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THERMODYNAMICS OF BINARY AND TERNARY ION EXCHANGE IN ZEOLITES: THE EXCHANGE OF SODIUM, AMMONIUM AND POTASSIUM IONS IN MORDENITE

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In many ion exchanges that involve zeolites, more than two types of exchanging ions are involved. Most work to date has been concerned with equilibria involving two different types of ion only. In this paper, a recently devised thermodynamic treatment for exchange equilibria involving three ions is tested experimentally. In §1 the most important aspects of this thermodynamic model are discussed, and after this the experimental techniques necessary to obtain a ternary exchange isotherm are summarized. Data for three binary exchanges in synthetic mordenite are presented in §3 (the ion pairs Na–NH_4, NA–K and K–NH_4) together with a ternary isotherm obtained for the simultaneous exchange of Na^+, NH_4^+ and K^+ ions in the same zeolite, all data being measured at a temperature of 25 °C. After some general considerations in §4 on the nature of non-ideality in the zeolite phase and its effects on the variation of observed ion selectivities as a function of exchanger composition, the experimental data are next used to test, first, the validity, and secondly the range of applicability of numerous models found in the literature, all of which attempt to predict multicomponent exchange equilibria from binary exchange data alone. In §5 models that were developed primarily with ion exchange resins in mind are discussed (Soldatov & Bychkova 1980). In §6 approaches that attempt to predict, from binary activity data, the coefficients of ternary exchanger systems are considered, especially those that have been used with some success on clays (Elprince & Babcock 1975; Chu & Sposito 1981). All of these models are shown to be, at best, only partially successful in predicting experimental data for the comparatively simple Na–NH_4–K–mordenite exchange system. The use of zeolites seems, therefore, to introduce additional complications. The recently developed model of Fletcher & Townsend (1981 b) is next used to determine directly the exchanger phase activity coefficients ϕ_{Na}, ϕ_{NH_4} and ϕ_K, and these are indeed found to vary with the exchanger phase composition in a complicated manner. Finally, in §8, the observed non-ideality of the ternary exchange system is rationalized in terms of site heterogeneity within the zeolite framework, and the consequences of this phenomenon are discussed, particularly with respect to the problems this presents in the successful prediction of multicomponent exchange phenomena, when only a limited quantity of data are available.

General introduction

Very many theoretical and experimental studies of ion exchange equilibria that involve just two exchanging ions can be found in the literature. However, it is only comparatively recently that much attention has been paid to the problem of understanding multicomponent ion exchange equilibria, despite the fact that many natural and industrial processes involve more than two types of exchanging ions. An important requirement of any successful model of multicomponent exchange is that it be able to predict equilibrium compositions of the system over a range of conditions, with use of, perhaps, a necessarily limited quantity of accurate experimental data. As such, it is natural that many of the models that have been derived have sought to predict multicomponent compositions from data obtained for binary ion exchange equilibria.

Theoretical studies of multicomponent exchange equilibria have been developed in parallel by workers primarily interested in either resins or clays or zeolites. The resulting models have similarities, but each have also their distinctive aspects, reflecting to some degree particular behavioural characteristics of the ion exchanger that was of primary interest. Detailed studies on multicomponent exchange equilibria in resins have been in progress for more than a decade (Soldatov & Bychkova 1971, 1980; Kol'nenkov & Bogomolov 1977) while studies on clays by a quite different approach were initiated somewhat more recently (Elprince & Babcock 1975; Wiedenfeld & Hossner 1978). Subsequently another model, which is designed to predict ternary equilibrium compositions in clays from binary exchange data, has been reported (Elprince *et al.* 1980; Chu & Sposito 1981). Some of these models will be discussed in greater detail later in this paper; all of them involve simplifying assumptions with regard to the behaviour of the activity coefficients that describe the non-ideality of the exchanger phase.

A series of theoretical studies on binary ion exchange in zeolites were made by Barrer & Klinowski (1972*a*, 1974*a*, 1979*a*) and by Barrer *et al.* (1973). A general statistical thermodynamic theory of isomorphous replacement in zeolites has also been given (Barrer & Klinowski 1977) and the subject has been considered also from the viewpoint of order–disorder theory (Barrer & Klinowski 1979*b*). The first detailed report of a ternary ion exchange system in a zeolite was by Barrer & Townsend (1978), and subsequently, detailed studies on the Na–Ca–Mg–A system have appeared (Rees 1980; Barri & Rees 1980). Other binary exchange studies (Barrer & Townsend 1976; Fletcher & Townsend 1980) have shown that the activity coefficients for ions in association with their equivalents of zeolite framework can vary in a complicated manner with exchanger composition, and considerations of other work (Barrer *et al.* 1973; Barrer & Klinowski 1977) led to the conclusion that these variations must be ascribed to changing populations and compositions within the exchanger site sets that comprise the zeolite (Fletcher & Townsend 1980). It appeared therefore that models for ternary or multicomponent exchange that had been developed for clays and resins might not be appropriate for zeolites (Fletcher & Townsend 1981*a*), and so an appropriate thermodynamic treatment, which makes no structural assumptions about the nature of the non-ideality of the exchanger phase, was derived (Fletcher & Townsend 1981*b*, 1981*c*).

This paper reports the first comprehensive experimental test of this new model. The ternary system Na–NH_4–K–mordenite was chosen for this test for two main reasons. First, mordenite is a highly siliceous zeolite, and is therefore particularly resistant to dealumination followed by consequent destruction of the lattice framework (McDaniel & Maher 1976). Hydronium ion exchange (Barrer & Klinowski 1975) was also minimized by using the above choice of ions, since the external pH was always close to neutral. (Both dealumination and hydronium ion exchange can lead to apparent non-stoichiometry of exchange, which would unnecessarily complicate this study). The second main reason for choosing this system is that it was already known (Barrer & Klinowski 1974*b*) that sodium, ammonium and potassium ions all exchange to 100% of the exchange capacity of the zeolite. So problems entailed in 'normalizing' the isotherms (Barrer *et al.* 1973) were avoided.

Some general points with regard to the thermodynamic model are emphasized here. First, the approach used for the exchanger phase involved essentially integrating Gibbs–Duhem type equations (Fletcher & Townsend 1981*b*). Such an approach relies for its precision on accurate data and reliable extrapolation to compositions involving limiting concentrations of one or more species. A degree of inherent uncertainty is therefore introduced into the calculations; this matter is discussed further in §5 and §7. A second consequence of employing Gibbs–Duhem-type equations is that the thermodynamic equilibrium constants so derived should be subject to an internal consistency test §5 and §7). Finally, it is emphasized (in common with a wide range of thermodynamic calculations) that the evaluation of the thermodynamic equilibrium constants themselves gives no information on the equilibrium concentrations of the system as a function of composition: for this, a knowledge of activity coefficients in both the solution and exchanger phases is required. Activity coefficient data for salts in the mixed electrolyte solution is not a matter that is considered in detail here; values were derived from a recent extension (Fletcher & Townsend 1981*c*, 1983) of the models of Guggenheim (1935) and Glueckauf (1949). In contrast, the means by which accurate values may be found for the activity coefficients of components in the exchanger phase is the major concern of this paper.

List of symbols

a_{u}	activity of ion u in the aqueous solution phase
$\bar{a}_{\mathrm{u}}$	activity of ion u in the zeolite phase
f_{u}	rational activity coefficient (i.e. from using a measurement scale involving mole fractions $\bar{X}_{\mathrm{u}}$) for ion u in zeolite phase
f_{ij}	rational activity coefficient for ion i at a composition $\bar{X}_{\mathrm{i}}$ for a binary exchange involving only ions i and j
f_{ij}^{∞}	value of f_{ij} as $\bar{X}_{\mathrm{i}} \rightarrow 0$
g_{u}	activity coefficient of ion u in exchanger phase with use of equivalent fraction $\bar{E}_{\mathrm{u}}$ as the measurement scale rather than mole fraction
$g_{\mathrm{A}}^{(\mathrm{B})}$	binary activity coefficient of ion A in the presence of ion B with use of the equivalent fraction convention (following Soldatov & Bychkova 1980)
g_{ij}	activity coefficient of ion i at a composition $\bar{E}_{\mathrm{i}}$ for a binary exchange involving ions i and j (cf. f_{ij})
g_{ij}^{∞}	value of g_{ij} as $\bar{E}_{\mathrm{i}} \rightarrow 0$
k	the Boltzmann constant
$k_{\mathrm{C-A}}, k_{\mathrm{C-B}}$	ratios of two Gaines & Thomas (1953) corrected selectivity quotients (see definition of K_{G} and also (10))
z_{u}	valency of cation u
z_{X}	valency of co-anion X in solution phase
A, B, C	labels for cations $\mathrm{M}_{\mathrm{A}}^{z_{\mathrm{A}}+}$, $\mathrm{M}_{\mathrm{B}}^{z_{\mathrm{B}}+}$, $\mathrm{M}_{\mathrm{C}}^{z_{\mathrm{C}}+}$, which are involved in a ternary exchange process (see equation (1))
E_{A}	equivalent fraction of ion A in solution
$\bar{E}_{\mathrm{u}}$	equivalent fraction of ion u in zeolite (defined in (7)). For binary exchanges $\bar{E}_{\mathrm{u}}+\bar{E}_{\mathrm{v}} = 1$; for ternary exchanges $\bar{E}_{\mathrm{u}}+\bar{E}_{\mathrm{v}}+\bar{E}_{\mathrm{w}} = 1$
$\bar{E}'_{\mathrm{u}}$	relative concentration term, expressed in equivalent fractions, and defined so that if (for example) $\bar{E}_{\mathrm{w}}$ is kept constant, then $\bar{E}'_{\mathrm{u}} = \bar{E}_{\mathrm{u}}/(1-\bar{E}_{\mathrm{w}})$
${}^{\mathrm{u}}_{\mathrm{v}}G^{\mathrm{E}}$	excess free energy term for binary exchange involving ions u (initially in solution) and v (initially in exchanger)
${}^{\mathrm{u}}_{\mathrm{v}}\Delta G^{\ominus}$	standard free energy change for binary exchange involving ions u (initially in solution) and v (initially in exchanger)
${}^{\mathrm{u}}_{\mathrm{v,w}}\Delta G^{\ominus}$	standard free energy change for ternary exchange involving ions u, v, w. Ion u is initially in solution and both v and w are in the exchanger (see equation (1))

K_a	thermodynamic equilibrium constant (i.e. in terms of activities a)
${}^{\mathrm{u}}_{\mathrm{v}}K_a$	thermodynamic equilibrium constant corresponding to ${}^{\mathrm{u}}_{\mathrm{v}}\Delta G^{\ominus}$
${}^{\mathrm{u}}_{\mathrm{v,w}}K_a$	thermodynamic equilibrium constant for ternary reaction corresponding to ${}^{\mathrm{u}}_{\mathrm{v,w}}\Delta G^{\ominus}$
K_{G}	corrected selectivity quotient in which solution phase concentrations are expressed in terms of activities, but zeolite phase concentrations are expressed in terms of equivalent fractions by using the Gaines & Thomas (1953) convention (hence the subscript G)
${}^{\mathrm{u}}_{\mathrm{v}}K_{\mathrm{G}}$	corrected selectivity quotient (Gaines & Thomas (1953) convention) for binary exchange involving ions u (initially in solution) and v (initially in exchanger)
${}^{\mathrm{u}}_{\mathrm{v,w}}K_{\mathrm{G}}$	corrected selectivity quotient (Gaines & Thomas (1953) convention) for ternary exchange reaction involving ions u, v, w. Ion u is initially in solution and v, w are in the exchanger (see equation (1))
${}^{\mathrm{u}}_{\mathrm{v}}\mathscr{K}_{\mathrm{G}}$	pseudobinary corrected selectivity quotient (Gaines & Thomas (1953) convention), formally identical to ${}^{\mathrm{u}}_{\mathrm{v}}K_{\mathrm{G}}$, but actually expressing the equilibrium compositions between ions u and v only *in the presence* of ion w; so for this function $\bar{E}_{\mathrm{u}}+\bar{E}_{\mathrm{v}} \neq 1$
K_m	mass action quotient, in which no corrections for non-ideality have been applied to ionic concentration terms in either phase
$K_{m,E}$	mass action quotient in which concentrations in the zeolite are expressed in terms of equivalent fractions
${}^{\mathrm{u}}_{\mathrm{v,w}}K_{m,E}$	mass action quotient for the ternary exchange reaction involving ions u, v, w. Ion u is initially in solution, and ions u, w are in the exchanger (see equation (1))
$\mathrm{M}_{\mathrm{u}}^{z_{\mathrm{u}}+}$	symbol for metal cation involved in exchange reaction, ion label u (see equation (1))
N	number of crystallographically distinct cation exchange sites within the zeolite
N_0	number of unit negative charges dispersed through the zeolite framework
$\mathscr{N}$	number of independent sets of experimental data to which polynomial equations are fitted
$\mathscr{P}$	order of fitting polynomial with respect to concentration variable $\bar{E}_{\mathrm{A}}$
${}^{\mathrm{u}}_{\mathrm{v}}\mathrm{Q}$	excess free energy term, following Soldatov & Bychkova (1980), defined in (34)
$\mathscr{Q}$	order of fitting polynomial with respect to concentration variable $\bar{E}_{\mathrm{B}}$
R	gas constant
$\mathscr{R}$	summation of residuals function, which gives a criterion for best fit
T	absolute temperature
$\bar{\mathrm{X}}_{\mathrm{A}}$	mole fraction of ion A in the zeolite. Thus $\bar{\mathrm{X}}_{\mathrm{A}} = \bar{m}_{\mathrm{A}}/\Sigma_i \bar{m}_i$, and should be distinguished from $\bar{E}_{\mathrm{A}}$
X	label for co-anion in solution
$\mathrm{X}_{\mathrm{L}}(i)$	the fraction of the total framework charge which is neutralized by all exchange cations found on the ith site group within the zeolite
X_{L}	quantity of anionic lattice holding one mole of unit charge
α_i, β_j γ_p, δ_q ϵ_i, ζ_j η_p, θ_q	coefficients of best-fitting polynomials of orders i, j, p, and q, respectively

${}^{\mathrm{u}}_{\mathrm{v}}\alpha$	separation factor defining the preference displayed by the exchanger for ion u over ion v; concentration in both phases is expressed in terms of equivalent fractions $E_{\mathrm{u}}, \bar{E}_{\mathrm{u}}$ etc.
${}^{\mathrm{u}}_{(\mathrm{v,w})}\tilde{\alpha}$	pseudobinary separation factor, in which the preference displayed by the exchanger for ion u over *both* v *and* w *combined* is defined. The separate effects of v, w are not considered, so this function is not a ternary separation factor in the strict sense of the term
γ_{u}	molal (i.e. moles per kilogram) activity coefficient for ion u in the aqueous solution
$\gamma_{\pm\mathrm{uX}}$	mean molal stoichiometric activity coefficient for a pure solution of salt uX at an ionic strength I. (To keep the symbol as simple in form as possible, the subscript ±uX does not show the stoichiometry of the salt. So, for example, if the salt is sodium chloride, the subscript is ±NaCl, but if the salt is lanthanum sulphate $La_2(SO_4)_3$, the subscript is still only written as $\pm LaSO_4$)
$\gamma^{(\mathrm{v,w})}_{\pm\mathrm{uX}}$	mean molal stoichiometric activity coefficient for salt uX in a *mixed* electrolyte solution that also contains the salts vX and wX.
η	ratio of number of cationic sites in zeolite framework to the framework charge in the same quantity of zeolite (after Barrer & Klinowski 1977)
λ_{uv}	interaction energy between the ion pair uv within the exchanger
ν_{u}	molar volume of homo-ionic u-form of the exchanger
$\xi^{(\mathrm{v,w})}_{\mathrm{uX}}$	activity correction factor for salt uX in the presence of vX and wX, defined in (16) (see Fletcher & Townsend 1981*c*)
ϕ_{u}	activity coefficient for ion u in association with its equivalent of anionic zeolite lattice X_L
$\chi_{\mathrm{C-A}}, \chi_{\mathrm{C-B}}$	composition dependent crystal phase selectivity function (evaluation of these parameters leads to the calculation of $\phi_{\mathrm{A}}, \phi_{\mathrm{B}}, \phi_{\mathrm{C}}$ (equations (20)–(24))
ω_{AA}	additional change in energy of the crystal, which occurs when two A ions occupy adjacent sites (Barrer & Klinowski 1977)
Γ	overall correction factor to allow for non-ideality in the aqueous solution phase
${}^{\mathrm{u}}_{\mathrm{v,w}}\Gamma$	overall correction for non-ideality in the aqueous solution phase for a ternary exchange reaction involving ions u, v and w. Ion u is initially in solution and both v and w are in the exchanger (see equation (1))
$\Gamma_{\mathrm{C-A}}, \Gamma_{\mathrm{C-B}}$	overall correction for non-ideality in the aqueous solution phase, implicit in the functions $k_{\mathrm{C-A}}, k_{\mathrm{C-B}}$ (see equations (10) and (11))
Λ_{uv}	Boltzmann function, which expresses the difference in interaction energies between like and unlike ion pairs in the exchanger (i.e. λ_{uu} and λ_{uv}; see equation (46))
Φ	overall correction for non-ideality in the zeolite phase
${}^{\mathrm{u}}_{\mathrm{v,w}}\Phi$	overall correction for non-ideality in the zeolite phase for a ternary exchange reaction involving ions u, v and w. Ion u is initially in solution and both v and w are in the exchanger.

1. THERMODYNAMIC MODEL FOR TERNARY ION-EXCHANGE

(*a*) *Basic definitions*

For an ion exchange process involving three different counter-ion species $M_A^{z_A+}$, $M_B^{z_B+}$ and $M_C^{z_C+}$ three exchange reactions may be written, each having a corresponding thermodynamic equilibrium constant and standard free energy (Fletcher & Townsend 1981 *a,b*). These may be generalized as

$$2z_v z_w M_u^{z_u+} + z_u z_w \overline{M}_v^{z_v+} + z_u z_v \overline{M}_w^{z_w+} \rightleftharpoons 2z_v z_w \overline{M}_u^{z_u+} + z_u z_w M_v^{z_v+} + z_u z_v M_w^{z_w+}, \tag{1}$$

where

$$\begin{bmatrix} A, & B, & C \\ B, & C, & A \\ C, & A, & B \end{bmatrix} = \begin{bmatrix} u \\ v \\ w \end{bmatrix},$$

z is the valency of the cation $M_u^{z_u+}$, $M_v^{z_v+}$ or $M_w^{z_w+}$ and the overbar denotes that the ion is in the exchanger phase. The thermodynamic equilibrium constants are then

$${}^{\,\,u}_{v,w}K_a = \frac{\bar{a}_u^{2z_v z_w}\, a_v^{z_u z_w}\, a_w^{z_u z_v}}{a_u^{2z_v z_w}\, \bar{a}_v^{z_u z_w}\, \bar{a}_w^{z_u z_v}}, \tag{2}$$

where a_i, $\bar{a}_i$ denote activity of ion i in solution and zeolite respectively. Each thermodynamic equilibrium constant can be expressed as the product of a mass action quotient (K_m), an activity coefficient factor for the solution phase (Γ) and an activity coefficient factor for the zeolite phase (ϕ)

$$K_a = K_m \Gamma \Phi, \tag{3}$$

where explicitly

$${}^{\,\,u}_{v,w}K_{m,E} = \frac{\bar{E}_u^{2z_v z_w}\, m_v^{z_u z_w}\, m_w^{z_u z_v}}{\bar{E}_v^{z_u z_w}\, \bar{E}_w^{z_u z_v}\, m_u^{2z_v z_w}} \tag{4}$$

$${}^{\,\,u}_{v,w}\Gamma = \gamma_v^{z_u z_w}\, \gamma_w^{z_u z_v} / \gamma_u^{2z_v z_w} \tag{5}$$

$${}^{\,\,u}_{v,w}\Phi = \phi_u^{2z_v z_w} / \phi_v^{z_u z_w}\, \phi_w^{z_u z_v}. \tag{6}$$

The subscript E on K_m indicates that the exchanger phase composition is expressed in terms of equivalent fractions $\bar{E}_{u,v,w}$, and m denotes concentrations (moles per kilogram) in solution. The equivalent fraction of (for example) ion $M_A^{z_A+}$ in the exchanger is then

$$\bar{E}_A = z_A \bar{m}_A \Big/ \sum_{u}^{w} z_i \bar{m}_i \tag{7}$$

with $\bar{m}_i$ being the concentration (in moles per kilogram) of ion i in the zeolite. The $\gamma_{u,v,w}$ are the 'activity coefficients' of the individual ions $M_u^{z_u+}$, $M_v^{z_v+}$ and $M_w^{z_w+}$ in solution, respectively. The means by which these can be evaluated is described in § 1 *b*.

The $\phi_{u,v,w}$ are the activity coefficients of equivalents of the respective cations in association with an equal quantity of oppositely charged lattice framework. Thus ϕ 'does not have the character of an individual ion activity coefficient but refers to the combination of that ion with the exchanger in a definite composition of the whole mass' (Gaines & Thomas 1953).

(*b*) *Evaluation of thermodynamic equilibrium constants*

It is also convenient to consider the quotient

$$K_G = K_m \Gamma, \tag{8}$$

which has been 'corrected' for the bulk phase non-ideality and which is solely dependent on non-ideality in the zeolite phase. Explicitly (Fletcher & Townsend 1981*a*)

$${}^{u}_{v,w}K_G = \frac{\bar{E}_u^{2z_v z_w}}{\bar{E}_v^{z_u z_w}\,\bar{E}_w^{z_u z_v}}\;\frac{a_v^{z_u z_w}\,a_w^{z_u z_v}}{a_u^{2z_v z_w}}. \tag{9}$$

The Gibbs–Duhem equation can then be applied to the ternary exchange equilibrium in the zeolite phase. Integration of all the resulting equations in terms of $\bar{E}_A$ and $\bar{E}_B$ only as the independent variables leads to a set of equations involving just two ratios (Fletcher & Townsend 1981*b*)

$$k_{C-A} = ({}^{C}_{A,B}K_G/{}^{A}_{B,C}K_G)^{\frac{1}{3}} = \Gamma_{C-A}({}^{C}_{A,B}K_{m,E}/{}^{A}_{B,C}K_{m,E})^{\frac{1}{3}} \tag{10}$$

$$k_{C-B} = ({}^{C}_{A,B}K_G/{}^{B}_{C,A}K_G)^{\frac{1}{3}} = \Gamma_{C-B}({}^{C}_{A,B}K_{m,E}/{}^{B}_{C,A}K_{m,E})^{\frac{1}{3}} \tag{11}$$

The use of the equivalent fraction convention has been criticized recently (Sposito & Mattigod 1979; Sposito 1981). However, the equivalent fraction refers only to the number of equivalents of cations in association with an equal number of moles of electrons. The approach is consistent with that of Gaines & Thomas (1953). The matter is discussed in detail elsewhere (Barrer & Townsend 1984).

To evaluate k_{C-A} and k_{C-B}, values of Γ_{C-A} and Γ_{C-B} are needed. These functions are defined as

$$\Gamma_{C-A} = ({}^{C}_{A,B}\Gamma/{}^{A}_{B,C}\Gamma)^{\frac{1}{3}}, \tag{12}$$

$$\Gamma_{C-B} = ({}^{C}_{A,B}\Gamma/{}^{B}_{C,A}\Gamma)^{\frac{1}{3}}. \tag{13}$$

(Note that k_{C-A}, k_{C-B} are not identical to the ratios (K_{C3}/K_{C1}) and (K_{C3}/K_{C2}) used in earlier work (Fletcher & Townsend 1981*b*), but are related through the cube root).

${}^{u}_{v,w}\Gamma$, defined in (5), contains the 'activity coefficients' of individual ions. In contrast to the ϕ terms (which, as explained above, are *not* individual ion activity coefficients) the γ terms obviously cannot be evaluated separately. Nevertheless, it is possible to evaluate the ${}^{u}_{v,w}\Gamma$ functions in terms of ratios of the mean molal stoichiometric activity coefficients for the salts in the *mixed* solution at the required ionic strength. The form of these ratios, and the magnitude of the correction, depends on the valencies of the three exchanging ions and also on the number of co-anions in solution (Fletcher & Townsend 1981*c*). For the present case of only one co-anion, (valence z_X) then

$$\Gamma_{C-A} = ({}^{C}_{A,B}\Gamma/{}^{A}_{B,C}\Gamma)^{\frac{1}{3}} = (\xi_{AX}^{(B,C)}/\xi_{CX}^{(A,B)})^{1/z_X}, \tag{14}$$

$$\Gamma_{C-B} = ({}^{C}_{A,B}\Gamma/{}^{B}_{C,A}\Gamma)^{\frac{1}{3}} = (\xi_{BX}^{(A,C)}/\xi_{CX}^{(A,B)})^{1/z_X}, \tag{15}$$

and

$$\xi_{uX}^{(v,w)} = [\gamma_{\pm uX}^{(v,w)}]^{z_v z_w (z_u + z_X)}, \quad \begin{bmatrix} A, & B, & C \\ B, & C, & A \\ C, & A, & B \end{bmatrix} = \begin{bmatrix} u \\ v \\ w \end{bmatrix}, \tag{16}$$

where $\gamma_{\pm\mathrm{uX}}^{(\mathrm{v},\mathrm{w})}$ ... are the mean molal stoichiometric activity coefficients of the respective salts in the *mixed* solution at the required ionic strength. General equations for the derivation of $\gamma_\pm$ values in the mixed salt solution have also been derived recently (Fletcher & Townsend 1981 *c*); however, for the system discussed in this paper $z_\mathrm{u} = z_\mathrm{v} = z_\mathrm{w}$, and it has been shown (Fletcher & Townsend 1983) that the ξ ratios in such a case are constant irrespective of the solution phase composition, and equal to

$$\Gamma_{\mathrm{C-A}} = (\gamma_{\pm\mathrm{AX}}/\gamma_{\pm\mathrm{CX}})^{[z^2(z+z_\mathrm{X})/2zz_\mathrm{X}]}, \tag{17}$$

and

$$\Gamma_{\mathrm{C-B}} = (\gamma_{\pm\mathrm{BX}}/\gamma_{\pm\mathrm{CX}})^{[z^2(z+z_\mathrm{X})/2zz_\mathrm{X}]}, \tag{18}$$

where $z = z_\mathrm{u} = z_\mathrm{v} = z_\mathrm{w}$.

A general expression for the thermodynamic equilibrium constants then follows, namely

$$\ln ({}_{\mathrm{v},\mathrm{w}}^{\mathrm{u}}K_a) = z_\mathrm{v}(z_\mathrm{w} - z_\mathrm{u}) + z_\mathrm{w}(z_\mathrm{v} - z_\mathrm{u}) + \int_0^1 I_1 \ln k_{\mathrm{C-A}}\,\mathrm{d}\bar{E}_\mathrm{A} + \int_0^1 I_2 \ln k_{\mathrm{C-B}}\,\mathrm{d}\bar{E}_\mathrm{B}, \tag{19}$$

where I_1 and I_2 are integers as indicated: for

$$\begin{bmatrix} \mathrm{A}, & \mathrm{B}, & \mathrm{C}, -2, +1 \\ \mathrm{B}, & \mathrm{C}, & \mathrm{A}, +1, -2 \\ \mathrm{C}, & \mathrm{A}, & \mathrm{B}, +1, +1 \end{bmatrix} = \begin{bmatrix} \mathrm{u} \\ \mathrm{v} \\ \mathrm{w} \\ \mathrm{I}_1 \\ \mathrm{I}_2 \end{bmatrix}$$

and the activity coefficients are respectively

$$\ln \phi_\mathrm{A}^{z_\mathrm{B} z_\mathrm{C}} = \int_1^{\bar{E}_\mathrm{A}} \ln \chi_{\mathrm{C-A}}\,\mathrm{d}\bar{E}_\mathrm{A} + \int_0^{\bar{E}_\mathrm{B}} \ln \chi_{\mathrm{C-B}}\,\mathrm{d}\bar{E}_\mathrm{B}, \tag{20}$$

$$\ln \phi_\mathrm{B}^{z_\mathrm{A} z_\mathrm{C}} = \int_0^{\bar{E}_\mathrm{A}} \ln \chi_{\mathrm{C-A}}\,\mathrm{d}\bar{E}_\mathrm{A} + \int_1^{\bar{E}_\mathrm{B}} \ln \chi_{\mathrm{C-B}}\,\mathrm{d}\bar{E}_\mathrm{B}, \tag{21}$$

$$\ln \phi_\mathrm{C}^{z_\mathrm{A} z_\mathrm{B}} = \int_0^{\bar{E}_\mathrm{A}} \ln \chi_{\mathrm{C-A}}\,\mathrm{d}\bar{E}_\mathrm{A} + \int_0^{\bar{E}_\mathrm{B}} \ln \chi_{\mathrm{C-B}}\,\mathrm{d}\bar{E}_\mathrm{B}, \tag{22}$$

with

$$\chi_{\mathrm{C-A}} = (k_{\mathrm{C-A}}/k^*_{\mathrm{C-A}}) \exp[-z_\mathrm{B}(z_\mathrm{C} - z_\mathrm{A})], \tag{23}$$

$$\chi_{\mathrm{C-B}} = (k_{\mathrm{C-B}}/k^*_{\mathrm{C-B}}) \exp[-z_\mathrm{A}(z_\mathrm{C} - z_\mathrm{B})], \tag{24}$$

$k^*_{\mathrm{C-A}}$, $k^*_{\mathrm{C-B}}$ are the values of $k_{\mathrm{C-A}}$, $k_{\mathrm{C-B}}$ at $\bar{E}_\mathrm{A}$, $\bar{E}_\mathrm{B}$, i.e. at the composition for which the values of ϕ_A, ϕ_B and ϕ_C are required.

2. EXPERIMENTAL

(*a*) *Materials and methods*

Synthetic mordenite in powder form ('Na–Zeolon') was supplied by Norton Chemicals U.S.A. Before chemical analysis, the material was exchanged with sodium chloride solution of concentration 0.5 mol dm^{-3}, then washed thoroughly with distilled water. This procedure ensured that the starting material was in the homoionic sodium form. After drying and equilibration of the material over a saturated sodium chloride solution in a desiccator for two weeks, to ensure an equilibrium uptake of water into the zeolite, the sodium mordenite was analysed (Barrer & Townsend 1976). The unit cell composition was $Na_{2.5}(AlO_2)_{7.4}(SiO_2)_{40.6}$ 25.6 H_2O. A small quantity of iron was also detected (5.6×10^{-4} moles of Fe_2O_3 per hectogram of zeolite).

To evaluate the respective equilibrium constants and exchanger phase activity coefficients for ternary exchange, it is necessary to obtain equilibrium data points covering the whole of the ternary crystal phase composition. Only then can the necessary integration procedures be effected (equations (19)–(22)) by using appropriate best-fitting polynomials (Fletcher & Townsend 1981 *b*). Equilibrium points were constructed over the complete crystal phase composition surface by equilibrating for three days sets of samples of the homoionic sodium mordenite (each sample an accurately weighed portion of *ca.* 0.2 g) with corresponding sets of 50 cm³ volumes of solution containing varying ratios of the three exchanging cations. All solutions had a constant total concentration of 0.1 mol dm⁻³ in the three chloride salts, and the temperature was maintained at 25 °C. Initial solution compositions were chosen in order to scan systematically over the whole composition range. So, for example, one set of solutions had, before equilibration, a constant 1:1 ratio of potassium: ammonium ions, but the sodium content varied through the set from 0% to 90% of the total. The total salt concentration was kept constant at 0.1 mol dm⁻³. A similar procedure was employed recently in studies on the Ca–Mg–Na–A system (Barri & Rees 1980).

After centrifugation, both separated phases were analysed for all three cations. For this purpose the mordenite samples were dissolved by digestion in a 1:1 nitric acid:H_2O mixture over a steam bath for about one week.

(*b*) *Tests for thermodynamic reversibility*

Before the experimental data can be subjected to a thermodynamic treatment, it is important that the exchange isotherms be shown to be reversible. For the three binary exchange isotherms reversibility was established by conventional techniques (Fletcher & Townsend 1981 *d*). Determining reversibility in ternary systems is problematical because equilibria are characterized by two linked surfaces representing equilibrium compositions for the two phases (Fletcher & Townsend 1981 *b*). The additional degree of freedom possessed by a ternary exchange means that it is not possible to force the composition back to the pure sodium form of the zeolite along the same path as was traversed for the forward exchange. Consequently there is no simple technique involving inspection of graphical data that can confirm that the system is reversible. Therefore reversibility was inferred from the observed reversibility of the three conjugate binary systems, and this inference was confirmed by calculating mass action quotients with either the pure potassium or the pure ammonium forms of the mordenite as the starting material. Reversibility was regarded as established if these mass action quotients agreed well with the values predicted from the polynomial derived from fitting the experimental data obtained with homoionic sodium mordenite as the starting material.

3. ION-EXCHANGE ISOTHERMS

(*a*) *Exchanges involving two ions only*

Binary exchange isotherms for the ion pairs $Na–NH_4$, Na–K and $NH_4–K$ are shown in figure 1. The data are plotted in terms of the equivalent fraction of one of the counter-ions in solution against the equivalent fraction of that same ion in the zeolite at equilibrium. Since the

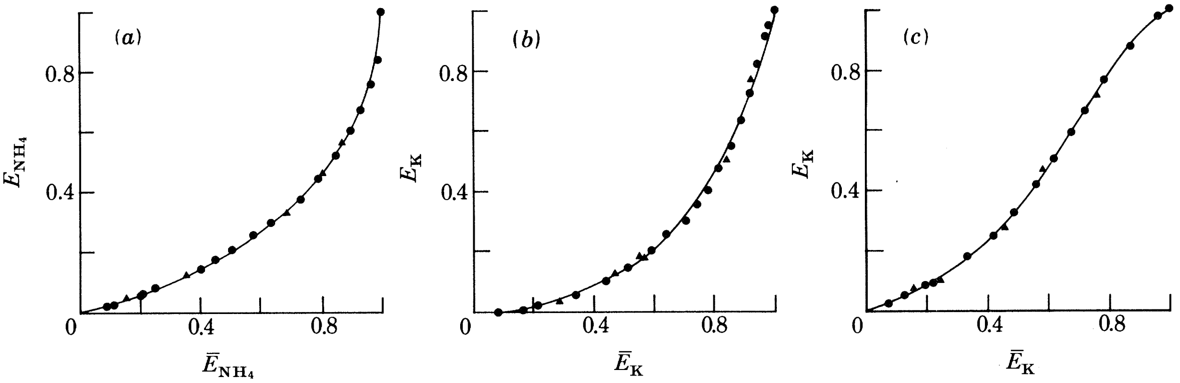


FIGURE 1. Binary isotherms for (*a*) Na–NH_4, (*b*) Na–K and (*c*) NH_4–K exchanges at 25 °C in synthetic mordenite. Forward points (●); reverse points (▲).

TABLE 1. THERMODYNAMIC DATA FOR BINARY EXCHANGE SYSTEMS

u	v	coefficients, c_n, for substitution in $\ln({}^{\mathrm{u}}_{\mathrm{v}}K_{\mathrm{G}}) = \sum_{n=0}^{3} c_n \bar{E}^n_{\mathrm{u}}$.				${}^{\mathrm{u}}_{\mathrm{v}}K_a$	${}^{\mathrm{u}}_{\mathrm{v}}\Delta G^\ominus$
		$n = 0$	1	2	3		J mol^{-1}
NH_4	Na	+1.33	+1.56	−5.69	+5.27	4.599	−3780
K	Na	+3.24	−6.53	+9.48	−5.24	7.482	−4986
K	NH_4	+0.870	+0.224	−0.774	−0.927	1.637	−1221

exchanges are binary, the other ion is also defined. The polynomial equations describing the dependence of the logarithm of the corrected selectivity quotient ${}^{\mathrm{u}}_{\mathrm{v}}K_{\mathrm{G}}$ on the crystal phase composition are given in table 1. Also shown are the corresponding values for the thermodynamic equilibrium constant and standard free energy, calculated from the approach of Gaines & Thomas (1953).

(*b*) *The* Na–NH_4–K *ternary isotherm*

When limited data on a ternary equilibrium are available, the results can be expressed by plotting the composition of both phases on one triangular coordinate diagram, with either tie-lines or numbers to join equivalent experimental points for each phase (Barri & Rees 1980). When there are a large number of data points this approach becomes confusing, but where clear and consistent trends in selectivity are discernible it is possible to depict the data by using a separate triangular plot for each phase, with only some data points numbered to correspond (Soldatov & Bychkova 1980). The data for the ternary system Na–NH_4–K–MOR are shown in this form in figure 2. A total of 82 experimental points for the ternary equilibrium were measured. The figure serves to show the numbers and distribution of points that are necessary to represent adequately the equilibrium characteristics of a ternary ion exchange system, but selectivity trends are still difficult to discern. A more satisfactory representation of the ternary equilibria can be obtained if the triangular coordinates of the solution phase are superimposed upon those of the crystal phase, with the coordinates of the former distorted so that any point on the solution phase falls on top of its corresponding equilibrium point for the crystal phase.

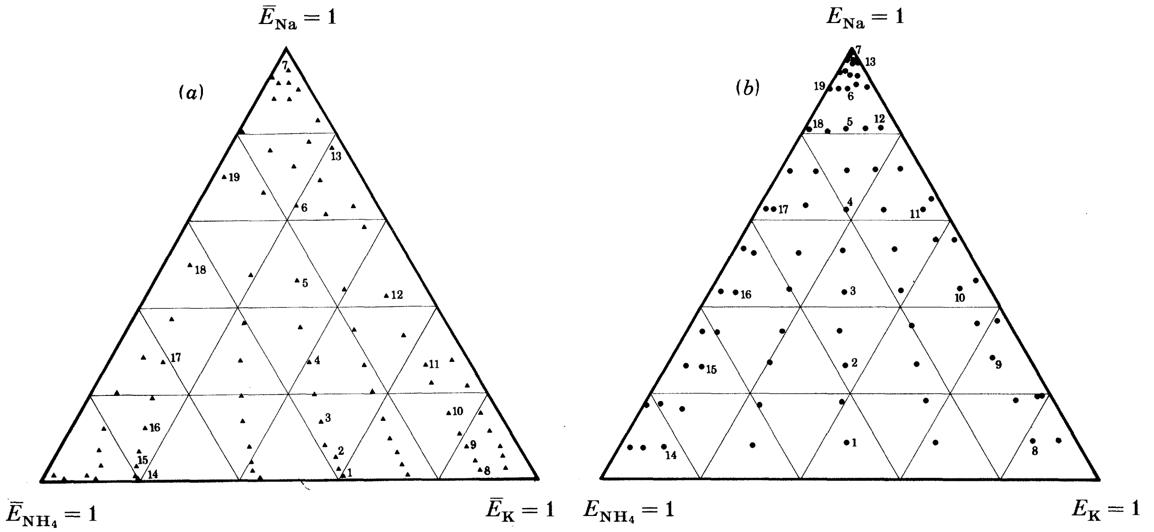


FIGURE 2. Ternary isotherm for the Na–NH_4–K equilibrium in synthetic mordenite at 25 °C. Examples of experimental data obtained for (*a*) crystal and (*b*) solution phase. Points numbered correspondingly represent tie lines between the two diagrams.

This procedure is shown diagramatically in figure 3. To achieve this transformation, two constants q_1 and q_2 were defined so that

$$q_1 = E_A \bar{E}_B / \bar{E}_A E_B = f(E_A, E_B), \qquad (25)$$

$$q_2 = E_A \bar{E}_C / \bar{E}_A E_C = f(E_A, E_B). \qquad (26)$$

The dependence of q_1 and q_2 on E_A and E_B was determined by best-fitting these terms to polynomials in E_A and E_B. Then E_A was varied in increments of 0.1 and for each of these increments q_1 and q_2 were calculated for small increments in E_B from $E_B = 1 - E_A$ to $E_B = 0$

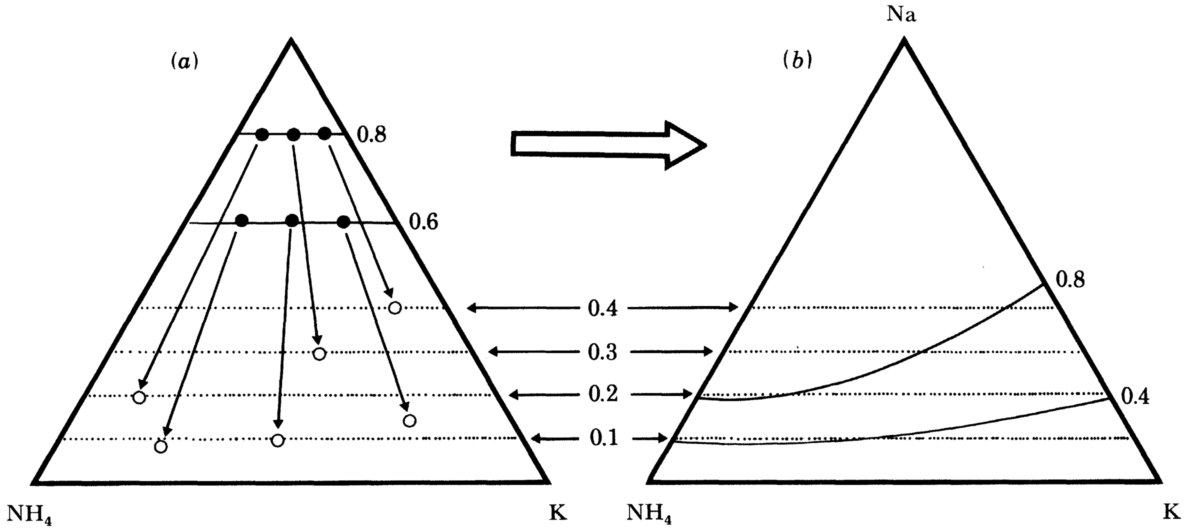


FIGURE 3. Diagram of the superimposition of distorted grid-lines for the solution phase on top of the crystal phase. In (*a*) examples of data for both the solution (●) and crystal (○) phases are shown, joined by tie lines. In (*b*) the resulting distorted gridlines for the solution phase are shown.

(E_C was defined in this way as well). For each increment, q_1 and q_2 were then solved simultaneously to yield values for $\bar{E}_A$ and $\bar{E}_B$. The same procedure was then repeated *in toto*, but with increments of 0.1 in E_B and E_A being varied from $1-E_B$ to zero for each E_B increment. In addition to all the ternary results, the data for the three binary isotherms were used to define q_1 and q_2 along the edges of the triangular coordinate diagram. The result (based on a total of 150 experimental data points) is depicted in figure 4.

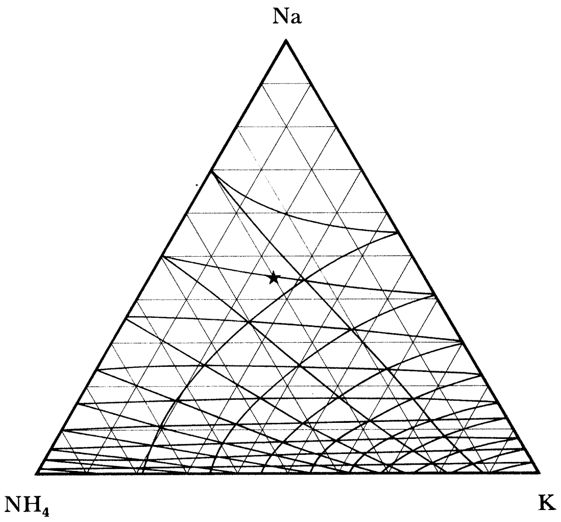


FIGURE 4. Ternary isotherm for the Na–NH_4–K equilibrium in synthetic mordenite at 25 °C, depicted with the 10% grid lines for the solution phase distorted with respect to the crystal phase.

The grid lines corresponding to high values of the equivalent fraction of sodium in solution E_{Na} are seen to be widely spaced, which indicates that the quantity of sodium ion found in solution at equilibrium remains high, even when the zeolite phase contains a large proportion of the other two ions. So, for example, consider the phase composition $\bar{E}_{NH_4} = 0.3$, $\bar{E}_K = 0.25$ (marked with a star on figure 4). Although the percentage of sodium in the zeolite at this point is only 45%, that in the bulk solution at equilibrium is 80%. In addition, note that for high $\bar{E}_{Na}$ values the spacing of the solution phase grid lines is more marked for low $\bar{E}_{NH_4}$ values than for low $\bar{E}_K$ values. This shows that a marked preference is displayed by mordenite for either potassium or ammonium over sodium, and that potassium is especially favoured.

The reversibility of the ternary exchange isotherm was confirmed by the procedure described in the previous section, starting with either the homoionic potassium or the ammonium forms of mordenite. The values of the ternary mass action quotients (equation (4)) so obtained are given in table 2. For comparison, values of ${}_{v,w}^{u}K_{m,E}$ are shown, which were predicted by appropriate interpolation of the polynomials that represent the dependence of the mass action quotients on the crystal phase composition by using only the data obtained with homoionic sodium mordenite as the starting material (figures 2 and 4). As a further check, data were obtained for the ternary exchange equilibrium at the higher and constant total solution concentration of 0.3 mol dm^{-3}. The concentration–valency effect (Barri & Rees 1980) does not operate when all the exchanging ions are univalent (Barrer & Klinowski 1974) and the correction for solution phase non-ideality ${}_{v,w}^{u}\Gamma$ is negligible at these concentrations (Fletcher

Table 2. Reversibility tests on the ternary isotherm

(Values when K–MOR was the starting material are in the top half; values for NH_4–Mor as starting material, in bottom half)

		${}^{\mathrm{Na}}_{\mathrm{NH_4,K}}K_{m,E}$		${}^{\mathrm{NH_4}}_{\mathrm{K,Na}}K_{m,E}$		${}^{\mathrm{K}}_{\mathrm{Na,NH_4}}K_{m,E}$	
$\bar{E}_{\mathrm{Na}}$	$\bar{E}_{\mathrm{NH_4}}$	predicted	measured	predicted	measured	predicted	measured
0.344	0.438	0.0352	0.0382	1.83	2.06	15.51	12.65
0.248	0.345	0.0433	0.0468	2.53	2.53	9.21	8.94
0.199	0.279	0.0460	0.0481	3.11	2.92	6.94	6.89
0.158	0.239	0.0440	0.0451	3.79	3.52	5.99	6.28
0.125	0.198	0.0410	0.0424	4.42	4.16	5.51	5.67
0.095	0.163	0.0362	0.0381	5.65	5.64	4.89	5.19
0.071	0.125	0.0328	0.0351	5.91	6.27	5.16	5.43
0.045	0.094	0.0326	0.0347	7.97	7.49	4.20	3.85
0.014	0.912	0.0019	0.0026	6.74	5.40	78.41	72.07
0.027	0.160	0.0281	0.0305	2.70	2.21	13.14	14.91
0.046	0.744	0.0089	0.0084	3.95	3.53	28.44	32.37
0.077	0.666	0.0161	0.0150	3.08	2.88	20.13	22.77
0.122	0.566	0.0287	0.0243	2.15	2.56	16.61	16.25
0.155	0.497	0.0390	0.0350	2.17	2.43	11.82	12.07
0.206	0.387	0.0426	0.0442	2.32	2.47	10.11	9.25
0.245	0.283	0.0474	0.0482	2.83	2.96	7.52	7.07

Table 3. Reversibility tests on the ternary isotherm from data obtained at higher solution concentrations

		${}^{\mathrm{Na}}_{\mathrm{NH_4,K}}K_{m,E}$		${}^{\mathrm{NH_4}}_{\mathrm{K,Na}}K_{m,E}$		${}^{\mathrm{K}}_{\mathrm{Na,NH_4}}K_{m,E}$	
$\bar{E}_{\mathrm{Na}}$	$\bar{E}_{\mathrm{NH_4}}$	predicted	measured	predicted	measured	predicted	measured
0.016	0.748	0.0050	0.0043	4.86	5.07	41.05	46.04
0.025	0.651	0.0065	0.0068	4.65	4.35	32.41	33.17
0.040	0.562	0.0130	0.0119	3.13	3.53	24.50	23.61
0.052	0.466	0.0180	0.0178	3.23	3.25	17.20	17.25
0.080	0.399	0.0255	0.0271	3.18	2.99	12.32	12.31
0.105	0.318	0.0336	0.0366	3.23	3.10	8.45	8.80
0.083	0.825	0.0025	0.0025	6.07	6.24	66.14	63.85
0.133	0.232	0.0451	0.0433	3.75	3.68	5.92	6.26
0.131	0.500	0.0281	0.0303	2.79	2.49	12.71	13.19
0.106	0.406	0.0291	0.0318	2.89	2.77	11.89	11.35
0.088	0.335	0.0331	0.0325	3.18	3.15	9.48	9.74
0.068	0.281	0.0319	0.0312	3.67	3.63	8.53	8.83
0.054	0.230	0.0296	0.0309	4.23	4.30	7.99	7.53
0.043	0.185	0.0292	0.0309	5.23	5.08	6.54	6.37
0.035	0.142	0.0321	0.0333	6.06	6.01	5.14	4.99

& Townsend 1981*c*, 1983), so mass action quotients obtained at this higher concentration could be compared directly with those predicted by interpolation of the polynomials. Again, reversibility was confirmed (table 3). In comparing these data, it should be remembered that a comparison of the ${}^{\mathrm{u}}_{\mathrm{v,w}}K_{m,E}$ values is a more sensitive test of reproducibility than a direct comparison of measured and predicted chemical compositions. This is because of the powers in $\bar{E}_{\mathrm{u}}$ and m_{u} (equation (4)).

4. Effects on selectivities of non-ideality in the exchanger phase

(*a*) *General considerations*

The isotherm shown in figure 4 gives an overall view of the selectivity properties of the ternary exchange system as a function of composition of the crystal phase. The selectivity manifested at any point on the isotherm is the combined result of several factors, these being:

(*a*) the innate properties of the exchanging ions and the co-ions in aqueous solution, as found in their defined Henry Law reference states (namely the hypothetical ideal molal solutions of the pure salts (Robinson & Stokes 1959)),

(*b*) the innate properties of the exchanging ions in the particular zeolite under study, as found in their defined Raoult Law reference states (namely the homoionic zeolites in equilibrium with an infinitely dilute solution of the same ion (Gaines & Thomas 1953));

(*c*) the departure from ideality of the ions in the actual mixed solution;

(*d*) the departure from ideality of the mixed $\mathrm{M}_{(1/z_i)}\mathrm{X_L}$ solid solution of zeolite.

Leaving aside steric exclusion effects (Barrer & Townsend 1978), the factors that affect the innate selectivity of the system are primarily electrical in character, and include the charge density, polarizability and ionic radius of each of the exchanging ions, together with the lattice charge density and the ratio of crystallographic cation sites to the framework charge within each site set in the zeolite. The first four properties can be adequately rationalized in terms of dielectric theory (Barrer & Falconer 1956; Barrer, Rees & Shamsuzzoha 1966; Barrer & Klinowski 1972*b*; Fletcher & Townsend 1981*d*) and the effect of the last property has been quantified in a statistical thermodynamic model (Barrer & Klinowski 1977).

In an ideal exchange, the mass action quotient will have some constant value greater than zero for all exchanger phase compositions, the actual magnitude of $K_{m,E}$ depending on the relative properties of the ions in the two phases in their reference states, and this value will be equal to the thermodynamic equilibrium constant. Variations in the mass action quotient with composition arise from non-ideality within the two phases. So if the correction for non-ideality in solution is applied to obtain the corrected selectivity quotients ${}_{\mathrm{v,w}}^{\mathrm{u}}K_{\mathrm{G}}$, it follows that any variation in these functions with crystal phase composition must arise from non-ideality in the exchanger itself. If the variations of the binary K_{G} functions with crystal phase composition are small or near monotonic, it is likely that a simple model will enable prediction of ternary equilibria from binary data alone; if not, it is probably necessary to effect the rigorous experimental procedure described in this paper.

(*b*) *Evidence for non-ideality from experimental selectivity trends*

Figures 6–8 are contour diagrams (derived by using third order polynomials in both $\bar{E}_{\mathrm{NA}}$ and $\bar{E}_{\mathrm{NH_4}}$), which show general trends in the logarithm of the corrected selectivity quotients ${}_{\mathrm{NH_4,K}}^{\mathrm{Na}}K_{\mathrm{G}}$, ${}_{\mathrm{K,Na}}^{\mathrm{NH_4}}K_{\mathrm{G}}$ and ${}_{\mathrm{Na,NH_4}}^{\mathrm{K}}K_{\mathrm{G}}$ with crystal phase composition. These K_{G} values were calculated from activity coefficient data for the three salts NaCl, KCl and $\mathrm{HN_4Cl}$ found in Robinson & Stokes (1959), and the corrections for the mixed electrolyte solutions were applied by using the equations of Fletcher & Townsend (1981*c*). It is apparent that the variation of these functions with the crystal phase composition is complicated, which indicates a degree of non-ideality in the crystal phase, which probably arises from the existence of different sets of ion sites within the zeolite (Barrer & Klinowski 1977; Fletcher & Townsend 1981*a*).

The ${}_{\mathrm{v,w}}^{\mathrm{u}}K_{\mathrm{G}}$ functions not only provide evidence of marked non-ideality in the mordenite,

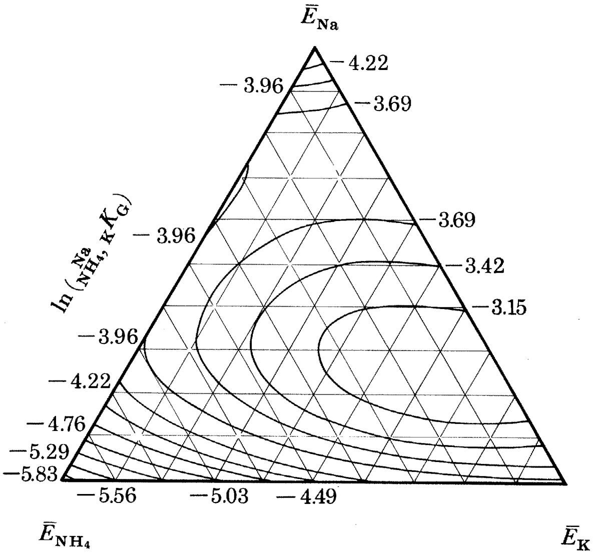
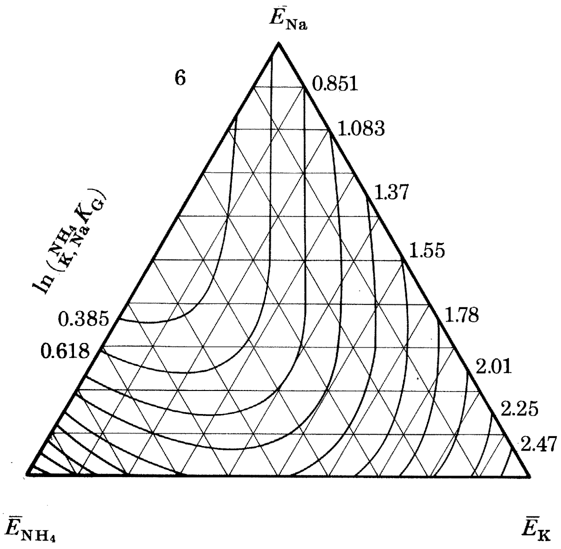


FIGURE 5. Contour map of the corrected selectivity quotient ln $({}_{\mathrm{NH_4,K}}^{\mathrm{Na}}K_{\mathrm{G}})$ as a function of crystal phase composition.



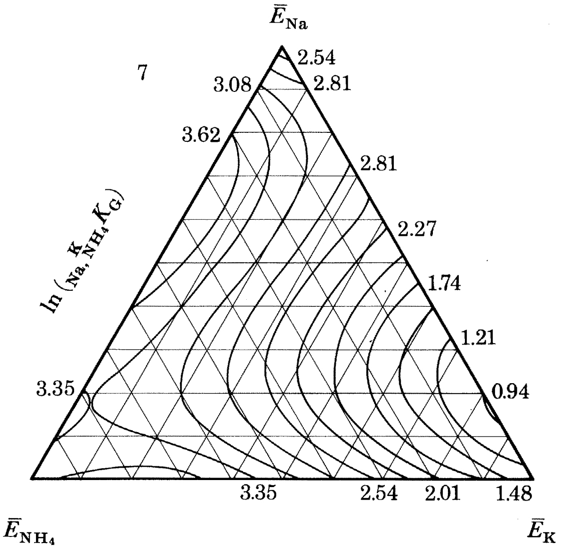


FIGURE 6. Contour map of the corrected selectivity quotient ln $({}_{\mathrm{K,Na}}^{\mathrm{NH_4}}K_{\mathrm{G}})$ as a function of crystal phase composition.

FIGURE 7. Contour map of the corrected selectivity quotient ln $({}_{\mathrm{Na,NH_4}}^{\mathrm{K}}K_{\mathrm{G}})$ as a function of crystal phase composition.

but they also give a general picture of the preference exhibited by the zeolite for each ion. In figure 5 the selectivity for ammonium or potassium, or both, over sodium is seen. The logarithmic function is always negative, which indicates that the latter two ions in any combination are always preferred over the sodium. The selectivity for sodium varies substantially, however, reaching a maximum in the region $\bar{E}_{\mathrm{Na}} \approx 0.3$, $\bar{E}_{\mathrm{NH_4}} \rightarrow 0$. The preference decreases slightly in the two regions $\bar{E}_{\mathrm{Na}} \rightarrow 1$, $\bar{E}_{\mathrm{K}} \rightarrow 1$, and the presence of ammonium ion in the mordenite seems always to affect adversely the already low selectivity for sodium. The lowest preference for sodium is exhibited in the region in which $\bar{E}_{\mathrm{NH_4}} \rightarrow 1$. The preference for

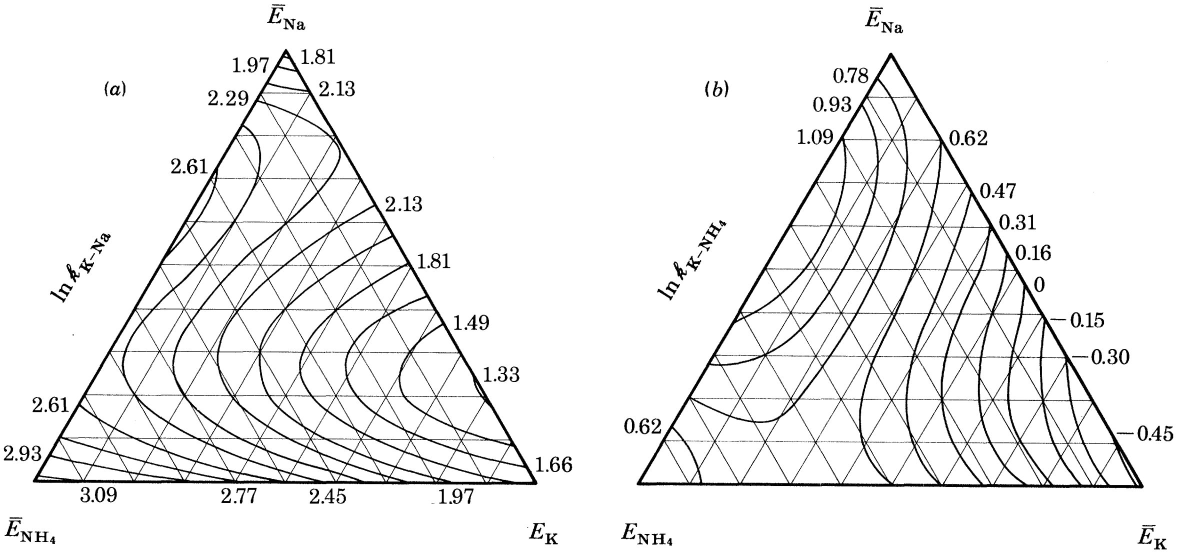


FIGURE 8. Contour maps of (*a*) $\ln k_{\mathrm{K-Na}}$ and (*b*) $\ln k_{\mathrm{K-NH_4}}$ as a function of crystal phase composition. These contour maps were derived by using third order polynomial fits.

ammonium ion over sodium and potassium is seen in figure 6. In contrast to the previous case the logarithm of the corrected selectivity quotient is now always positive, reflecting primarily the preference that mordenite displays for ammonium over sodium, since mordenite shows fairly similar selectivity behaviour for both ammonium and potassium (see the portion of figure 6 in which $\bar{E}_{\mathrm{Na}} \to 0$).

Selectivity for the ammonium ion is greatest when either $\bar{E}_{\mathrm{K}} \to 1$ or (surprisingly) when $\bar{E}_{\mathrm{NH_4}} \to 1$. The minimal preference for ammonium is displayed when $\bar{E}_{\mathrm{Na}} \to 0.5$ and $E_{\mathrm{K}} \to 0$. This may be connected with the relative populations of ions in different sites in the crystal. It is known that in the sodium form of mordenite, only half the exchangeable sodium ions are situated in the main channels (Meier 1961; Barrer & Klinowski 1974*b*). Although the preference of mordenite for ammonium and potassium over sodium is similar in magnitude, the values of $\ln ({}^{\mathrm{K}}_{\mathrm{Na,NH_4}}K_{\mathrm{G}})$ shown in figure 7 indicate that generally potassium is just preferred over ammonium. Selectivity for potassium over sodium and ammonium is seen to maximize in the region where $\bar{E}_{\mathrm{Na}} \sim \bar{E}_{\mathrm{NH_4}} \sim 0.5$ and $\bar{E}_{\mathrm{K}} \to 0$. In contrast to the case of the ammonium ion in figure 6, selectivity for potassium is seen to decrease as $\bar{E}_{\mathrm{K}} \to 1$.

By using (19), the standard free energy changes ${}^{\mathrm{Na}}_{\mathrm{NH_4,K}}\Delta G^{\ominus}$, ${}^{\mathrm{NH_4}}_{\mathrm{K,Na}}\Delta G^{\ominus}$ and ${}^{\mathrm{K}}_{\mathrm{Na,NH_4}}\Delta G^{\ominus}$ were found to be $+8.87$, -2.56 and -6.32 kJ mol^{-1}, respectively (§5*a*). These functions give an overall affinity sequence, namely that the affinity of mordenite for the ions increases in the order $\mathrm{Na^+} < \mathrm{NH_4^+} < \mathrm{K^+}$. This mirrors the general conclusions drawn above, but it is strongly emphasized that the overall order of thermodynamic affinity must not be confused with the selectivity sequence observed for a particular composition, because crystal and solution non-ideality may serve to alter the latter sequence. This may be seen from an examination of contour diagrams representing the variation of the functions $\ln k_{\mathrm{C-A}}$ and $\ln k_{\mathrm{C-B}}$ (equation (19)). For the Na–NH$_4$–K–MOR system,

$$k_{\mathrm{C-A}} = ({}^{\mathrm{K}}_{\mathrm{Na,NH_4}}K_{\mathrm{G}} / {}^{\mathrm{Na}}_{\mathrm{NH_4,K}}K_{\mathrm{G}})^{\frac{1}{3}} = a_{\mathrm{Na}}\,\bar{E}_{\mathrm{K}} / a_{\mathrm{K}}\,\bar{E}_{\mathrm{Na}} = k_{\mathrm{K-Na}} \tag{27}$$

and

$$k_{\mathrm{C-B}} = ({}^{\mathrm{K}}_{\mathrm{Na,NH_4}}K_{\mathrm{G}} / {}^{\mathrm{NH_4}}_{\mathrm{K,Na}}K_{\mathrm{G}})^{\frac{1}{3}} = a_{\mathrm{NH_4}}\,\bar{E}_{\mathrm{K}} / a_{\mathrm{K}}\,\bar{E}_{\mathrm{NH_4}} = k_{\mathrm{K-NH_4}}. \tag{28}$$

The functions $\mathscr{k}_{\mathrm{K-Na}}$ and $\mathscr{k}_{\mathrm{K-NH_4}}$ are seen to be pseudobinary corrected selectivity quotients, representing as such the preference that the mordenite displays for one of a particular pair of ions *in the presence of the third ion*. Thus $\mathscr{k}_{\mathrm{K-Na}}$ represents the preference of mordenite for potassium over sodium in the presence of ammonium, and figure 8*a* shows that for all values of $\bar{E}_{\mathrm{NH_4}}$ the preference order is $\mathrm{Na^+} \ll \mathrm{K}$, in agreement with the affinity sequence above. In contrast, figure 8*b* shows the effect on $\ln \mathscr{k}_{\mathrm{K-NH_4}}$ of varying the sodium content of the zeolite. Movement along any line of constant ratio $\bar{E}_{\mathrm{Na}}/\bar{E}_{\mathrm{NH_4}}$ towards $\bar{E}_{\mathrm{K}} = 1$ results in a steady decline in the value of $\ln \mathscr{k}_{\mathrm{K-NH_4}}$ until the values become negative. So, for example, at a composition of $\bar{E}_{\mathrm{Na}} = 0.2$ and $\bar{E}_{\mathrm{NH_4}} = 0.5$, the selectivity sequence (while taking into account figure 9 also) is $\mathrm{Na^+} < \mathrm{NH_4^+} < \mathrm{K^+}$, in line with the affinity sequence. However, at $\bar{E}_{\mathrm{Na}} = 0.08$, $\bar{E}_{\mathrm{NH_4}} = 0.2$ the selectivity sequence is $\mathrm{Na^+} < \mathrm{NH_4^+} \sim \mathrm{K^+}$, and at $\bar{E}_{\mathrm{Na}} = 0.04$, $\bar{E}_{\mathrm{NH_4}} = 0.1$ the order has reversed partially to give $\mathrm{Na^+} < \mathrm{K^+} < \mathrm{NH_4^+}$.

5. PREDICTION OF TERNARY EXCHANGE EQUILIBRIA

(*a*) *Fitting procedures and experimental uncertainty*

The evaluation of the thermodynamic equilibrium constants and free energies of exchange depend on the accurate integration of polynomials that have been best-fitted to the experimental data (see also a further discussion on this point in §7*b*). This matter has been considered previously for binary exchange processes (Fletcher & Townsend 1980), where it was noted that for cases where one ion is strongly preferred over the other, the experimental error is exaggerated towards the extrema of the isotherm, with a consequent poorer precision of fit by a suitable polynomial. For ternary exchanges the problem may be more serious, since it is now necessary to fit polynomials to *surfaces* that describe the dependency of the functions $\mathscr{k}_{\mathrm{C-A}}$ and $\mathscr{k}_{\mathrm{C-B}}$ on $\bar{E}_{\mathrm{A}}$ and $\bar{E}_{\mathrm{B}}$ (equation (19)). So, taking as an example $({}^{\mathrm{Na}}_{\mathrm{NH_4,K}}K_a)$, expressed as a polynomial, equation 19 becomes

$$\ln\left({}^{\mathrm{Na}}_{\mathrm{NH_4,K}}K_a\right) = -2\int_0^1\left[\sum_{i=0}^{m}\alpha_i(\bar{E}_{\mathrm{A}})^i + \sum_{j=1}^{n}\beta_j(\bar{E}_{\mathrm{B}})^j\right]\mathrm{d}\bar{E}_{\mathrm{A}} + \int_0^1\left[\sum_{p=0}^{r}\gamma_p(\bar{E}_{\mathrm{A}})^p + \sum_{q=1}^{s}\delta_q(\bar{E}_{\mathrm{B}})^q\right]\mathrm{d}\bar{E}_{\mathrm{B}} = \sum_{q=1}^{s}\frac{\delta_q}{q+1} - 2\sum_{i=0}^{m}\frac{\alpha_i}{i+1}. \tag{29}$$

Obviously, the accuracy of K_a and $\Delta G^{\ominus}$ values so derived depends on how accurately a given polynomial fits the experimental data. The 'goodness of fit' is therefore assessed by using a summation of residuals function $\mathscr{R}$, where, taking for example $\mathscr{k}_{\mathrm{C-A}}$,

$$\mathscr{R} = \left\{\frac{\sum\limits_{\mathscr{N}}\left[\ln\left(\mathscr{k}_{\mathrm{C-A\,(predicted)}}/\mathscr{k}_{\mathrm{C-A\,(measured)}}\right)\right]^2}{(\mathscr{N}-\mathscr{P}-\mathscr{Q}-1)}\right\}^{\frac{1}{2}}. \tag{30}$$

A minimum value in $\mathscr{R}$ with polynomial order gives one criterion for best fit. $\mathscr{N}$ is the number of sets of data (in this work $\mathscr{N} = 82$), and $\mathscr{P}$, $\mathscr{Q}$ are the orders of the polynomial in $\bar{E}_{\mathrm{Na}}$ and $\bar{E}_{\mathrm{NH_4}}$, respectively. A similar $\mathscr{R}$ function, but excluding $\mathscr{Q}$, has been used previously for binary exchange studies (Barrer & Munday 1971; Barri & Rees 1980).

Values of $\mathscr{R}$ were determined for the Na–NH$_4$–K–mordenite system for both $\ln \mathscr{k}_{\mathrm{K-Na}}$ and $\ln \mathscr{k}_{\mathrm{K-NH_4}}$, and are shown in table 4. For both functions, minima in $\mathscr{R}$ are seen when the polynomial orders in $\bar{E}_{\mathrm{Na}}$ and $\bar{E}_{\mathrm{NH_4}}$ are both 4. However, a very strong dependence of K_{a} (and

TABLE 4. VALUES OF SUM OF RESIDUALS $\mathscr{R}$, DEFINED IN (30), FOR POLYNOMIAL ORDER 1 TO 5 FOR THE FITS OF $\ln k_{\mathrm{K-Na}}$ AND $\ln k_{\mathrm{N-NH_4}}$ AS A FUNCTION OF $\bar{E}_{\mathrm{Na}}$ AND $\bar{E}_{\mathrm{NH_4}}$

order of polynomial for $\bar{E}_{\mathrm{Na}}$	order of polynomial for $\bar{E}_{\mathrm{NH_4}}$	$\mathscr{R}$ for $\ln k_{\mathrm{K-Na}}$	$\mathscr{R}$ for $\ln k_{\mathrm{K-NH_4}}$
1	1	0.3667	0.3073
2	2	0.3553	0.2703
3	3	0.3150	0.2630
4	4	0.2827	0.2540
5	5	0.2833	0.2543

TABLE 5. VALUES OF $\Delta G^{\ominus}$ CALCULATED BY USING DIFFERENT FITTING POLYNOMIAL ORDERS FOR $\ln k_{\mathrm{K-Na}}$ AND $\ln k_{\mathrm{K-NH_4}}$ AS A FUNCTION OF $\bar{E}_{\mathrm{Na}}$ AND $\bar{E}_{\mathrm{NH_4}}$

(orders of polynomial for $\bar{E}_{\mathrm{Na}}$, $\bar{E}_{\mathrm{NH_4}}$ respectively for (i) $\ln k_{\mathrm{K-Na}}$ and (ii) $\ln k_{\mathrm{K-NH_4}}$)

	(i) 1,1 (ii) 1,1	(i) 2,2 (ii) 2,2	(i) 3,3 (ii) 3,3	(i) 4,4 (ii) 3,3	(i) 4,4 (ii) 4,4	(i) 5,5 (ii) 5,5
${}^{\mathrm{Na}}_{\mathrm{K,NH_4}}\Delta G^{\ominus}$	+7.85	+7.70	+7.86	+9.12	+8.87	+9.70
${}^{\mathrm{NH_4}}_{\mathrm{K,Na}}\Delta G^{\ominus}$	−2.87	−2.68	−2.42	−3.04	−2.56	−3.18
${}^{\mathrm{K}}_{\mathrm{Na,NH_4}}\Delta G^{\ominus}$	−4.98	−5.02	−5.45	−6.07	−6.32	−6.52
$\Sigma^{\mathrm{w}}_{\mathrm{u}}\,{}^{\mathrm{u}}_{\mathrm{v,w}}\Delta G^{\ominus}$	0.00	0.00	−0.01	+0.01	−0.01	0.00

therefore $\Delta G^{\ominus}$) on the polynomial orders is seen in table 5, it is important, therefore, to have, if possible, an additional criterion on which to base the choice of 'best-fitting' polynomial. For binary exchanges it has been common practice to compare the best-fit analytic function based on a minimal $\mathscr{R}$ value with a 'by eye' assessment of the fit. For cases where the isotherm is highly selective it has occasionally proved better to use a 'by-eye' fit and integrate the equation numerically, even though this is admittedly a somewhat subjective procedure (Fletcher & Townsend 1980). For those binary exchange systems where the selectivities are not so marked, such as those shown in figure 1, such a procedure is not necessary, since thermodynamic consistency requires that $\Sigma^{u}_{v}\,\Delta G^{\ominus}$ for the three binary systems be zero. The three $\Delta G^{\ominus}$ values were each derived independently by using best-fit polynomials, chosen on the basis of minimal $\mathscr{R}$ values, and from table 1, $\Sigma^{u}_{v}\,\Delta G^{\ominus} = 15\ \mathrm{J\ mol^{-1}}$, which is within experimental uncertainty. It appears therefore that the polynomial equations (given in table 1) are an adequate description of the selectivity behaviour of these three binary exchanges.

For a ternary exchange, assessments 'by eye' are highly subjective, if not meaningless (figure 9). Fortunately, however, an objective second criterion for choosing the best-fit polynomials is available for the ternary case, given reliable data on the conjugate binary systems (figure 1). The thermodynamic treatment for ternary exchange (Fletcher & Townsend 1981 *b*) employs the same reference states as the binary exchange model of Gaines & Thomas (1953). It should therefore be possible to predict the standard free energies of exchange for the ternary reactions (defined in equation (1)) from the standard free energies of the three conjugate binary exchanges. From data given in table 1.

$$\left.\begin{aligned} {}^{\mathrm{Na}}_{\mathrm{NH_4,K}}\Delta G^{\ominus} &= -{}^{\mathrm{NH_4}}_{\mathrm{Na}}\Delta G^{\ominus} - {}^{\mathrm{K}}_{\mathrm{Na}}\Delta G^{\ominus} = +8.77\ \mathrm{kJ\ mol^{-1}},\\ {}^{\mathrm{NH_4}}_{\mathrm{K,Na}}\Delta G^{\ominus} &= {}^{\mathrm{NH_4}}_{\mathrm{Na}}\Delta G^{\ominus} - {}^{\mathrm{K}}_{\mathrm{NH_4}}\Delta G^{\ominus} = -2.56\ \mathrm{kJ\ mol^{-1}},\\ {}^{\mathrm{K}}_{\mathrm{Na,NH_4}}\Delta G^{\ominus} &= {}^{\mathrm{K}}_{\mathrm{Na}}\Delta G^{\ominus} + {}^{\mathrm{K}}_{\mathrm{NH_4}}\Delta G^{\ominus} = -6.21\ \mathrm{kJ\ mol^{-1}}. \end{aligned}\right\} \qquad (31)$$

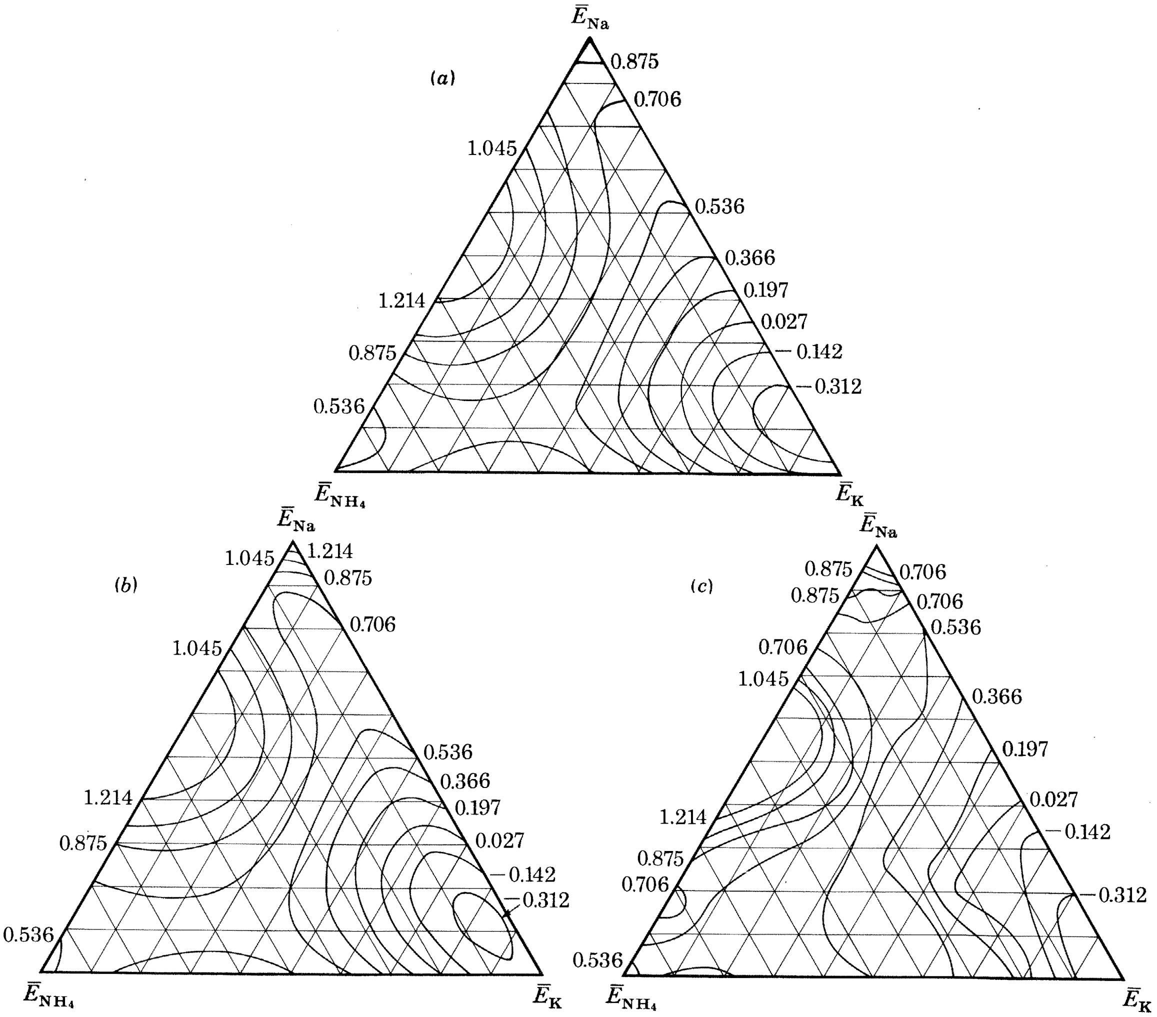


FIGURE 9. Contour maps for $\ln k_{\mathrm{K-NH_4}}$ from polynomial fits that were (*a*) fourth order in $\bar{E}_{\mathrm{Na}}$ and $\bar{E}_{\mathrm{NH_4}}$, and (*b*) fifth order in $\bar{E}_{\mathrm{Na}}$ and $\bar{E}_{\mathrm{NH_4}}$. In (*c*) the contours for this function as estimated from the data 'by eye' are shown.

These predicted values should now be compared with measured ${}_{\mathrm{v,w}}^{\mathrm{u}}\Delta G^{\ominus}$ values, found from the ternary model. Closest agreement between these and the predicted values given in (31) are found for the 4,4 polynomials fit (table 5), the measured values of ${}_{\mathrm{v,w}}^{\mathrm{u}}\Delta G^{\ominus}$ are respectively $+8.87$, -2.56 and -6.32 kJ mol^{-1}, in excellent agreement with (31). The coefficients for these best-fitting 4,4 polynomial fits are given in table 6. This is a successful example of the application of the so-called 'triangle rule' (Barrer & Klinowski 1974*b*; Golden & Jenkins 1981).

TABLE 6. COEFFICIENTS OF BEST-FITTING POLYNOMIALS FOR $k_{\mathrm{K-Na}}$ AND $k_{\mathrm{K-NH_4}}$

	coefficients of $\bar{E}^{m}_{\mathrm{Na}}$ for dependent variables:			coefficients of $\bar{E}^{n}_{\mathrm{NH_4}}$ for dependent variable:	
m	$\ln k_{\mathrm{K-Na}}$	$\ln k_{\mathrm{K-NH_4}}$	n	$\ln k_{\mathrm{K-Na}}$	$\ln k_{\mathrm{K-NH_4}}$
0	2.197	−0.2029	1	−3.501	−0.5595
1	−10.97	−3.849	2	21.78	14.03
2	48.32	22.55	3	−31.83	−23.05
3	−67.98	−32.68	4	14.91	10.38
4	31.11	15.24			

Successful prediction of standard free energies for the ternary exchange does not, however, permit the prediction of equilibrium compositions for the ternary two-phase mixture, for the reasons discussed in the previous section. Two main approaches have been adopted therefore to allow such prediction. The first of these takes several different forms, but in principle uses combinations of corrected selectivity quotients to predict the ternary quotients (Kol'nenkov & Bogmolov 1977; Kataoka & Yashida 1980; Barri & Rees 1980). The second method involves making use of solid solution models to predict ternary activity coefficients from appropriate binary data (Elprince & Babcock 1975; Chu & Sposito 1981).

The first approach entails defining pseudobinary coefficients, formally identical to the corresponding binary corrected selectivity quotients, which implies that

$$\mathrm{Lim}\,({}^{\mathrm{u}}_{\mathrm{v}}\tilde{K}_{\mathrm{G}})_{(\bar{E}_{\mathrm{u}}/\bar{E}_{\mathrm{v}})} = ({}^{\mathrm{u}}_{\mathrm{v}}K_{\mathrm{G}})_{(\bar{E}_{\mathrm{u}}/\bar{E}_{\mathrm{v}})} \quad (\bar{E}_{\mathrm{w}} \to 0), \tag{32}$$

where the superscript $\tilde{}$ implies that a pseudobinary function is being considered, i.e. the third ion $\mathrm{M}_{\mathrm{w}}^{z_{\mathrm{w}}+}$ is present. (It is important to note the definition of $\bar{E}_{\mathrm{i}}$ changes in the pseudobinary coefficient. Thus, for example, when the pseudobinary coefficient is being considered $\bar{E}_{\mathrm{u}} = 1-\bar{E}_{\mathrm{v}}-\bar{E}_{\mathrm{w}}$, but for the true binary quotient $\bar{E}_{\mathrm{u}} = 1-\bar{E}_{\mathrm{v}}$. This follows from the limiting condition given above.) If the magnitude of

$$\left[\frac{\partial}{\partial \bar{E}_{\mathrm{w}}}({}^{\mathrm{u}}_{\mathrm{v}}\tilde{K}_{\mathrm{G}})\right]_{(\bar{E}_{\mathrm{u}}/\bar{E}_{\mathrm{v}})}$$

can be *a priori* estimated, it follows that one can calculate ${}^{\mathrm{u}}_{\mathrm{v}}\tilde{K}_{\mathrm{G}}$ at any point along a 'parametric line' (Soldatov & Bychkova 1980) across the triangular coordinate diagram, the parametric line being one for which the ratio $\bar{E}_{\mathrm{u}}/\bar{E}_{\mathrm{v}}$ is constant. In its simplest form, this method assumes that along any parametric line

$$\left[\frac{\partial}{\partial \bar{E}_{\mathrm{w}}}({}^{\mathrm{u}}_{\mathrm{v}}\tilde{K}_{\mathrm{G}})\right]_{(E_{\mathrm{u}}/E_{\mathrm{v}})} = 0.$$

Obviously, this is implying ideal behaviour in the exchanger phase, so in this form this approach is very limited as far as zeolites are concerned, even for a relatively simple system such as Na–$\mathrm{NH_4}$–K–MOR.

(*b*) *The model of Soldatov & Bychkova* (1980)

A useful modification of this over-simple approach has been developed (Soldatov & Bychkova 1970, 1980). In this method, one of the ions (for example $\mathrm{M}_{\mathrm{A}}^{z_{\mathrm{A}}+}$) involved in the ternary exchange is assumed to affect the other two near-identically. The other two must be the ones that have the closest properties of the three. Then the following relation is suggested (Soldatov & Bychkova 1980)

$$\ln(\phi_{\mathrm{B}}/\phi_{\mathrm{C}}) = b + a\ln(g_{\mathrm{B}}^{(\mathrm{A})}/g_{\mathrm{C}}^{(\mathrm{A})}), \tag{33}$$

where $g_{\mathrm{B}}^{(\mathrm{A})}$, $g_{\mathrm{C}}^{(\mathrm{A})}$ are the activity coefficients (convention of Gaines & Thomas 1953) of the corresponding ions in the *binary* exchange involving ion $\mathrm{M}_{\mathrm{A}}^{z_{\mathrm{A}}+}$. The terms ϕ_{B}, ϕ_{C} are, as before, the activity coefficients of the corresponding ions in the ternary system. The term b is a function of an excess free energy of mixing term of the form

$${}^{\mathrm{u}}_{\mathrm{v}}Q = ({}^{\mathrm{u}}_{\mathrm{v}}G^{\mathrm{E}}/RT) = \bar{E}_{\mathrm{u}}\ln g_{\mathrm{u}}^{(\mathrm{v})} + \bar{E}_{\mathrm{v}}\ln g_{\mathrm{v}}^{(\mathrm{u})}; \tag{34}$$

since $\bar{E}_{\mathrm{v}} = 1-\bar{E}_{\mathrm{u}}$, then

$$\mathrm{d}({}^{\mathrm{u}}_{\mathrm{v}}Q) = \ln(g_{\mathrm{u}}^{(\mathrm{v})}/g_{\mathrm{v}}^{(\mathrm{u})})\,\mathrm{d}\bar{E}_{\mathrm{u}}. \tag{35}$$

Equation (35) implies that $\bar{E}_{\mathrm{w}}$ is zero. If, however, ${}^{\mathrm{u}}_{\mathrm{v}}Q$ is differentiated across a section of the ternary composition diagram for which $\bar{E}_{\mathrm{w}}$ = constant, then

$$\mathrm{d}({}^{\mathrm{u}}_{\mathrm{v}}Q)/(1-\bar{E}_{\mathrm{w}}) = \ln(\phi_{\mathrm{u}}/\phi_{\mathrm{v}})\,\mathrm{d}\bar{E}'_{\mathrm{u}}, \tag{36}$$

where $\bar{E}'_{\mathrm{u}}$ is now a relative concentration term (Soldatov & Bychkova 1970). The function can then be integrated along a line $\bar{E}_{\mathrm{w}}$ = constant across the triangular diagram from $\bar{E}'_{\mathrm{u}} = 0$ to $\bar{E}'_{\mathrm{w}} = 1$ to give

$$\int_0^1 \ln(\phi_{\mathrm{u}}/\phi_{\mathrm{v}})\,\mathrm{d}\bar{E}'_{\mathrm{u}} = \ln(g^{(\mathrm{w})}_{\mathrm{u}}/g^{(\mathrm{w})}_{\mathrm{v}}). \tag{37}$$

The right side of (37) follows because at the extrema of the line the ternary activity coefficients tend to the activity coefficients for the binary systems, u–w and v–w respectively. Also

$$\int_{Q(\bar{E}'_{\mathrm{u}}=0)}^{Q(\bar{E}'_{\mathrm{u}}=1)} \mathrm{d}Q/(1-\bar{E}_{\mathrm{w}}) = \frac{{}^{\mathrm{w}}_{\mathrm{u}}Q-{}^{\mathrm{w}}_{\mathrm{v}}Q}{1-\bar{E}_{\mathrm{w}}}, \tag{38}$$

where ${}^{\mathrm{w}}_{\mathrm{u}}Q-{}^{\mathrm{w}}_{\mathrm{v}}Q$ is the difference in excess free energies between the two binary systems at the extrema of the line across the triangular diagram at constant composition $\bar{E}_{\mathrm{w}}$. This is the term b in (33). The term a in (33) is a transformation coefficient involving $\bar{E}_{\mathrm{v}}$. In the simplest case, it is arguable that since ions $\mathrm{M}^{z+}_{\mathrm{u}}$ and $\mathrm{M}^{z+}_{\mathrm{v}}$ are chosen as having the closest properties of the three in the ternary system it is reasonable (Soldatov & Bychkova 1980) to assume a linear relation to hold along the parametric line $\bar{E}_{\mathrm{w}}$ = constant. This makes a linear transform in $\bar{E}_{\mathrm{v}}$, and overall (Soldatov & Bychkova 1980)

$$\ln\left(\frac{\phi_{\mathrm{B}}}{\phi_{\mathrm{C}}}\right) = \left(\frac{{}^{\mathrm{A}}_{\mathrm{B}}Q-{}^{\mathrm{A}}_{\mathrm{C}}Q}{1-\bar{E}_{\mathrm{A}}}\right)+(1-\bar{E}_{\mathrm{B}})\ln\left(\frac{g^{(\mathrm{C})}_{\mathrm{B}}}{g^{(\mathrm{B})}_{\mathrm{C}}}\right). \tag{39}$$

For the system Na–$\mathrm{NH_4}$–K–MOR the ions most similar in behaviour are ammonium and potassium. It is of interest therefore to see if it is possible to transform selectivity quotients for the Na–$\mathrm{NH_4}$ and Na–K binary systems in a linear manner along different parametric lines for which $\bar{E}_{\mathrm{Na}}$ is held constant. A convenient function to use for this purpose is the separation factor α, where

$$^{\mathrm{Na}}_{\mathrm{NH_4}}\alpha = \bar{E}_{\mathrm{Na}}E_{\mathrm{NH_4}}/\bar{E}_{\mathrm{NH_4}}E_{\mathrm{Na}} \tag{40}$$

and

$$^{\mathrm{Na}}_{\mathrm{K}}\alpha = \bar{E}_{\mathrm{Na}}E_{\mathrm{K}}/\bar{E}_{\mathrm{K}}E_{\mathrm{Na}}. \tag{41}$$

(The use of these functions assumes, of course, that the solution phase correction is not significant. This is a valid assumption, since for exchange involving ions of one valency only, ${}^{\mathrm{u}}_{\mathrm{v,w}}\Gamma$ is not a function of the exchanger phase composition (Fletcher & Townsend 1983) and therefore the solution phase correction cannot adversely affect any linear relation between the α values above). If, to a first approximation, the ammonium and potassium ions are regarded as behaving identically, then a pseudobinary separation factor ${}^{\mathrm{Na}}_{(\mathrm{NH_4K})}\tilde{\alpha}$ may be defined as

$$^{\mathrm{Na}}_{(\mathrm{NH_4,K})}\tilde{\alpha} = \frac{\bar{E}_{\mathrm{Na}}(E_{\mathrm{NH_4}}+E_{\mathrm{K}})}{E_{\mathrm{Na}}(\bar{E}_{\mathrm{NH_4}}+\bar{E}_{\mathrm{K}})} = \frac{\bar{E}_{\mathrm{Na}}(1-E_{\mathrm{Na}})}{E_{\mathrm{Na}}(1-\bar{E}_{\mathrm{Na}})} = \frac{({}^{\mathrm{Na}}_{\mathrm{NH_4}}\alpha)\,\bar{E}_{\mathrm{NH_4}}+({}^{\mathrm{Na}}_{\mathrm{K}}\alpha)\,\bar{E}_{\mathrm{K}}}{(1-\bar{E}_{\mathrm{Na}})}. \tag{42}$$

Since a complete ternary isotherm of the Na–K–$\mathrm{NH_4}$–MOR system has been determined (figure 4) it is possible to predict values of ${}^{\mathrm{Na}}_{(\mathrm{NH_4,K})}\tilde{\alpha}$ by (42) and to compare these with actual experimental data. Experimental data were obtained by interpolation of the best-fitting

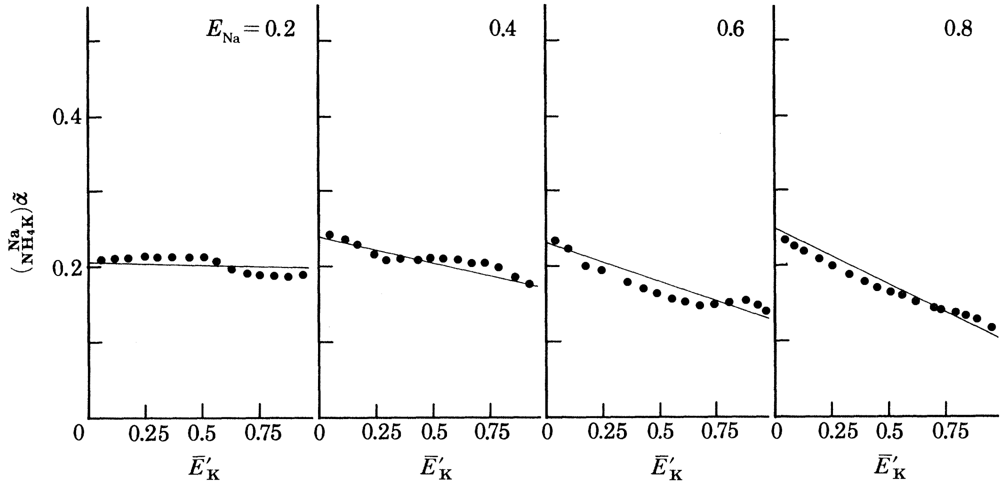


FIGURE 10. Plots of the separation factor $({}^{\mathrm{Na}}_{\mathrm{NH_4,\,K}})\tilde{\alpha}$ as a function of the normalized equivalent fraction of potassium in the crystal phase ($\bar{E}'_{\mathrm{K}}$) and for different (but in each case constant) values of $\bar{E}_{\mathrm{Na}}$. The predicted line of Soldatov & Bychkova (1980) (solid line) agrees well with measured data from the ternary isotherm.

polynomial for the plot of ln $({}^{\mathrm{Na}}_{\mathrm{NH_4,\,K}}K_{\mathrm{G}})$ in figure 5. As explained above, for a homovalent ternary exchange in dilute solution $({}^{\mathrm{u}}_{\mathrm{v,w}}K_{\mathrm{G}}) \simeq ({}^{\mathrm{u}}_{\mathrm{v,w}}K_{m,\,E})$. Also, when the exchange involves univalent ions only, $({}^{\mathrm{u}}_{\mathrm{v,w}}K_{m,\,E}) = ({}^{\mathrm{u}}_{\mathrm{v,w}}\,\alpha)$. The results are shown in figure 10; it is seen that for all four chosen parametric lines of constant $\bar{E}_{\mathrm{Na}}$, the preference for sodium is predicted accurately by (42), in agreement with the expectations of Soldatov & Bychkova (1980). It is of interest that Barri & Rees (1980) use a similar rationale in their studies on the Na–Ca–Mg–zeolite A system. In their predictions they join together the $\bar{E}_{\mathrm{Ca}}$ and $\bar{E}_{\mathrm{Mg}}$ values, and of the three ions in this exchange system the calcium and magnesium are indisputably the most similar. Using this approach, they achieved a considerable degree of success in predicting ternary compositions. However, they also emphasized the marked differences in preferences

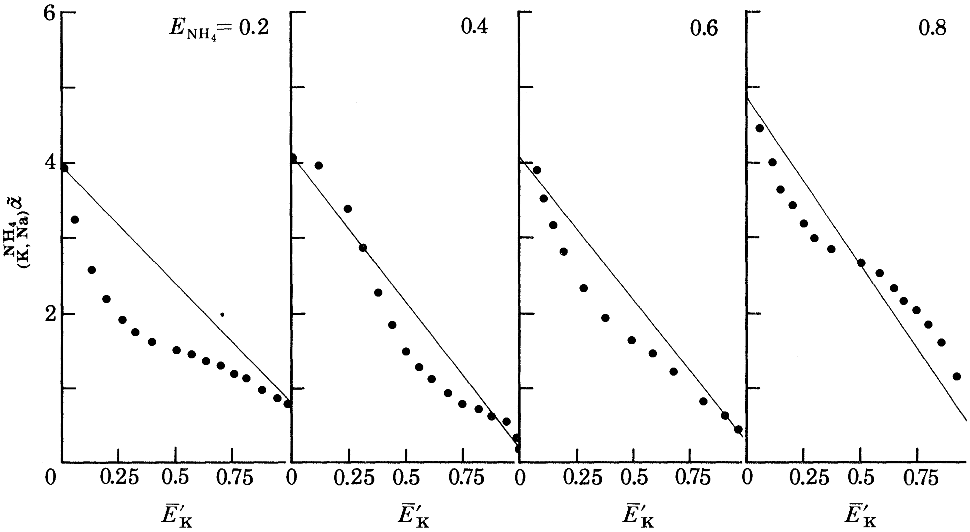


FIGURE 11. Plots of the separation factor ${}_{(\mathrm{K,\,Na})}^{\mathrm{NH_4}}\tilde{\alpha}$ as a function of $\bar{E}'_{\mathrm{K}}$, and for different (but in each case constant) values of $\bar{E}_{\mathrm{NH_4}}$. The predictions (solid line) agree poorly with measured data taken from the ternary isotherm.

for different sites within the zeolite framework, which are manifested by the divalent ions, and they concluded that as far as zeolite exchange is concerned, 'the prediction of both zeolite and solution phase compositions for a ternary exchange from a knowledge of only binary exchange data still awaits a solution' (Barri & Rees 1980).

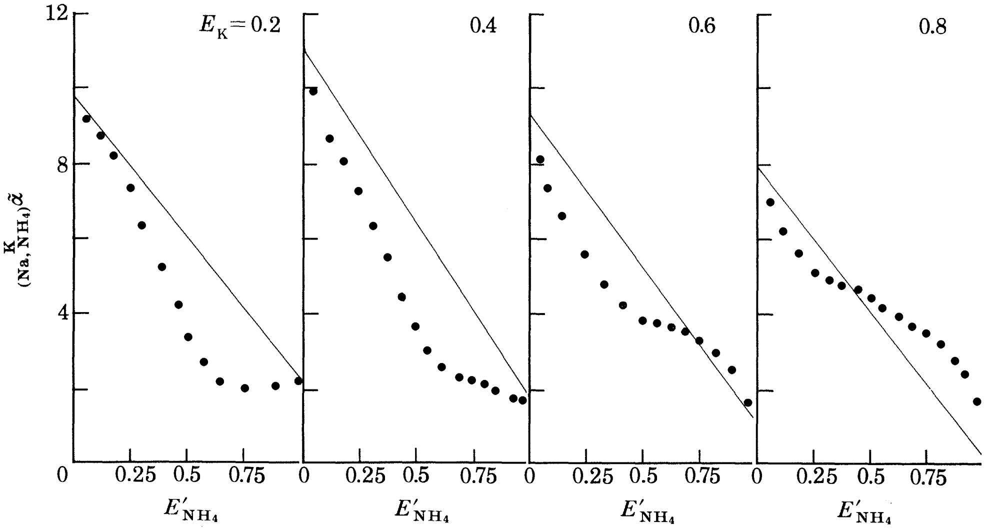


FIGURE 12. Plots of the separation factor ${}_{(\mathrm{Na},\mathrm{NH_4})}^{\mathrm{K}}\tilde{\alpha}$ as a function of the normalized equivalent function of ammonium in the crystal phase ($\bar{E}'_{\mathrm{NH_4}}$), and for different (but in each case constant) values of $\bar{E}_{\mathrm{K}}$. (The predictions (solid line) agree poorly with measured data from the ternary isotherm.

For comparison, values of ${}_{(\mathrm{K},\mathrm{Na})}^{\mathrm{NH_4}}\tilde{\alpha}$ and ${}_{(\mathrm{Na},\mathrm{NH_4})}^{\mathrm{K}}\tilde{\alpha}$ were also predicted by using the procedure described above, and these data plotted against experimental data taken from the polynomials depicted in figures 6 and 7. The results are shown in figures 11 and 12. Bearing in mind that the $\mathrm{NH_4}$–K pair is the most alike in properties (figures 6 and 7), the observed much poorer correlations are the expected results.

(*c*) *The need for other models*

A problem with the above approaches is that to choose which two ions in a ternary mixture are behaving most similarly in a zeolite it is important to obtain a quantity of experimental data on the ternary equilibrium as well as the binary exchange isotherms before any prediction can be safely attempted. Some data on the ternary compositions are absolutely necessary for Barri & Rees' (1980) approach. Even when it is possible to choose the most alike ion pair unambiguously, the predictions can be quite approximate, and certainly it would be dangerous to attempt to further predict from these data the effects that changes in the ionic strength of the external solution may have on the zeolite selectivity. This, however, is an important requirement of a useful model for equilibrium ternary ion exchange (Fletcher & Townsend 1981*d*). For this reason models such as the above can be inadequate and therefore other approaches have been developed. Among these, solid solution models, designed to predict equilibrium compositions by calculating ternary exchange activity coefficients from binary data, have achieved some success (Elprince & Babcock 1975; Elprince *et al.* 1980).

The rationale behind these approaches follows from the discussion at the beginning of this section. It is possible to calculate the free energies of exchange for ternary exchange reactions from data for the appropriate binary systems (the 'triangle rule'). If, therefore, a suitable model for the calculation of ternary activity coefficients can be developed, then the actual selectivity of the exchanger for any ternary composition can be determined, since from (3) and (8)

$$ {}_{\mathrm{v,w}}^{\mathrm{u}}K_{\mathrm{G}(\bar{E}_{\mathrm{u}},\,\bar{E}_{\mathrm{v}})} = ({}_{\mathrm{v,w}}^{\mathrm{u}}\varPhi)^{-1}_{(\bar{E}_{\mathrm{u}},\,\bar{E}_{\mathrm{w}})} \times \exp\left[\frac{-z_{\mathrm{u}}\,z_{\mathrm{v}}\,z_{\mathrm{w}}({}_{\mathrm{v,w}}^{\mathrm{u}}\Delta G^{\ominus})}{RT}\right], \tag{43} $$

where $({}_{\mathrm{v,w}}^{\mathrm{u}}\Delta G^{\ominus})$ is a standard free energy per equivalent of exchange. (This equals the standard free energy change per mole when only univalent ions are concerned in the process).

The thermodynamic model of Fletcher & Townsend (1981*b*) enables values of ϕ_{A}, ϕ_{B} and ϕ_{C} to be determined directly from experimental data. Nevertheless, for accurate results, many experimental data are required. It appears that for some cases involving resins or clays the solid solution models (which are easy to apply) are very adequate (Elprince & Babcock 1975; Chu & Sposito 1981). It is important therefore to see if these models can be applied readily to zeolite exchangers, or at least to define the conditions under which they may be applicable to these materials. These matters are discussed in the next two sections.

6. PREDICTION OF ACTIVITY COEFFICIENTS FOR THE TERNARY EXCHANGE EQUILIBRIUM FROM BINARY DATA ONLY

(*a*) *The model of Elprince & Babcock* (1975)

The solid solution model of Elprince & Babcock (1975) consists of a set of equations that relate the activity coefficients of ions in the exchanger to a series of constants that represent energies of interaction between the exchangeable cations in the system. Their approach developed an earlier model (Wilson 1964). The Wilson model represented non-ideality in terms of the Raoult law and used additive interaction terms to describe the non-ideality. Guggenheim (1935) and later Pitzer (1973*a*, *b*), both also derived models for strong aqueous solutions of electrolytes involving ion–ion interaction terms, but used instead the Henry law as the criterion for ideality. For exchanges involving two ions only, the equations of Elprince & Babcock (1975) are (for the *uni-univalent* case):

$$ \ln g_{\mathrm{A}} = -\ln(\bar{E}_{\mathrm{A}} + \varLambda_{\mathrm{AB}}\bar{E}_{\mathrm{B}}) + \bar{E}_{\mathrm{B}}\left(\frac{\varLambda_{\mathrm{AB}}}{\bar{E}_{\mathrm{A}} + \bar{E}_{\mathrm{B}}\varLambda_{\mathrm{AB}}} - \frac{\varLambda_{\mathrm{BA}}}{\bar{E}_{\mathrm{B}} + \bar{E}_{\mathrm{A}}\varLambda_{\mathrm{BA}}}\right), \tag{44} $$

$$ \ln g_{\mathrm{B}} = -\ln(\bar{E}_{\mathrm{A}}\varLambda_{\mathrm{BA}} + \bar{E}_{\mathrm{B}}) + \bar{E}_{\mathrm{A}}\left(\frac{\varLambda_{\mathrm{BA}}}{\bar{E}_{\mathrm{A}}\varLambda_{\mathrm{BA}} + \bar{E}_{\mathrm{B}}} - \frac{\varLambda_{\mathrm{AB}}}{\bar{E}_{\mathrm{A}} + \bar{E}_{\mathrm{B}}\varLambda_{\mathrm{AB}}}\right). \tag{45} $$

(Note that the second bracketed term in (45) differs from that given in the original paper (Elprince & Babcock 1975), where the signs were inadvertently reversed). The $\varLambda$ values represent differences in interaction energies between pairs of like and unlike ions. So, for example,

$$ \varLambda_{\mathrm{AB}} = (\nu_{\mathrm{B}}/\nu_{\mathrm{A}})\exp\left[-[\lambda_{\mathrm{AB}} - \lambda_{\mathrm{AA}})/RT\right], \tag{46} $$

where ν_{A}, ν_{B} are the molar volumes of the pure components and $\lambda_{\mathrm{AB}} - \lambda_{\mathrm{AA}}$ is the difference in interaction energies between unlike and like ion pairs within the exchanger. The terms g_{A}, g_{B} are the activity coefficients of ions $\mathrm{A}^{z_{\mathrm{A}}^{+}}$, $\mathrm{B}^{z_{\mathrm{B}}^{+}}$ in association with their equivalents of exchanger framework (Gaines & Thomas (1953) convention).

The equations can be generalized for multicomponent exchange (Elprince & Babcock 1975). For exchange involving three univalent ions, the general equation is

$$\ln\phi_u = 1 - \left(\ln \sum_{i=u}^{w} \bar{E}_i \Lambda_{ui}\right) - \sum_{i=u}^{w} \left[\bar{E}_u \Lambda_{iu} \Big/ \sum_{j=u}^{w} (\bar{E}_j \Lambda_{ij})\right] \tag{47}$$

for

$$\begin{bmatrix} A, & B, & C \\ B, & C, & A \\ C, & A, & B \end{bmatrix} = \begin{bmatrix} u \\ v \\ w \end{bmatrix}.$$

Given, therefore, experimental data for the three binary exchanges $A \rightleftharpoons B$, $B \rightleftharpoons C$ and $C \rightleftharpoons A$, the values of Λ_{AB}, Λ_{BA} can be evaluated by using (44) and (45). These values can then be inserted into (47) to obtain ϕ_A, ϕ_B and ϕ_C. Implicit in this method is the assumption that the Λ values so obtained are constant. However, this approach has been applied successfully to clays not only by Elprince & Babcock (1975) but also by Wiedenfeld & Hossner (1978).

The procedure was therefore applied also to the Na–NH_4–K–MOR system. To obtain the Λ values, an iterative procedure was adopted, since (44) and (45) do not lend themselves to simple simultaneous solution. Λ_{ij} values were calculated as a function of crystal phase composition for each of the three binary exchanges $NH_4 \rightleftharpoons Na$, $K \rightleftharpoons Na$ and $K \rightleftharpoons NH_4$ (shown in figure 1). Activity coefficients for the three binary systems were obtained by using the procedure of Gaines & Thomas (1953), and the results are shown as a function of crystal phase composition in figure 13, together with the respective plots showing the corresponding variations of the corrected selectivity coefficient ${}_{u}^{v}K_G$. Figure 14 shows values of Λ_{ij} predicted from the activity coefficient data depicted in figure 13.

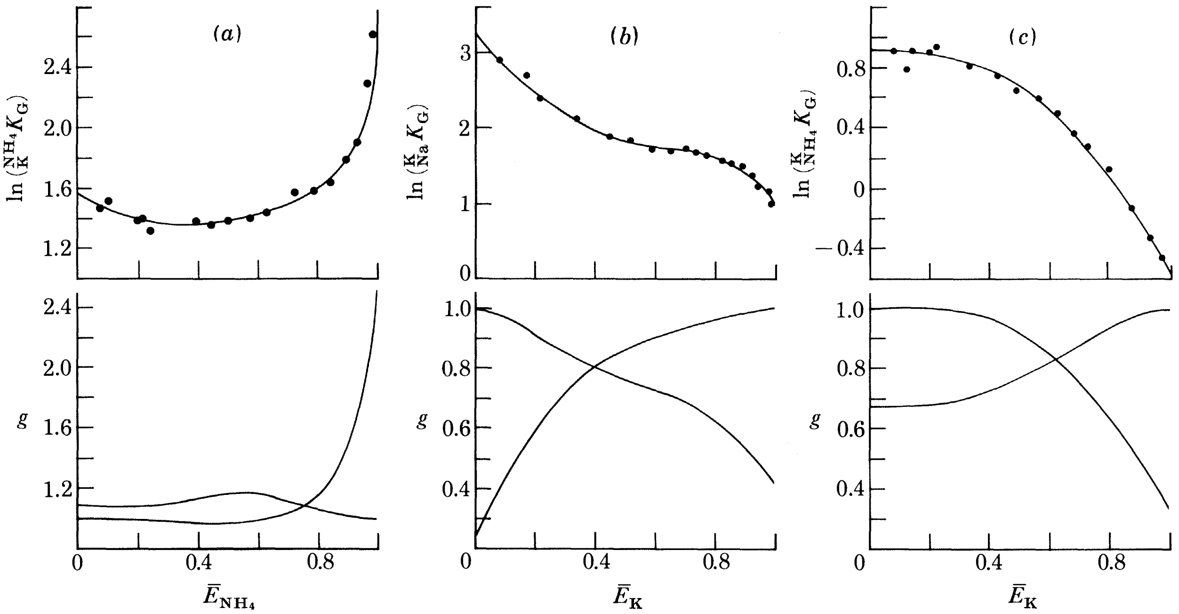


FIGURE 13. Plots of the binary corrected selectivity quotient as a function of (*a*) $\bar{E}_{NH_4}$, (*b*) $\bar{E}_K$ and (*c*) $\bar{E}_K$, obtained by using the procedure of Gaines & Thomas (1953) on the data shown in the corresponding figure 1*a*, *b*, *c*. Also shown are plots of the activity coefficients (*a*) g_{Na}, g_{NH_4}, (*b*) g_{Na}, g_K and (*c*) g_{NH_4}, g_K.

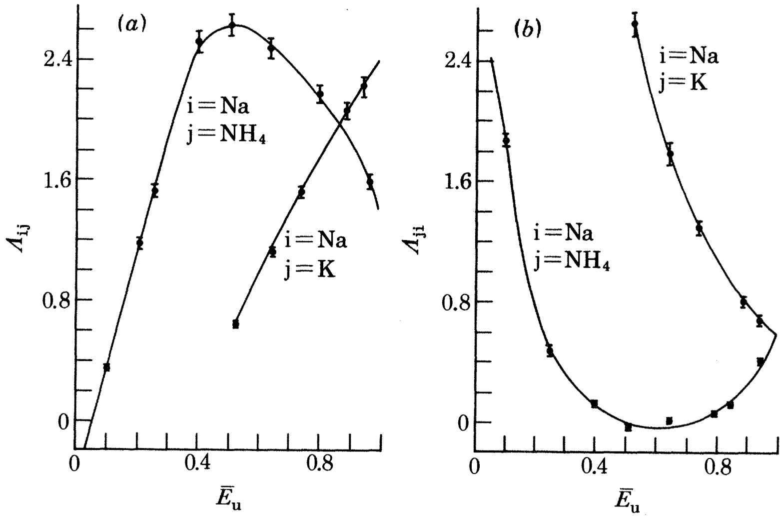


FIGURE 14. (*a*) Plots of the interaction terms Λ_{NaNH_4} and Λ_{NaK} obtained by using the data in figure 1*a*, *b* and the procedure of Elprince & Babcock (1975). Λ values are plotted against $\bar{E}_u$, where u = NH$_4$ and K respectively. The equations could not be solved for values of Λ_{NaK} corresponding to $\bar{E}_K < 0.5$. (*b*) Plots of Λ_{NH_4Na} and Λ_{KNa} corresponding to data in figure 14*a* with $\bar{E}_u$ as for figure 14*a*. Again, Λ_{KNa} values could not be obtained for $\bar{E}_K < 0.5$.

It is evident that the Λ_{ij} values are a strong function of the crystal phase composition, even for the binary exchanges. Indeed, for the K$\rightleftharpoons$Na and K$\rightleftharpoons$NH$_4$ exchanges the equations proved to be insoluble over certain composition ranges of the isotherm. The approach of Elprince & Babcock (1975) thus appears inapplicable to the Na–NH$_4$–K–MOR system on two counts. First, the Λ_{ij} and Λ_{ji} values are not constant even for the binary exchanges. Secondly, it is frequently impossible to obtain unique solutions for Λ_{ij} and Λ_{ji} for some crystal phase compositions. This failure of the model is in marked contrast to its successful application to clay minerals (Elprince & Babcock 1975). Possible reasons for this failure are discussed in the next section.

(*b*) *Predictions of activity coefficients from the 'sub-regular' solution model*

More recently, another procedure for the prediction of ternary activity coefficients in clays has been reported (Elprince *et al.* 1980). This procedure uses a convergent power series (Margules equation) to represent the behaviour of activity coefficients in a multi-component solid solution, and is an extension of the 'sub-regular' solution model of Hardy (1953). The general form of the equation for a multi-component system is (Elprince *et al.* 1980)

$$\ln f_u = \sum_{i,\,j\,\neq\,u} c_{ij}^{(u)}\,\bar{X}_i\,\bar{X}_k + \sum_{i,\,j,\,k\,\neq\,u} d_{ijk}^{(u)}\,\bar{X}_i\,\bar{X}_j\,\bar{X}_k + \ldots, \tag{48}$$

where f_u is the activity coefficient of ion u in the multicomponent system, c_{ij} and d_{ijk} are coefficients and $\bar{X}_i$ is the mole fraction of ion i in the mixture. If the convergent series is truncated after the cubic terms, then for ion u in a ternary mixture the corresponding ternary activity coefficient is

$$\ln \phi_u = c_{vv}^{(u)}\,\bar{X}_v^2 + c_{ww}^{(u)}\,\bar{X}_w^2 + c_{vw}^{(u)}\,\bar{X}_v\,\bar{X}_w + d_{vvv}^{(u)}\,\bar{X}_v^3 + d_{www}^{(u)}\,\bar{X}_w^3 + d_{vvw}^{(u)}\,\bar{X}_v^2\,\bar{X}_w + d_{vww}^{(u)}\,\bar{X}_v\,\bar{X}_w^2, \tag{49}$$

where

$$c_{\mathrm{ii}}^{(\mathrm{u})} = 2\ln f_{\mathrm{iu}}^{\infty} - \ln f_{\mathrm{ui}}^{\infty}, \tag{50}$$

$$d_{\mathrm{iii}}^{(\mathrm{u})} = 2(\ln f_{\mathrm{ui}}^{\infty} - \ln f_{\mathrm{iu}}^{\infty}), \tag{51}$$

$$c_{\mathrm{ij}}^{(\mathrm{u})} = \tfrac{1}{2}(3\ln f_{\mathrm{iu}}^{\infty} + 3\ln f_{\mathrm{ju}}^{\infty} - \ln f_{\mathrm{ui}}^{\infty} - \ln f_{\mathrm{uj}}^{\infty} - \ln f_{\mathrm{ij}}^{\infty} - \ln f_{\mathrm{ji}}^{\infty}), \tag{52}$$

$$d_{\mathrm{iij}}^{(\mathrm{u})} = 3(\ln f_{\mathrm{ui}}^{\infty} - \ln f_{\mathrm{iu}}^{\infty}) + (\ln f_{\mathrm{uj}}^{\infty} - \ln f_{\mathrm{ju}}^{\infty} + \ln f_{\mathrm{ij}}^{\infty} - \ln f_{\mathrm{ji}}^{\infty}), \tag{53}$$

where, for example, f_{ij}^{∞} is the binary activity coefficient (mole fraction convention) of component i when its mole fraction approaches zero in a binary mixture of i and j.

By using this model, good agreement was obtained between experimentally-determined and predicted data for the ternary system $\mathrm{NH_4}$–Ba–La–montmorillonite (Elprince *et al.* 1980). As for the earlier model of Elprince & Babcock (1975) it was assumed that no experimental data for the ternary exchange equilibrium were required *a priori* for the application of the model. Subsequently, however, the Margules equation model has been refined by Chu & Sposito (1981), who contradicted this assumption and asserted that 'the sub-regular model for the ternary system cannot be expressed solely in terms of parameters that depend only on data obtained for binary systems'. A new and extra parameter was introduced (Chu & Sposito 1981) that requires some experimental data on the ternary exchange equilibrium for its evaluation. For the $\mathrm{NH_4}$–Ba–La–montmorillonite system this parameter was found to approximate to zero, which explained the good agreement observed earlier (Elprince *et al.* 1980).

Since the 'sub-regular model' has been applied quite successfully to clays, it seemed logical to apply the model also to the experimental data reported here for the three binary exchanges $\mathrm{NH_4} \rightleftharpoons \mathrm{Na}$, $\mathrm{K} \rightleftharpoons \mathrm{Na}$ and $\mathrm{K} \rightleftharpoons \mathrm{NH_4}$ in mordenite (figure 1) to calculate values of ϕ_{Na}, $\phi_{\mathrm{NH_4}}$ and ϕ_{K} and hence predict ternary equilibrium behaviour. These results could then be compared with the experimental data (figures 2 and 4). For exchanges involving univalent ions only, $f_{\mathrm{ij}} = g_{\mathrm{ij}}$, etc., so values of $f_{\mathrm{ij}}^{\infty}, f_{\mathrm{ji}}^{\infty}$ for each binary exchange can in principle be taken from the extrema of the plots of g_{ij}, g_{ji} shown in figure 13. (So, for example, with figure 13*a*, $g_{\mathrm{ij}} = g_{\mathrm{NH_4}}$ and $g_{\mathrm{ij}}^{\infty} = g_{\mathrm{NH_4}}$ as $\bar{E}_{\mathrm{NH_4}} \rightarrow 0$). However, since the depicted curves are best-fitting polynomials that are minimally constrained because of the lack of experimental data in the limits $\bar{E}_{\mathrm{i}}$, $\bar{E}_{\mathrm{j}} \rightarrow 0$, this is not a good approach.

A much better procedure is outlined by Elprince *et al.* (1980). The standard expression for the excess free energy of a binary system is

$${}^{\mathrm{i}}_{\mathrm{j}}G^{E} = RT(\bar{X}_{\mathrm{i}} \ln f_{\mathrm{i}} + \bar{X}_{\mathrm{j}} \ln f_{\mathrm{j}}). \tag{54}$$

Also, the activity coefficients of the ions in the binary exchange may be expressed in terms of a Margules equation so that (for example)

$$\ln f_{\mathrm{u}} = \bar{X}_{\mathrm{v}}^{2}[(2\ln f_{\mathrm{vu}}^{\infty} - \ln f_{\mathrm{uv}}^{\infty}) + 2\bar{X}_{\mathrm{v}}(\ln f_{\mathrm{uv}}^{\infty} - \ln f_{\mathrm{vu}}^{\infty})]. \tag{55}$$

Since for exchange involving ions of only one valency, $\bar{X}_{\mathrm{i}} = \bar{E}_{\mathrm{i}}$ and $f_{\mathrm{i}} = g_{\mathrm{i}}$, substitution of suitable Margules-type expressions into (54) leads, for a given pair of exchanging ions, to

$${}^{\mathrm{u}}_{\mathrm{v}}G^{E} = \bar{E}_{\mathrm{u}}\bar{E}_{\mathrm{v}} RT[\ln g_{\mathrm{uv}}^{\infty} + \bar{E}_{\mathrm{u}}(\ln g_{\mathrm{vu}}^{\infty} - \ln g_{\mathrm{uv}}^{\infty})]. \tag{56}$$

Equation (56) not only enables g_{uv}^{∞} and g_{vu}^{∞} to be evaluated, but provides a test of the theory itself, since a plot of ${}^{\mathrm{u}}_{\mathrm{v}}G^{E}/RT\bar{E}_{\mathrm{u}}\bar{E}_{\mathrm{v}}$ against $\bar{E}_{\mathrm{u}}$ should be linear.

By using the data depicted in figure 13, values of G^{E} and ${}^{\mathrm{u}}_{\mathrm{v}}G^{E}/RT\bar{E}_{\mathrm{u}}\bar{E}_{\mathrm{v}}$ were therefore calculated, and plotted against $\bar{E}_{\mathrm{u}}$. The results for the three binary exchanges in mordenite are shown in figure 15. The plots of ${}^{\mathrm{u}}_{\mathrm{v}}G^E/RT\bar{E}_{\mathrm{u}}\bar{E}_{\mathrm{v}}$ against $\bar{E}_{\mathrm{u}}$ for the $NH_4 \rightleftharpoons Na$ and $K \rightleftharpoons Na$ exchanges are parabolic, which shows that the above model is not an adequate description of these exchange equilibria in the zeolite. In contrast, the plot of ${}^{\mathrm{u}}_{\mathrm{v}}G^E/RT\bar{E}_{\mathrm{K}}\bar{E}_{\mathrm{NH_4}}$ against $\bar{E}_{\mathrm{K}}$ (figure 16*c*) conforms fairly well to a straight line. (It is of interest that when the theoretical approach of Soldatov & Bychkova (1980) was applied to these same exchange equilibria in mordenite, their model also succeeded best with this pair of ions (see §5)). The very substantial deviations from linearity observed for two of the binary exchange systems (figures 15*a*, *b*) made the meaning of any subsequent predictions of activity coefficients for the ternary exchange difficult to ascertain.

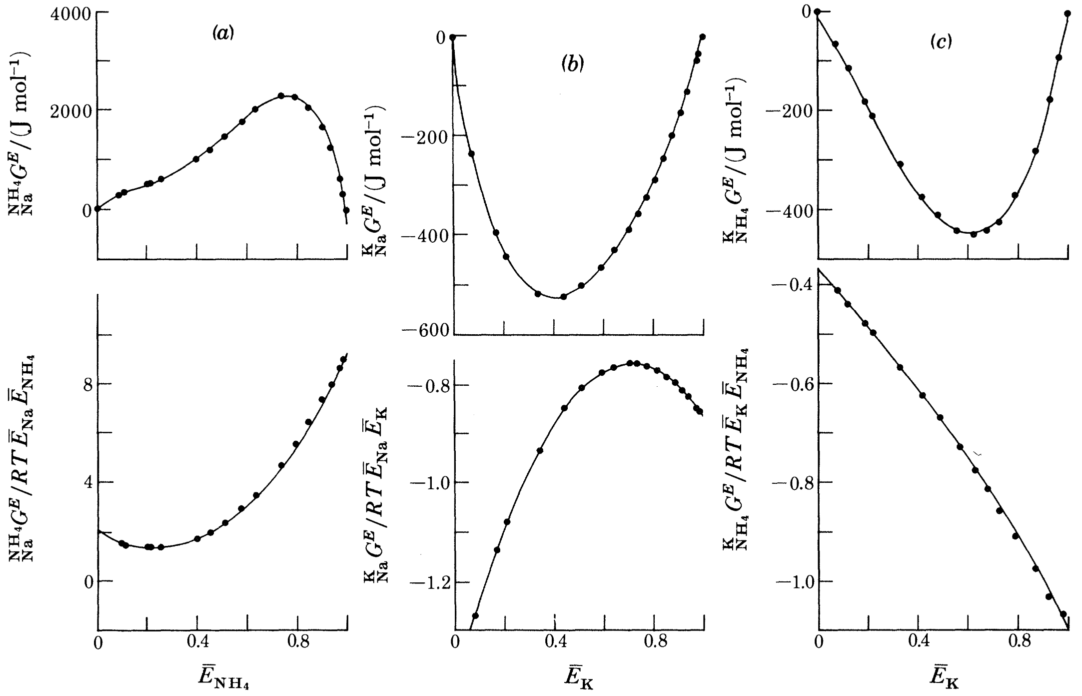


FIGURE 15. Plots of ${}^{\mathrm{u}}_{\mathrm{v}}G^E$ and $({}^{\mathrm{u}}_{\mathrm{v}}G^E/RT\bar{E}_{\mathrm{u}}\bar{E}_{\mathrm{v}}$ as a function of equivalent fraction, based on activity coefficient data shown in figure 13. Figure 15*a* corresponds to 13*a et seq.* The plots of ${}^{\mathrm{u}}_{\mathrm{v}}G^E/RT\bar{E}_{\mathrm{u}}\bar{E}_{\mathrm{v}}$ should be linear for agreement with theory; only for the $K–NH_4$ pair is this seen (cf. figure 10).

(*c*) *Concluding remarks*

The failure of the models of both Elprince & Babcock (1975) and of Elprince *et al.* (1980) when they are applied to the $Na–NH_4–K–MOR$ system should not be taken to imply general criticisms of these approaches. As emphasized above, these models worked quite well for clays, even when the exchanges involved multivalent ions. Rather, the failure should be ascribed to differences in the properties of a typical zeolite compared to a clay. The probable cause of the failure is the existence of a much more marked site heterogeneity in the zeolite, a phenomenon that has been briefly discussed elsewhere (Fletcher & Townsend 1981*a*). This can, of course, arise in a clay or resin and has been used by workers to explain minor deviations from ideal behaviour in these materials (Soldatov & Bychkova 1971, 1980*a*; Elprince *et al.* 1980; Goulding & Talibudeen 1980). Site heterogeneity is however an *intrinsic* property of zeolites (Barrer &

Klinowski 1977, 1979*a*, *b*). This matter is discussed further below, in terms of experimentally measured activity coefficients for the ternary exchange of sodium, ammonium and potassium ions in mordenite.

7. EXPERIMENTAL DETERMINATION OF TERNARY ACTIVITY COEFFICIENTS IN EXCHANGERS

(*a*) *Introduction*

In addition to the thermodynamic treatment adopted by Fletcher & Townsend (1981*a*, *b*), which was derived with zeolites primarily in mind, other workers have published procedures for determining activity coefficients of ions in a multi-component exchanger phase. So, when considering in particular exchange in organic resins, Bychkova & Soldatov (1980) described a method like that of Fletcher & Townsend, which also uses the equivalent fraction convention as the concentration scale in the exchanger. More recently, Chu & Sposito (1981) published a similar formulation in a study of ternary ion exchange in clays, which used the mole fraction scale (Sposito & Mattigod 1979). All three approaches derive basically from an application of the Gibbs–Duhem equation to the exchanger phase. Obviously, such treatments cannot be dependent on the particular chemical properties of the phase under investigation. It is instructive therefore to compare the three treatments, and check that they are indeed fully compatible.

Both the treatment of Bychkova & Soldatov (1980) and that of Chu & Sposito (1981) begin by defining pseudobinary coefficients, which are related to three binary coefficients by the relation shown in (32). Equations for the activity coefficients are then derived in terms of the pseudobinary coefficients. Evaluation of activities required knowledge of the dependence of the pseudobinaries on the ternary composition. For accurate work, detailed experimental data on the equilibrium between the exchanger and solution phase are required over the whole ternary composition plot. The treatment of Fletcher & Townsend (1981*b*) begins from the opposite side, by defining constants for the ternary equilibrium ${}_{\mathrm{v,w}}^{\mathrm{u}}K_{\mathrm{a}}$ (see equation (2)). Subsequent application of the Gibbs–Duhem equation leads, however, to two quotients, each of which involves just two of the ${}_{\mathrm{v,w}}^{\mathrm{u}}K_{\mathrm{a}}$ terms. Simplification of these quotients then gives rise also to pseudobinaries (see equations (27) and (28)), which are very similar in form to those of other workers (Bychkova & Soldatov 1980; Chu & Sposito 1981).

Nevertheless, some differences remain. First, because Chu & Sposito use the mole fraction convention, their equations (rightly) do not have terms involving only the valencies of the exchanging ions, and for a given system, therefore, the numerical values of the activity coefficients so derived differ from these calculated with the equivalent fraction scale (Barrer & Townsend 1983). (The valence term is not seen in the equations of Bychkova & Soldatov (1980) either, but this is apparently because they are considering exchanges involving univalent ions only (Bychkova & Soldatov 1980).)

A second and important procedural difference is seen when either Chu & Sposito (1981) or Bychkova & Soldatov (1980) are compared with Fletcher & Townsend (1981). Following, for example, Bychkova & Soldatov, the activity coefficient for the third ion is

$$\frac{1}{z_{\mathrm{C}}}(\ln \phi_{\mathrm{C}}) = \int_{l_3}^{l_1} \bar{E}_{\mathrm{A}}\,\mathrm{d}\ln({}_{\mathrm{C}}^{\mathrm{A}}\mathscr{K}_{\mathrm{G}}) + \int_{l_4}^{l_2} \bar{E}_{\mathrm{B}}\,\mathrm{d}\ln({}_{\mathrm{C}}^{\mathrm{B}}\mathscr{K}_{\mathrm{G}}), \tag{57}$$

where

$$l_1 = \ln [{}^{\mathrm{A}}_{\mathrm{C}}\tilde{\mathscr{K}}_{\mathrm{G}(\bar{E}_{\mathrm{C}})}], \quad l_2 = \ln [{}^{\mathrm{B}}_{\mathrm{C}}\tilde{\mathscr{K}}_{\mathrm{G}(\bar{E}_{\mathrm{C}})}],$$

$$l_3 = \ln [{}^{\mathrm{A}}_{\mathrm{C}}\tilde{\mathscr{K}}_{\mathrm{G}(\bar{E}_{\mathrm{C}}=1)}], \quad l_4 = \ln [{}^{\mathrm{B}}_{\mathrm{C}}\tilde{\mathscr{K}}_{\mathrm{G}(\bar{E}_{\mathrm{C}}=1)}]$$

and where (for example) ${}^{\mathrm{A}}_{\mathrm{C}}\tilde{\mathscr{K}}_{\mathrm{G}}$ is a corrected selectivity quotient for the pseudobinary equilibrium between ions $\mathrm{C}^{z_{\mathrm{C}}^{+}}$ and $\mathrm{A}^{z_{\mathrm{A}}^{+}}$. Thus

$${}^{\mathrm{A}}_{\mathrm{C}}\tilde{\mathscr{K}}_{\mathrm{G}} = \bar{E}_{\mathrm{A}}^{1/z_{\mathrm{A}}} a_{\mathrm{C}}^{1/z_{\mathrm{C}}} / \bar{E}_{\mathrm{C}}^{1/z_{\mathrm{C}}} a_{\mathrm{A}}^{1/z_{\mathrm{A}}}. \tag{58}$$

Comparison of this definition with (10) shows that

$$\mathscr{k}_{\mathrm{C-A}} = z_{\mathrm{A}} z_{\mathrm{B}} z_{\mathrm{C}} ({}^{\mathrm{A}}_{\mathrm{C}}\tilde{\mathscr{K}}_{\mathrm{G}})^{-1}. \tag{59}$$

By inserting this result into (57) and transforming differentials

$$\ln \phi_{\mathrm{C}}^{z_{\mathrm{A}} z_{\mathrm{B}}} = \int_0^{\bar{E}_{\mathrm{A}}} \ln \mathscr{k}_{\mathrm{C-A}} \,\mathrm{d}\bar{E}_{\mathrm{A}} + \int_0^{\bar{E}_{\mathrm{B}}} \ln \mathscr{k}_{\mathrm{C-B}} \,\mathrm{d}\bar{E}_{\mathrm{B}} - \bar{E}_{\mathrm{A}} \ln \mathscr{k}_{\mathrm{C-A}(\bar{E}_{\mathrm{A}})} - \bar{E}_{\mathrm{B}} \ln \mathscr{k}_{\mathrm{C-B}(\bar{E}_{\mathrm{B}})}, \tag{60}$$

which is identical with (22) provided $z_{\mathrm{A}} = z_{\mathrm{B}} = z_{\mathrm{C}}$. However, it is not possible by the same procedure to so easily prove the identity of the two treatments (namely those of Fletcher & Townsend (1981 *b*) and Bychkova & Soldatov (1981)) for ϕ_{A} and ϕ_{B}. This is because Bychkova & Soldatov always express each activity coefficient in terms of the concentrations of the other two ions.

(*b*) *Direct determination of activity coefficients from the isotherm*

In the treatment of Fletcher & Townsend (1981 *b*) values of ϕ_{A}, ϕ_{B} and ϕ_{C} are in terms of $\bar{E}_{\mathrm{A}}$ and $\bar{E}_{\mathrm{B}}$ only. This effectively simplifies the calculation of the values of the activity coefficients, since it is only necessary to know the variation of just *two* functions with the crystal phase composition to evaluate all three activity coefficients. The dependencies of these two functions $\ln \chi_{\mathrm{C-A}}$ and $\ln \chi_{\mathrm{C-B}}$ can be expressed in terms of just two polynomials in $\bar{E}_{\mathrm{A}}$ and $\bar{E}_{\mathrm{B}}$ (*not* identical to the polynomials described in §5a), namely

$$\ln \chi_{\mathrm{C-A}} = \sum_{i=0}^{m} \epsilon_i (\bar{\mathrm{E}}_{\mathrm{A}})^i + \sum_{j=1}^{n} \zeta_j (\bar{E}_{\mathrm{B}})^j \tag{61}$$

and

$$\ln \chi_{\mathrm{C-B}} = \sum_{p=0}^{r} \eta_p (\bar{E}_{\mathrm{A}})^p + \sum_{q=1}^{s} \theta_q (\bar{E}_{\mathrm{B}})^q. \tag{62}$$

(Note that the polynomials above incorporate the valence terms and the values of $\mathscr{k}^*_{\mathrm{C-A}}$ and $\mathscr{k}^*_{\mathrm{C-B}}$. The procedure outlined here is therefore different to, and simpler than, that suggested originally (Fletcher & Townsend 1981 *b*)). Integration of the polynomials within the prescribed limits shown in (20)–(22) then leads to values of ϕ_{A}, ϕ_{B} and ϕ_{C} for any given exchanger phase composition. When doing the integrations, it is important to remember that $\bar{E}_{\mathrm{A}}$ and $\bar{E}_{\mathrm{B}}$ are inter-dependent. For any valid solution of the equations, $\bar{E}_{\mathrm{A}} + \bar{E}_{\mathrm{B}} \leqslant 1$. Certain terms in the equations can therefore disappear, since when $\bar{E}_{\mathrm{A}} = 1$ then $\bar{E}_{\mathrm{B}} = 0$, and the converse. So, for example, from (20), (61) and (62)

$$\ln \phi_{\mathrm{A}}^{z_{\mathrm{B}} z_{\mathrm{C}}} = \sum_{i=0}^{m} \frac{\epsilon_i}{i+1} [(\bar{E}_{\mathrm{A}})^{(i+1)} - 1] + \bar{E}_{\mathrm{B}} \left[\sum_{j=1}^{n} \zeta_j \bar{E}_{\mathrm{A}} (\bar{E}_{\mathrm{B}})^{(j-1)} + \sum_{p=0}^{r} \eta_p (\bar{E}_{\mathrm{A}})^p + \sum_{q=1}^{s} \frac{\theta_q}{q+1} (\bar{E}_{\mathrm{B}})^q \right]. \tag{63}$$

By using these procedures, values of ϕ_{Na}, ϕ_{NH_4} and ϕ_K were evaluated as a function of crystal phase composition for the system Na–NH_4–K–MOR. The results are shown as contour diagrams in figures 16–18. The polynomials of best-fit from which the contour diagrams were constructed were derived from the 82 experimental points obtained for the ternary equilibrium only (see figure 2).

These contour diagrams provide an approximate picture of the variation of ϕ values with crystal composition. In examining them it is important, therefore, to recognize that not every detail of the contours is necessarily an accurate reflection of some intrinsic property of the

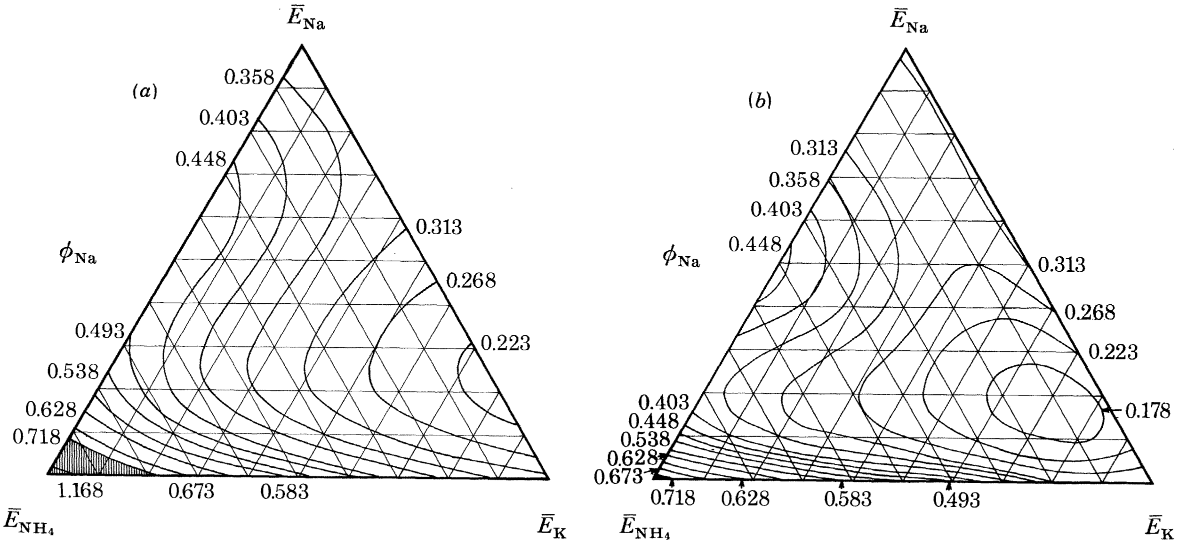


FIGURE 16. Contour maps of experimentally obtained values of the activity coefficient for sodium in mordenite, ϕ_{Na}, as a function of the composition. The maps were constructed with (*a*) (3,3) and (*b*) (4,4) polynomials. The contours become very close together in the shaded area in figure 16(*a*).

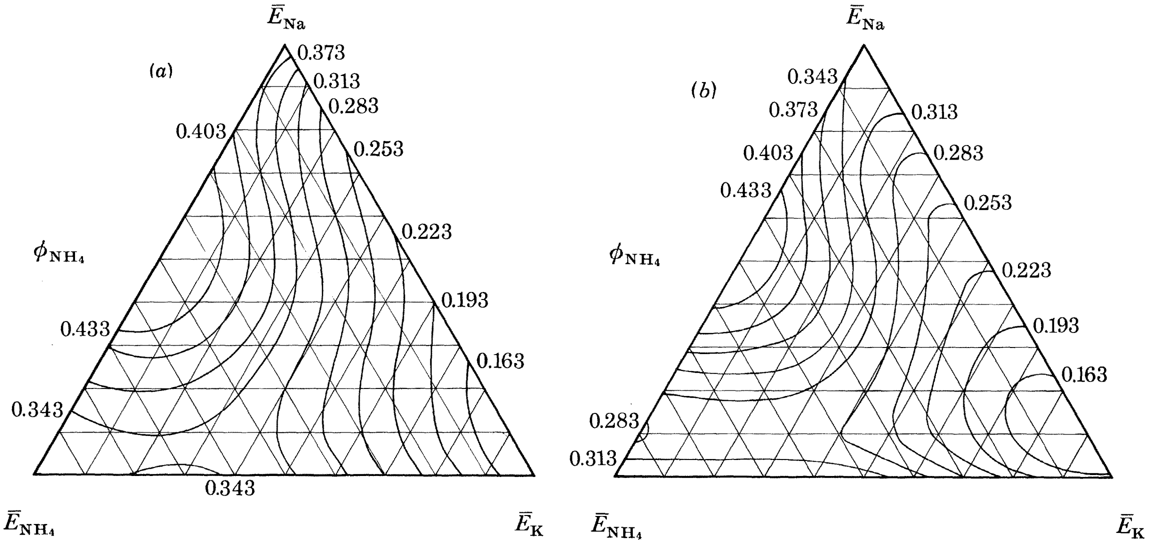


FIGURE 17. Contour maps for ϕ_{NH_4} with (*a*) and (*b*) corresponding to (3,3) and (4,4) polynomial fits, respectively.

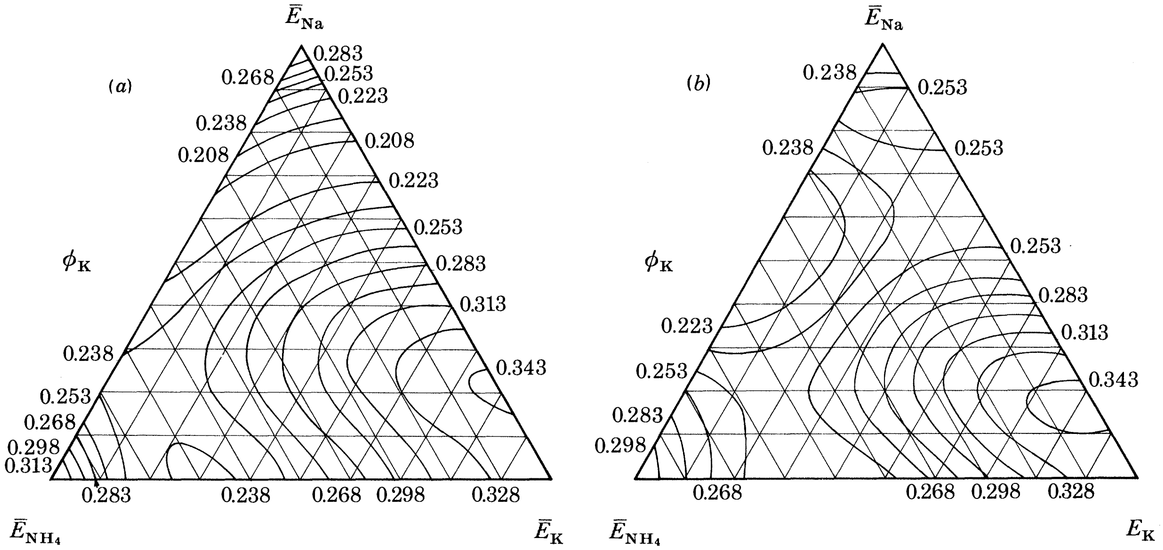


FIGURE 18. Contour maps for ϕ_{K}, with (*a*) and (*b*) corresponding to (3,3) and (4,4) polynomial fits, respectively.

TABLE 7. ACTIVITY COEFFICIENTS CALCULATED BY USING DIFFERENT ORDER POLYNOMIALS FOR $k_{\text{N-Na}}$ AND $k_{\text{K-NH}_4}$

Crystal composition		activity coefficients from third order polynomial data			activity coefficients from fourth-order polynomial data		
$\bar{E}_{\mathrm{Na}}$	$\bar{E}_{\mathrm{NH_4}}$	ϕ_{Na}	$\phi_{\mathrm{NH_4}}$	ϕ_{K}	ϕ_{Na}	$\phi_{\mathrm{NH_4}}$	ϕ_{K}
0.882	0.053	1.064	1.003	0.691	0.865	0.982	0.769
0.692	0.084	1.092	0.875	0.650	0.851	0.838	0.735
0.463	0.247	1.046	1.035	0.823	0.885	0.936	0.760
0.377	0.549	1.341	1.342	0.721	1.205	1.269	0.662
0.267	0.216	0.796	0.778	0.967	0.583	0.674	0.957
0.279	0.458	1.072	1.113	0.814	0.883	1.032	0.777
0.074	0.107	0.808	0.525	0.996	0.564	0.451	1.013
0.082	0.388	1.091	0.859	0.853	0.799	0.763	0.849
0.071	0.846	2.174	1.001	0.776	1.484	0.868	0.830

exchanger. The dependence of ϕ values on the correct choice of best-fitting polynomial orders is more marked than for the K_a values. This follows from (29) and (53): whereas ${}^{\mathrm{Na}}_{\mathrm{NH_4,K}}K_{\mathrm{a}}$ can be evaluated from a knowledge of the polynomial coefficients α_i and δ_q only, for ϕ_{A} *all* the coefficients for *both* polynomials corresponding to (20) are required. The marked dependence of the ϕ values on polynomial orders is seen by comparing the results derived from (3,3) fits (i.e. third order in $\bar{E}_{\mathrm{Na}}$ and $\bar{E}_{\mathrm{NH_4}}$; see discussion in §5*a*) with the corresponding (4,4) results (see figures 16–18 and table 7).

Inevitably, the effects of the best-fitting procedures is to 'smooth out' the actual non-ideality to some degree (Franklin & Townsend 1984). A test of whether the best-fit ϕ values do therefore give a reasonable description of non-ideality is to compare measured selectivity quotients with those predicted by using the best-fit ϕ data and (43). It is most important to note that in assessing the degree of agreement between measurement and prediction that which has been attained by using (43), consideration must be given to the considerable sensitivity of ${}^{\mathrm{u}}_{\mathrm{v,w}}\Phi$ to small changes in ϕ_{u}, ϕ_{v}, and ϕ_{w} (see equation (6)).

From table 8, a significant improvement in predictive accuracy is seen when (4,4) polynomials are used rather than the (3,3) equations. On the basis of the earlier discussion on the dependence of free energy values on polynomial orders (see discussion after (31)), this is the expected result. By taking all the experimental data (figure 2) into account the average percentage errors in predictions were (respectively for the (3,3) and (4,4) fits) ${}^{\mathrm{Na}}_{\mathrm{NH_4,K}}K_{\mathrm{G}}$ (28.7 % and 21.1 %), ${}^{\mathrm{NH_4}}_{\mathrm{K,Na}}K_{\mathrm{G}}$ (14.1 % and 14.0 %) and ${}^{\mathrm{K}}_{\mathrm{Na,NH_4}}K_{\mathrm{G}}$ (25.9 % and 23.9 %). Ways of improving further the degree of agreement between measurements and predictions, and of establishing reliable *a priori* methods of choosing the most appropriate polynomial order, are currently under study, and are further discussed elsewhere (Franklin & Townsend 1984).

Table 8. Error in ${}^{\mathrm{u}}_{\mathrm{v,w}}K_{\mathrm{G}}$ predicted from polynomials of $k_{\mathrm{K-Na}}$ and $k_{\mathrm{K-NH_4}}$

(Values in the top half are for third order fits; those in the lower half are for fourth order fits)

	average percentage error	largest error	error distribution under 10 %	number of points in group 10–20 %	over 20 %
${}^{\mathrm{Na}}_{\mathrm{NH_4,K}}K_{\mathrm{G}}$	28.65	128.76	24	16	41
${}^{\mathrm{NH_4}}_{\mathrm{K,Na}}K_{\mathrm{G}}$	14.05	71.64	34	30	17
${}^{\mathrm{K}}_{\mathrm{Na,NH_4}}K_{\mathrm{G}}$	25.85	122.30	20	21	40
${}^{\mathrm{Na}}_{\mathrm{NH_4,K}}K_{\mathrm{G}}$	21.12	100.28	25	23	33
${}^{\mathrm{NH_4}}_{\mathrm{K,Na}}K_{\mathrm{G}}$	14.02	75.23	35	29	17
${}^{\mathrm{K}}_{\mathrm{Na,NH_2}}K_{\mathrm{G}}$	23.93	84.85	28	13	40

8. Site heterogeneity in the exchanger phase

(*a*) *Introduction*

The activity coefficient data for ϕ_{Na}, $\phi_{\mathrm{NH_4}}$ and ϕ_{K}, depicted in figures 16–18, and determined for the ternary exchange by application of the Gibbs–Duhem equation (Fletcher & Townsend 1981*b*), are purely phenomenological quantities, representing experimentally-determined deviations from ideality of the three ions within the mordenite crystal framework. The complicated dependence of these functions on the exchanger phase composition is most likely due to site heterogeneity in the exchanger. Site heterogeneity has been noted in resins (Soldatov & Bychkova 1971); these materials are, however, amorphous in nature, so that non-ideality cannot be correlated easily with specific sets of ion sites within the resin beads.

In clays, pH-dependent site heterogeneity is a well known phenomenon (Peigneur *et al.* 1975; Goulding & Talibudeen 1980; Maes & Cremers 1975, 1977) and this was used to explain the failure of the sub-regular model to describe adequately the Ba–$\mathrm{NH_4}$ exchange in montmorillonite (Elprince *et al.* 1980). In zeolites, site heterogeneity can be very marked, giving rise to partial exchange (Barrer *et al.* 1973; Barrer & Klinowski 1977) and also to phenomena in which some ions are irreversibly 'locked' into certain sites within the framework (Maes & Cremers 1975; Lai & Rees 1976*a*, *b*). This heterogeneity arises from the existence of 'crystallographically distinct cation sites intimately mixed throughout an anionic framework' (Barrer & Klinowski 1979*a*).

(*b*) *General theoretical considerations*

From Barrer *et al.* (1973), for an exchange involving three types of ions within a zeolite that has *n* crystallographically distinct yet intimately mixed sub-lattices, the equilibrium constant may be factorized as

$$ {}^{\mathrm{u}}_{\mathrm{v,w}}K_a = \prod_{i=1}^{n} ({}^{\mathrm{u}}_{\mathrm{v,w}}K_{ai})^{X_{\mathrm{L}}(i)}, \tag{64}$$

where ${}^{\mathrm{u}}_{\mathrm{v,w}}K_{ai}$ refers to the equilibrium between ions in the *i*th site and those in solution. The function $X_{\mathrm{L}}(i)$ expresses the proportion of the total framework charge, which is neutralized by *all* ions that are exchanged into the *i*th site group. So, for example

$$\bar{E}_{\mathrm{u}i} = z_{\mathrm{u}}\,\bar{m}_{\mathrm{u}i} / \sum_{i=1}^{n} \sum_{\mathrm{j=u}}^{\mathrm{w}} (\bar{E}_{\mathrm{j}i}) = z_{\mathrm{u}}\,\bar{m}_{\mathrm{u}i} / \sum_{i=1}^{n} X_{\mathrm{L}}(i). \tag{65}$$

Hence

$$ {}^{\mathrm{u}}_{\mathrm{v,w}}K_a = \prod_{i=1}^{n} ({}^{\mathrm{u}}_{\mathrm{v,w}}K_{\mathrm{G}i})^{X_{\mathrm{L}}(i)} \prod_{i=1}^{n} ({}^{\mathrm{u}}_{\mathrm{v,w}}\varPhi_i)^{X_{\mathrm{L}}(i)} \tag{66}$$

$$ {}^{\mathrm{u}}_{\mathrm{v,w}}K_a = \left(\frac{a_{\mathrm{v}}^{z_{\mathrm{u}} z_{\mathrm{w}}} a_{\mathrm{w}}^{z_{\mathrm{u}} z_{\mathrm{v}}}}{a_{\mathrm{u}}^{2 z_{\mathrm{v}} z_{\mathrm{w}}}}\right) \prod_{i=1}^{n} \left[\frac{(\bar{E}_{\mathrm{u}i}\,\phi_{\mathrm{u}i})^{2 z_{\mathrm{v}} z_{\mathrm{w}}}}{(\bar{E}_{\mathrm{v}i}\,\phi_{\mathrm{v}i})^{z_{\mathrm{u}} z_{\mathrm{w}}} (\bar{E}_i\,\phi_{\mathrm{w}i})^{z_{\mathrm{u}} z_{\mathrm{v}}}}\right]^{X_{\mathrm{L}}(i)}. \tag{67}$$

Equation (66) shows that when ions exchange in a zeolite containing *i* crystallographically distinct site groups, it is possible for the ions in each site to behave non-ideally, and yet overall the exchanges appear to behave ideally. For this to occur, it is only necessary that the product of the ${}^{\mathrm{u}}_{\mathrm{v,w}}K_{\mathrm{G}i}\ {}^{\mathrm{u}}_{\mathrm{v,w}}\varPhi_i$ terms be near constant. This situation has been discussed by Barrer & Klinowski (1972*a*) for binary exchange. (Note that the factorization of (for example) ϕ_{u} into a set of formal $\phi_{\mathrm{u,i}}$ terms does *not* imply that it is permissible to therefore write down a 'chemical potential' in terms of a particular ion in a given sub-lattice within the crystal. For further discussion on this, see Barrer & Klinowski (1979*b*), Sersale *et al.* (1981) and Barrer & Townsend (1984)).

The opposite case is, however, at least as likely. The overall activity coefficients are seen (equation (67)) to be complicated functions of both the total population of ions in each site group at a given overall crystal composition, and of the composition of the ions within those site groups. It is not surprising, therefore, that ϕ values shown in figures 16 to 18 behave in a complex manner, and that both the approach of Elprince & Babcock (1975) and the 'sub-regular' model (Elprince 1980) fail to predict ϕ values adequately since crystallographic studies have proved that the proportion of charge neutralized on each site group and the composition of each site group is a function of the overall composition of the zeolite (Costenoble & Maes 1978).

(*c*) *Statistical thermodynamic considerations*

Barrer & Klinowski (1977) used statistical mechanics to relate the phenomenological activity coefficients for a binary ion exchange reaction to the framework charge density. If a random siting of cations is assumed (which is a consistent model for a homogeneous or near-homogeneous exchanger) the equations are

$$\ln g_{\mathrm{A}} = (z_{\mathrm{A}}\,\eta - 1)\ln\left(\frac{z_{\mathrm{A}}\,z_{\mathrm{B}}\,\eta - z_{\mathrm{B}}\,\bar{E}_{\mathrm{A}} - z_{\mathrm{A}}\,\bar{E}_{\mathrm{B}}}{z_{\mathrm{A}}\,z_{\mathrm{B}}\,\eta - z_{\mathrm{B}}}\right) - \frac{\omega_{\mathrm{AA}}\,\bar{E}_{\mathrm{B}}^2}{z_{\mathrm{B}}\,\eta\,kT} \tag{68}$$

and

$$\ln g_{\mathrm{B}} = (z_{\mathrm{B}}\,\eta - 1)\ln\left(\frac{z_{\mathrm{A}}\,z_{\mathrm{B}}\,\eta - z_{\mathrm{B}}\,\bar{E}_{\mathrm{A}} - z_{\mathrm{A}}\,\bar{E}_{\mathrm{B}}}{z_{\mathrm{A}}\,z_{\mathrm{B}}\,\eta - z_{\mathrm{A}}}\right) - \frac{z_{\mathrm{B}}\,\omega_{\mathrm{AA}}\,\bar{E}_{\mathrm{A}}^2}{z_{\mathrm{A}}^2\,\eta k T}, \tag{69}$$

where ω_{AA} is an excess interaction energy that arises when pairing of the entering $A^{z_A^+}$ ions occurs. The term η is related to the framework charge density by

$$\eta = N/N_0, \tag{70}$$

where N is the number of ion sites and N_0 the number of unit charges in the crystal. For uni-univalent exchange, the equations reduce to the terms involving ω_{AA} only and equations (68) and (69) then imply that for a *homogeneous* exchanger $\ln g_A$ and $\ln g_B$ should vary with $\bar{E}_A$, $\bar{E}_B$ in a symmetrical manner, according to the relative values of ω_{AA} and η (Fletcher & Townsend 1982). (This behaviour was observed also by Elprince & Babcock (1975) in their studies of the Na–Rb–Cs–montmorillonite systems, for which their model worked).

In contrast, if the exchanger consists of n sets of crystallographically distinct yet intimately mixed cation sites, equations (68) and (69) will then become

$$\ln g_A = -\frac{1}{kT}\sum_{i=1}^{n}\left[\frac{\bar{E}_{Bi}^2(\bar{E}_{Ai}+\bar{E}_{Bi})\,\omega_{AA,\,i}}{\eta_i}\right] \tag{72}$$

and

$$\ln g_B = -\frac{1}{kT}\sum_{i=1}^{n}\left[\frac{\bar{E}_{Ai}^2(\bar{E}_{Ai}+\bar{E}_{Bi})\,\omega_{AA,\,i}}{\eta_i}\right] \tag{73}$$

and the activity coefficients need no longer vary with $\bar{E}_A$ in a symmetrical manner, since both $\bar{E}_{Ai}+\bar{E}_{Bi}$ and $\bar{E}_{Ai}$ can also be functions of $\bar{E}_A$ (Fletcher & Townsend 1981 *d*)).

9. *Final comments*

In addition to the other properties that characterize them, zeolites are found generally to contain crystallographically distinct sets of sites throughout the exchanger framework. Normally, each set of sites is populated only partially by exchanging ions, and the extent of population as well as the composition within any site set are both functions of the overall composition of the exchanger. As a consequence, activity coefficients for a multicomponent exchange reaction cannot be predicted from appropriate binary data for a heterogeneous exchanger, since the phenomenological binary coefficients are complicated functions of each site set, population and composition, and both these properties will change on introducing other species of ion into the exchanger. This has been shown to be true for the ternary Na–NH_4–K–MOR system by comparing phenomenological (i.e. experimentally measured) activity coefficient data with those values predicted from binary data. It appears, therefore, unavoidable that an adequate description of a multicomponent exchange equilibrium in a heterogeneous exchanger requires of necessity a very substantial quantity of accurate experimental data over the whole range of the multicomponent exchanger composition. Given these data, the thermodynamic approach of Fletcher & Townsend (1981 *b*) enables relevant thermodynamic parameters to be evaluated relatively easily.

For binary exchange equilibria, Barrer & Klinowski (1974) have shown that for relatively low electrolyte concentrations in aqueous solution the *ratio* of activity coefficients for the ions in a zeolite should be virtually independent of that external electrolyte concentration. By using this assumption and also a mathematical model that facilitates the evaluation of activity coefficients in an aqueous solution containing any number of cation or anion, or both, species (Fletcher & Townsend 1981 *c*), exchange equilibria can be successfully predicted over a range of ionic strengths by using different co-ions (Townsend *et al.* 1984). Provided the temperature is kept constant, such predictions do not in fact require the evaluation of the activity coefficients for ions in the exchanger phase. Currently, further studies are therefore under way to examine if similar predictive procedures can be applied to multicomponent exchange equilibria.

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REFERENCES

Barrer, R. M. & Falconer, J. 1956 *Proc. R. Soc. Lond.* A **236**, 227–249.
Barrer, R. M. & Klinowski, J. 1972*a* *J. chem. Soc. Faraday Trans.* I **68**, 73–87.
Barrer, R. M. & Klinowski, J. 1972*b* *J. chem. Soc. Faraday Trans.* I **68**, 1956–1963.
Barrer, R. M. & Klinowski, J. 1974*a* *J. chem. Soc. Faraday Trans.* I **70**, 2080–2091.
Barrer, R. M. & Klinowski, J. 1974*b* *J. chem. Soc. Faraday Trans.* I **70**, 2362–2367.
Barrer, R. M. & Klinowski, J. 1975 *J. chem. Soc. Faraday Trans.* I **71**, 690–698.
Barrer, R. M. & Klinowski, J. 1977 *Phil. Trans. R. Soc. Lond.* A **285**, 637–676.
Barrer, R. M. & Klinowski, J. 1979*a* *J. chem. Soc. Faraday Trans.* I **75**, 247–251.
Barrer, R. M. & Klinowski, J. 1979*b* *Geochim. cosmochim. Acta* **43**, 755–766.
Barrer, R. M., Klinowski, J. & Sherry, H. S. 1973 *J. chem. Soc. Faraday Trans.* II **69**, 1669–1676.
Barrer, R. M. & Munday, B. M. 1971 *J. chem. Soc.* A, 2904.
Barrer, R. M., Rees, L. V. C. & Shamsuzzoha, M. 1966 *J. inorg. nucl. Chem.* **28**, 629–643.
Barrer, R. M. & Townsend, R. P. 1976 *J. chem. Soc. Faraday Trans.* I **72**, 661–673.
Barrer, R. M. & Townsend, R. P. 1978 *J. chem. Soc. Faraday Trans.* I **74**, 745–755.
Barrer, R. M. & Townsend, R. P. 1984 *J. chem. Soc. Faraday Trans.* II, **80**, 629–640.
Barri, S. A. I. & Rees, L. V. C. 1980 *J. Chromatogr.* **201**, 21–34.
Bychkova, V. A. & Soldatov, V. S. 1980 *Vest. Akad. Nauk. BSSR., Ser. Khim*, 1980, 35–40.
Chu, S. Y. & Sposito, G. 1981 *J. Soil Sci. Soc. Am.* **45**, 1084–1089.
Costenoble, M. L. & Maes, A. 1978 *J. chem. Soc. Faraday Trans.* I **74**, 131–135.
Elprince, A. M. & Babcock, K. L. 1975 *Soil Sci.* **120**, 332–338.
Elprince, A. M., Vanselow, A. P. & Sposito, G. 1980 *J. Soil Sci. Soc. Am.* **44**, 964–969.
Fletcher, P. & Townsend, R. P. 1980 *J. Chromatogr.* **201**, 93–105.
Fletcher, P. & Townsend, R. P. 1981*a* *J. chem. Soc. Faraday Trans.* II **77**, 955–963.
Fletcher, P. & Townsend, R. P. 1981*b* *J. chem. Soc. Faraday Trans.* II **77**, 965–980.
Fletcher, P. & Townsend, R. P. 1981*c* *J. chem. Soc. Faraday Trans.* II **77**, 2077–2089.
Fletcher, P. & Townsend, R. P. 1981*d* *J. chem. Soc. Faraday Trans.* I **77**, 497–509.
Fletcher, P. & Townsend, R. P. 1982 *J. chem. Soc. Faraday Trans.* I **78**, 1741–1753.
Fletcher, P. & Townsend, R. P. 1983 *J. chem. Soc. Faraday Trans.* II **79**, 419–432
Franklin, K. R. & Townsend, R. P. 1984 (Paper in preparation.)
Gaines, G. L. & Thomas, H. C. 1953 *J. chem. Phys.* **21**, 714–718.
Glueckauf, E. 1949 *Nature, Lond.* **163**, 414.
Golden, T. C. & Jenkins, R. G. 1981 *J. chem. Engng. Data* **26**, 366–367.
Goulding, K. W. T. & Talibudeen, O. 1980 *J. Colloid Interface Sci.* **78**, 15–24.
Guggenheim, E. A. 1935 *Phil. Mag.* **19**, 588–643.
Hardy, H. K. 1953 *Acta metall.* **1**, 202–208.
Katoaka, T. & Yoshida, H. 1980 *J. chem. Engng. Japan* **13**, 328–330.
Kol'nenkov, V. P. & Bogomolov, G. V. 1977 *Dokl. Akad. Nauk SSSR* **236**, 1144–1147.
Lai, P. P. & Rees, L. V. C. 1976*a* *J. chem. Soc. Faraday Trans.* I **72**, 1818–1826.
Lai, P. P. & Rees, L. V. C. 1976*b* *J. chem. Soc. Faraday Trans.* I **72**, 1827–1839.
Maes, A. & Cremers, A. 1975 *J. chem. Soc. Faraday Trans.* I **71**, 265–277.
Maes, A. & Cremers, A. 1977 *J. chem. Soc. Faraday Trans.* I **73**, 1807–1814.
Maier, W. M. 1961 *Z. Kristallogr. Kristallgeom.* **115**, 439–450.
McDaniel, C. V. & Maher, P. K. 1976 In *Zeolite chemistry and catalysis*, p. 283. A.C.S. Monograph vol. 171.
Mortier, W. J. 1982 In *Compilation of extra framework sites in zeolites*, p. 29. London: Butterworths.
Peigneur, P., Maes, A. & Cremers, A. 1975 *Clays Clay Miner.* **23**, 71.
Pitzer, K. S. 1973*a* *J. phys. Chem.* **77**, 268–277.
Pitzer, K. S. & Mayorga, G. 1973*b* *J. phys. Chem.* **77**, 2300–2308.
Rees, L. V. C. 1980 In *Properties and applications of zeolites* (ed. R. P. Townsend), p. 218. Chemical Society Spec. Publ. no. 33.

Robinson, R. A. & Stokes, R. H. 1959 *Electrolyte solutions*. London: Butterworths.

Sersale, R., Collela, C. & Aiello, R. (editors) 1981 *Recent Progress Reports and Discussion, 5th Int. Conf. Zeolites, Naples 1980*, p. 226.

Soldatov, V. S. & Bychkova, V. A. 1970 *Russ. J. phys. Chem.* **44**, 1297–1300.

Soldatov, V. S. & Bychkova, V. A. 1971 *Russ. J. phys. Chem.* **45**, 707–709.

Soldatov, V. S. & Bychkova, V. A. 1980 *Sep. Sci. Technol.* **15**, 89–110.

Sposito, G. 1981 In *Chemistry in the soil environment* (ed. M. Stelly), p. 13. Amer. Soc. Agron. Spec. Publ. no. 40.

Sposito, G. & Mattigod, S. N. 1979 *Clays Clay Miner.* **27**, 125–127.

Townsend, R. P., Fletcher, P. & Loizidou, M. 1984 Proc. 6th Int. Conf. Zeolites, Reno, Nevada, U.S.A. 1983. (In the press.)

Wiedenfeld, R. P. & Hossner, L. R. 1978 *J. Soil Sci. Soc. Am.* **42**, 709–712.

Wilson, G. M. 1964 *J. Am. chem. Soc.* **86**, 127.