear approximation of the equilibrium curve

$$c_a = \Gamma c_2 + A_1. \tag{9}$$

The use of the result of Eq. (9) leads to the well-known system

$$\begin{cases} \frac{\partial c_2}{\partial t} = D^* \nabla^2 c_2, \\ D_1^*\left(\frac{\partial c_2}{\partial n}\right)_s = k(c_1 - c_{2s}), \\ c_2(x, y, z, 0) = c_0, \end{cases} \tag{10}$$

where

$$D^* = \frac{D_c + \Gamma D_a}{1 + \Gamma}, \tag{11}$$

and

$$D_1^* = D_{1c} + \Gamma D_{1a}. \tag{12}$$

The solution of this system for spherical exchanger particles under conditions when $C_1 = C_n = \text{const}$ and $C_0 = 0$ gives the result

$$1 - \frac{c_a}{c_{ap}} = 1 - \frac{q}{q_0} = \sum_{n=1}^{\infty} B_n \exp\left(-\mu_n^2 \frac{D^* t}{R^2}\right). \tag{13}$$

In this equation

$$B_n = \frac{6\,\mathrm{Bi}^{*2}}{\mu_n^2(\mu_n^2 + \mathrm{Bi}^{*2} - \mathrm{Bi}^*)}, \tag{14}$$

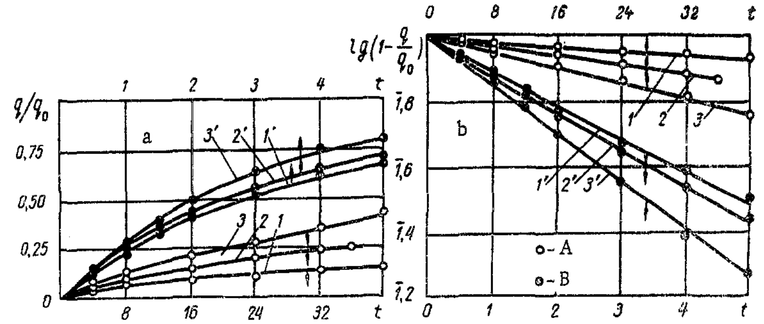

Fig. 3. Kinetic curves of the ion exchange of Hg^{++} by cationite KU-2 [a) relation $q/q_0 = f(t)$; b) relation $(1-q/q_0) = f(t)$ in semi-log coordinates]: 1, 1') with equilibrium flow of liquid; 2, 2') with pulsed motion of flow (2: $\omega A = 0.6$; 2': 0.12 cm/sec); 3, 3') with pulsed flow leading to the creation of an internal diffusion cycle (3: $\omega A = 1.55$ cm/sec; 3': $\omega A = 0.33$ cm/sec: A) with $\Gamma = 1.1 \cdot 10^5$; B) with $\Gamma \approx 0$; t in min.

where

$$\mathrm{Bi}^* = \frac{kR}{D_{1c} + \Gamma D_{1a}}, \tag{15}$$

and a_n are the roots of the characteristic equation

$$\mathrm{tg}\,\mu = -\frac{1}{\mathrm{Bi}^* - 1}\mu. \tag{16}$$

The coefficients D* and Bi* which occur in Eq. (13) have a complex structure and reflect the kinetics of ion exchange. According to theory we must observe the following special features of ion exchange:

1) The kinetics of the process are determined by the range of the change of concentration. Experimental data on the equilibrium show that the range of change of concentration of C_2 can be divided into two parts: a) the region $\Gamma \gg 1$ and b) the region $T = 0$.

In the first of these regions, in accordance with Eq. (11), $D^* = D_a$ and in the second region $D^* = D_c$. If the coefficients D_a and D_c differ considerably in magnitude, then different rates of exchange should be observed in accordance with the differences in the coefficients.

2) It is well-known that Biot's criterion determines the nature of the kinetics of the process. For small values of this criterion the kinetics are of external diffusion and for large values they are of internal diffusion. It follows from Eq. (15) that in the region $\Gamma \gg 1$, when $D_{1a} \neq 0$ conditions are probable for which $\mathrm{Bi} < 1$ and the mechanism is of external diffusion. A powerful hydrodynamic effect is necessary (acceleration of the flow of liquid, formation of pulsations, mixing) [4, 5] to achieve an internal diffusion cycle. In the region $\Gamma \approx 0$ the cycle in the majority of cases is of internal diffusion or relatively weak hydrodynamic effects are necessary to convert it to an internal diffusion cycle.

As we shall see later, the mechanisms listed here have been confirmed by experiment.

In order to verify the theoretical mechanisms obtained above, a number of experiments on the kinetics of ion exchange were undertaken on cationite KU-2 with solutions of $Ca(NO_3)_2$ and $Hg(NO_3)_2$ in the special experimental apparatus shown in Fig. 2. The apparatus consists of a flow column 1 in which a weighed quantity of cationite was placed, 3. The solution from a pressurized flask after heating in the thermostat 4 to a temperature of 298°K was fed into the column by means of the pipe 5 passing through the "short" layer of cationite and entering the receiver from a free discharge 6. Pulsations of the liquid in the column were created by means of a diaphragm pulsator 7.

Cationite KU-2 in hydrogenous form with size $0.05 < d < 0.1$ cm was used as the exchanger. The starting solutions were prepared from the salts $Ca(NO_3)_2$ and $Hg(NO_3)_2$ at two different concentrations. The first concentrations (0.000189 g·equiv. Hg^{++}/liter and 0.0068 g·equiv·Ca^{++}/liter) corresponded on the equilibrium

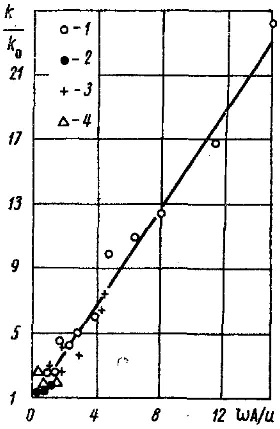

Fig. 4. Dependence of relative increase of mass exchange coefficient on the dimensionless complex $\omega A/u$: 1) for exchange with mercury ions when $\Gamma = 1.1 \cdot 10^5$; 2) the same, when $\Gamma \approx 0$; 3) for exchange with calcium ions when $\Gamma = 2.1 \cdot 10^3$; 4) the same, when $\Gamma \approx 0$.

curve to the values $\Gamma_{Hg^{++}} = 1.1 \cdot 10^5$ and $\Gamma_{Ca^{++}} = 2.1 \cdot 10^3$ and the second concentrations (0.0141 g • equiv. Hg^{++}/liter and 0.0254 g • equiv • Ca^{++}/liter) corresponded to the value $\Gamma \approx 0$.

One series of experiments was carried out with equilibrium motion of the solution through the layer of 0.104–0.416 cm/sec, and the other at the same rate but under conditions of pulsations applied to the flow. The pulsation frequency varied from 0.4 to 14 Hz and the amplitude varied within the limits 0.05 to 1.25 cm. The ion concentrations in the outlet solutions were determined for calcium by a complexnometric method and for mercury by a photocolorimetric method in the case of low concentrations and by titration with a solution of NH_4CNS in the region of high concentrations. The effluent kinetic curves obtained were recalculated from the outcome of the relation (Fig. 3a)

$$q/q_0 = f(t). \tag{17}$$

Curves 1 and 1' characterize the kinetics of the process under conditions of equilibrium liquid flow, when the process is limited by external diffusion. The change of hydrodynamic environment due to the creation of low-frequency pulsations of the liquid promotes intensification of the process (curves 2 and 2'). Further increase of amplitude of the pulsation rate ωA leads to the formation of an internal diffusion cycle (curves 3 and 3').

The plot of relation (17) in semilog coordinates shows that over the lapse of a certain time a linear relation is established (Fig. 3b). This also would be expected in accordance with Eq. (13) and [3].

We shall use first of all the experimental data obtained in the region $\Gamma \approx 0$ and also with stronger flow pulsations, when the exchange cycle is one of internal diffusion. In this case $D^* = D_c$ and Eq. (13) assumes the simpler form

$$1 - \frac{q}{q_0} = \sum_{n=1}^{\infty} \frac{6}{\pi^2 n^2} \exp\left(-\pi^2 n^2 \frac{D^* t}{R^2}\right). \tag{18}$$

In the region of normal cycle we have the following relation

$$D^* = \frac{R^2 \operatorname{tg} \alpha_I}{\pi^2 \cdot 0.4343}. \tag{19}$$

The values of the coefficients determined by formula (19) were found to be $0.26 \cdot 10^{-5}$ cm^2/sec for calcium ions and $0.075 \cdot 10^{-5}$ cm^2/sec for mercury ions.

Let us return now to the region $\Gamma \gg 1$ in which the effect of diffusion through the pore walls and, consequently, the effect of the coefficient D_a is apparent.

In considering the experiments carried out under the conditions of the internal diffusion cycle, i.e., at high values of ωA, it was found that Eq. (18) and (19) remain suitable also for determining the coefficient $D^* = D_a$ (formula (11)). Its value was found to be $0.1 \cdot 10^{-5}$ cm^2/sec for Ca^{++} and $0.003 \cdot 10^{-5}$ cm^2/sec for Hg^{++}.

It is interesting to compare the results obtained. The ratio of the coefficients D_c for Ca^{++} and Hg^{++} was found to be 3.4 whilst the ratio of the D_a coefficients for the same substances was 33. It follows from this, that the weight of the ions ($M_{Ca} = 40.08$; $M_{Hg} = 200.61$) has a considerably stronger effect on diffusion of the substance over the surface of the solid phase than on diffusion in solution. Theoretical considerations had shown previously, that the differences in value of the coefficients D_c and D_a should lead to differences in the kinetics for the regions $\Gamma \approx 0$ and $\Gamma \gg 1$. The data in Fig. 3 shows conclusively that this mechanism actually takes place.

We now determine Bi, the value of which defines the kinetics of the process. It follows from Eq. (15) that

$$\mathrm{Bi} = \frac{kR}{D_{1c}} \quad \text{and } \mathrm{Bi}^* = \frac{\mathrm{Bi}}{1 + \Gamma \dfrac{D_a}{D_c}} . \tag{20}$$

Thus, we establish that $\mathrm{Bi}^* = 0.0012\mathrm{Bi}$ and $\mathrm{Bi}^* \approx 75k$ for exchange with calcium ions; $\mathrm{Bi}^* = 0.00023\mathrm{Bi}$ and $\mathrm{Bi}^* \approx 50k$ for exchange with mercury ions.

It follows from comparison of both expressions that with one and the same value of Bi the value of Bi* is considerably less in the case of Hg^{++} diffusion. It can be expected therefore that external diffusion mass exchange is more probable for the process of Hg^{++} absorption than for Ca^{++}. Greater pulsation effects are necessary for converting this process to an internal diffusion process. Experiments confirm this situation. Thus, for Ca^{++} exchange the internal diffusion cycle is achieved when $\omega A = 1.08$ cm/sec, while for Hg^{++} exchange the cycle is achieved when $\omega A = 1.55$ cm/sec for one and the same ratio of liquid flow.

According to the results of ion exchange intensification by means of an oscillatory process, the relative increase of the mass exchange coefficients can be assessed as

$$k_p/k_0 = \mathrm{Bi}^*/\mathrm{Bi}_0^* \tag{21}$$

(Bi* corresponds to the absence of pulsations). For this, the normal cycle region was selected, for which the equation

$$\lg\left(1 - \frac{q}{q_0}\right) = \lg B_1 - 0.4343\mu_1^2 \frac{D^*t}{R^2}$$

holds, and the angle of slope of the straight line was established for the normal cycle a, related to μ_1 by the relation

$$\operatorname{tg} \alpha = 0.4343\mu_1^2 \frac{D^*}{R^2} .$$

Comparing the two processes, the first of which is an internal diffusion process ($\alpha = \alpha_B$ and $\mu_1 = \pi$) and the second one takes place in the intermediate region and is defined by the parameters α and μ_1, we obtain

$$\mu_1 = \pi \sqrt{\frac{\operatorname{tg}\alpha}{\operatorname{tg}\alpha_I}} .$$

Values of μ_1 can be used for determining Bi* by Eq. (16) or by Table 6.5 in [6]. The operation mentioned can be carried out both in the presence and absence of pulsations. A value of Eq. (21) was established which was compared with the dimensionless complex $\omega A/u$ [5] (Fig. 4). As we can see, the use of pulsation effects also in the case of ion exchange is an effective means of intensifying external mass exchange.

NOTATION

Bi	is the Biot criterion;
j_c, j_a	are the ion flow densities in the liquid and absorption phases;
w_{ca}, w_{ac}	are the specific strengths of sources and sinks of substances associated with interphase transfers;
D_{1c}, D_{1a}	are the coefficients of mass conductivity in the liquid and absorption phases;
m	is the porosity of exchanger;
$D_c = D_{1c}/m$;	
$D_a = D_{1a}/m$;	
c_0 and C_{a0}	are the initial concentrations of ions inside the pores and at the surface of the exchanger;
c_a, c_{ap}	are the ion concentrations on the exchanger at a given time t and under equilibrium conditions;

q, q_0	are the masses of substance absorbed by the exchanger relative to the given time t and under equilibrium conditions;
c_i	is the initial concentration of original solution;
c_1	is the concentration of absorbed ions outside a granule of exchanger;
c_{2s}	is the ion concentration at the outer surface of a granule of exchanger;
n	is the normal to the surface of the granule;
Γ	is the average slope of the equilibrium isotherm in a given range of concentration;
R	is the radius of a particle of exchanger;
$d = 2R$;	
α	is the angle of slope of straight line for the normal cycle, in semilog coordinates;
k	is the mass exchange coefficient;
k_0	is the mass exchange coefficient with equilibrium flow of liquid pulsation frequency;
A	is the amplitude;
u	is the linear flow rate;
x, y, z	are the coordinates.

Subscripts

s	denotes the surface of exchanger granule;
I	denotes the internal diffusion process;
p	denotes the pulsed process.

LITERATURE CITED

1. Boyd, Adamson, and Meyers, Chromatographic Method for Separation of Ions [Russian translation], IL (1949), p. 333.
2. F. Helferik, Ionites. Principles of Ion Exchange [Russian translation], IL (1962).
3. G. A. Aksel'rud, Zhur. Fizich. Khimii, 37, 1251 (1963).
4. G. A. Aksel'rud, Theory of Diffusion Extraction of Substances from Porous Substances [in Russian], Izd. Politekhnicheskogo Institute, L'vov (1959).
5. I. N. Fiklistov and G. A. Aksel'rud, Inst. Fiz. Zhur., 10, No. 4, 531 (1966).
6. A. V. Lykov, Theory of Heat Conduction [in Russian], Vysshaya Shkola, Moscow (1967).