

MATHEMATICAL DESCRIPTION OF THE PROCESS OF REMOVING SOME IONS FROM AQUEOUS-ALCOHOL SOLUTIONS BY MEANS OF CATION-EXCHANGE RESINS

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Abstract The constant of ion exchange (IE) equilibrium and the total exchange capacity of an ionit are important characteristics of ion exchange process [1-3].

For their determination the (IE) equations, which correspond to one or another of their adsorption isotherm, are used. Knowing these values one describes the ion exchange equilibrium in double or triple ions system, i.e. calculates the equilibrium relation of ions quantity in solid to this one in solution.

The most widely used equation of (IE) isotherm was obtained by P. Nikolsky

$$\frac{X_1^{1/z_1}}{X_2^{1/z_2}} = k_{1,2} \cdot \frac{a_1^{1/z_1}}{a_2^{1/z_2}}, \quad (1)$$

where

$X_{1,2}$ – the quantity of absorbed ions;

$z_{1,2}$ – the charge of the same ions;

$k_{1,2}$ – the exchange ions constant of these;

$a_{1,2}$ – the activities of ions in equilibrium solution.

In this work the (IE) equilibrium of ions of Ca and Fe on the cation-exchange U – 2.8 and C 100 in H – form has been studied.

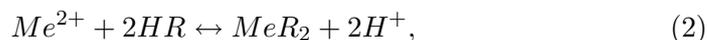
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At the ionit introduction into the solution at some time the equilibrium settles that characterizes by the certain distribution of cations between the cationit and the solution.

The quantitative dependence of the exchange degree on the ions concentration in the solution is expressed by the law of acting masses.

For the exchange of bivalent Ca and Fe in the solution (Me^{2+}) to univalent hydrogen ions (H^+) of the cationit we can write



where Me^{2+} and H^+ are exchanging ions; R is the insoluble anionic matrix of the cationit.

Then the thermodynamic constant of equilibrium of this equation is

$$k_T = \frac{C_{H^+}^2 \cdot C_{MeR_2}}{C_{Me^{2+}} \cdot C_{HR}^2} \cdot \frac{f_{H^+}^2 \cdot f_{MeR_2}}{f_{Me^{2+}} \cdot f_{HR}^2}, \quad (3)$$

where C_H^+ , C_{Me}^{2+} are the concentrations of ions in the solution; C_{MeR} , C_{HR} are the concentrations of these ions in the cationit; f_i are the coefficients of activity of corresponding ions in the cationit and in the solution.

The main difficulty when using equation (3) is the determination of the activity coefficients in the ionit phase. Often in order to solve this problem it is assumed the ionit phase as an ideal solid solution of exchanging ions and that ions activities are proportional to their concentration in the ionit phase. In this case the activity coefficients in equation (3) is omitted.

On the other hand, the relation of average activity coefficients of ions in the solution, if their concentrations are not so high ($\leq 0,01$ N), is close to 1. Then, under these hypotheses, equation (3) is

$$k_C = \frac{C_{H^+}^2 \cdot C_{MeR_2}}{C_{Me^{2+}} \cdot C_{HR}^2}. \quad (4)$$

Thus, at the exchange of ions equal to their charge at rather low concentrations of initial salts the value of concentration constant (IE) k_C is close to the value of thermodynamic constant (k_T).

In general, in order to determine experimentally the equilibrium constant (IE) one must know equilibrium concentrations of ions both in ionit phase and in solution that is difficult to do sometimes. If the cationit in H form is used, such a calculation becomes possible.

Consider from this point of view the equation (4). In this equation denote the full exchange capacity by X_m (in mg-equiv) for the corresponding mass of the ionit (m), the initial quantity of ions in the solution by C_o (in mg-equiv); the quantity of exchanging ions ($Me^{2+} \rightarrow 2H^+$) by X (in mg-equiv).

Then the equilibrium concentrations of ions Me^{2+} and H^+ in the ionit phase and in the solution (according to equation (2)) is equal to

$$C_{Me}^{2+} = C_o - \frac{X}{2}; \quad C_{HR} = X_m - X; \quad C_{MeR_2} = \frac{X}{2}; \quad C_H^+ = X.$$

Substituting these values into equation (4) we obtain the expression for constant k_C

$$k_C = \frac{X^2 \cdot \frac{X}{2}}{(C_o - \frac{X}{2}) \cdot (X_m - X)^2}, \tag{5}$$

whence

$$(X_m - X)^2 = \frac{X^3}{k_C \cdot (2C_o - X)}, \tag{6}$$

or

$$X_m - X = \frac{X \cdot \sqrt{X}}{\sqrt{k_C \cdot (2C_o - X)}}. \tag{7}$$

By dividing both parts of equation (7) by $X_m \cdot X$ we obtain

$$\frac{1}{X} - \frac{1}{X_m} = \frac{1}{X_m \sqrt{k_c}} \sqrt{\frac{X}{2C_o - X}} \tag{8}$$

and, finally,

$$\frac{1}{X} = \frac{1}{X_m} + \frac{1}{X_m \sqrt{k_c}} \sqrt{\frac{X}{2C_o - X}}. \tag{9}$$

This is an equation of isotherm of ion exchange. If the initial concentrations of ions in the solution (C_o) are known and when determining experimentally the quantity of exchanging ions (Me^{2+}), that is equal to the quantity of evolving hydrogen ions (X), we can calculate the total exchangeable capacity of ionit (X_m) and the (IE) equilibrium constant (k_c).

Equation (9) represents an equation with two independent variables: X_m - the total exchangeable capacity of ionit, k_c - equilibrium constant of (IE). As

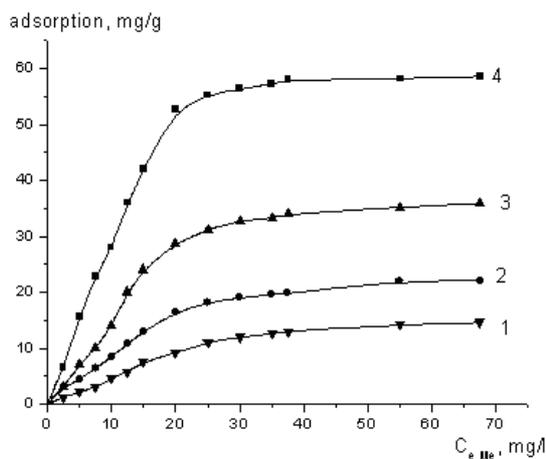


Fig. 1. Isotherms of adsorption of Ca (3, 4) and Fe (1, 2) on cationites KU-2*8H (1, 4) and C100H (2, 3). Weight of ionit - 0,25 g, volume of solution - 200 ml, time of contact of ionit with solution - 24 h.

any equation, it requires the determination of two parameters – X and C_0 . Parameter X can be obtained from data of experimental adsorption isotherm of Me^{2+} (fig. 1), and C_0 - the quantity of Me^{2+} ions in initial solution is assigned in advance.

In order to verify the applicability of equation (9) at the description of (IE) equilibrium in the triple ion system Ca, Fe, H we studied the dependencies of quantities of ions of bivalent metals Ca and Fe adsorbed by the ionits KU-2*8H – Ca and C 100H – Fe on their equilibrium concentration in the solution. The experiments were carried out in static conditions. The procedure of preparing of alcohol –aqueous solutions of Ca and Fe and the carrying out of experiments, and the calculation of values of ions adsorption are described in [4]. The maximal concentration of Ca and Fe in mixture was about 200mg/l, and the minimal one – 10 mg/l for each ion.

Fig. 1 shows the obtained experimental data.

Apparently the entire experimental points well coincide with the straight line, that testifies that the studied process of ion exchange of H ions from cationits with Ca and Fe ions is satisfactory described by the given equation.

Table 1 is under consideration.

Table 1 Total exchangeable capacity (X_m , mg/g) of the ionits.

X_m , mg/g						
Ionits \ Ions	KU 2*8H			C100H		
	Theoretic	Experimen- tal	Deviation, %	Theoretic	Experimen- tal	Deviation, %
Ca ²⁺	53,2	58,6	9,2	35,0	35,8	2,2
Fe ²⁺	21,5	22,9	6,3	16,1	14,5	9,3

In Table 1 the values of total exchange capacity X_m of cationits against Ca and Fe ions, calculated according to equation (9) and determined experimentally are shown. As can be seen the difference between values X_m calculated theoretically and those obtained experimentally does not exceed 10% what means that the proposed equation can be used for the determination of the total exchangeable capacity of ionits.

So, knowing the constants X_m and k_C one can calculate the value of adsorption of Me^{2+} ions by the ionit KU-2*8H and C100H at any of their concentrations in the initial solution and find the distribution of these ions in ionit phase and in the solution.

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