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## Abstract

## Full Text

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# STATICS OF EXCHANGE OF A MIXTURE OF IONS

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As is known, the main purpose of applying ordinary ion-exchange processes and ion-exchange chromatography is the absorption and separation of mixtures; nevertheless, up to the present time the statics of ion exchange has been studied for ions separately. In doing so, the independence of the exchange of each pair of ions is assumed (1–7). The degree of validity of such an approximation for solutions of different concentrations has been insufficiently studied, in many respects because of the need for cumbersome calculations.

Fig. 1. Nomograms for calculating equilibrium concentrations of ions during exchange in multicomponent systems

The aim of the present work was to find a simple method for calculating equilibrium ratios in a multicomponent system with known initial concentrations, for given values of the exchange constants, and to compare the calculated data with experimental data.

The calculation was reduced to solving a system of equations that includes the material-balance equations and the exchange isotherms for each ion, under the assumption that the activity coefficients of the ions in solution and in the resin are equal to unity:

$$\frac{A_i^{1/z_i}}{A_j^{1/z_j}} = K_{ij}\frac{C_i^{1/z_i}}{C_j^{1/z_j}}, \qquad i,\ j = 1,\ 2, \ldots,\ n; \tag{1}$$

$$m(A_i - A_{0i}) = V(C_{0i} - C_i); \tag{2}$$

Figure 2 graph: exchange isotherms of sodium and cesium on hydrogen in a three-component system.

Figure 2: Figure 2 graph: exchange isotherms of sodium and cesium on hydrogen in a three-component system.

$$A_0 = \sum_{i=1}^{n} A_i = \sum_{i=1}^{n} A_{0i}; \tag{3}$$

$$C_0 = \sum_{i=1}^{n} C_i = \sum_{i=1}^{n} C_{0i}; \tag{4}$$

$A_i, A_j$ are the sorbed amounts of the $i$-th and $j$-th ions per unit mass of ion exchanger; $C_i, C_j$ are the equilibrium concentrations of the $i$-th and $j$-th ions in solution; $A_{0i}, A_{0j}$ are the initial amounts of the $i$-th and $j$-th ions per unit mass of ion exchanger; $C_{0i}, C_{0j}$ are the initial concentrations of the $i$-th and $j$-th ions in solution; $A_0$ is the static exchange capacity of the ion exchanger; $V$ is the volume of solution; $m$ is the mass of ion exchanger; $z_i, z_j$ are the charges of the ions.

Since in processes of absorption and separation of mixtures of elements an ion exchanger is usually used in the form of a singly charged ion, the ion in the form in which the initial ion exchanger is present is denoted by the subscript 1, $A_{01} = A_0$; $A_{02} = A_{03} = ... = A_{04} = 0$, and $z = 1$ is taken.

The solution of the system of equations (1), (2), (3), and (4) is found by the following method. From the equation

**Fig. 2.** Exchange isotherms of sodium and cesium for hydrogen during exchange in a three-component system. 1 —experimental data, 2 —data calculated from nomograms

$$\left(\frac{C_{0i}}{C_i} - 1\right)^{1/z_i} = K_{i1}\left(\frac{V}{m}\right)^{1-1/z_i} \frac{1}{\dfrac{A_0}{A_1}(1+b) - 1}. \tag{5}$$

(where $b = \dfrac{V}{m}\dfrac{C_{01}}{A_0}$), which is a consequence of equations (1)–(4), the set of values of all $C_i$ is calculated for an arbitrarily specified value of $A_1$. Then, from the found $C_i$, the quantity is calculated

$$A_1^1 = A_0 - \frac{V}{m}\left(\sum_{i=2}^{n} C_{0i} - \sum_{i=2}^{n} C_i\right). \tag{6}$$

Figure 3 graph: exchange isotherms of sodium and calcium on hydrogen in a three-component system in the presence of 0.1 N hydrochloric acid.

Figure 3: Figure 3 graph: exchange isotherms of sodium and calcium on hydrogen in a three-component system in the presence of 0.1 N hydrochloric acid.

Then, constructing graphically the dependence of $A_1^1$ on $A_1$, we find the solution of the system of equations at the point for which $A_1 = A_1^1$. Calculation by equation (6) is facilitated by the use of nomograms (Fig. 1).

We studied exchange in a three-component system on a cation exchanger in a hydrogen form.

**Fig. 3.** Exchange isotherms of sodium and calcium for hydrogen during exchange in a three-component system in the presence of 0.1 N hydrochloric acid. 1 —experimental data, 2 —data calculated from nomograms

The quantities of the individual ion-exchange constants in the mixture that are necessary for calculating the equilibrium ratios were determined experimentally under static conditions and calculated from equation (1).

The experimental equilibrium ratios were studied using the systems NaCl—CsCl—RH and NaCl—$CaCl_2$—HCl—RH on the cation exchanger KU-2 under static conditions, at salt concentrations up to 1 N and an equivalent metal ratio of 1 : 1. The equilibrium concentrations of sodium and cesium were determined radiometrically; the equilibrium concentrations of Ca, by complexometric titration with Trilon B (in the resin phase, after desorption with NaCl solution). For exchange in concentrated solutions ($> 0.2$ N), where the smallest quantity is the hydrogen concentration in the cation exchanger, the latter was determined directly by washing the hydrogen from the cation exchanger with 2N NaCl solution and titrating it with alkali.

The experimental data obtained on exchange in three-component systems and their comparison with calculations based on the assumption of independence of ion exchange are presented in Figs. 2 and 3. It is clearly seen that there is complete agreement between the experimental and calculated data up to an equilibrium solution concentration of, on average, 0.05 N, and a regular divergence at higher solution concentrations, which, apparently, cannot be explained solely by the behavior of the activity coefficients of the substances.

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## CITED LITERATURE

[1] B. P. Nikol' skii, V. I. Paramonova, *Usp. khim.*, **8**, No. 10, 1535 (1939).
[2] A. M. Trofimov, in: *Chromatography*, Leningrad State University Press, 1956, p. 15.
[3] T. F. Antipova-Karataeva, I. N. Antipov-Karataev, *Koll. zhurn.*, **5**, 419 (1939).
[4] J. Dranoff, L. Lapidus, *Industr. and Eng. Chem.*, **49**, No. 8, 1297 (1957).
[5] G. Jangg, *Österr. Chem. Ztg.*, **59**, Nos. 23-24, 331 (1958).
[6] K. M. Saldadze, A. B. Pashkov, V. S. Titov, *Ion-Exchange High-Molecular Compounds*, Moscow, 1960, p. 38.
[7] A. T. Davydov, I. Ya. Levin, *Tr. N.-i. inst. khimii Khar' kovsk. gos. univ.*, **10**, 221 (1953); **12**, 309 (1954); **12**, 316 (1954).

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