On Ion Exchange Equilibria

III *. An Investigation of Some Empirical Equations

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    Empirical equations by the following authors for representing ion exchange equilibria are discussed: Kroeker, Vageler, Weisz, Boedeker, "Freundlich", Wiegner-Jenny, van Dranen and Rothmund-Kornfeld (*cf.* Table 1). Also an empirical equation recently given by Yamabe and Sato is discussed in a note. Discussion is limited to exchange between monovalent ions except when discussing the Rothmund-Kornfeld equation. It is shown that the linear plots used for determining the constants in the empirical equations are too insensitive to be used for testing the applicability of the equation under consideration. A more sensitive plot is obtained if the constants in the empirical equation are used for calculating the equilibrium quotient curve $\varkappa$ (β). There are three different kinds of equilibrium quotient curves recorded in literature: falling, rising and curves with maximum or minimum (*cf.* Fig. 1). No empirical equation except the one of "Freundlich" is capable of representing all of these types. The most useful equation seems to be that of Rothmund and Kornfeld which can be extended in a very simple manner to all three types of equilibrium quotient curves. In connection with this equation some different methods for finding an approximate value of the thermodynamic equilibrium constant are discussed, and it is shown that $k^{1/p}$ (where k and p are the empirical constants in the Rothmund-Kornfeld equation) and $\varkappa_{B,A(\beta = 0.5)}$ may be useful first approximations to the thermodynamic equilibrium constant.

In the earlier work on ion exchange a number of empirical equations were used for representing equilibrium data. Later various forms of the law of mass action were used and, at present, it is very common to represent ion exchange equilibrium data by plotting the equilibrium quotient (see eq. (2) below) against some function of the ionic concentrations. Such plots show that, in most cases, the equilibrium quotient varies. For cases where the variation is large it has been suggested [1] that other expressions *e.g.* some empirical equation, may be more useful. The present paper deals with the possibility of representing variations in the equilibrium quotient by empirical equations.

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* For parts I and II see Refs. 7 and 18.

Discussion is limited to cation exchange equilibria and, for the sake of simplicity, to exchange between monovalent ions. Only when discussing the Rothmund-Kornfeld equation will exchange between multivalent ions be considered.

For the ion exchange reaction:

$$B^+ + AR \rightleftharpoons A^+ + BR \tag{1}$$

where A^+ and B^+ are the two exchanging cations and R the anion framework of the exchanger an equilibrium quotient can be defined as follows:

$$\varkappa_{B,A} = \frac{\{A^+\} \cdot [BR]}{\{B^+\} \cdot [AR]} \tag{2}$$

where $\{\}$ denotes activity and [] concentration.

The following mole fractions are used:

$$\alpha = \frac{[B^+]}{[A^+] + [B^+]} = \frac{[B^+]}{a_0} ; \quad \beta = \frac{[BR]}{[AR] + [BR]} = \frac{[BR]}{s_0} \tag{3}$$

where a_0 is the total ionic concentration of the solution (which is here equal to the ionic strength) and s_0 is the saturation capacity of the exchanger. From (2) and (3) the following expression for $\varkappa_{B,A}$ is obtained:

$$\varkappa_{B,A} = \frac{f_A(1-\alpha)\beta}{f_B\alpha(1-\beta)} \tag{4a}$$

where f_A and f_B are the activity factors of A^+ and B^+ in the liquid phase. In dilute solutions $f_A = f_B$ and

$$\varkappa_{B,A} = \frac{(1-\alpha)\beta}{\alpha(1-\beta)} \tag{4b}$$

CHOICE OF GRAPHICAL REPRESENTATION

It has proved convenient to plot $\varkappa$ against β, and the three different types of $\varkappa(\beta)$-curves reported in the literature are given in Fig. 1. In the following, curves with $\dfrac{d\varkappa}{d\beta} < 0$ are referred to as type I, with $\dfrac{d\varkappa}{d\beta} > 0$ as type II and curves with a maximum or minimum as type III. Hitherto type I has been most usual but examples of the other two types can be found in papers by Argersinger et al.[2,3], Bonner and Rhett [4], Duncan and Lister [5,6], Högfeldt et al.[7] and Marinsky [8].

The empirical equations used give a simple relation either between the amount of a certain ion added and the amount sorbed by the exchanger at equilibrium, or between the equilibrium concentration in solution and the amount sorbed by the exchanger. In the latter case the empirical equation gives a relation of the type:
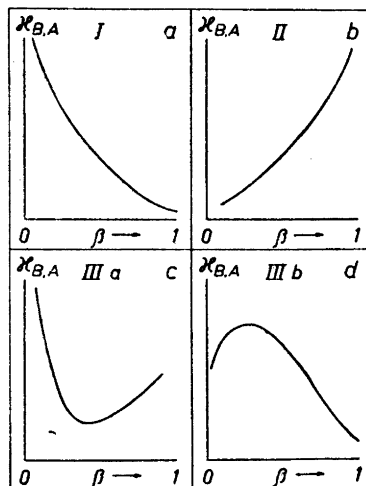
$$\alpha = \varphi(\beta) \tag{5}$$

Fig. 1. The three different types of $\varkappa(\beta)$-curves. Fig. 1a represents a falling curve, Fig. 1b a rising curve and Figs. 1c and 1d are examples of curves with a minimum or maximum.

where $\varphi(\beta)$ is a function of β, which inserted in (4b) gives a function $\varkappa(\beta)$ which can be studied and compared with curves obtained experimentally. In the first case a relation between α,β and the total amount of the ion under consideration is required. Such a relation is given by the conservation of mass and takes the following form if the exchanger saturated with A^+ is equilibrated with V litres of solution of B^+ of initial concentration c_0, and A^+ of initial concentration $a_0—c_0$:

$$\beta s_0 + V\alpha a_0 = Vc_0 \qquad (6)$$

From (6) and the empirical equation:

$$Vc_0 = \psi(\beta) \qquad (7)$$

where $\psi(\beta)$ is a function of β, an expression for $\varkappa(\beta)$ can be obtained.

In order to be able to use (6) one must make experiments under such conditions that V, a_0 and s_0 are held constant.

The type of curve obtained if $\varkappa_{A,B} = \varkappa_{B,A}^{-1}$ is plotted against $(1—\beta)$ instead of $\varkappa_{B,A}$ against β may now be considered. The three types of $\varkappa(\beta)$-curves are characterized by the sign of $\dfrac{d\varkappa}{d\beta}$. For $\dfrac{d\varkappa}{d\beta} < 0$ we have type I, for $\dfrac{d\varkappa}{d\beta} > 0$ type II and for $\dfrac{d\varkappa}{d\beta} \gtrless 0$ type III.

The sign of $\dfrac{d\varkappa}{d\beta}$ is known and the sign of $\dfrac{d\varkappa^{-1}}{d(1—\beta)}$ is required:

$$\frac{d\varkappa^{-1}}{d(1—\beta)} = \frac{—d(1/\varkappa)}{d\beta} = \frac{1}{\varkappa^2}\frac{d\varkappa}{d\beta}$$

Thus $\dfrac{d\varkappa}{d\beta}$ has the same sign as $\dfrac{d\varkappa^{-1}}{d(1—\beta)}$. If $\varkappa(\beta)$ belongs to type I or II, $\varkappa^{-1}(1—\beta)$ belongs to the same type. If, however, $\varkappa(\beta)$ belongs to type IIIa,

$\varkappa^{-1}(1-\beta)$ belongs to type IIIb and *vice versa*. This depends upon the reversal in orientation to the two axes. The corresponding $\varkappa^{-1}(1-\beta)$-curves can be visualised by turning the $\varkappa(\beta)$-curves in Fig. 1 upside down.

It is of course an arbitrary matter which kind of curve one chooses to plot. One conveniently takes B^+ as the most strongly sorbed ion. The equilibrium quotient then becomes larger than unity and the $\varkappa(\beta)$-curve gives the variation of selectivity with concentration for that ion over the other. For curves with a maximum or minimum the distinction between types IIIa and IIIb is only a consequence of this convention as one could equally well plot the reciprocal function and transform IIIa to IIIb, or *vice versa*, and only make use of one of them.

RESULTS

Expressions for $\varkappa(\beta)$ have been calculated as outlined above from the empirical equations given by the following authors: Boedeker[9], van Dranen[10], "Freundlich"[11], Kroeker[12], Rothmund-Kornfeld[13-14], Vageler[15], Weisz[16] and Wiegner-Jenny[17].

In Table 1 the different empirical equations and the corresponding $\varkappa(\beta)$-functions are summarized. From this table it can be seen that the equations of Kroeker and van Dranen contain only one constant whereas all others contain two constants which may be determined from the linear plots indicated in the fourth column. For the equations of Kroeker, Vageler, Boedeker and Wiegner-Jenny one must keep a_0, V and s_0 constant in order to be able to use (6) for calculating $\varkappa(\beta)$. The numbers I—III in the last column but one refer to the different types of $\varkappa(\beta)$-curves given in Fig. 1. From the last column but one of Table 1 it can be seen that no empirical equation but the one of "Freundlich" is capable of representing all types of $\varkappa(\beta)$-curves found in the literature. These results suggest the possibility of arranging the empirical equations according to the type of $\varkappa(\beta)$-curve which may be derived from them.

The applicability of the different empirical equations for representing experimental data has been tested by using the data of Högfeldt *et al.*[7] for the Ag^+—H^+ exchange on Wofatit KS and Dowex 50, for which the $\varkappa(\beta)$-curves belong to types I and III respectively. These measurements were made at so low an ionic strength that the variation in the activity of water could be neglected[18] at least to a first approximation. Also the condition $f_{H^+} \cdot f_{Ag^+}^{-1} \approx 1$ is approximately valid[35] and (4b) has been used for calculating $\varkappa$.

The Kroeker equation: This equation was tested by calculating $\log \dfrac{[Ag]^+_{tot}}{[Ag^+]} =$

$\log \dfrac{Vc_0}{V\alpha a_0} = q_1$ using the data in Tables 7a and 8a in Ref. 7. Some corresponding values of β and q_1 are given in Table 2. β is the mole fraction of silver in the resin. If the Kroeker equation were valid q_1 should be constant but it is apparent that q_1 decreases with increasing mole fraction. This decrease is systematic and so large that it cannot be due to experimental error, but must be taken as an indication of the inapplicability of the Kroeker equation to the data under consideration. That the Kroeker equation cannot be strictly applicable to either of the two systems is evident from the fact that it must give

Table 1. The relation between the empirical equations and the function $\varkappa(\beta)$.

Author	Equation	Linear plot	$\varkappa(\beta)$	Type	Condition
Kroeker [13]	$\log(Vc_0/Va\alpha_0) = km = q_1$		$\varkappa_{B,A} = \dfrac{(1-q_2\beta)}{q_2(1-\beta)}$ $q_2 = s_0/(Va_0(10^{q_1}-1))$	(I) (II)	$q_2 > 1$ $q_2 < 1$
Vageler [15]	$\beta s_0 = SVc_0/(Vc_0+k)$	$1/\beta s_0 ; 1/Vc_0$	$\varkappa_{B,A} = \dfrac{[q_1-(1+q_2q_3)\beta-q_2\beta^2]}{q_2(1-\beta)(q_3+\beta)}$ $q_1 = S/s_0; q_2 = s_0/Va_0; q_3 = (k-S)/s_0$	I III	$q_1 \lesssim 1+q_2+q_2q_3$ $q_1 > 1+q_2+q_2q_3$
Weisz [16]	$\beta = Sa/(a+k)$	$1/\beta ; 1/a$	$\varkappa_{B,A} = \dfrac{S-(1+k)\beta}{k(1-\beta)}$	(I) (II)	$k+1 > S$ $k+1 < S$
Boedeker [9]	$\beta s_0 = k(Vc_0)^p$	$\log \beta s_0 ; \log Vc_0$	$\varkappa_{B,A} = \dfrac{(1+q_2q_2\beta-q_1\beta^{1/p})}{q_1(1-\beta)(\beta^{1/p-1}-q_2)}$ $q_1 = s_0^{1/p}/Va_0 k^{1/p}; q_2 = k^{1/p}/s_0^{1/p-1}$	II III	$p \gtrless 1$ $p < 1$
"Freundlich" [11]	$\beta = ka^p$	$\log \beta ; \log a$	$\varkappa_{B,A} = \dfrac{k^{1/p}-\beta^{1/p}}{\beta^{1/p-1}(1-\beta)}$	II III (I) (III)	$\left.\begin{array}{l}p \gtrless 1\\ p \lesssim 1\end{array}\right\} k > 1$ $\left.\begin{array}{l} \\ p \gtrless 1\end{array}\right\} k < 1$
Wiegner-Jenny [17]	$\beta s_0 = k \cdot [Va\alpha_0/(Vc_0-Va\alpha_0)]^p$	$\log \beta ; \log a$	$\varkappa_{B,A} = \dfrac{(1-q_1\beta^{1/p+1})}{q_1(1-\beta)\beta^{1/p}}$; $q_1 = \dfrac{s_0^{1/p+1}}{Va_0 k^{1/p}}$	III (I)	$q_1 < 1$ $q_1 \gtrsim 1$
van Dranen [10]	$\sec\dfrac{\pi}{2}\beta = (\cos\dfrac{\pi}{2}\beta)^{-1} = ka+1$	$\sec\dfrac{\pi}{2}\beta ; a$	$\varkappa_{B,A} = \dfrac{\beta(k+1-\sec\dfrac{\pi}{2}\beta)}{(1-\beta)(\sec\dfrac{\pi}{2}\beta-1)}$	(I)	
Rothmund-Kornfeld [13-14]	$\beta/(1-\beta) = k[a/(1-a)]^p$	$\log\dfrac{\beta}{1-\beta} ; \log\dfrac{a}{1-a}$	$\varkappa_{B,A} = k^{1/p}\left(\dfrac{1-\beta}{\beta}\right)^{1/p-1}$	I II	$p < 1$ $p > 1$

The symbols for the empirical constants are not always the original ones, but are those used in the present work. The terms q_i, $i = 1, 2, 3$ are derived quantities, which are constant under certain experimental conditions. S, k and p are constants, and m is the mass of exchanger. In the last column but one giving the type of $\varkappa(\beta)$-curve obtained the values within parenthesis refer to those curves, which are not valid within the whole concentration range $0 \leq \beta \leq 1$ because of lacking physical meaning.

Table 2. Determination of q_1 in the Kroeker equation.

Wofatit KS		Dowex 50	
$\beta = \dfrac{[AgR]}{s_0}$	q_1	$\beta = \dfrac{[AgR]}{s_0}$	q_1
0.002429	0.79	0.002186	0.81
0.01143	0.69	0.01053	0.72
0.05699	0.52	0.05945	0.64
0.1056	0.41	0.1170	0.60
0.2075	0.33	0.1905	0.58
0.3211	0.28	0.2763	0.57
0.4033	0.23	0.3643	0.53
0.5102	0.24	0.4402	0.52
0.6193	0.16	0.5153	0.47
0.7088	0.13	0.6601	0.40
0.7931	0.12	0.8252	0.33
0.9153	0.08	0.9038	0.25

$\varkappa(\beta)$-curves belonging to type II for q_1-values less than 1, whereas the two systems studied belong to types I and III.

Wiegner [19] has tested the Kroeker equation on the ammonium-calcium-permutit system and also obtained decreasing q_1-values with increasing ammonium concentration in the exchanger.

The Vageler equation: The test of this equation was performed as follows. As indicated in Table 1 a plot of $1/\beta s_0 = 1/[AgR]$ against $1/Vc_0 = 1/[Ag^+]_{tot}$ would be a straight line if the Vageler equation were applicable. Quite good straight lines were obtained for the two sets of measurements, but the data for Wofatit KS showed a greater spread than those for Dowex 50. The best straight lines were drawn through the experimental points, and the constants S and k were determined. Experimental conditions were such that $a_0 = 100.0$ mC, $V = 0.100$ litre and $s_0 = 1.75$ for Wofatit KS and $s_0 = 3.83$ for Dowex 50. The s_0-values are average values taken from Tables 7a and 8a in Ref. 7. Using these values for a_0, V and s_0 and the values of S and k from the linear plots, the constants q_1, q_2 and q_3 (see Table 1) and the function $\varkappa(\beta)$ were calculated. In Figs. 2 and 3 the full curves give $\varkappa(\beta)$ calculated from the Vageler equation. From these figures it is apparent that the Vageler equation is applicable to a rather large concentration range. Agreement seems to be better for Wofatit KS despite the larger spread in the linear plot. According to Vageler [15], S in his equation should be equal to the saturation capacity s_0. From the linear plots S was found to be 2.0 for Wofatit KS and 10.1 for Dowex 50. These figures are not in agreement with the values of s_0 determined experimentally, especially for Dowex 50. An analogous result was obtained by Weisz [16] for zeolites.

The Weisz equation: The constants S and k (see Table 1) were determined from the plot of $1/\beta$ against $1/a$. This plot yielded a good straight line for Dowex 50, but for Wofatit KS the deviations were greater. From Table 1 it is seen that for $k + 1 > S$ the $\varkappa(\beta)$-curve belongs to type I and for $k + 1 < S$ it belongs to type II. These two conditions were fulfilled for the data on Wofatit KS and Dowex 50 respectively. From Table 1 it is seen that for $\beta = S/(1 + k)$
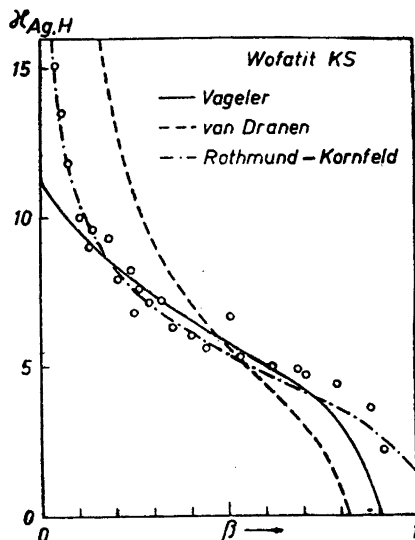
Fig. 2. Comparison[.] between experimental and approximate $\varkappa(\beta)$-curves using the data on Wofatit KS.

    O   *Experimental points*
—————— *$\varkappa(\beta)$ calculated from the Vageler equation.*
— — — —   »   »   »   » *van Dranen* »
— · — · —   »   »   »   » *Rothmund-Kornfeld equation.*

$\varkappa(\beta) = 0$. This means that the curve has physical meaning only in the range $0 \leq \beta \leq S/(1 + k)$. For Wofatit KS this value of β is ~ 0.47, a value for which $\varkappa(\beta) = 0$ differs so largely from that for $\beta = 0.47$ in Fig. 2 that the Weisz equation does not appear to be applicable in this case. Although the data on Dowex 50 give a $\varkappa(\beta)$-curve of type III it seems worth-while to test the Weisz equation on the rising part of the curve. In Fig. 3, $\varkappa(\beta)$ is given for Dowex 50 and there is good agreement with the Weisz equation within the interval $0.2 \leq \beta \leq 0.8$. For lower and larger β-values the deviations are large. The occurrence of deviations for small β-values follows from the existence of the minimum in the $\varkappa(\beta)$-curve which cannot be accounted for by the Weisz equation.

Weisz introduced the equation discussed above in his study of various empirical equations [16]. When comparing it with the Vageler equation, he found the latter to give a better numerical agreement. This may perhaps be due to the fact that the Vageler equation is capable of describing curves of both types I and III, while the Weisz equation can only describe part of a curve of type I and curves of type II and should thus have less applicability.

The equation introduced by Weisz can be considered to be a special case of the one used by Wolff [20]:

$$\beta s_0 - k_0 = \frac{S \cdot a}{a + k} \qquad (8)$$

where k_0 is a third empirical constant.

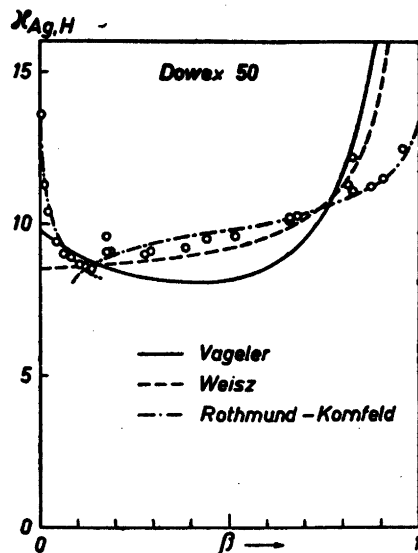Fig. 3. *Comparison between experimental and approximate* $\varkappa(\beta)$*-curves using the data on Dowex 50.*

     O   *Experimental points.*
    ——————— $\varkappa(\beta)$ *calculated from the Vageler equation.*
    — — — —   »   »   »   *Weisz*   »
    — · — · —   »   »   »   »   *Rothmund-Kornfeld equation.*
When using the Rothmund-Kornfeld equation the two parts of the $\varkappa(\beta)$*-curve have been approximated with two different equations, one for the falling and the other for the rising part.*

The existence of the constant k_0 means that the equilibrium quotient tends towards infinity as $\beta \rightarrow k_0/s_0$. For a number of cases $\varkappa(\beta)$ increases largely with decreasing β, but in the cases studied right down to the tracer level [21],[22] finite and constant limiting values of $\varkappa$ have been obtained. These results imply that k_0 must be very small and the Wolff equation becomes practically equal to the Weisz equation. For such cases the Weisz equation must be preferred even if a better numerical agreement can be obtained from the Wolff equation over a limited concentration range since it contains three empirical constants.

The Boedeker equation: The constants k and p (see Table 1) were first determined from the plot of log βs_0 against log $[Ag^+]_{tot}$ for the two systems. Quite good straight lines were obtained except for the highest values of β, where the experimental points tend towards the log $[Ag^+]_{tot}$-axis. Agreement was better for the data on Dowex 50 than on Wofatit KS, and this can be understood from the fact that the Boedeker equation is applicable to $\varkappa(\beta)$-curves of types II and III only. For this reason the $\varkappa(\beta)$-curve was calculated for Dowex 50 but not for Wofatit KS. The graphical method for finding the constants proved to be too insensitive as it gave a $\varkappa(\beta)$-curve far from the one obtained experimentally. For that reason the method of averages [23] was used for the calculation of k and p. In Fig. 4 the corresponding $\varkappa(\beta)$-curve is plotted. As is seen from this figure agreement is quite good for values of $\beta \lesssim 0.4$. For
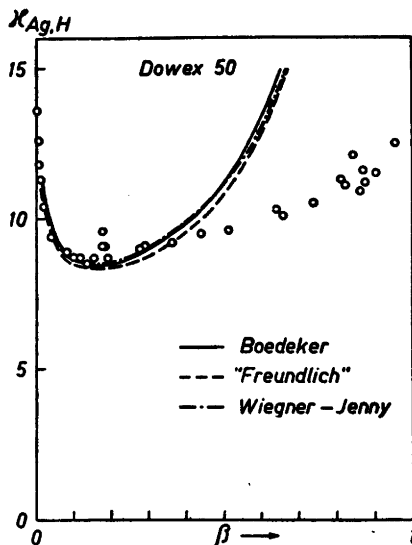
Fig. 4. Comparison between experimental and approximate $\varkappa(\beta)$-curves using the data on Dowex 50.

O	*Experimental points.*
——————	$\varkappa(\beta)$ *calculated from the Boedeker equation.*
— — — —	» » » » *"Freundlich" equation.*
— · — · —	» » » » *Wiegner-Jenny equation.*

higher values of β the curve tends rapidly towards infinity and deviations from the experimental curve are large. This might be ascribed to the fact that the Boedeker equation (as well as the "Freundlich" and Wiegner-Jenny equations discussed below) is of an exponential type and does not indicate the existence of an upper limit for the amount to be exchanged. ·

The "Freundlich" equation: The constants k and p (see Table 1) were determined from the plot of log β against log α for Dowex 50. The $\varkappa(\beta)$-curve has been plotted in Fig. 4. The close agreement with the $\varkappa(\beta)$-curve obtained from the Boedeker equation is to be noted and the same arguments are applicable to them both. When testing the equation with the data on Wofatit KS k proved to be > 1 and for $k > 1$ the "Freundlich" equation is inapplicable to a $\varkappa(\beta)$-curve of type I and the $\varkappa(\beta)$-curve was not calculated.

Freundlich's name is given within quotation marks, because van Bemmelen [24] (as is pointed out by McBain [25]) was the originator of the equation, although it has become associated with Freundlich's name.

The Wiegner-Jenny equation: This is a modification of the "Freundlich" equation put forward in order to indicate that the ion exchange equilibrium is independent of dilution for exchange between ions of equal valence. The quantities p and q_1 (q_1 constant under the experimental conditions) were determined from the plot of log α against log β. That this plot should give a straight line is seen by the following argument:

The Wiegner-Jenny equation:

$$\beta s_0 = k \cdot \left(\frac{V a a_0}{V c_0 - V a a_0} \right)^p$$

and the requirement of conservation of mass (6) give:

$$\alpha = q_1 \beta^{1/p+1} \qquad q_1 = \frac{s_0^{1/p+1}}{V a_0 k^{1/p}} \qquad (9)$$

From (9) it is seen that for the case of constant V and a_0 the Wiegner-Jenny equation becomes a special case of the "Freundlich" equation. It is also seen that by plotting log α against log β a straight line should be obtained giving the values of $1/p + 1$ and q_1. $\varkappa(\beta)$ calculated from the Wiegner-Jenny equation, is plotted in Fig. 4 for the Ag^+—H^+ exchange on Dowex 50. The measurements on Wofatit KS were not used for the same reasons as for the Boedeker and "Freundlich" equations. The $\varkappa(\beta)$-curves in Fig. 4 from the "Freundlich" and Wiegner-Jenny equations should have coincided. The observed differences are due to small differences in the constants ($\sim 1\%$) depending upon the limited accuracy in their determination from the linear plot and shows the sensitivity of the $\varkappa(\beta)$-curve to variations in the constants.

The van Dranen equation: Recently van Dranen [10] has proposed the equation given in Table 1 containing only one parameter and having an upper limit equal to the saturation capacity. The equation was tested by calculating $k = (\sec \frac{\pi}{2} \beta - 1)/\alpha$ for the two sets of measurements. No constant values were obtained as is shown in Table 3, where some of the results for Wofatit KS are given. The variation in k is large and the results show that this equation is not applicable to the data under consideration. An analogous result was obtained for Dowex 50, but this can be understood from the inapplicability of the van Dranen equation to a $\varkappa(\beta)$-curve of type III.

The form of a $\varkappa(\beta)$-curve calculated from the van Dranen equation, has been obtained by using the value $k = 2.74$ and the resulting curve is given in Fig. 2.

Table 3. Determination of $k = (\sec \frac{\pi}{2} \beta - 1)/\alpha$ in the van Dranen equation using the data on Wofatit KS.

$\beta = \frac{[AgR]}{s_0}$	$(\sec \frac{\pi}{2} \beta - 1)/\alpha$	$\beta = \frac{[AgR]}{s_0}$	$(\sec \frac{\pi}{2} \beta - 1)/\alpha$
0.002429	0	0.2075	1.74
0.006871	0.323	0.2515	1.78
0.009246	0.254	0.3211	2.31
0.01336	0.298	0.4033	2.36
0.01946	0.362	0.5102	3.23
0.02810	0.537	0.6193	3.18
0.04129	0.740	0.6858	3.56
0.05699	0.817	0.7088	3.73
0.07582	1.02	0.7931	4.60
0.1056	1.19	0.8825	6.58
0.1419	1.51	0.9153	7.81

The Rothmund-Kornfeld equation: Monovalent ions. In Fig. 2 the curve denoted by —·—·— gives $\varkappa(\beta)$ obtained by applying the Rothmund-Kornfeld equation (for brevity called the R—K equation in the following) to the data on Wofatit KS. k and p were determined from the plot of $\log \dfrac{\beta}{1-\beta}$ against $\log \dfrac{\alpha}{1-\alpha}$ which yielded a good straight line. Agreement is seen to be good over the whole concentration range. That the R—K equation (types I or II) is not applicable to the data on Dowex 50 (type III) can be seen as a small non-linearity of the insensitive double-logarithmic plot. The R—K equation can, however, be applied to curves of type III by proceeding as follows. The rising part of the curve is approximated by a R—K equation with $p > 1$ and the falling part by a R—K equation with $p < 1$. The four parameters k_1, p_1 and k_2, p_2 can all be determined from the double-logarithmic plot because, in the case of a curve of type III, the double-logarithmic plot can be approximated by two straight lines intersecting at the point corresponding to the minimum or maximum.

In Fig. 3 the curve denoted by —·—· gives $\varkappa(\beta)$ obtained using two different R—K equations intersecting at $\beta = 0.12$. Agreement is seen to be quite good.

Multivalent ions: The R—K equation seems to be the most useful one, as it can be applied to all three types of $\varkappa(\beta)$-curves and gives good numerical agreement for the two experimental studies considered here. For that reason, the discussion concerning multivalent ions will be limited to this equation. When considering multivalent ions, two approaches are possible as discussed in a previous paper [18]: "choice" (E) ("equivalents") and "choice" (M) ("moles").

Choice (E) gives the following ion exchange reaction:

$$z_A B^{z_B+} + z_A z_B (A_{1/z_A})R \rightleftharpoons z_B A^{z_A+} + z_A z_B (B_{1/z_B})R \tag{10}$$
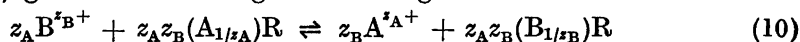
The equilibrium quotient $\varkappa_{B,A}$ for reaction (10) is defined by:

$$\varkappa_{B,A} = \frac{\{A^{z_A+}\}^{z_B}}{\{B^{z_B+}\}^{z_A}} \left(\frac{[(B_{1/z_B})R]}{[(A_{1/z_A})R]} \right)^{z_A z_B} = \frac{\{A^{z_A+}\}^{z_B}}{\{B^{z_B+}\}^{z_A}} \left(\frac{\beta}{1-\beta} \right)^{z_A z_B} \tag{11}$$

if the concentrations in the exchanger are expressed by the equivalent fractions:

$$\beta = \frac{[(B_{1/z_B})R]}{s_0} \quad \text{and} \quad 1-\beta = \frac{[(A_{1/z_A})R]}{s_0} \tag{12}$$

The R—K equation then takes the following form:

$$\left(\frac{[(B_{1/z_B})R]}{[(A_{1/z_A})R]} \right)^{z_A z_B} = k \left(\frac{\{B^{z_B+}\}^{z_A}}{\{A^{z_A+}\}^{z_B}} \right)^{p} \tag{13}$$
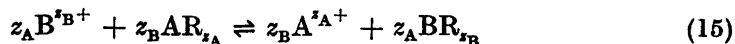
where k and p are empirical constants.

From (11) and (13) the following expression for $\varkappa(\beta)$ can be deduced:

$$\varkappa_{B,A} = k^{1/p} \left(\frac{(1-\beta)}{\beta} \right)^{z_A z_B (1/p-1)} \tag{14}$$

$\varkappa_{B,A}$ belongs to type I if $p < 1$
  »   »   »   »   II » p > 1

Choice (M) gives the following ion exchange reaction:

$$z_A B^{z_B+} + z_B AR_{z_A} \rightleftharpoons z_B A^{z_A+} + z_A BR_{z_B} \tag{15}$$

and the equilibrium quotient for reaction (15) is defined by:

$$\lambda_{B,A} = \frac{\{A^{z_A+}\}^{z_B} [BR_{z_B}]^{z_A}}{\{B^{z_B+}\}^{z_A} [AR_{z_A}]^{z_B}} \tag{16}$$

The R—K equation now gives:

$$\frac{[BR_{z_B}]^{z_A}}{[AR_{z_A}]^{z_B}} = k \left(\frac{\{B^{z_B+}\}^{z_A}}{\{A^{z_A+}\}^{z_B}} \right)^p \tag{17}$$

From (16) and (17):

$$\lambda_{B,A} = k^{1/p} \frac{(1-X_B)^{z_B(1/p-1)}}{X_B^{z_A(1/p-1)}} \tag{18}$$

where the mole fractions X_B and $(1-X_B)$ are defined by:

$$X_B = \frac{[BR_{z_B}]}{[AR_{z_A}] + [BR_{z_B}]} \text{ and } 1-X_B = \frac{[AR_{z_A}]}{[AR_{z_A}] + [BR_{z_B}]} \tag{19}$$

From (18) it is seen:

For p < 1 $\lambda_{B,A}$ belongs to type I
» p > 1 $\lambda_{B,A}$ » » » II

For these two cases too, curves of type III can be approximated using the extension discussed for monovalent ions.

The thermodynamic equilibrium constant: The R—K equation can also be used for obtaining an approximate value for the thermodynamic equilibrium constant for the ion exchange process. This quantity is of value when discussing ion exchange affinities.

Argersinger et al.[26,27] as well as Högfeldt et al.[18,28-30] have shown that the thermodynamic equilibrium constant ($K_{B,A}$) can be obtained by graphical integration of the log $\varkappa_{B,A}(\beta)$-curve. For the calculation of $K_{B,A}$ the following expression can be used:

$$\ln K_{B,A} = \int_0^1 \ln \varkappa_{B,A}(\beta) d\beta \tag{20}$$

When taking the variation in the activity of water into consideration a more complex expression may be obtained [27,31].

Inserting the expression for $\varkappa_{B,A}$ from the R—K equation in (20) and integrating the following expression for $K_{B,A}$ is obtained:

$$K_{B,A} = k^{1/p} \tag{21}$$

This quantity, $k^{1/p}$, can be obtained directly from the double-logarithmic plot, where the intercept on the abscissa gives —log $k^{1/p}$. For multivalent ions only choice (E) gives the same result as that given by (21).

Equation (20) can also be applied to the other empirical equations discussed in this paper, but the R—K equation gives the simplest and most straight-forward method for getting an approximate value for $K_{B,A}$.

In connection with equation (21) it may be noted that it has been proposed [32] that the $\varkappa$-value for $\beta = 0.5$ is a good measure for the relative affinity of the ions for the exchanger. For a system, which can be approximated by the R—K equation, it is found from equation (21) that:

$$\varkappa_{B,A(\beta=0.5)} = K_{B,A} \tag{22}$$

For systems with a maximum or minimum in the $\varkappa(\beta)$-plot, the following approximate expression obtained from (20) and the R—K equation may be useful:

$$\log K_{B,A} \approx \beta_m \log k_1^{1/p_1} + (1-\beta_m) \log k_2^{1/p_2} \tag{23}$$

where β_m is the β-value for the maximum or minimum and k_1, p_1 and k_2, p_2 are the parameters for the two parts of the $\varkappa(\beta)$-curve.

In order to test the usefulness of the different approximate expressions for $K_{B,A}$, $K_{Ag,H}$ was calculated for the two studies of the Ag^+—H^+ exchange on Wofatit KS and Dowex 50 and compared with $\varkappa_{Ag,H(\beta=0.5)}$ and $K_{Ag,H}$-values obtained by graphical integration [18]. The results are given in Table 4.

Table 4. A comparison between approximate and integrated $K_{Ag,H}$-values.

Exchanger	k_1	p_1	k_2	p_2	β_m	$\varkappa_{Ag,H}$ $\beta = 0.5$	$K_{Ag,H}$ from (21) or (23)	$K_{Ag,H}$ integrated
Wofatits KS	3.59	0.75	—	—	—	5.4	5.50	5.16
Dowex 50	5.01	0.89	11.2	1.04	0.14	9.6	9.42	9.90

From Table 4 it is seen that, for the two cases studied, the approximation from the R—K equation gives results in agreement with the integration within $\pm$ 10 % — an accuracy which may often be sufficient. It is also seen that the simpler method using $\varkappa_{B,A(\beta=0.5)}$ is also of sufficient accuracy and for a first approximation it may be useful in a large number of cases.

Recently the authors attention has been called to a paper by Yamabe and Sato [33] which describes the use of an empirical equation which in our notation becomes:

$$\log \frac{\beta}{a} = p \log \frac{(1-\beta)}{(1-a)} + \log k \tag{24}$$

where p and k are empirical constants. A plot of $\log \dfrac{\beta}{a}$ against $\log \dfrac{(1-\beta)}{(1-a)}$ should be a straight line. In their test of the equation to exchange between mono- and divalent ions the authors claim that better agreement was obtained by plotting $\log \dfrac{\beta s_0}{V a a_0}$ against $\log \dfrac{s_0(1-\beta)}{V a_0(1-a)}$. In testing this equation with the data of Högfeldt et al.[7] V, a_0 and s_0

are practically constant so that the test can equally well be performed on (24) as on the alternative. In order to calculate $\varkappa(\beta)$ from (24) it is convenient to express $\beta(\varkappa)$ as:

$$\beta = \frac{\varkappa(k^{1/(p-1)} - \varkappa^{1/(p-1)})}{k^{1/(p-1)}(\varkappa - 1)} \qquad (25)$$

From (25) it can be deduced that:

$$\left.\begin{array}{l} p > 1 \\ k > 1 \end{array}\right\} \quad \text{type I} \qquad \left.\begin{array}{l} p > 1 \\ k < 1 \end{array}\right\} \quad \text{type II} \qquad \left.\begin{array}{l} p < 1 \\ k > 1 \end{array}\right\} \quad \text{type II} \qquad \left.\begin{array}{l} p < 1 \\ k < 1 \end{array}\right\} \quad \text{type I}$$

and thus (24) can be used on $\varkappa(\beta)$-curves of types I and II.

The equation was tested with the data on Wofatit KS but no straight line was obtained. It did not seem worth-while calculating $\varkappa(\beta)$ as the insensitive double-logarithmic plot showed large deviations from linearity. As Yamabe [34] has obtained good agreement with experimental data for higher concentrations than 0.1 C the present results suggest that his equation may be less useful at lower concentrations.

It is a pleasure to acknowledge the valuable aid of Professor Hidetake Kakihana with the translation and discussion of the Japanese paper.

DISCUSSION

From Figs. 2—4 it is seen that it always seems possible to find an empirical equation applicable to a limited concentration range, whereas it may be hard to find one applicable to the whole concentration range. An indispensible condition is that the empirical equation can give a $\varkappa(\beta)$-curve of the same type, I—III, (see Fig. 1 and Table 1) as the experimental one.

The linear plots (which are often logarithmic) used to determine the constants in the empirical equations seem to be too insensitive to test agreement between the empirical equation and the experimental data. They may, however, be used for smoothing out experimental data.

For the two sets of measurements on which the empirical equations have been tested the best agreement is found with the R—K equation. Although the R—K equation is only applicable to $\varkappa(\beta)$-curves of types I and II it is relatively easy to extend its usefulness to all types. None of the other equations seems to offer this extension in such a simple manner. However, from a test on only two experimental $\varkappa(\beta)$-curves, no general deductions can be made about its accuracy in other cases.

The present conclusion, that the R—K equation is the most useful one, is in contradiction with the results of Weisz [16], who found that the Vageler equation gave better numerical agreement with experimental data on zeolites than the equations of "Freundlich", Rothmund-Kornfeld, Wiegner-Jenny and himself. Weisz tested the empirical equations on several systems containing both monovalent and multivalent ions, but the concentration ranges were not as broad as in the present investigation. However, Weisz found, as in this investigation, that the exponential curves ("Freundlich", Wiegner-Jenny) did not give as good an agreement as curves of the hyperbolic type (Vageler, Weisz). This may be due to the fact that the hyperbolic curves (in agreement with experience) have an upper limit for the exchange not shown by the exponential ones.

Future work: There are a number of theoretical approaches in the literature giving a functional connection between α and β. In a following paper they will be discussed in an analogous manner.

REFERENCES

1. Samuelson, O. *Ion exchangers in analytical chemistry*, Uppsala 1952, p. 33.
2. Lowen, W. K., Stoenner, R. W., Argersinger, Jr., W. J., Davidson, A. W. and Hume, D. N. *J. Am. Chem. Soc.* **73** (1951) 2666.
3. Bonner, O. D., Argersinger, Jr., W. J. and Davidson, A. W. *J. Am. Chem. Soc.* **74** (1952) 1044.
4. Bonner, O. D. and Rhett, V. *J. Phys. Chem.* **57** (1953) 254.
5. Duncan, J. F. and Lister, B. A. J. *J. Chem. Soc.* **1949** 3285.
6. Duncan, J. F. and Lister, B. A. J. *Discussions Faraday Soc.* **7** (1949) 104.
7. Högfeldt, E., Ekedahl, E. and Sillén, L. G. *Acta Chem. Scand.* **4** (1950) 1471.
8. Marinsky, J. A. Diss., Report to the Office of Naval Research, NR-026-001 (1949).
9. Boedeker, C. *J. Landwirtschaft* **7** (1859) 48.
10. van Dranen, J. *Rec. trav. chim.* **71** (1952) 1157.
11. Freundlich, H. *Kapillarchemie*, Leipzig 1909.
12. Kroeker, K. Diss., Berlin 1892.
13. Rothmund, V. and Kornfeld, C. *Z. anorg. allgem. Chem.* **103** (1918) 129.
14. Rothmund, V. and Kornfeld, C. *Ibid.* **108** (1919) 215.
15. Vageler, P. *Der Kationen- und Wasserhaushalt des Mineralbodens*, Berlin 1932.
16. Weisz, L. Diss. (E. T. H., Zürich) Budapest 1932.
17. Jenny, H. *Kolloid. Beih.* **23** (1926) 428.
18. Högfeldt, E. *Arkiv Kemi* **5** (1952) 147.
19. Wiegner, G. *J. Landwirtschaft* **60** (1912) 111.
20. Wolff, T. O. G. *Landwirtschaftliche Zeitung für Nord- und Mitteldeutschland* **1859** 250.
21. Tompkins, E. R. and Mayer, S. W. *J. Am. Chem. Soc.* **69** (1947) 2859.
22. Högfeldt, E. *Arkiv Kemi.* **7** (1954) 561.
23. Scarborough, B. J. *Numerical mathematical analysis*, 2nd Ed., Baltimore 1950, p. 446.
24. van Bemmelen, J. M. *Landwirtsch. Vers. Sta.* **35** (1888) 69.
25. McBain, J. W. *The sorption of gases and vapours by solids*, London 1932, p. 5.
26. Argersinger, Jr., W. J., Davidson, A. W. and Bonner, O. D. *Trans. Kansas Acad. Sci.* **53** (1950) 404.
27. Davidson, A. W. and Argersinger, Jr., W. J. *Ann. N. Y. Acad. Sci.* **57** (1953) 105.
28. Ekedahl, E., Högfeldt, E. and Sillén, L. G. *Acta Chem. Scand.* **4** (1950) 556.
29. Högfeldt, E., Ekedahl, E. and Sillén, L. G. *Acta Chem. Scand.* **4** (1950) 828.
30. Högfeldt, E., Ekedahl, E. and Sillén, L. G. *Acta Chem. Scand.* **4** (1950) 829.
31. Gaines, L. G. and Thomas, H. C. *J. Chem. Phys.* **21** (1953) 714.
32. Samuelson, O. *Ion exchangers in analytical chemistry*, Uppsala 1952, p. 34.
33. Yamabe, T. and Sato, S. *J. Chem. Soc. Japan, Ind. Chem. Sect.* **54** (1951) 483.
34. Yamabe, T. *Private communication.*
35. Bonner, O, D., Davidson, A. W. and Argersinger, Jr., W. J. *J. Am. Chem. Soc.* **74** (1952) 1047.