Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Ternary Ion-Exchange Equilibria

V. S. Soldatov[a]; V. A. Bichkova[a]
[a] INSTITUTE OF GENERAL AND INORGANIC CHEMISTRY, BSSR ACADEMY OF SCIENCES MINSK, USSR

To cite this Article Soldatov, V. S. and Bichkova, V. A.(1980) 'Ternary Ion-Exchange Equilibria', Separation Science and Technology, 15: 2, 89 — 110

To link to this Article: DOI: 10.1080/01496398008056084

URL: http://dx.doi.org/10.1080/01496398008056084

SEPARATION SCIENCE AND TECHNOLOGY, 15(2), pp. 89–110, 1980

Ternary Ion-Exchange Equilibria

V. S. SOLDATOV and V. A. BICHKOVA

INSTITUTE OF GENERAL AND INORGANIC CHEMISTRY
BSSR ACADEMY OF SCIENCES
MINSK, USSR

Abstract

The shape of parametric lines in both phases of ternary ion-exchange systems are discussed for both ideal and nonideal systems. It has been shown that deviations of the parametric lines from linearity correspond to nonideality of the system while the converse is not necessarily valid. Conditions of linearity for nonideal systems are derived. Equations for calculating activity coefficients of resinates in ternary mixtures are given. Triangular diagrams and three-dimensional diagrams of the dependence of activity coefficients on composition are illustrated by the systems NH_4^+–Na^+–H^+ and Ba^{2+}–Cu^{2+}–Co^{2+} on sulfostyrene-type exchangers. Methods for prediction of ternary ion-exchange equilibria are discussed. A comparison of these methods for the systems studied shows that consideration of the nonideality of the systems is required for accurate prediction.

INTRODUCTION

Nearly all practical, important, and natural ion-exchange processes deal with more than two exchangeable ions. At the same time, most of our knowledge of the regularities of ion exchange comes from investigation of binary exchanges. Few systematic studies have been done on multicomponent ion exchange because of the complexity of both experimental and theoretical multiionic systems.

The prediction of multicomponent equilibria from the data of binary exchange was the main goal of the works published on this problem. Little attention has been paid to the problem of the influence of resin composition on the affinity of ions in multiionic resin.

In this paper we summarize our work on multicomponent exchange equilibria carried out since 1966 in the Laboratory of Ion Exchange and Sorption of the Institute of General and Inorganic Chemistry of the BSSR Academy of Sciences.

IDEAL MULTIIONIC EXCHANGE

We define ideal exchange as a process in which the activity coefficients of all the components remain constant. This corresponds to constant values of concentration equilibrium constants of both binary and "pseudobinary" exchanges. The term "pseudobinary exchange" is used to discuss exchange in the presence of the third ion.

Complete information on the distribution of ions 1, 2, and 3 between ion exchanger and solution can conveniently be given by a couple of triangular diagrams for both phases where the composition of one of the phases changes along some lines, i.e., x_i, $\bar{x}_i$ = const or x_i/x_j, $\bar{x}_i/\bar{x}_j$ = const, which is denoted as a line of thermodynamic simplification (*1*, *2*). Here x_i, x_j are equivalent fractions of the ions exchanging; the bars denote quantities within the resin phase, and $\sum_i x_i = 1$. These lines of thermodynamic simplification of properties are also called parametric lines (*1*, *2*). By definition, points on the lines corresponding to the same equilibrium in the two phases should be numbered identically as in Fig. 1. For a complete description of the system, the value of the total concentrations of the components in each phase is also required.

It has been shown (*3*, *4*) that straight parametric lines in triangular diagrams correspond to ideal exchange in the case of homovalent ions. At the same time, the converse is not necessarily true. For heterovalent ternary exchange it is easily seen that a constant value of a pseudobinary heterovalent concentration constant does not lead to straight parametric lines in the triangular diagram.

The equation

$$k_x = \frac{\bar{x}_1 x_2}{\bar{x}_2 x_1} = \text{const} \tag{1}$$

is the condition of linearity of the parametric lines. If $z_1 \neq z_2$, for ideal systems we have

$$K = \frac{\bar{c}_1^{\,1/z_1} c_2^{\,1/z_2}}{\bar{c}_2^{\,1/z_2} c_1^{\,1/z_1}} = k_x \left(\frac{\bar{x}_1}{x_1}\right)^{(1/z_1-1)} \left(\frac{x_2}{\bar{x}_2}\right)^{(1/z_2-1)} \left(\frac{z_1\bar{c}_1 + z_2\bar{c}_2}{z_1 c_1 + z_2 c_2}\right)^{(1/z_1-1/z_2)} \tag{2}$$

where c is concentration on the chosen scale. Since K = const, k_x cannot be constant because of the presence of another variable part in the equation, and the parametric lines are not straight.

If two of the three ions (e.g., 1 and 3) in the ternary system have the same charge, it is clear that some parametric lines are straight: x_1/x_3 = const, $\bar{x}_1/\bar{x}_3$ = const, etc.

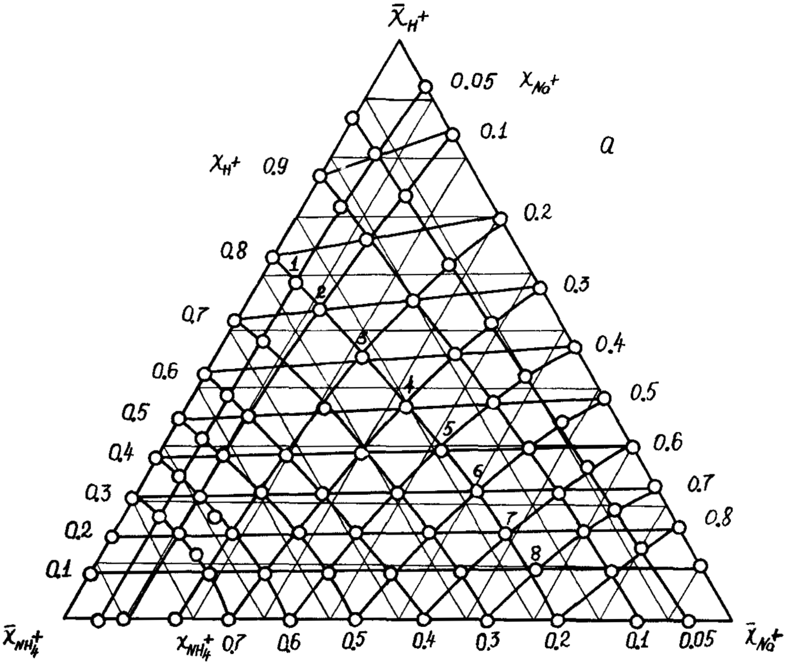

FIG. 1a. Composition of ion exchanger Dowex 50w x 12 in equilibrium with 0.1 *M* solution of NH^+_4, Na^+, and H^+ chlorides; $t=25.0°C$. Lines in the triangle correspond to constant equivalent fractions (shown in the figure) of the ion in the solution.

NONIDEAL ION EXCHANGE SYSTEMS

These simple deductions can help in the interpretation of experimental data for ternary exchanges presented in the form of triangular diagrams. Direct analysis of the dependences of pseudobinary concentration constants on the phase composition is rather difficult, because each system is characterized by at least two three-dimensional diagrams [e.g., $\tilde{K}_3^1 = f(\bar{x}_1, \bar{x}_2)$ and $\tilde{K}_2^1 = f(\bar{x}_1, \bar{x}_2)$].

Several examples of triangular diagrams for the systems of different complexity are given in Figs. 1–3. The highly cross-linked cation exchanger KU-2x25 (Soviet production similar to Dowex 50x25) is used because the largest nonideality is expected in this case.

Deviations from ideality in binary systems (Fig. 4) correlate well with

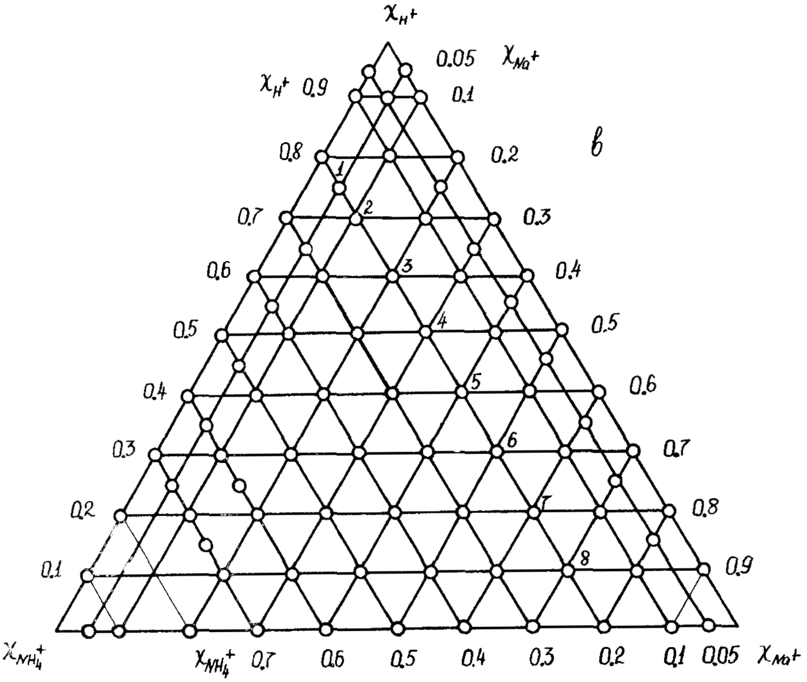

FIG. 1b. Composition of 0.1 *M* NH_4^+, Na^+, and H^+ chloride solution equilibrium with Dowex 50w x 12. Connected equilibrium points are numbered identically in Figs. 1a and 1b.

nonlinearity of the parametric lines in the triangular diagrams. It is also seen that in the case of hetervalent ternary exchange with two ions of equal charge, lines corresponding to a constant ratio of these ions are close to straight, while, if $x_{NH_4}{}^{+}/x_{Mg}{}^{2+}$ is constant, straight parametric lines are not obtained (*5*) (Fig. 5).

It has been mentioned that straight lines in triangular diagrams do not necessarily correspond to ideal exchange. Here we shall look upon some special cases where straight parametric lines can appear in nonideal systems. (*6*, *7*).

The condition of linearity of parametric lines in triangular diagrams is

$$\Delta\bar{x}_1/\Delta\bar{x}_2 = \text{const} \tag{3}$$

If we find $\bar{x}_i = \bar{x}_i(\tilde{K}_2{}^1, \tilde{K}_3{}^1, x_1, x_2)$ ($\tilde{K}$ is an apparent equilibrium constant) and substitute it into (3), we have

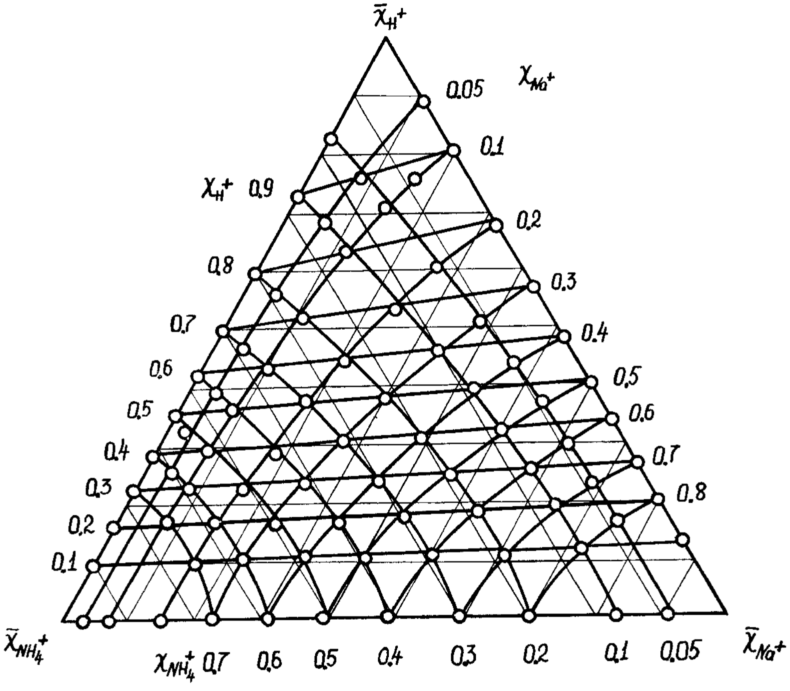

FIG. 2 Resin KU-2x25. See text to Fig. 1a.

$$\frac{\tilde{K}_3^1(-\tilde{K}_3^2+1)}{\tilde{K}_3^2(\tilde{K}_3^1+b)}=\text{const},\qquad \frac{\tilde{K}_3^1(-\tilde{K}_3^2+1)}{-\tilde{K}_3^1-\tilde{K}_3^2 b}=\text{const},$$

$$\text{if}\quad x_1=\text{const}\tag{4a}$$

$$\frac{\tilde{K}_3^1(\tilde{K}_3^2+b)}{\tilde{K}_3^2(-\tilde{K}_3^1+1)}=\text{const},\qquad \frac{\tilde{K}_3^2(-\tilde{K}_3^1+1)}{-\tilde{K}_3^1 b-\tilde{K}_3^2}=\text{const},$$

$$\text{if}\quad x_2=\text{const}\tag{4b}$$

$$\frac{\tilde{K}_3^1(\tilde{K}_3^2 b+1)}{-\tilde{K}_3^1+\tilde{K}_3^2}=\text{const},\qquad \frac{-\tilde{K}_3^1+\tilde{K}_3^2}{\tilde{K}_3^2(-\tilde{K}_3^1 b-1)}=\text{const},$$

$$\text{if}\quad x_3=\text{const}\tag{4c}$$

where

$$b=\frac{x_2^{\mathrm{II}}x_3^{\mathrm{I}}-x_2^{\mathrm{I}}x_3^{\mathrm{II}}}{x_1|(x_2^{\mathrm{I}}-x_2^{\mathrm{II}})|}$$

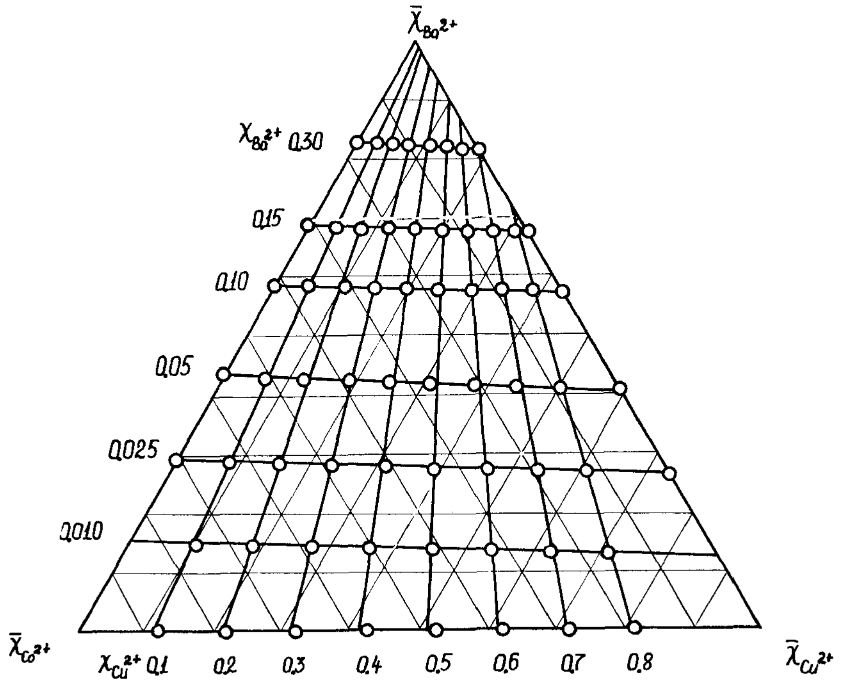

FIG. 3 Resin Dowex 50x x 12. System Ba^{2+}–Cu^{2+}–Co^{2+}. See text to Fig. 1a.

x^{I} and x^{II} are defined by

$$\Delta x_i = x_i^{\mathrm{I}} - x_i^{\mathrm{II}}$$

Δx_i corresponds to $\Delta \bar{x}_i$ (Eq. 3).

Suppose that ions 2 and 3 are close in properties, then the value $\tilde{K}_3{}^1$ must be approximately constant where x_1 = const. Under these conditions, (4a) is an equation of a straight line. At the same time, the other two parametric lines are approximately linear if $\tilde{K}_3{}^1 \gg \tilde{K}_3{}^2$ and $\tilde{K}_3{}^1 \gg 1$ (see Figs. 3 and 4). This is important to know for prediction of ternary equilibria.

ACTIVITY COEFFICIENTS

The examples given in Figs. 3 and 4 show that nonideality of ternary resinate mixtures has to be taken into consideration. The methods of calculation of activity coefficients in multiionic systems has been described in previous works (*8*, *9*). It is a generalization of the method suggested earlier for binary systems (*10a*, *10b*).

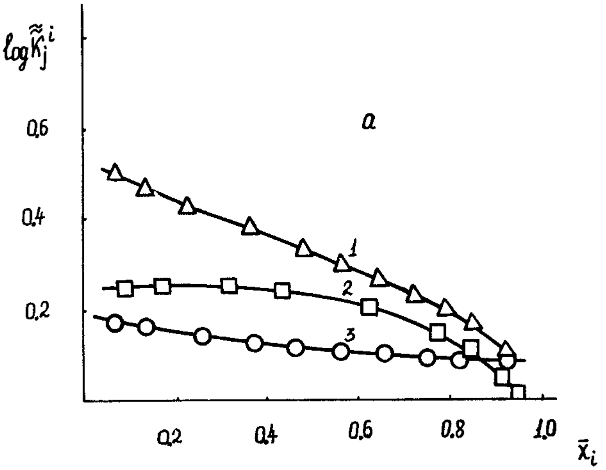

FIG. 4a. The concentration equilibrium constant in binary systems as a function of ionic fraction of the first ion given. Fig. 4a: Dowex 50x x 12, (1) NH_4^+–H^+, (2) Na^+–H^+, (3) NH_4^+–Na^+. Fig. 4b: KU-2x25, (1) NH_4^+–H^+, (2) Na^+–H^+ (3) NH_4^+–Na^+. Fig. 4c: Dowex 50w x 12, (1) Ba^{2+}–Co^{2+}, (2) Ba^{2+}–Cu^{2+}, (3) Cu^{2+}–Co^{2+}. In all cases the exchange was studied at an ionic strength of 0.1 of the solution of chlorides, $t = 25.0°C$.

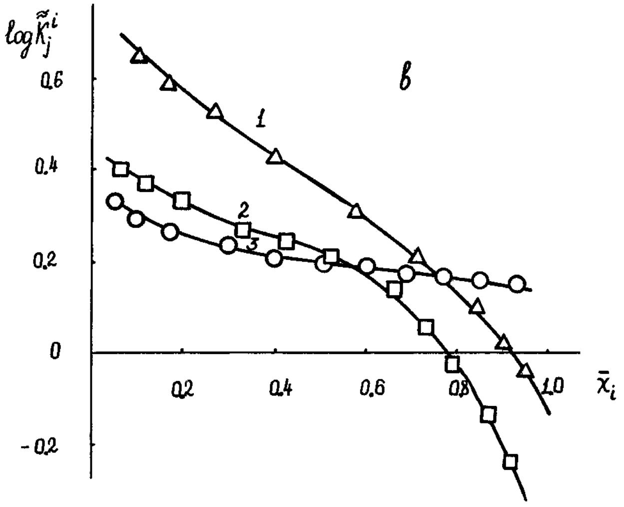

FIG. 4b. See Fig. 4a.

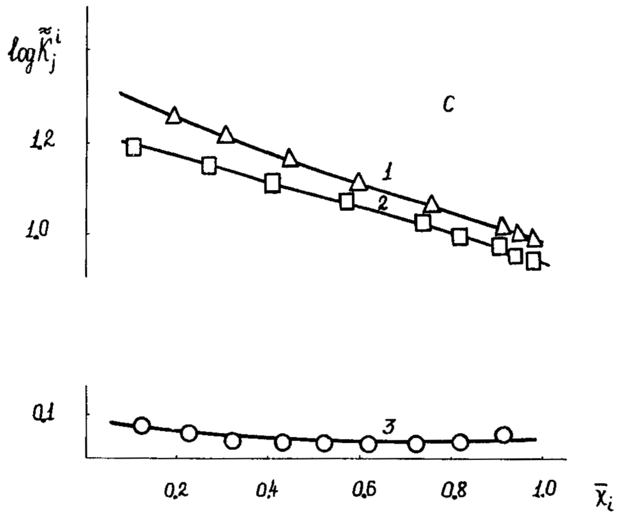

FIG. 4c. See Fig. 4a.

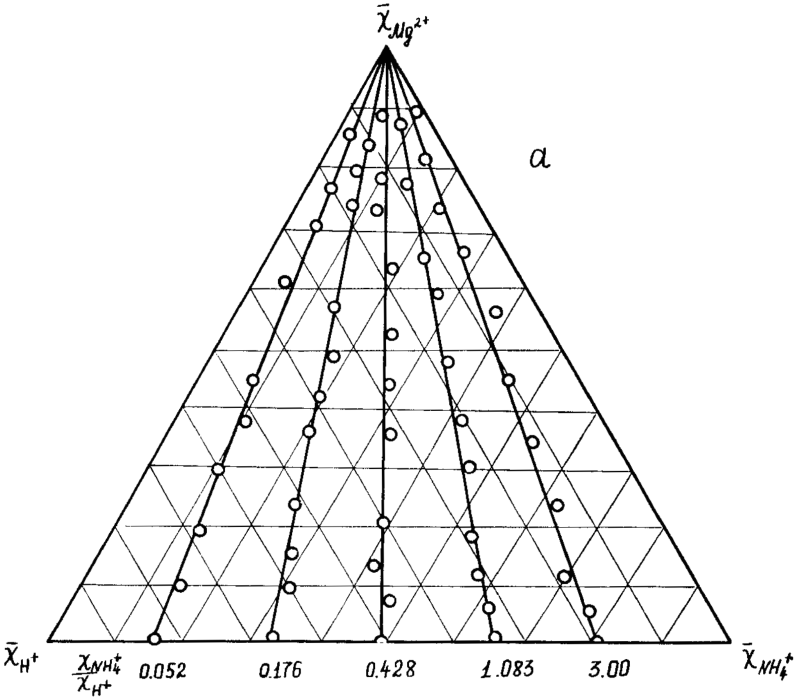

FIG. 5a. Composition of ion exchanger KU-2x25 in equilibrium with mixed Mg^{2+}, NH_4^+, and H^+ chloride solutions with an ionic strength of 0.1 at $t = 25.0°C$. Fig. 5a: Constant ratio $X_{NH_4^+}/X_{H^+}$. Fig. 5b: Constant $X_{NH_4^+}/X_{Mg^{2+}}$. Fig. 5c: Constant $X_{Mg^{2+}}$.

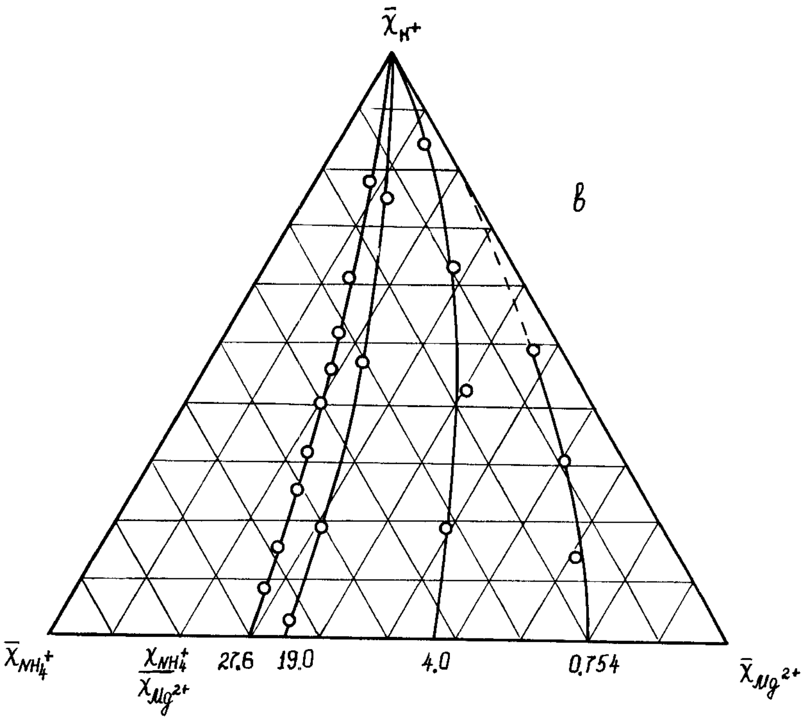

FIG. 5b. See Fig. 5a.

Activity coefficients for ternary monovalent resinate mixtures are calculated from the following equations:

$$\ln \varphi_1 = \int_{\ln \tilde{K}_1{}^2(\bar{x}_1=1)}^{\ln \tilde{K}_1{}^2(\bar{x}_1)} \bar{x}_2 d \ln \tilde{K}_1{}^2 + \int_{\ln \tilde{K}_1{}^3(\bar{x}_1=1)}^{\ln \tilde{K}_1{}^3(\bar{x}_1)} \bar{x}_3 d \ln \tilde{K}_1{}^3 \tag{5a}$$

$$\ln \varphi_2 = \int_{\ln \tilde{K}_2{}^1(\bar{x}_2=1)}^{\ln \tilde{K}_2{}^1(\bar{x}_2)} \bar{x}_1 d \ln \tilde{K}_2{}^1 + \int_{\ln \tilde{K}_2{}^3(\bar{x}_2=1)}^{\ln \tilde{K}_2{}^3(\bar{x}_2)} \bar{x}_3 d \ln \tilde{K}_2{}^3 \tag{5b}$$

$$\ln \varphi_3 = \int_{\ln \tilde{K}_3{}^1(\bar{x}_3=1)}^{\ln \tilde{K}_3{}^1(\bar{x}_3)} \bar{x}_1 d \ln \tilde{K}_3{}^1 + \int_{\ln \tilde{K}_3{}^2(\bar{x}_3=1)}^{\ln \tilde{K}_3{}^2(\bar{x}_3)} \bar{x}_2 d \ln \tilde{K}_3{}^2 \tag{5c}$$

In these equations the apparent constant of pseudobinary exchange $\tilde{K}_j{}^i$ is given by

$$\tilde{K}_j{}^i = \frac{\bar{x}_i a_j}{\bar{x}_j a_i} \tag{6}$$

where a is activity.

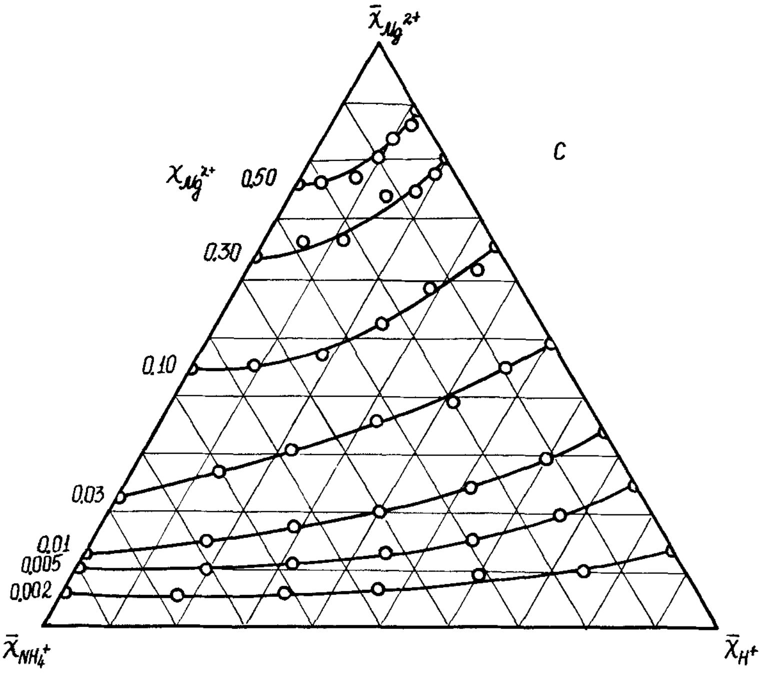

FIG. 5c. See Fig. 5a.

The values of the activity coefficients in Eqs. (5a)–(5c) do not depend on the path of integration, but it is important to notice that the most convenient path in practical calculations lies along a line of constant concentration of one of the ions in the ternary system and one side of the triangular diagram.

Values of log φ in the ternary systems mentioned above are given in Figs. 6–8.

All the systems studied are substantially nonideal. The activity coefficient of the ion most different in its properties from the other two is either constant or depends linearly on the composition along the line of its constant content (e.g., H^+ in the system NH_4^+–Na^+–H^+, Figs. 6 and 7; Ba^{2+} in the system Ba^{2+}–Cu^{2+}–Co^{2+}, Fig. 8).

Some specific interactions between resinates in the mixture NH_4^+–Na^+–H^+ [similar to other systems of this type (*8*, *11*, *12*)] are indicated by the complexity of the dependence of log φ on the composition of the resinate mixtures.

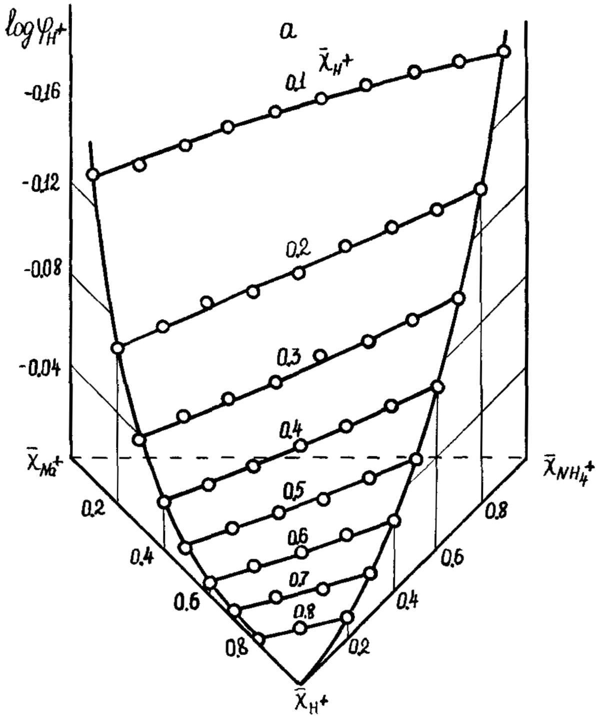

Fig. 6a. Log φ as a function of composition Dowex 50w x 12 in the NH_4^+-Na^+-H^+ form. Fig. 6a: φ_{H^+}. Fig. 6b: φ_{Na^+}. Fig. 6c: $\varphi_{NH_4^+}$.

PRECALCULATION OF TERNARY EXCHANGE EQUILIBRIA

It is possible to divide all methods for the prediction of ternary exchange equilibria from the data for binary systems into three groups.

The first group of methods (*13–16*) is based on the assumption of ideality of the exchange equilibria.

In the second group of methods (*14*, *17–20*), linear transformation of composition of binary systems is used to obtain the composition of the ternary systems.

The third method (*21–24*) takes nonideality or real systems directly into account.

Practical calculation of the composition of one of the phases at a chosen composition of another phase for ideal systems is achieved by solving the following system of equations:

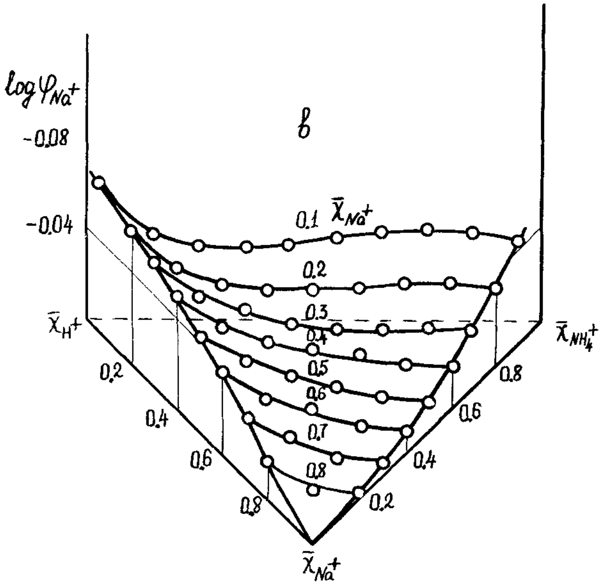

FIG. 6b. See Fig. 6a.

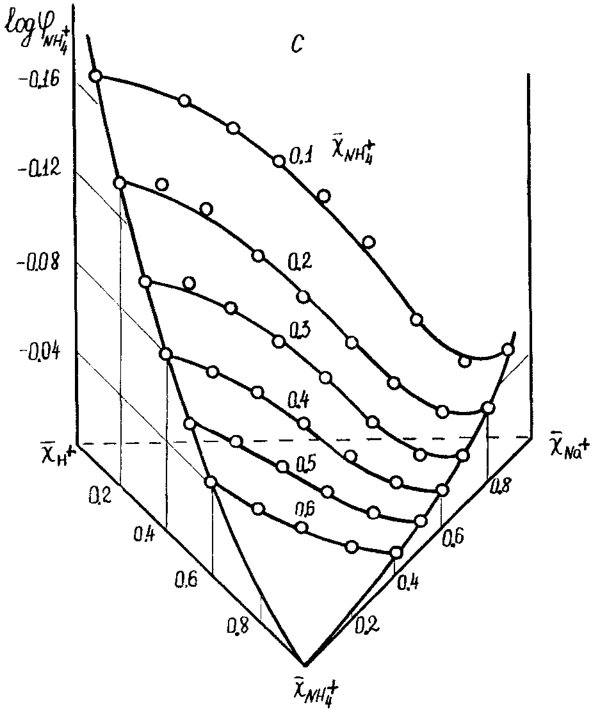

FIG. 6c. See Fig. 6a.

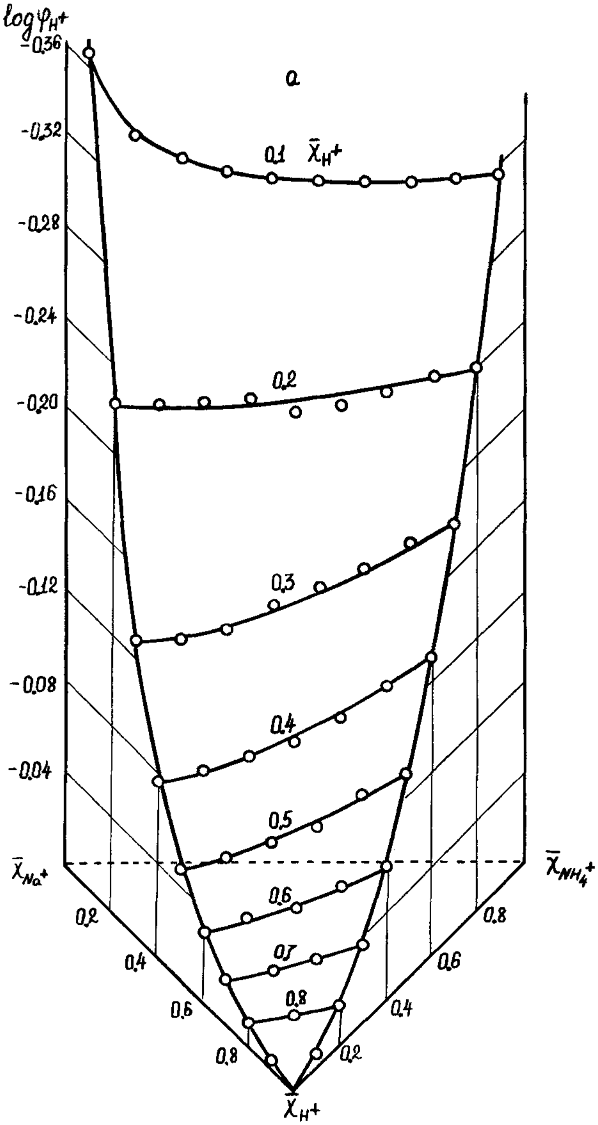

FIG. 7a. Log φ as a function of composition of KU-2x25 in the NH_4^+-Na^+-H^+ form. Fig. 7a: φ_{H^+}. Fig. 7b: φ_{Na^+}. Fig. 7c: $\varphi_{NH_4^+}$.

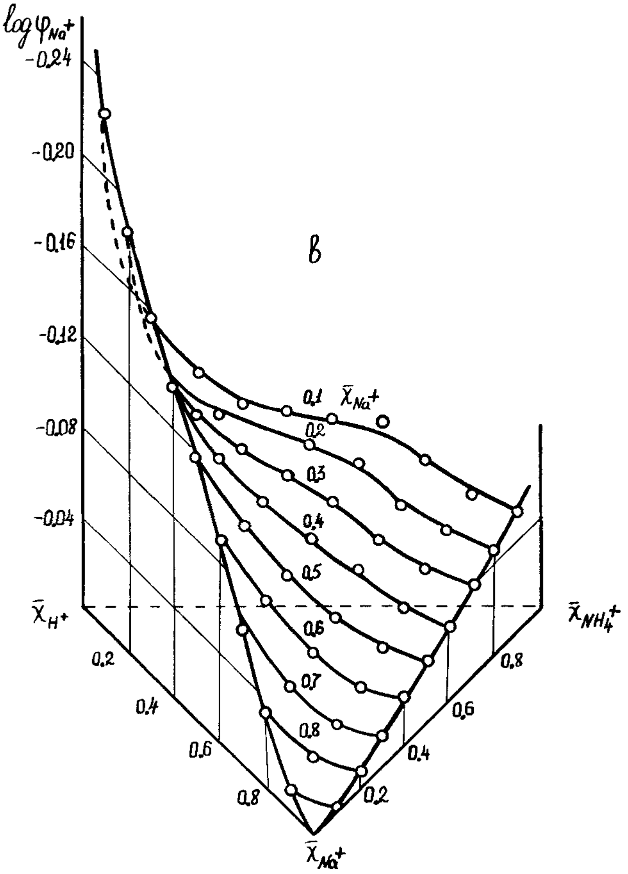

FIG. 7b. See Fig. 7a.

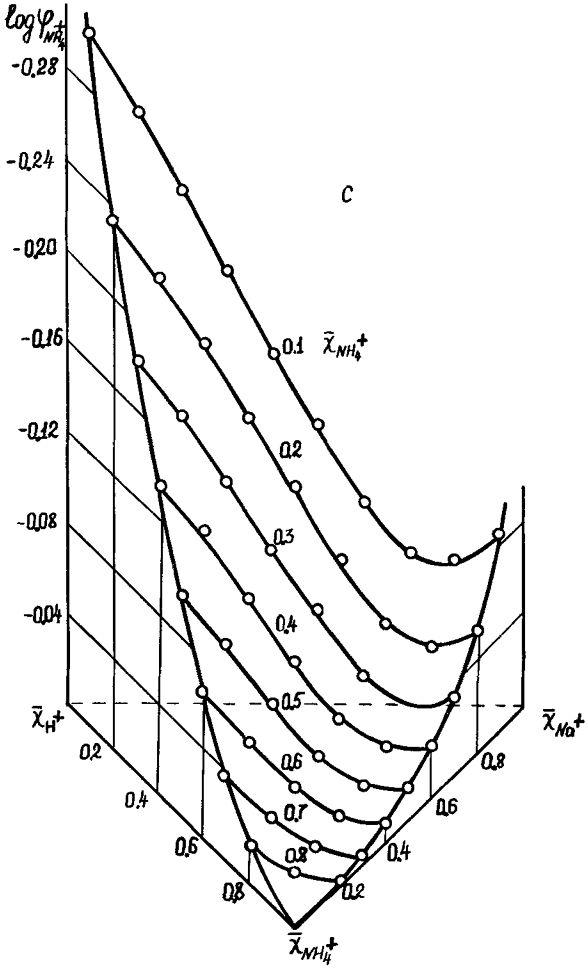

FIG. 7c. See Fig. 7a.

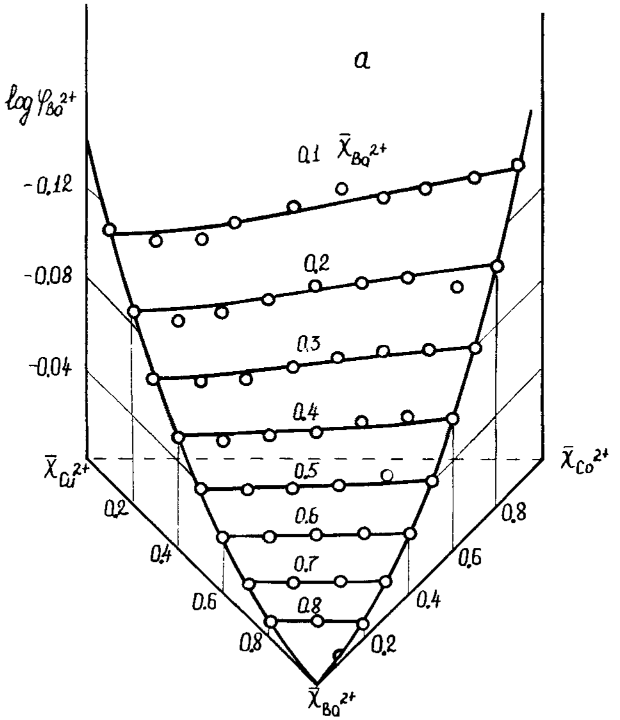

FIG. 8a. Log φ as a function of composition of Dowex 50w x 12 in the Ba^{2+}–Cu^{2+}–Co^{2+} form. Fig. 8a: $\varphi_{Ba^{2+}}$. Fig. 8b: $\varphi_{Cu^{2+}}$. Fig. 8c: $\varphi_{Co^{2+}}$.

$$K_2^1 = \frac{\bar{x}_1^{1/z_1} x_2^{1/z_2}}{\bar{x}_2^{1/z_2} x_1^{1/z_1}} f_2^1(w) \tag{7a}$$

$$K_3^1 = \frac{\bar{x}_1^{1/z_1} x_3^{1/z_3}}{\bar{x}_3^{1/z_3} x_1^{1/z_1}} f_3^1(w) \tag{7b}$$

$$\bar{x}_1 + \bar{x}_2 + \bar{x}_3 = 1 \tag{7c}$$

or

$$x_1 + x_2 + x_3 = 1 \tag{7d}$$

In these equations $f_2^1(w)$ is a given function of swelling of the resin. Choosing $\bar{x}_1$ and $\bar{x}_3$, values x_1 and x_3 can be computed by solving the Eqs. (7a)–(7c). If x_1 and x_3 are chosen, values $\bar{x}_1$ and $\bar{x}_3$ can be computed from Eqs. (7a), (7b) and (7d).

Since K_2^1 and K_3^1 are not often constant for real systems, some average

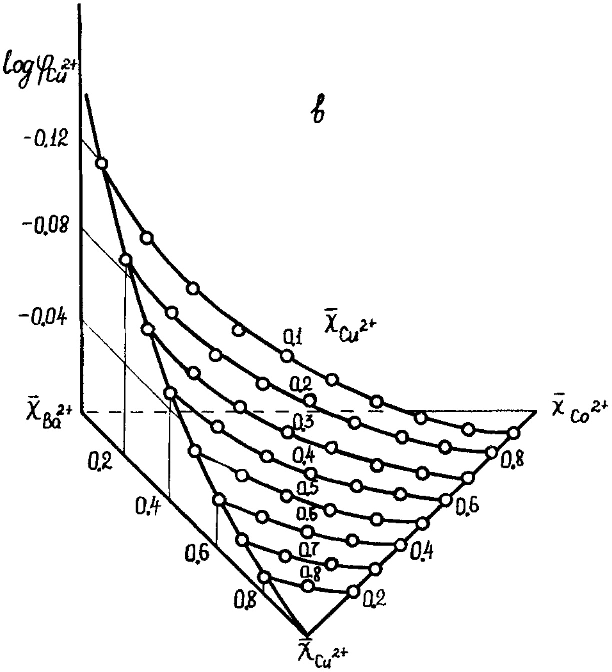

FIG. 8b. See Fig. 8a.

values have to be taken for practical calculations. This can cause large discrepancies between theory and practice, and this method should only be used for rough estimations.

The second method is applicable only in some special cases. The conditions for its application are homovalency of the exchange and ideality of the systems.

In view of the fact that parameteric lines may be linear, the following theoretical considerations can be used.

If ions 2 and 3 in the triplet 1–2–3 are similar in their properties, the apparent equilibrium constant $\tilde{K}_3{}^2$ is close to 1 ($\tilde{K}_3{}^2 \cong 1$). For this case, System (5) can be rewritten:

$$\ln \varphi_1 \cong \int_{\ln \tilde{K}_1{}^3(\bar{x}_1=1)}^{\ln \tilde{K}_1{}^3(\bar{x}_1)} \bar{x}_3 d \ln \tilde{K}_1{}^3 + \int_{\ln \tilde{K}_1{}^2(\bar{x}_1=1)}^{\ln \tilde{K}_1{}^2(\bar{x}_1)} \bar{x}_2 d \ln \tilde{K}_1{}^2 \qquad \text{(8a)}$$

$$\ln \varphi_2 \cong \int_{\ln \tilde{K}_2{}^1(\bar{x}_2=1)}^{\ln \tilde{K}_2{}^1(\bar{x}_2)} \bar{x}_1 d \ln \tilde{K}_2{}^1 \qquad \text{(8b)}$$

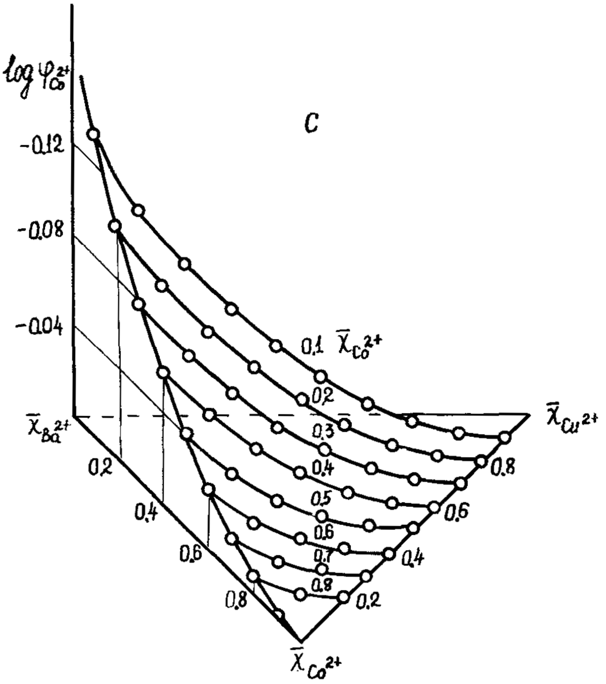

FIG. 8c. See Fig. 8a.

$$\ln \varphi_3 \cong \int_{\ln \tilde{K}_3{}^1(\bar{x}_3 = 1)}^{\ln \tilde{K}_3{}^1(\bar{x}_3)} \bar{x}_1 d \ln \tilde{K}_3{}^1 \tag{8c}$$

Since along the line $\bar{x}_1 = \text{const}$, $\tilde{K}_3{}^1 \cong \tilde{K}_2{}^1$ then

$$\ln \varphi_2 \cong \ln \varphi_3$$

and the system tends to degenerate into a bicomponent one because ions 2 and 3 behave as one component. The activity coefficient of the first ion is independent of the ratio of fractions of ions 2 and 3, provided that $\bar{x}_1$ (i.e., $\bar{x}_2 + \bar{x}_3$) is constant. This results in a linear parametric line, corresponding to $\bar{x}_1 = \text{const}$ in the triangular diagram for the solution.

Hence mixing of the components along the line $\bar{x}_1 = \text{const}$ is pseudo-ideal in the sense that it takes place without a change of the activity coefficients.

On the other hand, if $\tilde{K}_3{}^2$ is approximately constant, a line in the triangular diagram for the exchanger phase, corresponding to $\bar{x}_2/\bar{x}_3 = \text{const}$, must be a straight line $x_2/x_3 = \text{const}$ if $z_2 = z_3$.

This gives a simple method for calculation of x_1, x_2 for nonideal systems from the data for binary exchanges.

The point required is located at the intersection of the two straight lines in the solution phase triangle corresponding to lines $\bar{x}_1$ = const and $\bar{x}_2/\bar{x}_3$ = const in the triangular diagram of the resin phase. The end points of these lines lie on the sides of these triangles and can be found from the binary exchanges.

In the third group of methods it is assumed (*21*) that a foreign ion influences the activity coefficients of the other two ions (2 and 3) identically. Ions 2 and 3 must be chosen to have the closest properties in the triplet. The following equation is suggested:

$$\log \frac{\varphi_2}{\varphi_3} = b + a \log \frac{\varphi_{23}}{\varphi_{32}} \tag{9}$$

where φ_2 and φ_3 are activity coefficients in the ternary system, and φ_{23} and φ_{32} are the corresponding values in the binary system. a and b are constants. It has been shown in the theory of nonelectrolyte mixtures (*25*) that b is given by

$$b = \frac{Q_{12} - Q_{13}}{1 - \bar{x}_1} \tag{10}$$

where Q is proportional to the excess free energy of mixing in the binary systems:

$$Q_{ij} = \bar{x}_{ij} \log \varphi_{ij} + \bar{x}_{ji} \log \varphi_{ji} \tag{11}$$

a is a transformation coefficient; it is constant at $\bar{x}_3$ = const and is equal to $1 - \bar{x}_3$ (*25*).

φ_1 can be estimated by using the formal thermodynamics of ternary mixtures (*26*).

The activities of the components in ternary mixtures can be obtained in the same way as the concentrations in ideal systems were obtained in the first method. Using these data together with activity coefficients, the composition in the phase can be computed for a given composition of the other (solution or resin).

The empirical suggestion that the activity coefficient of component i in the ternary system can be obtained by summarizing this value taken from the binary exchanges *i-j* and *i-k* was obtained in the following way by Bajpai and Gupta (*22*):

$$\varphi_i = \frac{\bar{x}_i}{\bar{x}_j + \bar{x}_k} \varphi_{ij} + \frac{\bar{x}_K}{\bar{x}_j + \bar{x}_k} \varphi_{ik} \tag{12}$$

Table 1 gives the average absolute deviation (Δx) of computed x_{ij} from

TABLE 1

No.	Ternary systems	Resins	Δx I	 II	 III [21]	 III [22]
1	Ba^{2+}–Cu^{2+}–Co^{2+}	Dowex 50w x 12	0.011	0.002	0.004	0.007
2	Na^{+}–NH_4^{+}–H^{+}	. .	0.020	0.006	0.005	0.006
3	Li^{+}–NH_4^{+}–H^{+}	KRS-25[a]	0.056	0.023	0.008	0.007
4	Na^{+}–NH_4^{+}–H^{+}	. .	0.042	0.010	—	0.005
5	K^{+}–NH_4^{+}–H^{+}	. .	0.060	0.011	0.005	0.012
6	Cs^{+}–NH_4^{+}–H^{+}	. .	0.073	0.023	0.003	0.016

[a] Analog of Dowex 50 x 25 (Soviet production).

experimental values for systems of different complexity (increasing from top to bottom):

$$\Delta x = \sum_{i=1}^{n} \sum_{j=1}^{m} \frac{|(x_{ij(\mathrm{comp})} - x_{ij(\mathrm{exp})})|}{nm} \qquad (13)$$

where n is the number of ions ($n = 3$ in our case) and m is the number of experimental points. Twelve points regularly distributed in the triangular diagrams of the exchanger phase for each system were taken.

It is seen that the method taking into account the nonideality of exchange systems is the most accurate one. At the same time, the second method gives acceptable results provided that the properties of the exchanging ions are appropriately considered.

REFERENCES

1. V. S. Soldatov and L. V. Novitskaya, *Thermodynamics of Ion Exchange*, Minsk, 1968, p. 217.

2. V. P. Kolnenkov and V. S. Soldatov, *Izv. Akad. Nauk B SSR Ser. Khim. Nauk*, *6*, 36 (1970).

3. D. Tondeur and G. Klein, *Ind. Eng. Chem., Fundam.*, *6*(3), 351 (1967).

4. V. P. Kolnenkov and N. S. Serzhinskaya, *Izv. Akad. Nauk B SSR Ser. Khim. Nauk*, *4*, 126 (1976).

5. V. P. Kolnenkov, "Ion Exchange in Systems of Type I_1^{2}–I_2^{+}–I_3^{+} on Sulfostyrene Ion Exchangers," Dissertation, Minsk, 1972, p. 99.

6. V. A. Bichkova and V. S. Soldatov, *Izv. Akad. Nauk B SSR Ser. Khim. Nauk*, *5*, 39 (1972).

7. V. A. Bichkova and V. S. Soldatov, *Ibid.*, *2*, 44 (1973).

8. V. S. Soldatov and V. A. Bichkova, *Z. Phys. Chem.*, *45*(5), 1251 (1971).

9. V. S. Soldatov, *Simple Ion Exchange Equilibria*, Minsk, 1972, p. 186.

10a. E. Ekedahl, E. Högfeldt, and L. G. Sillén, *Acta Chem. Scand.*, *4* 828 (1950).

10b. A. W. Davidson and W. J. Argersinger, *Ann. N. Y. Acad. Sci.*, *57*(A3), 3105 (1953).

11. V. A. Bichkova and V. S. Soldatov, *Izv. Akad. Nauk B SSR Ser. Khim. Nauk*, *3*, 105 (1977).

12. V. A. Bichkova and V. S. Soldatov, *Ibid.*, *4*, 22 (1979).

13. B. P. Nikolsky and V. I. Paramonova, *Usp. Khim.* 8(10), 1535 (1939).

14. G. Jangg, Oesterr. Chem. -Ztg., *59*(23–24), 331 (1958).

15. L. J. Pieroni and J. S. Dranof, *AIChE J.*, *9*(1), 42 (1963).

16. Yu. A. Kokotov and V. A. Pasechnic, *Equilibrium and Kinetics of Ion Exchange*, Leningrad, 1970, p. 100.

17. V. I. Sokolova, V. P. Kolnenkov, and V. S. Soldatov, *Izv. Akad. Nauk B SSR Ser. Khim. Nauk*, *6*, 31 (1969).

18, V. P. Kolnenkov and V. S. Soldatov, *Z. Phys. Chem.*, *49*(2), 397 (1975).

19. V. P. Kolnenkov and V. A. Shchekoldin, *Dokl. Akad. Nauk B SSR*, *20*(6), 545 (1976).

20. W. J. Brignal, A. K. Gupta, and M. Streat, "The Theory and Practice of Ion Exchange," Presented at an International Conference Held at Churchill College, University of Cambridge, London, July 25–30, 1976.

21. V. S. Soldatov and V. A. Bichkova, *Z. Phys. Chem.*, *44*(9), 2293 (1970).

22. R. K. Bajpai, A. K. Gupta, and M. Gopala Rao, *J. Phys. Chem.*, *77*(10), 1288 (1973).
23. V. P. Kolnenkov and G. V. Bogomolov, *Dokl. Akad. Nauk B SSR*, *236*(5), 1144 (1977).
24. R. P. Smith and E. T. Woodburn, *AIChE J.*, *24*(4), 577 (1978).
25. V. B. Kogan, *Heterogeneous Equilibria*, Leningrad, 1968, p. 347.
26. V. P. Zharov and A. G. Morachevsky, *Physicochemical Properties of Solutions*, Leningrad, 1964, p. 28.

Received by editor September 12, 1979