Determination of the Thermodynamic Equilibrium Constants of Ion Exchange Processes

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Ion exchange reactions are considered on the basis of chemical equivalents (i), where n and m are

$$nM^+ + nm(N/n)R \rightleftharpoons mN^{n+} + nm(M/m)R \qquad \text{(i)}$$

the valencies of the respective ion, N^{n+} and M^{m+}, and R^- represents the negative ion of the resin framework. The corresponding thermodynamic equilibrium constant expression is rearranged in the form (ii). Plotting experimental data as $\log(a_N{}^m/a_M{}^n)$ *versus* equivalent fraction of the ion

$$\log(a_N{}^m/a_M{}^n) = \log K + nm\log(a_{NR}/a_{MR}) \qquad \text{(ii)}$$

exchanged leads to the appearance of an inflexion point. It is mathematically found that the quotient a_{NR}/a_{MR}, from the equilibrium constant expression, may be substituted by the ratio of equivalent fraction of $(N/n)R$ over equivalent fraction of $(M/m)R$ at the inflexion point. The calculated thermodynamic ion exchange constants are in very good agreement with the values obtained by other methods.

This work presents a novel method for the direct determination of thermodynamic ion exchange equilibrium constants which is not based upon any previously known approach. Therefore, the problem of calculating the activity coefficients of the species in the solid phase and determination of the thermodynamic equilibrium constants of ion exchange processes, considered in a number of scientific papers, has not been reviewed here. The original idea, communicated in its elementary conception by Ruvarac and Vesely,[1] has recently been considerably developed and applied by Petković to solvent extraction[2] and strong acid dissociation[3] equilibria. In this paper an improved version of the method formerly invented by Ruvarac and Vesely[1] is introduced.

Theoretical

The ion exchange reaction, involving exchange of two ions only, may be written in the form of reaction (1), where n and m are the

$$nM^{m+} + mNR_n \rightleftharpoons mN^{n+} + nMR_m \qquad (1)$$

valencies of the respective ions N^{n+} and M^{m+}. The ions are considered to be exchanged in equivalent amounts and the exchanger contains no other negative ion but R^- of the resin framework.

Difficulties in selecting the concentration scale for the equilibria where reacting species exist in different phases have been avoided by expressing the concentrations of the species in the exchanger by equivalent fractions and those in the aqueous phase by mol dm^{-3}. Therefore, the ion exchange equilibrium has been presented in terms of chemical equivalents, equation (2), and the corresponding thermodynamic equilibrium constant expression is given in equation (3), where a is the chemical

$$nM^{m+} + nm(N/n)R \rightleftharpoons mN^{n+} + nm(M/m)R \qquad (2)$$

$$K = \frac{a_N{}^m (a^E_{MR})^{nm}}{a_M{}^n (a^E_{NR})^{nm}} \qquad (3)$$

activity. The particular species to which an activity refers is indicated by the corresponding subscript. Charges are omitted from the subscript ions and an indication of the existence of the species in the aqueous or solid phase is left out to simplify notation. M^{m+} and N^{n+} (written M and N) are always related to the aqueous phase and MR_m and NR_n (written MR and NR) to the solid phase. The superscript E is introduced to denote activities on the equivalent fraction concentration scale. The consequence of the presentation of the components in the exchanger by means of chemical equivalents is that the ratio a^E_{MR}/a^E_{NR}, appearing in equation (3), is dimensionless.

The standard state of an ion in the aqueous phase is chosen so that at infinite dilution the ratio of the activity to the measured concentration of the ion is unity. The standard state of the components in the exchanger is represented by the pure component. The concentrations of $(N/n)R$ and $(M/m)R$ species in the exchanger are conveniently represented by the equivalent fractions, x^E_{NR} and x^E_{MR}, respectively. The ion concentrations in the aqueous phase are given in mol dm^{-3}.

The starting point for determining the thermodynamic equilibrium constants of ion exchange processes is equation (3), conveniently rearranged as in equation (4). The method is based

$$\log\frac{a_N{}^m}{a_M{}^n} = y = \log K + nm\log\frac{a^E_{NR}}{a^E_{MR}} \qquad (4)$$

on the application of a mathematical procedure to the condition for the appearance of an inflexion point in the presentation of experimental data by equation (4) as $y = f(a^E_{MR})$. The purpose of the procedure is to evaluate the value of the quotient a^E_{NR}/a^E_{MR} at the inflexion point. The existence of the inflexion point enables the use of a further equation, *i.e.* the second derivative of equation (4) equalized to zero.

Equation (5), the first derivative of equation (4), contains the expression $\mathrm{dln}\,a^E_{NR}/\mathrm{d}a^E_{MR}$ which can be evaluated separately using the Gibbs–Duhem equation (6) applied to the binary

$$2.303\frac{\mathrm{d}y}{\mathrm{d}a^E_{MR}} = nm\frac{\mathrm{dln}\,a^E_{NR}}{\mathrm{d}a^E_{MR}} - \frac{nm}{a^E_{MR}} \qquad (5)$$

$$x^E_{MR}\,\mathrm{dln}\,a^E_{MR} + x^E_{NR}\,\mathrm{dln}\,a^E_{NR} = 0 \qquad (6)$$

mixture of $(N/n)R$ and $(M/m)R$. The term for the water activity variation in the wet exchanger has been omitted from equation (6). Högfeldt[4] has found that no serious error is introduced by omitting this term. Inserting equation (6) into equation (5) gives equation (7) which, using the additional equation (8), gives equation (9). Further differentiation of equation (9) led to the

$$2.303\frac{dy}{da^{E}_{MR}} = -\frac{nm}{a^{E}_{MR}}\left(\frac{x^{E}_{MR}}{x^{E}_{NR}} + 1\right) \tag{7}$$

$$x^{E}_{MR} + x^{E}_{NR} = 1 \tag{8}$$

$$2.303\frac{dy}{da^{E}_{MR}} = -\frac{nm}{a^{E}_{MR}}\frac{1}{x^{E}_{NR}} \tag{9}$$

second derivative expression given in equation (10). When $d^2y/d(a^{E}_{MR})^2 = 0$, to fulfil the condition valid at the inflexion point, rearrangement gives equation (11).

Following the same pattern as in equations (4)—(11), but considering the functionality $y = f(a^{E}_{NR})$, equation (12) is obtained.

$$2.303\frac{d^2y}{d(a^{E}_{MR})^2} = -\frac{1}{x^{E}_{NR}a^{E}_{MR}}\left(\frac{1}{a^{E}_{MR}} + \frac{1}{x^{E}_{NR}}\frac{dx^{E}_{NR}}{da^{E}_{MR}}\right) \tag{10}$$

$$d\ln a^{E}_{MR} + d\ln x^{E}_{NR} = 0 \tag{11}$$

$$d\ln a^{E}_{NR} + d\ln x^{E}_{MR} = 0 \tag{12}$$

Integrating equations (11) and (12) and dividing the solution gives equation (13), where P represents the integration constant.

$$\frac{a^{E}_{NR}}{a^{E}_{MR}} = \frac{x^{E}_{NR}}{x^{E}_{MR}}P \tag{13}$$

The integration of equations (11) and (12) is allowed since a number of different pairs of exchangeable ions make a family of sigmoid curves whose inflexion points also form a curve.

Evaluation of the integration constant, P, has been realized on the basis that the chemical activities of the species in the ion exchanger, in the case of ideality of the solid phase, are equal to corresponding concentrations. Then, equation (4) transforms to equation (14) whose second derivative equalized to zero leads to

$$y = \log K + nm\log\frac{1 - x^{E}_{MR}}{x^{E}_{MR}} \tag{14}$$

the equality $x^{E}_{MR} = x^{E}_{NR}$. Introducing this equality into equation (13) the integration constant, P, is equal to unity. As a consequence, equation (13) is transformed into equation (15),

$$\frac{a^{E}_{NR}}{a^{E}_{MR}} = \frac{x^{E}_{NR}}{x^{E}_{MR}} \tag{15}$$

showing that at the inflexion point the ratio of equivalent activities of the species in the ion exchanger phase may be substituted by the ratio of the analytical concentrations of the same species.

In fact the activities of the species in the ion exchanger phase are not known, but they are demanded in the presentation of experimental data as $y = f(a^{E}_{MR})$ according to equation (4). The use of a^{E}_{MR} may be avoided provided that a fixed number of exchanged sites is maintained constant throughout. Then x^{E}_{NR} is a function of x^{E}_{MR} and a^{E}_{NR} is also a function of a^{E}_{MR}. Hence, we may approximate a^{E}_{MR} to x^{E}_{MR} and plot experimental data as $y = f(x^{E}_{MR})$. The expression for the calculation of the thermodynamic equilibrium constant, given by equation (16),

$$\log K = y^* - nm\log\frac{(x^{E}_{NR})^*}{(x^{E}_{MR})^*} \tag{16}$$

results from equations (4) and (15). Here, y^* represents the ordinate value of the inflexion point and $(x^{E}_{MR})^*$ is the abscissa of the point. The value of $(x^{E}_{NR})^*$ is easily calculated from equation (8).

Table 1. Data on two ion exchange processes[a]

(*a*) K^+–H^+ exchange data on amorphous zirconium phosphate[b]

c_H	c_K	x^{E}_{H}	x^{E}_{K}	y
0.245	0.055	0.827	0.183	0.729
0.159	0.098	0.725	0.275	0.292
0.159	0.142	0.662	0.338	0.134
0.130	0.170	0.579	0.421	−0.014
0.102	0.199	0.554	0.446	−0.208
0.087	0.213	0.529	0.471	−0.310
0.074	0.226	0.454	0.546	−0.398
0.060	0.240	0.404	0.596	−0.522
0.046	0.254	0.333	0.667	−0.658
0.039	0.261	0.395	0.705	−0.743
0.033	0.267	0.272	0.728	−0.825
0.024	0.276	0.237	0.763	−0.978
0.018	0.282	0.184	0.816	−1.112

(*b*) Ba^{2+}–H^+ exchange data on Dowex 50[c]

c_H	c_{Ba}	x^{E}_{H}	x^{E}_{Ba}	y
0.1036	1.27×10^{-7}	0.996	0.003	12.840
0.1036	2.62×10^{-7}	0.993	0.006	12.061
0.1037	5.12×10^{-7}	0.987	0.012	11.597
0.1037	0.39×10^{-7}	0.997	0.022	11.072
0.1039	2.39×10^{-6}	0.955	0.045	10.260
0.1043	3.92×10^{-6}	0.924	0.075	9.836
0.1048	8.10×10^{-6}	0.888	0.111	9.204
0.1069	2.16×10^{-5}	0.779	0.220	8.360
0.1102	6.65×10^{-5}	0.638	0.361	7.396
0.1190	7.70×10^{-4}	0.275	0.724	5.303
0.1271	5.25×10^{-3}	0.103	0.896	3.663
0.1313	2.86×10^{-2}	0.048	0.951	2.207

[a] Here c denotes concentration (mol dm^{-3}) in the aqueous phase and y is calculated according to equation (4). [b] From ref. 7. [c] From ref. 8.

In order to prove that a^{E}_{MR} may be substituted by x^{E}_{MR} we have calculated a^{E}_{MR} values from the experimental data on x^{E}_{NR} and x^{E}_{MR} by means of a lengthy graphical integration as suggested by Högfeldt.[4] It has been found that differences between the K values obtained by plotting experimental data as either $y = f(a^{E}_{MR})$ or $y = f(x^{E}_{MR})$ are within the error of the inflexion point location.

The y values, defined by equation (4), are easily calculated from the concentrations of exchangeable ions in the aqueous phase and corresponding activity coefficients given in the literature[5] and recalculated for mutual influence.[6] The location of the inflexion point is well established by means of the best fit of experimental data with the least-squares procedure on the third degree polynomial.

Results

In order to demonstrate the application of our method we have treated examples of experimental data[7,8] on monovalent and divalent ion exchange with hydrogen by means of equation (16). The data of Ba^{2+}–H^+ exchange on Dowex 50 and K^+–H^+ exchange on amorphous zirconium phosphate are presented in Table 1. The values of y, calculated from the concentrations of exchangeable ions in the aqueous phase and corresponding activity coefficients as $y = \log(a^{m}_{H}/a_{M})$, are plotted *versus*

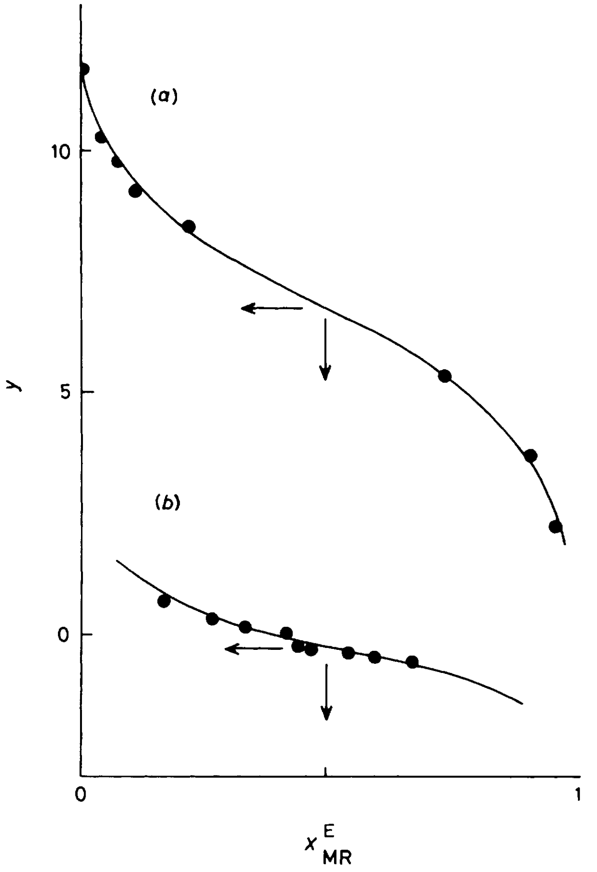

Figure. The presentation of experimental data on Ba^{2+}–H^+ exchange on Dowex 50 (*a*) and K^+–H^+ exchange on amorphous zirconium phosphate (*b*) by means of equation (4)

equivalent fractions of the ion in the exchanger phase (Figure). The ordinate value of the inflexion point, y^*, and the values of $(x^E_{MR})^*$ from the abscissa and $(x^E_{NR})^*$ obtained from equation (8) are introduced into equation (16) enabling the calculation of K.

For the Ba^{2+}–H^+ exchange $\log K = 6.63—2\log(0.52/0.48) = 6.56$ and for the the K^+–H^+ exchange $\log K = -0.31 - \log(0.45/0.55) = -0.31$. These two examples show how simple it is to calculate ion exchange equilibrium constants utilizing data for solutions which are neither dilute nor close to the saturation of the exchanger phase (*i.e.* corresponding to the *middle* of the exchange isotherm).

Further illustration of the validity of our method is presented in Table 2. The equilibrium constants calculated in a traditional manner and published for different ion exchange systems[4,9–14] are in very good agreement with those obtained using the published experimental data but processing them by the method presented here.

As a conclusion we wish to emphasize that the proposed method has nothing to do either with the extrapolation of the apparent equilibrium constants to infinite dilution or with the graphical integration of the apparent constants in order to calculate activity coefficients of the species in the ion exchanger phase. In the application of our method one needs to have the distribution data precisely determined in the middle part of the ion exchange isotherm. Such measurements are more certain than determining the exchangeable ion concentrations of very dilute solutions or determining the concentrations under conditions near the saturation of the ion exchanger.

Table 2. The ion exchange equilibrium constants, defined by equation (3), for different systems (T = 298 K)

		K		
Ion exchanger	System	Published values	Our method	Ref.
Montmorillonite	Sr^{2+}–K^+	1.8×10^{-3}	1.6×10^{-3}	9
Wofatit KS	Ag^+–H^+	5.2	5.3	4
Dowex 50	Ag^+–H^+	9.9	9.8	4
Zirconium phosphate				
amorphous	UO_2^{2+}–H^+	6.3×10^{-3}	6.8×10^{-3}	10
semicrystalline	Li^+–H^+	4.3×10^{-2}	4.1×10^{-2}	11
	K^+–H^+	2.2×10^{-1}	2.2×10^{-1}	11
	Cs^+–H^+	1.9	1.8	11
Hydrous zirconia	SCN^-–NO_3^-	1.9	2.0	12
	SCN^-–Cl^-	1.5	1.6	12
	Cl^-–NO_3^-	1.0	1.1	12
Greensand soil	Cs^+–NH_4^+	1.3×10^{-1}	1.4×10^{-1}	13
Vermiculite	Sr^{2+}–Ba^{2+}	1.0	8.2×10^{-1}	14

The thermodynamic equilibrium constants obtained by our method are as reliable as the activities found in the literature[5] representing quantities needed to evaluate y defined in equation (4). Likewise, different methods for determining the maximum exchange capacity of an ion exchanger can give rise to a slight change in K. These and similar problems do not influence the general validity of the method presented.

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