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

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To cite this Article Dyer, A. , Enamy, H. and Townsend, R. P.(1981) 'The Plotting and Interpretation of Ion-Exchange Isotherms in Zeolite Systems', Separation Science and Technology, 16: 2, 173 — 183
To link to this Article: DOI: 10.1080/01496398108058111
URL: http://dx.doi.org/10.1080/01496398108058111

SEPARATION SCIENCE AND TECHNOLOGY, 16(2), pp. 173–183, 1981

The Plotting and Interpretation of Ion-Exchange Isotherms in Zeolite Systems

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Abstract

This paper describes the method whereby ion-exchange isotherms may be plotted and interpreted in the light of modern developments in the literature. It pays particular attention to the problems presented by ion-exchange phenomena in zeolites but should provide a definitive text whereby ion-exchange reactions in other media may be sensibly compared. A detailed example of the application of modern theory to ion-exchange equilibria for a uni-divalent exchange has been given.

INTRODUCTION

Ion exchange has been recognized from the earliest scientific studies made by man. The earliest description of an ion-exchange process has been ascribed to Pliny, and the phenomenon is of utility in chemistry, biology, horticulture, geology, as well as to well-known technological applications such as water purification. Despite this deep importance, the theory of ion exchange remains incomplete. Many authors attempt to quantify ion exchange by reference to ion-exchange equilibria but find that no modern, definitive text is available for them to follow. This

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is particularly problematic in the area of zeolite exchange where problems arise due to heteroenergetic sites and incomplete exchange.

This paper attempts to present methods whereby workers in the field can successfully apply a modern interpretation to zeolite ion-exchange equilibria involving two ions. As a summary, it will not be unhelpful to other exchangers (organic, biological, and inorganic).

EXPERIMENTATION

Production of Ion-Exchange Isotherms

To obtain ion-exchange isotherms for a zeolite system, the following procedures should be followed.

Chemical Analyses

These include:

(a) Wet chemical analysis for SiO_2 and Al_2O_3 should be carried out; x-ray fluorescence is an alternative method of analysis but considerable care should first be taken to ensure correct calibration.
(b) Accurate determination of the initial cation content of the zeolite (usually sodium by flame photometry).
(c) Assay of water content by thermogravimetry.
(d) Analyses of exchanging metal ion content in both solution and zeolite phases after equilibration.

Method

It is required to study the equilibrium distribution of ions between zeolite and aqueous phases. This is carried out by contacting tared amounts of homoionic zeolite (pre-equilibrated for at least 1 week over saturated NaCl solution to ensure a constant water content) with metal chloride or nitrate solutions or, better still, to study radiochemically the displacement of a radio-isotope of, say, sodium from the zeolite by ingoing ions. This, of course, provides an easy analysis of the distribution of metal ions between the two phases. All equilibrations should be in shaken polyethylene containers in a water bath maintained at constant temperature (usually 298 ± 0.1 K).

The exchange solutions must have known, and varying, proportions of the competing ions to the same total normality (hence isonormal). For uni-univalent exchange, since normality $\equiv$ molarity (viz., mol/dm^3), the ionic strength stays constant. When multivalent exchanges are being studied the ionic strength changes even though the total normality is kept constant. The samples should be shaken until equilibrium has been reached, and the time needed for this should be measured from kinetic experiments carried out beforehand. Probably seven days may be adequate for uni- univalent exchange in zeolites, but when divalent transitional elements are being exchanged hydrolysis and/or precipitation may well occur if solutions are in contact with the zeolite phase for long periods.

After equilibration the phases are separated, a further day being allowed before analysis of the liquid phase is effected, in order to allow time for small zeolite particles to separate out.

Reversibility

Before equilibrium thermodynamic interpretation can be applied, it is necessary to establish that the exchanges are reversible. Thus some points are plotted for the (say) $M^{n+} \rightleftarrows nNa^+$ exchange. The term "reversible" implies that equilibrium conditions are found to exist over the whole isotherm, i.e., forward and reverse isotherms are coincident within the limits of experimental uncertainty.

It is undesirable to dry zeolite samples before using them to find a "reverse isotherm" point, as this can result in a redistribution of ions within the lattice which will give rise to an irreversible isotherm, not because the system is intrinsically irreversible, but because of the preparative methods invoked (*7*).

Construction of Isotherm

Exchange between ion A^{Z_A+} (initially in solution) and ion B^{Z_B+} (initially in the zeolite) may be written

$$Z_B A^{Z_A+}_{(s)} + Z_A B^{Z_B+}_{(c)} \rightleftharpoons Z_B A^{Z_A+}_{(c)} + Z_A B^{Z_B+}_{(s)} \qquad (1)$$

where subscripts (s) and (c) refer to "solution" and "crystal" respectively.

The exchange equilibrium for these ions can be characterized conveniently by the ion-exchange isotherm, which is an equilibrium plot of the concentration of an exchanging ion in solution against the concentration of that same ion in the exchanger at constant temperature and constant solution normality. Usually the isotherm is plotted in terms of the equivalent fraction of the entering ion in solution (A_s) against that in the zeolite (A_c). The equivalent fraction of A^{Z_A+} in solution is given by

$$A_s = Z_A m_A/(Z_A m_A + Z_B m_B) \qquad (2)$$

where $m_{A,B}$ is the concentration (mol/dm^3) of the respective ions in solution. A similar expression holds for the zeolite phase except that it is more convenient to express concentrations in terms of the ion-exchange capacity of the exchanger thus:

$$A_c = Z_A M_A/(Z_A M_A + Z_B M_B) = Z_B M_A/Q \tag{3}$$

where $M_{A,B}$ is the concentration (mol kg^{-1}) of the respective ions in the zeolite, and Q is the ion exchange capacity (Q is expressed as the number of charges per 100 g of zeolite after equilibration over saturated salt solution, as previously mentioned).

The ion-exchange isotherm can then be plotted from the equilibrium values of A_s against A_c. Since it must be true that

$$1 - A_s = B_s \tag{4}$$

and

$$1 - A_c = B_c \tag{5}$$

it is apparent that such a plot fully defines the equilibrium at a specified temperature and total normality.

The selectivity of a zeolite for the entering ion A^{Z_A+} may be defined conveniently by a selectivity coefficient α (sometimes referred to as a separation factor) which is defined as

$$\alpha = A_c m_B/B_c m_A \tag{6}$$

Since $m_B = B_c/Z_B$, and $m_A = A_c/Z_A$, it is apparent that

$$\alpha = (Z_A/Z_B)A_c B_s/B_c A_s \tag{7}$$

or, from Fig. 1:

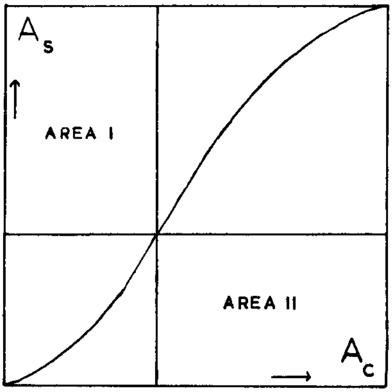

FIGURE 1.

$$\alpha = Z_A/Z_B \text{ (Area I/Area II)} \tag{8}$$

In addition, it is obvious that normally α is not invariant with the level of exchange (A_c). Using α, the conditions for selectivity are

$\alpha > (Z_A/Z_B)$, zeolite selective for A^{Z_A+}

$\alpha = (Z_A/Z_B)$, zeolite shows no preference

$\alpha < (Z_A/Z_B)$, zeolite selective for B^{Z_B+}

THEORY AND INTERPRETATION

The mass action quotient (K_m) for the ion-exchange reaction is

$$K_m = A_c^{Z_B} m_B^{Z_A} / B_c^{Z_A} m_A^{Z_B} \tag{9}$$

which is related to the selectivity quotient (α) by (*3*)

$$\alpha = K_m^{(1/Z_A)} (A_c/m_A)^{(Z_A - Z_B/Z_A)} \tag{10}$$

Since α is a function of A_c, it is obvious that the same will be true for K_m. The inconstancy of K_m is, of course, a reflection of the degree of departure from ideality of the system for a given A_c value.

It is convenient to define the ideal solution in terms of Henry's law, so that the reference state for the solution phase becomes, for each salt involved, the hypothetical ideal molar solution (mol/dm^3) of that salt. The ideal exchanger can then be defined in relation to the ideal solution, since the activity of water in the ideal molar solution is equal to that in the infinitely dilute solution; viz., unity (however, the infinitely dilute solution is *not* the reference state, since in this solution the activity of the dissolved salt is not 1 but tends to 0). Since for equilibrium it must be true that the chemical potentials of the water be the same in all phases, i.e.,

$$\mu_{w(v)} = \mu_{w(s)} = \mu_{w(c)} \tag{11}$$

where (v) refers to the vapor phase, then the reference state for the zeolite phase must involve water in the exchanger with an activity of unity. Thus a convenient definition of the standard state in the zeolite phase is the homoionic form of the exchanger immersed in an infinitely dilute solution of the same ion. The thermodynamic equilibrium constant is then defined as

$$K_a = a_{A(c)}^{Z_B} a_{B(s)}^{Z_A} / a_{B(c)}^{Z_A} a_{A(s)}^{Z_B} = A_c^{Z_B} f_A^{Z_B} m_B^{Z_A} \gamma_B^{Z_A} / B_c^{Z_A} f_B^{Z_A} m_A^{Z_B} \gamma_A^{Z_B} \tag{12}$$

where *a* is activity, or

$$K_a = K_m \Gamma (f_A^{Z_B} / f_B^{Z_A}) \tag{13}$$

where $\Gamma = (\gamma_B{}^{Z_A}/\gamma_A{}^{Z_B})$, $\gamma_{A,B}$ are the single ion activity coefficients in the solution of the ions A^{Z_A+} and B^{Z_B+}, respectively, and $f_{A,B}$ are the activity coefficients for ions A^{Z_A+} and B^{Z_B+} in the crystal phase associated with their equivalents of zeolite anionic framework.

It is apparent that an evaluation of K_a involves two procedures; viz., a *solution* activity correction followed by an *exchanger* (crystal) activity correction.

Considering first the solution activity correction, it is obvious that γ_A and γ_B cannot be evaluated separately by experiment, since the positive ions are always found in solution in association with an equivalent number of negative ions. Fortunately the ratio Γ can be evaluated in terms of the mean molar stoichiometric salt activity coefficients $\gamma_\pm$.

For a given salt A_mX_n, where X is the anion and *m*, *n* refer to the salt stoichiometry, by definition (*4*) the mean molar salt activity coefficient is

$$\gamma_{\pm(A_mX_n)} = [\gamma_A{}^{Z_X}\cdot\gamma_X{}^{Z_A}]^{(1/(Z_A+Z_X))} \tag{14}$$

Substitution and transformations finally yield

$$\Gamma = (\gamma_B{}^{Z_A}/\gamma_A{}^{Z_B}) = [\gamma_{\pm(BX)}]^{Z_A(Z_B+Z_X)/Z_X}[\gamma_{\pm(AX)}]^{-Z_B(Z_A+Z_X)/Z_X} \tag{15}$$

[For simplicity, in (*15*) the stoichiometries of the salts A_mX_n and B_pX_q are ignored in the subscripts of $\gamma_\pm$.]

Now Eq. (15) does not give Γ for the *mixed* solution, which is the reality, but rather gives Γ in terms of *pure* and *separate* solutions of the two salts (A_mX_n and B_pX_q). What is required is Γ in terms of the activity coefficients for the salts in *mixed* solutions, so that the effects of the accompanying salt B_pX_q on the activity of A_mX_n, and vice versa, are taken into account. For a mixture of two salts, Glueckauf (*1*) extended Guggenheim's original theory to yield expressions for the required activity coefficients of the salts in mixed solutions. These are

$$\log \gamma^{(BX)}_{(\pm AX)} = \log \gamma_{\pm(AX)} - \left(\frac{m_B}{4I}\right)\left\{k_1 \log \gamma_{\pm(AX)} - k_2 \log \gamma_{\pm(BX)} - \frac{k_3}{(1 + I^{-1/2})}\right\} \tag{16}$$

and

$$\log \gamma^{(AX)}_{(\pm BX)} = \log \gamma_{\pm(BX)} - \left(\frac{m_A}{4I}\right)\left\{k_4 \log \gamma_{\pm(BX)} - k_5 \log \gamma_{\pm(AX)} - \frac{k_6}{(1 + I^{-1/2})}\right\} \tag{17}$$

where

$$\begin{aligned}
k_1 &= Z_B(2Z_B - Z_A + Z_X)\\
k_2 &= Z_A(Z_B + Z_X)^2(Z_A + Z_X)^{-1}\\
k_3 &= 0.5[Z_AZ_BZ_X(Z_A - Z_B)^2(Z_A + Z_X)^{-1}]\\
k_4 &= Z_A(2Z_A - Z_B + Z_X)\\
k_5 &= Z_B(Z_A + Z_X)^2(Z_B + Z_X)^{-1}\\
k_6 &= 0.5[Z_AZ_BZ_X(Z_B - Z_A)^2(Z_B + Z_X)^{-1}]
\end{aligned}$$

and I is ionic strength.

For (16) and (17) the following should be noted: (a) the equations are expressed in terms of decadic logarithms, and (b) the values of the mean molar stoichiometric activity coefficients for the pure salts, $\gamma_{\pm(AX)}$ and $\gamma_{\pm(BX)}$, to be inserted are those that are found for the relevant pure salt at the same ionic strength as the *mixed* solution of interest. If the exchange is not uni-univalent, I will change with A_s and so should the values of $\gamma_{\pm(AX)}$ and $\gamma_{\pm(BX)}$ that are inserted.

$\gamma^{(BX)}_{(\pm AX)}$ and $\gamma^{(AX)}_{(\pm BX)}$ are the mean molar activity coefficients of salt AX in the presence of salt BX at the given ionic strength (I) and the converse. The bracketed superscripts, (BX) and (AX), do not denote powers. The ionic strength is defined in the normal way as

$$I = 0.5\Sigma_i m_i Z_i^2 \tag{18}$$

and the summation is carried out over *all* the ions present, m being concentration (mol/dm^3).

To summarize, the solution activity correction entails the following:

(1) The ionic strength of each solution should be calculated as a function of A_s (and hence m_A).

(2) For each solution, values of $\gamma_{\pm(AX)}$ and $\gamma_{\pm(BX)}$ should be obtained from the literature for that ionic strength.

(3) These should then be inserted into Eqs. (16) and (17) to obtain values of the mean molar stoichiometric activity coefficients in the mixed solutions.

(4) Finally, Γ for each solution (i.e., at each point on the isotherm) may be calculated from Eq. (15), viz.:

$$\ln \Gamma = (1/Z_X)[Z_A(Z_B + Z_X) \ln [\gamma^{(AX)}_{(\pm BX)}] - Z_B(Z_A + Z_X) \ln [\gamma^{(BX)}_{(\pm AX)}]] \tag{19}$$

It is now convenient to define a new function, the so-called Kielland quotient (K_c), where

$$K_c = K_m\Gamma \tag{20}$$

and it is apparent that following the above procedure yields, for a given isotherm, a set of values of K_c as a function of $\mathrm{A_c}$.

From (13) and (20),

$$K_a = K_c(f_{\mathrm{A}}^{Z_{\mathrm{B}}}/f_{\mathrm{B}}^{Z_{\mathrm{A}}}) \tag{21}$$

and evaluation of K_a (which is invariant with $\mathrm{A_c}$) involves the second correction, i.e., the exchanger activity correction. This correction uses the Gibbs-Duhem equation, viz.,

$$\Sigma_i n_i \, d\mu_i = 0 \tag{22}$$

which was first applied to the ion-exchange problem in depth by Gaines and Thomas (*2*). The summation should include all the components within the exchanger which affect the equilibrium. In practice, for zeolite ion-exchangers, salt imbibition may be ignored provided that the total solution concentration is < 1 mol/dm, and Barrer and Klinowski (*3*) have proved that the water activity terms are not significant in most cases.

Application of (22) finally yields values for f_{A}, f_{B}, and K_a:

$$\ln f_{\mathrm{A}}^{Z_{\mathrm{B}}} = (\mathrm{Z_B} - \mathrm{Z_A})\mathrm{B_c} - \ln K_{c(\mathrm{A_c})} + \mathrm{A_c} \ln K_{c(\mathrm{A_c})} + \int_{\mathrm{A_c}}^{1} \ln K_c \, d\mathrm{A_c} \tag{23}$$

$$\ln f_{\mathrm{B}}^{Z_{\mathrm{A}}} = -(\mathrm{Z_B} - \mathrm{Z_A})\mathrm{A_c} + \mathrm{A_c} \ln K_{c(\mathrm{A_c})} - \int_{0}^{\mathrm{A_c}} \ln K_c \, d\mathrm{A_c} \tag{24}$$

and

$$\ln K_a = (\mathrm{Z_B} - \mathrm{Z_A}) + \int_{0}^{1} \ln K_c \, d\mathrm{A_c} \tag{25}$$

Equation (25) enables the calculation of K_a from isotherm data to which the solution activity coefficient corrections have been applied. K_a may be determined by graphical integration of the plot of ln K_c against $\mathrm{A_c}$, or analytically by integrating the polynomial which gives the best fit to the experimental data.

The standard free energy per equivalent of exchange ($\Delta G^{\ominus}$) may then be found from

$$\Delta G^{\ominus} = -(RT \ln K_a)/\mathrm{Z_A Z_B} \tag{26}$$

In principle, $\Delta H^{\ominus}$ may be found from the Van't Hoff equation since

$$\Delta H^{\ominus} = \Delta U^{\ominus} + \Delta(PV^{\ominus}) = -R|\partial \ln K_a/\partial(1/T)| + \Delta(PV^{\ominus}) \tag{27}$$

and for ion-exchange processes $\Delta(PV^{\ominus}) \to 0$. However, frequently (in zeolites especially) the level of maximal ion exchange changes with temperature. This means that the standard states also change and, if this is the case, Eq. (27) cannot be used.

Two further points need to be made:

(a) Solution activity corrections. Frequently activity coefficient data that are available in the literature (*4*) do not extend over the appropriate range of ionic strength. In these cases values must be obtained by extrapolation rather than interpolation. This can be done if available data are best-fitted, *not* with a polynomial, but with the modified Debye-Huckel relationship:

$$\log \gamma_{\pm(\mathrm{AX})} = \frac{-A|\mathrm{Z_A Z_B}|\sqrt{I}}{(1 + Ba\sqrt{I})} + bI \tag{28}$$

where

$$A = \sqrt{2\pi L/1000}\,[e^3/2.303(4\pi\varepsilon kT)^{3/2}] \tag{29}$$

and

$$B = (Le^2/500\varepsilon kT)^{1/2} \tag{30}$$

L is the Avogadro constant, e is the charge on the electron, ε is the permittivity (i.e., $\varepsilon = \varepsilon_r \varepsilon_0$, where ε_r is the relative permittivity or "dielectric constant," and ε_0 is the permittivity of free space, 8.854×10^{-12} kg^{-1} m^{-3} s^4 A^2). a and b are essentially fitting parameters, although a is identified with the so-called "ionic atmosphere" of the original Debye-Huckel theory (*4*), and normally has a value of ~0.4 nm.

The use of Eq. (26), in the form shown above, requires decadic logarithms, and note that it is, as shown, the *modulus* of the product of charges ($\mathrm{Z_A}$ and $\mathrm{Z_X}$) that is inserted into the first term.

Best-fitting the above to literature experimental data can be achieved by taking sets of values of $\gamma_{\pm(\mathrm{AX})}$ and I and solving simultaneously for a and b. Estimation of $\gamma_{\pm(\mathrm{AX})}$ at values of I outside the experimental range quoted may then be carried out.

(b) Normalization. If exchange of ion B^{Z_B+} by A^{Z_A+} does not proceed to completion, it is necessary to "normalize" the isotherm. This involves dividing all values of $\mathrm{A_c}$ by the maximal value observed experimentally to give normalized $\mathrm{A_c}$ values, viz.:

$$\mathrm{A_c}^N = \mathrm{A_c}/\mathrm{A_c}(\max) \tag{31}$$

This procedure does not, of course, affect the solution activity correction, but does affect the Gaines and Thomas treatment. Equations

(12) to (25) are still applicable but normalized parameters must be used throughout. Thus, for example, (23) becomes

$$\ln f_A{}^{Z_B} = (Z_B - Z_A)B_c{}^N - \ln K^N_{c(A_c)} + A_c{}^N \ln K^N_{c(A_c)} + \int_{A_c{}^N}^{1} \ln K_c{}^N \, dA_c{}^N \qquad (32)$$

The superscript N refers to normalized values.

This procedure is necessary to conform to the definition of the exchanger phase standard state stated previously. In effect, normalization results in the B^{Z_B+} ions which are *not* involved in exchange being regarded as part of the exchanger framework. They can still affect the exchange equilibrium, of course, but these effects are allowed for in f_A and f_B. An alternative procedure suggested by Vansant and Uytterhoeven (*5*) and discussed extensively by Breck (*6*) is incorrect.

CONCLUSION AND EXAMPLE

Barrer and Townsend (*7*) considered the exchange

$$M^{2+}_{(s)} + 2NH^+_{4(c)} \rightleftarrows 2NH^+_{4(s)} + M^{2+}_{(c)} \qquad (33)$$

where M signifies a transition metal. The normality of all solutions was kept constant at 0.08 equiv/dm^3. The molar concentration (mol/dm^3) was not, however, constant, but changed from a lower limit of 0.04 (at $M_c = 1$) to an upper limit of 0.08 mol/dm^3 (at $(NH_4)_c = 1$). It follows, therefore, that the ionic strength also varied from a value of 0.12 mol/dm^3 at $M_c = 1$ to 0.08 mol/dm^3 at $M_c = 0$.

Considering, for example, the determination of values of $\gamma^{(MCl_2)}_{\pm(NH_4Cl)}$, and keeping the formalism of Eqs. (1) and (33) the same, then Eq. (17) is the appropriate one to use. k_4, k_5, and k_6 have values of 8, 9/2, and 1/2, respectively, and for (say) $M_c = 0.5$, $I = 0.1$ mol/dm^3. Then

$$[\log \gamma^{(MCl_2)}_{\pm(NH_4Cl)}]_{M_c=0.5} = 0.6[\log \gamma_{\pm(NH_4Cl)}]_{I=0.1} + 0.225[\log \gamma_{\pm(MCl_2)}]_{I=0.1} + 0.00645 \qquad (34)$$

For the case of $M_c = 1$, $(NH_4)_c = 0$, and Eq. (17) becomes

$$\mathscr{L}\underset{[(NH_4)_c \to 0]}{\mathrm{im}} [\log \gamma^{(MCl_2)}_{\pm(NH_4Cl)}] = 0.3336[\log \gamma_{\pm(NH_4Cl)}]_{I=0.12} + 0.3749[\log \gamma_{\pm(MCl_2)}]_{I=0.12} + 0.0107 \qquad (35)$$

Equation (35) shows that for a mixed solution, in contrast to that seen in a solution of just one electrolyte, as the activity of a salt tends to zero, its activity coefficient does not normally tend to unity. A finite value is obtained which is a function of the activity coefficients of the two unmixed salt solutions at the same ionic strength as the mixed solution.

Having obtained values for the mean molar stoichiometric activity coefficients in mixed solution, Barrer and Townsend (*5*) then calculated Γ as a function of *I* from (cf. Eq. (19) in this paper)

$$\ln \Gamma_{(I)} = 4[\ln \gamma^{(\mathrm{NH_4Cl})}_{(\pm \mathrm{MCl_2})}]_I - 3[\ln \gamma^{(\mathrm{MCl_2})}_{(\pm \mathrm{NH_4Cl})}]_I \qquad (36)$$

thus obtaining solution activity corrections over the whole range of M_c for these uni-divalent exchanges.

The above examples are provided as quick and convenient checks on the general equations given in this paper.

CORRIGENDUM

In the original paper of Barrer and Townsend (*7*), Eqs. (3) and (4) refer to the limiting conditions of $M_c \rightarrow 1$ and $M_c \rightarrow 0$, respectively. The "limit" symbols were accidentally omitted. The error in no way affects any data reported therein.

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Received by editor June 3, 1980