

SOME CHARACTERISTICS OF THE KINETICS OF ION EXCHANGE IN THE CASE OF PULSATING MOTION OF A LIQUID

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An approximate mathematical model is discussed for the kinetics of exchange under conditions of an intradiffusion process in the case of pulsating motion of a liquid.

The kinetics of ion exchange between a layer of exchanger and a pulsating flow of liquid is considered in [1]. With a defined amplitude of the pulsation rate, an intradiffusion exchange cycle originates. An approximate mathematical model of the process was developed for conditions when $c_1 = c_1 = \text{const}$.

Careful analysis of the results of experiments in the region $\Gamma \gg 1$ showed that despite the presence of an intradiffusion cycle (the velocity of the process was unchanged with increase of amplitude of the pulsation rate), the kinetics are dependent on the supply of liquid moving along the exchanger. Contrary to the traditional representation of the intradiffusion cycle, an increase of the speed of movement of the liquid increases the rate of exchange.

The proposed mathematical model explains this apparent contradiction. For a system with spherical symmetry, the kinetic equation of ion exchange can be written as follows [2, 3]:

$$\frac{\partial c_2}{\partial t} = D * \left(\frac{\partial^2 c_2}{\partial r^2} + \frac{2}{r} \frac{\partial c_2}{\partial r} \right). \quad (1)$$

We supplement Eq. (1) with the initial and boundary conditions:

$$\begin{aligned} c_2(r, 0) &= 0; \\ \left(\frac{\partial c_2}{\partial r} \right)_{r=0} &= 0; \\ \frac{\partial (Vc_a)}{\partial t} &= w(c_1 - c_1). \end{aligned} \quad (2)$$

The last balance equation determines the concentration c_1 in the liquid after passing through a "short" layer of exchanger. Liquid with this concentration again is involved in exchange because of the presence of pulsations. Therefore, at the boundaries of the particles of exchanger, the concentration environment is determined by the condition $c_2 = c_1$ and not by the condition $c_2 = c_1$.

The solution of system (1) and (2) by the Laplace transform method leads to the following results:

$$\frac{c_1}{c_i} = 1 - \sum_{n=1}^{\infty} \frac{2\alpha}{\alpha(\alpha/3-1) + 3\mu_n^2} \exp(-\mu_n^2 \tau), \quad (3)$$

$$\frac{\bar{c}_a}{c_p} = 1 - \sum_{n=1}^{\infty} \frac{2\alpha^2}{\mu_n^2 [\alpha(\alpha/3-1) + 3\mu_n^2]} \exp(-\mu_n^2 \tau), \quad (4)$$

where $\tan \mu = (-\mu)/(\alpha/3-1)$; $c_a = \Gamma c_2$; $\bar{c}_a = \Gamma \bar{c}_2$;

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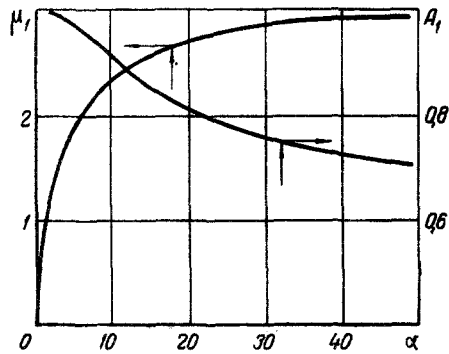


Fig. 1

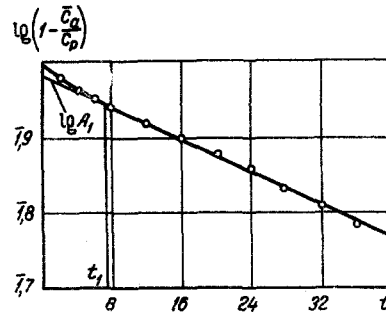


Fig. 2

Fig. 1. Dependence of μ_1 and A_1 on the dimensionless complex α .

Fig. 2. Function $(1 - \overline{c_a/c_p}) = f(t)$ in semilogarithmic coordinates when $w = 0.5 \text{ cm}^3/\text{sec}$ (t , min).

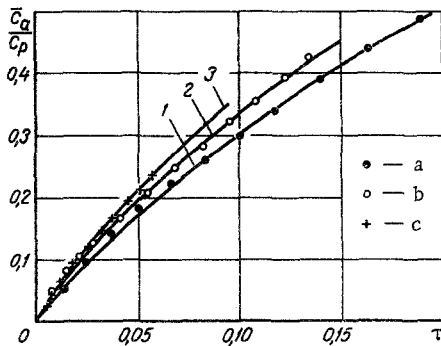


Fig. 3. Comparison of theoretical (solid lines) and experimental data: 1) $\alpha_1 = 4.5$; 2) $\alpha_2 = 5.1$; 3) $\alpha_3 = 6.0$; a) $w_1 = 0.25$; b) $w_2 = 0.5$; c) $w_3 = 1.0 \text{ cm}^3/\text{sec}$.

$$c_p = \Gamma c_i; \quad \alpha = \frac{w r_0^2}{V D^* \Gamma}; \quad \tau = \frac{D^* t}{r_0^2}.$$

When $\alpha \rightarrow \infty$ the latter equation reduces to the well-known equation

$$\frac{\overline{c_a}}{c_p} = 1 - \sum_{n=1}^{\infty} \frac{6}{\mu_n^2} \exp(-\mu_n^2 \tau); \quad (5)$$

$$\mu_n = \pi n.$$

Figure 1 shows the relation between the first root of the characteristic equation for μ_1 and the quantity A_1 , which was determined by the formula:

$$A_1 = \frac{2\alpha^2}{\mu_1^2 [\alpha(\alpha/3 - 1) + 3\mu_1^2]}. \quad (6)$$

We compare the results obtained with the experimental data on the kinetics of ion exchange on cationite KU-2 in H-form by its interaction with the pulsating liquid (solution of $\text{Hg}(\text{NO}_3)_2$ with an initial concentration of $0.000189 \text{ g-eq/liter}$). The scheme of the experimental equipment and the experimental procedure are described in [1].

The application of Eq. (5) for explaining the experimental data on ion exchange encountered specific difficulties. According to these equations, in the region of the normal cycle when $t > t_1$ (see Fig. 2), the kinetics of exchange in semilogarithmic coordinates should be described by a straight line [4]. This line makes an intercept on the axis of ordinate when $A_1 = 0.606$. Its slope should be independent of the supply of liquid and is determined for all flows by one and the same diffusion coefficient. The experimental data show that the normal cycle actually is evolved, however A_1 is greater than the value 0.606 and frequently approaches unity, but the magnitude of the slope depends on the flow of liquid.

By means of Eq. (4) we can easily explain the special features of exchange kinetics. Actually, according to Eq. (4) the quantity A_1 (Eq. (6)) varies within the limits $A_1 = 0.606$ when $\alpha \rightarrow \infty$; $A_1 = 0.98$ when $\alpha = 3$. With increase of α the slope of the straight line of the normal cycle is also increased. The diffusion coefficient, determined in this way, proves to be approximately identical and equal to $0.9 \cdot 10^{-7} \text{ cm}^2/\text{sec}$.

Figure 3 shows the curves of the absorption kinetics of mercury ions by an exchanger for different liquid flows (0.25 ; 0.5 and $1.0 \text{ cm}^3/\text{sec}$). The corresponding values of the parameter α , found by experimentally determined values of A_1 (see Fig. 1), are $\alpha_1 = 4.5$; $\alpha_2 = 5.1$ and $\alpha_3 = 6.0$.

Thus, a more accurate theoretical explanation is found for the experimental relations of ion exchange.

NOTATION

c_i	is the initial concentration of solution;
c_1	is the concentration of solution beyond the bounds of the particles of exchanger;
c_2	is the concentration of substance in solution in the pores of the exchanger at distance r ;
\bar{c}_2	is the average concentration of substance in solution in the pores of the exchanger;
D^*	is the internal diffusion coefficient;
Γ	is the average slope of equilibrium isotherm over a given range of concentration;
r_0	is the radius of granule of exchanger;
$0 \leq r \leq r_0$;	
w	is the flow rate of liquid;
V	is the volume of pores inside exchanger;
μ_n	are the roots of characteristic equation;
t	is the time.

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