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Thermodynamics of ion exchange in clays

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As an introduction, the general thermodynamic treatments for binary cation exchange are reviewed. The normal choice of standard states for the cations in the clay phase, and commonly used thermodynamic formulations with different scales of measurement are both discussed. The definition of standard states for the clay phase which is due to Gaines & Thomas (*J. chem. Phys.* **21**, 714 (1953)) is considered in most detail; the effect of water activity changes in the homo-ionic forms of the clay on the magnitude of the cation activity coefficients is considered. In the main part of the paper, three topics of current interest are considered. First, the current controversies regarding the appropriate choice of measurement scale for exchange reactions in clays are reviewed, together with the consequent implications that a particular choice of concentration scale have regarding the definition of ideal behaviour in the exchange phase. It is emphasized that thermodynamic formulations in terms of either the cationic mole fraction scale or the equivalent function scale are equally valid.

Second, some recent developments concerning the thermodynamics of ternary and multicomponent exchange are reviewed. The question as to whether multicomponent equilibria may be predicted from binary data alone is briefly discussed, and recent rigorous thermodynamic formulations of Chu & Sposito (*J. Soil Sci. Soc. Am.* (1981)) and Fletcher & Townsend (*J. chem. Soc. Faraday Trans.* II **77**, 955; 965; 2077 (1981)) are compared. These formulations, also based on different measurement scales, are shown to be compatible and complementary. Finally, the question of site heterogeneity in clays is considered briefly, and some current attempts to interpret non-ideal behaviour in the exchange reaction in terms of this phenomenon are discussed.

INTRODUCTION

The ubiquity of clays in the environment, and the consequent importance of understanding how their properties influence the overall properties of soils, has resulted in extensive studies of their equilibrium cation exchange properties, the earliest of which precede this century. Thus despite the overwhelming importance today of organic-based resins for ion exchange applications, the basic thermodynamic formulations of ion exchange which are used so widely today are based on precepts and principles which were enunciated long ago by researchers on inorganic exchange materials, especially clays. The names of Vanselow (1932), Gapon (1933), Kielland (1935) and Gaines & Thomas (1953) still appear widely in current ion exchange literature, irrespective of the nature of the exchanger under study.

This serves to emphasize a most important basic principle concerning thermodynamic studies and one which is frequently overlooked. This principle has been reiterated recently by Sposito (1981 *a*, *b*): because thermodynamics is concerned with the measurement of changes in certain physical quantities which describe the macroscopic system under study, it is not possible thence to speculate from these thermodynamic data regarding the fundamental nature of the microscopic mechanisms which underlie the observed behaviour. Thus any properly conceived thermodynamic formulation of ion exchange should be of general application to ion exchangers, irrespective of their chemical nature.

In what sense then can one consider the thermodynamics of ion exchange in clays in particular? First, experience may show that a particular choice either of reference states or of concentration scale is specially convenient for studies on clay minerals, even though there is nothing wrong with alternative choices, and even when these alternatives may be preferred for other types of ion exchangers. Second, although it is wrong to use thermodynamic data to infer mechanisms that occur on the microscopic scale within the exchanging phases, nevertheless the characteristic behaviour of different clays is manifested in the thermodynamic data obtained for cation exchange within these materials. A recognition of this characteristic behaviour enables one to appreciate the limits to which one can then predict exchange properties from a necessarily limited quantity of basic thermodynamic data.

This paper is concerned with recent developments in these areas, and specially with the questions of choice of standard reference states, definitions of ideal behaviour, multicomponent cation exchange properties and site heterogeneity within the exchanger.

1. Basic theoretical considerations

(a) *The thermodynamic equilibrium constant*

By considering first an exchange involving only two different types of cations, the basic reaction is

$$z_{\mathrm{v}}\mathrm{M}_{\mathrm{u}}^{z_{\mathrm{u}}+}+z_{\mathrm{u}}\overline{\mathrm{M}}_{\mathrm{v}}^{z_{\mathrm{v}}+}\rightleftharpoons z_{\mathrm{v}}\overline{\mathrm{M}}_{\mathrm{u}}^{z_{\mathrm{u}}+}+z_{\mathrm{u}}\mathrm{M}_{\mathrm{v}}^{z_{\mathrm{v}}+}, \qquad (1)$$

where $\mathrm{M}_{\mathrm{u}}^{z_{\mathrm{u}}+}$, $\mathrm{M}_{\mathrm{v}}^{z_{\mathrm{v}}+}$ are cations of valency z_{u}, z_{v} respectively. The superscripted bar refers to the exchanger phase. The thermodynamic equilibrium constant then follows:

$$K_a = (a_{\mathrm{v}}^{z_{\mathrm{u}}}/a_{\mathrm{u}}^{z_{\mathrm{v}}})\,(\bar{a}_{\mathrm{u}}^{z_{\mathrm{v}}}/\bar{a}_{\mathrm{v}}^{z_{\mathrm{u}}}), \qquad (2)$$

where $\bar{a}$ and a refer to the relative activities of the species in the clay and external solution respectively. The magnitude of K_a for a given pair of exchanging cations in a particular clay must then depend not only on the intrinsic properties of the system itself, but also on the choice of the reference states to which the relative activities $\bar{a}$, a refer. This (apparently) obvious point is overlooked frequently. Thus choosing, for example, similar criteria for ideal behaviour of the ions in *both* the exchanging phases leads to a standard free energy change of approximately zero for all exchanging pairs of cations (Helfferich 1962). Such a choice has not been favoured for studies on clays.

(b) *Non-ideality in the solution phase*

For the solution of electrolyte exterior to the clay exchanger, it has been normal practice in ion exchange studies to adopt the usual Henry law reference state to define ideal behaviour of the exchanging species, in which the relative activity of a species is regarded as becoming numerically equal to its concentration as its concentration tends to zero. The standard state is then the 'hypothetical ideal molal solution' of the appropriate species (Robinson & Stokes 1970), in which the ion is regarded as still behaving in the one molal solution (1 mol kg^{-1}) as it does when it is infinitely diluted with solvent. (If one prefers, one can of course use other concentration units such as mol dm^{-3}, provided the choice made is clearly specified.) To allow for non-ideality in the real solution, the activity coefficient γ is also introduced, so that for any solution concentration $a_{\mathrm{i}} = \gamma_{\mathrm{i}} m_{\mathrm{i}}/m_{\mathrm{i}}^{\ominus}$, where m_{i}, $m_{\mathrm{i}}^{\ominus}$ are the concentrations of species i in the real solution and the hypothetical ideal molal solution respectively. The relative activity ratio for the solution phase (equation (2)) then becomes

$$(a_{\mathrm{v}}^{z_{\mathrm{u}}}/a_{\mathrm{u}}^{z_{\mathrm{v}}}) = (\gamma_{\mathrm{v}} m_{\mathrm{v}}/m_{\mathrm{v}}^{\ominus})^{z_{\mathrm{u}}}/(\gamma_{\mathrm{u}} m_{\mathrm{u}}/m_{\mathrm{u}}^{\ominus})^{z_{\mathrm{v}}}, \tag{3}$$

and for any solution concentration and for one co-anion $\mathrm{A}^{z_{\overline{\mathrm{x}}}}$ (valency z_{x}) the activity coefficient ratio is (Robinson & Stokes 1970):

$$(\gamma_{\mathrm{v}}^{z_{\mathrm{u}}}/\gamma_{\mathrm{u}}^{z_{\mathrm{v}}}) = [(\gamma_{\pm\mathrm{v}}^{(\mathrm{u})})^{z_{\mathrm{u}}(z_{\mathrm{v}}+z_{\mathrm{x}})}/(\gamma_{\pm\mathrm{u}}^{(\mathrm{v})})^{z_{\mathrm{v}}(z_{\mathrm{u}}+z_{\mathrm{x}})}]^{1/z_{\mathrm{x}}}, \tag{4}$$

where $\gamma_{\pm\mathrm{vx}}^{(\mathrm{ux})}$, $\gamma_{\pm\mathrm{ux}}^{(\mathrm{vx})}$ are the mean activity coefficients of the salts $\mathrm{M_xA_v}$ and $\mathrm{M_xA_u}$ respectively in the *mixed electrolyte solution* at the experimental ionic strength (Dyer *et al.* 1981). For binary mixtures of two electrolytes with a common anion, the values of these functions may be found by using the model of Glueckauf (1949). Other model-dependent methods are available to determine these functions for multicomponent cation–anion systems (Fletcher & Townsend 1981*c*) or for solutions of high ionic strength (Pitzer 1973; Scatchard 1961).

(*c*) *Non-ideality in the clay exchanger*

For clays or soils, with very few exceptions (see, for example, Babcock & Duckart 1980) the normal practice has been to follow Gaines & Thomas (1953) and make the standard reference state for each exchanging cation within the clay the appropriate homo-ionic form of the clay in equilibrium with an infinitely dilute solution of the same cation, so that the thermodynamic equilibrium constant is then a measure of the relative affinity between the clay and the two cations involved in the exchange (Helfferich 1962; Bolt 1967).

Despite the near-universal use of these reference states as standards, two different measurement scales are employed commonly by different researchers to describe concentrations of cations within the clay phase. The first of these was adopted by Vanselow (1932) and Kielland (1935) and involves the mole fraction $\overline{\mathrm{X}}$ of ion in the exchange, so that for a binary exchange

$$\overline{\mathrm{X}}_{\mathrm{u}} = \overline{m}_{\mathrm{u}}/(\overline{m}_{\mathrm{u}}+\overline{m}_{\mathrm{v}}), \tag{5}$$

where $\overline{m}_{\mathrm{u}}$, $\overline{m}_{\mathrm{v}}$ are the concentrations of the respective ions in the clay. A more precise term for this function might be 'cationic mole fraction', as it should be noted that no account is taken in (5) of adsorbed or imbibed solvent (Barrer & Townsend 1984). In contrast, Gaines & Thomas employed the equivalent cation fraction $\bar{E}$ to describe cation concentrations in the clay. This is defined as

$$\bar{E}_{\mathrm{u}} = z_{\mathrm{u}}\overline{m}_{\mathrm{u}}/(z_{\mathrm{u}}\overline{m}_{\mathrm{u}}+z_{\mathrm{v}}\overline{m}_{\mathrm{v}}). \tag{6}$$

Again, a perhaps better name for $\bar{E}$ might be 'charge fraction', since the function is a measure of the proportion of the anionic charge on the clay which is neutralized by a given cation (and therefore of the mole fraction of clay associated with that cation).

In terms of cationic mole fractions, (2) becomes

$$K_a = (a_{\mathrm{v}}^{z_{\mathrm{u}}}/a_{\mathrm{u}}^{z_{\mathrm{v}}})\,(\overline{\mathrm{X}}_{\mathrm{u}}^{z_{\mathrm{v}}} f_{\mathrm{u}}^{z_{\mathrm{v}}}/\overline{\mathrm{X}}_{\mathrm{v}}^{z_{\mathrm{u}}} f_{\mathrm{v}}^{z_{\mathrm{u}}}) = K_{\mathrm{V}}(f_{\mathrm{u}}^{z_{\mathrm{v}}}/f_{\mathrm{v}}^{z_{\mathrm{u}}}), \tag{7}$$

where $f_{\mathrm{u}}, f_{\mathrm{v}}$ are the activity coefficients of cations $M_{\mathrm{u}}^{z_{\mathrm{u}}^+}$, $M_{\mathrm{v}}^{z_{\mathrm{v}}^+}$ in association with their equivalents of anionic exchanger framework and K_{V} is a corrected selectivity quotient, sometimes referred to as the Vanselow coefficient (Sposito 1977). Argersinger *et al.* (1950) were first to use the

Gibbs–Duhem equation to obtain expressions which enabled the functions f_u, f_v and K_a to be evaluated from appropriate experimental data for K_V, namely

$$\ln f_u^{z_v} = -\bar{E}_v \ln K_V^* + \int_{\bar{E}_u}^{1} \ln K_V \, d\bar{E}_u, \tag{8}$$

$$\ln f_v^{z_u} = \bar{E}_u \ln K_V^* - \int_{0}^{\bar{E}_u} \ln K_V \, d\bar{E}_u \tag{9}$$

and

$$\ln K_a = \int_0^1 \ln K_V \, d\bar{E}_u, \tag{10}$$

where the superscript $*$ refers to the value of K_V at a particular composition $\bar{E}_u$, $\bar{E}_v$. (Note that although K_V is defined in terms of $\bar{X}_u$, $\bar{X}_v$, (8)–(10) require a knowledge of this coefficient as a function of *charge* fraction $\bar{E}_u$ also.)

By using equivalent, or charge, fractions to define the concentrations of the cations in the clay, (2) becomes

$$K_a = (a_v^{z_u}/a_u^{z_v})\,(\bar{E}_u^{z_v} g_u^{z_v}/\bar{E}_v^{z_u} g_v^{z_u}) = K_G(g_u^{z_v}/g_v^{z_u}), \tag{11}$$

where g_u, g_v are the activity coefficients of cations $M_u^{z_u^+}$, $M_v^{z_v^+}$ in association with their equivalents of exchanger framework and K_G is another corrected selectivity coefficient. If $z_u \neq z_v$, then $K_V \neq K_G$ and f_u, f_v will also differ in magnitude from their corresponding g_u, g_v functions (except in the case of the common standard states).

If (in order to allow comparison with (8)–(10)), the effects of sorbed solvent(s) in the exchanger are neglected, then Gaines & Thomas (1953) showed that

$$\ln g_u^{z_v} = (z_v - z_u)\,\bar{E}_v - \bar{E}_v \ln K_G^* + \int_{\bar{E}_u}^{1} \ln K_G \, d\bar{E}_u, \tag{12}$$

$$\ln g_v^{z_u} = -(z_v - z_u)\,\bar{E}_u + \bar{E}_u \ln K_G^* - \int_{0}^{\bar{E}_u} \ln K_G \, d\bar{E}_u, \tag{13}$$

and

$$\ln K_a = (z_v - z_u) + \int_0^1 \ln K_G \, d\bar{E}_u. \tag{14}$$

Equations (8)–(10) are simpler than the alternative formulation of Gaines & Thomas, although the latter formulation has the compensating advantage of employing charge fractions only, rather than both $\bar{E}$ and $\bar{X}$.

(*d*) *Activity of sorbed solvent*

Gaines & Thomas's treatment is more comprehensive than that of Argersinger *et al.* (1950) in that it encompassed the effects of either sorbed or imbibed solvent, and of imbibed salts (Gaines & Thomas 1953). Both these factors may be significant in ion exchange studies at higher solution ionic strengths. It is here that it becomes especially important to specify that the homo-ionic forms of the clay be in equilibrium with an infinitely dilute solution of the same ion in the standard state. If the ionic strength of the electrolyte is not zero, then the activity coefficient g_u (or f_u) will *not* normally be unity even when the clay is in the homo-ionic $M_u^{z_u^+}$ form. Considering for example Gaines & Thomas's first case (Gaines & Thomas 1953), in which solvent only may be sorbed, then if $g_{\mathrm{u}(I_\mathrm{u})}$ is the activity coefficient of ion $M_\mathrm{u}^{z_\mathrm{u}+}$ in the homo-ionic M_u-exchanged clay at a solution ionic strength of I,

$$\ln\,(g_{\mathrm{u}(I_\mathrm{u})}/g_{\mathrm{u}(\infty)}) = z_\mathrm{u}\int_{a_{\mathrm{w}(\infty)}}^{a_{\mathrm{w}(I_\mathrm{u})}}\left[\frac{\bar{V}}{V}-\bar{v}_\mathrm{w}\right]\mathrm{d}\ln a_\mathrm{w}; \tag{15}$$

V is the molar volume of the sorbed solvent vapour, $\bar{V}$ and $\bar{v}_\mathrm{w}$ are (per exchange *equivalent*) the volume and water content of the clay, and $g_{\mathrm{u}(\infty)}$, $a_{\mathrm{w}(\infty)}$ are respectively the values of g_u and the water activity when the homo-ionic clay is immersed in an infinitely dilute solution of $M_\mathrm{u}^{z_\mathrm{u}+}$ ions (i.e. $g_{\mathrm{u}(\infty)} = a_{\mathrm{w}(\infty)} = 1$). When the bathing electrolyte solution is dilute, neglect of the correction shown in (15) is justified (Barrer & Klinowski 1974; Fletcher & Townsend 1981*b*; Sposito 1981*b*). For solutions of higher ionic strength, the deviation of $g_{\mathrm{u}(I_\mathrm{u})}$ from unity can be significant. Thus Fletcher & Townsend (1981*b*) found that at solution concentrations of 1 mol dm^{-3}, activity coefficients for the ions Na$^+$, K$^+$ and Li$^+$ in homo-ionic forms of zeolite A deviated by *ca.* 8% from unity at 298 K. At the same solution strength, the deviation for Ca^{2+} was more than 30%.

Even when the absolute magnitudes of the activity coefficients for the homo-ionic forms of the clay deviate significantly from unity, the overall effect on K_a may only be small, as the water activity terms tend to be self-cancelling. One may use the mean value theorem to effect the integrations, and assume that the volume per exchange equivalent of the clay is negligible compared with the molar volume of the vapour of the sorbed water. Then, providing the water vapour behaves as a perfect gas, the expression for K_a approximates to

$$\begin{aligned}\ln K_a = {} & (z_\mathrm{v}-z_\mathrm{u}) + z_\mathrm{u}\,z_\mathrm{v}\{\bar{v}_{\mathrm{w(b)}}\ln\,(p/p_0)_{\mathrm{(b)}} - \bar{v}_{\mathrm{w(a)}}\ln\,(p/p_0)_{\mathrm{(a)}} \\ & - \bar{v}_{\mathrm{w}(\overline{\mathrm{uv}})}\ln\,[(p/p_0)_{\mathrm{(b)}}/(p/p_0)_{\mathrm{(a)}}]\} + \int_0^1 \ln K_\mathrm{G}\,\mathrm{d}\bar{E}_\mathrm{u},\end{aligned} \tag{16}$$

where $\bar{v}_{\mathrm{w}(\overline{\mathrm{uv}})}$ is the mean water content of the mixed u, v clay exchanger, and (p/p_0) the relative pressure. Evaluations of the water terms have been carried out for binary exchanges in zeolites and resins by Barrer & Klinowski (1974) and similar ternary exchange studies have been undertaken by Fletcher & Townsend (1981*b*). The *total* effect of the water terms on the magnitude of K_a was never found to be significant, even though the individual activity coefficient values do change markedly. Since it is activity coefficient data rather than the standard free energies which are of importance when one is mathematically modelling changes in the selectivity of a system as a function of electrolyte concentrations (Townsend *et al.* 1984; Fletcher *et al.* 1984), the greater sensitivity of activity coefficient values to water activity changes must be borne in mind if one is working with concentrated electrolyte solutions.

2. USE OF DIFFERENT IONIC CONCENTRATION SCALES

(*a*) *Introduction*

Questions have been raised recently as to whether the equivalent fraction scale is indeed an appropriate choice for a rigorous thermodynamic formulation of ion exchange (Sposito & Mattigod 1979; Sposito 1981*b*). Sposito & Mattigod re-examined data obtained by Maes *et al.* (1975) for exchange equilibria involving different transition metals on montmorillonite. Maes *et al.* (1975) found that the function $\ln K_\mathrm{G}$ increased nearly linearly with the equivalent fraction of exchanging cation up to an exchange level of *ca.* 75%. Using cationic mole fractions rather than equivalent fractions, Sposito & Mattigod (1979) showed that within experimental uncertainty, plots of ln K_V against $\bar{E}_u$ for the same exchanges were near constant for $\bar{E}_u < 0.7$. They concluded therefore that 'ideality in a cation exchanger must be studied in terms of the Vanselow selectivity coefficient', and not K_G. As a direct result of these comments, Goulding (1983) has reinterpreted some earlier thermodynamic studies on clays (see, for example, Goulding & Talibudeen 1980) using the Vanselow coefficient K_V rather than the originally used K_G function.

There are two separate important issues that must be considered here. The first is whether there is anything *intrinsically* wrong with using K_G rather than K_V to describe the selectivity (and non-ideality) of the exchange process. Sposito implies that there is something intrinsically wrong when he states that the Gaines & Thomas activity coefficients g_u, g_v 'are only formal parameters without a strict thermodynamic meaning within themselves' (Sposito 1981*b*). The second issue is quite different: if both approaches are thermodynamically rigorous and compatible it may nevertheless be more *convenient* to use one measurement scale rather than the other for a particular type of exchanger (e.g. a clay).

(*b*) *Comparison of Vanselow with Gaines & Thomas approaches*

Considering first the question as to whether there is anything fundamentally wrong with the use of the equivalent fraction scale, and in particular whether the functions g_u, g_v are indeed activity coefficients rather than (*sic*) 'formal parameters' (Sposito 1981*b*) the standard free energy change per equivalent of exchange for the reaction in (1) is

$$\Delta G^{\ominus} = [(1/z_u)\,\bar{\mu}_u^{\ominus} + (1/z_v)\,\mu_v^{\ominus} - (1/z_u)\,\mu_u^{\ominus} - (1/z_v)\,\bar{\mu}_v^{\ominus}]. \tag{17}$$

Since the reference states for $\mu_u^{\ominus}$, $\mu_v^{\ominus}$ in the solution and for $\bar{\mu}_u^{\ominus}$, $\bar{\mu}_v^{\ominus}$ in the clay are the same irrespective of whether the Vanselow or Gaines & Thomas formulations are used, then the K_a value derived from each formulation *must* be the same for a given exchange system, as must the functions $\Delta G^{\ominus}$, $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$. However, Goulding (1983) derives an expression

$$\ln K_a' = \ln K_a'' + \int_0^1 f(\bar{E}_u)\,\mathrm{d}\bar{E}_u - (z_v - z_u), \tag{18}$$

where K_a', K_a'' are the values found for the thermodynamic constant K_a by using respectively the Vanselow and Gaines & Thomas approaches. Goulding next writes

$$\left.\begin{aligned} \ln K_a' &= \ln K_a'' + C_1, \\ \Delta G^{\ominus\prime} &= \Delta G^{\ominus\prime\prime} + C_2, \end{aligned}\right\} \tag{19}$$

and thence concludes that there is a constant difference between the standard thermodynamic functions K_a, $\Delta G^{\ominus}$ and $\Delta S^{\ominus}$ for a given exchange reaction when these functions are calculated using both the Vanselow and the Gaines & Thomas formulations. However, from (7) and (11)

$$K_V = K_G(z_v^{z_v}/z_u^{z_u})\,(z_u + (z_v - z_u)\,\bar{E}_u)^{(z_u - z_v)}, \tag{20}$$

so that the integral in (18) is

$$\int_0^1 f(\bar{E}_u)\,\mathrm{d}\bar{E}_u = \int_0^1 \ln\,(z_v^{z_v}/z_u^{z_u})\,\mathrm{d}\bar{E}_u + \int_0^1 (z_u - z_v)\,\ln\,[z_u + (z_v - z_u)\,\bar{E}_u]\,\mathrm{d}\bar{E}_u. \tag{21}$$

This function is in fact equal to $(z_v - z_u)$ (Barrer & Townsend 1984) which means that C_1 and C_2 in (19) are both zero, a conclusion that must follow from (17). Therefore the conclusions drawn by Goulding (1983) regarding K_a, $\Delta G^{\ominus}$ and $\Delta S^{\ominus}$ are erroneous. Regarding the activity coefficients g_u, g_v, these are indeed different from f_u, f_v in magnitude for a given clay composition $\bar{E}_u$, $\bar{E}_v$ (except, as again *must* follow, in the standard states when $f_{u(\infty)} = g_{u(\infty)} = 1$, etc.). However, the behaviour of g_u, g_v on the one hand and of f_u, f_v, on the other are entirely symmetric and complementary (Barrer & Townsend 1984) and there are therefore no grounds for stating that only f_u, f_v are 'true' (*sic*) activity coefficients (Sposito & Mattigod 1979). A detailed study of this matter is presented elsewhere (Barrer & Townsend 1984).

(*c*) *Definitions of ideal exchange behaviour in a clay*

The question as to whether one should use equivalent fractions rather than cationic mole fractions for thermodynamic studies is not therefore a fundamental one. The important point to remember is that when one chooses a particular concentration scale in a thermodynamic formulation, then usually one is setting up a criterion for ideal behaviour in terms of that scale. Thus using cationic mole fractions, the criterion for ideal behaviour is that the relative activity of cation i equals its cationic mole fraction for all values of $\bar{X}_i$. Similarly, for equivalent fractions the criterion is that $a_i = \bar{E}_i$ for all $\bar{E}_i$. For exchange levels of transition metal ion less than 70%, Sposito & Mattigod (1979) showed that if the cationic mole fraction scale is used, near-ideal behaviour is observed in Camp Berteau montmorillonite, whereas if equivalent fractions are used for these data, the dependence of K_G on $\bar{E}_u$ is monotonic (Maes *et al.* 1975). For exchange levels up to 70% therefore, use of $\bar{X}_u$ yields a simpler description of this system than does the use of $\bar{E}_u$. Generally, however, which of the two scales to use must be a matter of personal preference and convenience.

3. MULTICOMPONENT EXCHANGE REACTIONS

(*a*) *Introduction*

In recent years, the importance of developing adequate thermodynamic formulations for multicomponent exchange processes in clays, zeolites and resins has been recognized. Any detailed consideration of cation exchange processes in soils must involve multicomponent exchange studies, and in fact many apparently binary exchanges are in reality at least ternary. Thus (Talibudeen 1981) the well-known pH-dependent negative charge on clays (which arises from the ionization of surface hydroxyls as the pH is raised) not only leads to site heterogeneity in the exchanger, but also to participation in the exchange reaction of hydronium ions at higher pH values (Elprince *et al.* 1980). Another common cause for apparent binary exchanges being in actuality ternary has been demonstrated by some elegant studies on the Na–Cu, Na–Ca and Na–Mg exchange equilibria in Wyoming bentonite (Sposito *et al.* 1981; Sposito *et al.* 1983). Sposito *et al.* comment on the frequent observation that as a clay exchanged with alkali metal is saturated with a bivalent metal cation, both the cation exchange capacity and the selectivity of the clay for the bivalent cation increase (see, for example, Maes *et al.* 1975), and they demonstrate that these effects are due to the participation of metal complexes (e.g. $CuCl^+$) in the exchange reaction. This has of course the effect of converting what is apparently a binary (M^{2+}–Na^+) exchange into a ternary (M^{2+}–MCl^+–Na^+) one.

Attempts have been made, with varying degrees of success, to predict ternary or multicomponent exchange equilibria from experimental data obtained from the component binary exchanges using different model-based approaches (Elprince & Babcock 1975; Wiedenfeld &

Hossner 1978; Soldatov & Bychkova 1980; Barri & Rees 1980; Elprince *et al.* 1980; Chu & Sposito 1981; Fletcher *et al.* 1984). It now appears generally agreed that *a priori* prediction of multicomponent equilibria is not normally possible with binary data alone (Barri & Rees 1980; Chu & Sposito 1981; Fletcher *et al.* 1984). Direct measurements of multicomponent equilibrium compositions combined with a comprehensive and rigorous thermodynamic formulation (i.e. independent of any particular microscopic model for the system) is the best means of mathematically predicting the exchange behaviour of the clay, zeolite or resin over a range of experimental conditions.

(*b*) *Thermodynamic formulations of ternary ion exchange*

Systematic thermodynamic formulations for multicomponent ion exchange have been developed independently by three groups of workers. Soldatov & Bychkova (1980) developed theirs with resins particularly in mind; the model is considered elsewhere (Fletcher *et al.* 1984). The formulations of Fletcher & Townsend (1981 *a–c*) and Chu & Sposito (1981) complement each other in that the former uses the equivalent fraction scale, whereas the latter employs ionic mole fractions. Chu & Sposito (1981) develop their equations in terms of the three component binary reactions of the appropriate ternary exchange system; they obtain finally a general expression for the three binary thermodynamic equilibrium constants in terms of pseudo-binary Vanselow selectivity coefficients ${}^cK^T_{ij}$, where

$$K_{a,ij} = (a_j^{z_i}/a_i^{z_j})\,(\overline{\mathrm{X}}_i^{z_j} f_i^{z_j}/\overline{\mathrm{X}}_j^{z_i} f_j^{z_i}) = {}^cK^T_{ij}(f_i^{z_j}/f_j^{z_i}). \tag{22}$$

(Note that although ${}^cK^T_{ij}$ appears identical to K_{V} in (7) the similarity is deceptive. In (7) $\overline{\mathrm{X}}_{\mathrm{u}}+\overline{\mathrm{X}}_{\mathrm{v}} = 1$ whereas in (22) $\overline{\mathrm{X}}_i+\overline{\mathrm{X}}_j+\overline{\mathrm{X}}_k = 1$. Also f_i, f_j differ from $f_{\mathrm{u}}, f_{\mathrm{v}}$ in that they allow for the presence of other exchanging ions in addition to the *i*th and *j*th cations.) However, $\lim\limits_{(\overline{\mathrm{X}}_k\to 0)} {}^cK^T_{ij} = K_{\mathrm{V}}$). Considering then three different exchanging cations $\mathrm{M}_1^{z_1+}$, $\mathrm{M}_2^{z_2+}$ and $\mathrm{M}_3^{z_3+}$ in the clay, the general expression for the binary equilibrium constants is (Chu & Sposito 1981):

$$\ln K_{a,ij} = \underset{\text{(any path)}}{\int_{\bar{E}_i=1,\bar{E}_j=0,\bar{E}_k=0}^{0,1,0}} \left[\ln\,({}^cK^T_{ij})\,\mathrm{d}\bar{E}_j - \frac{z_j}{z_i}\ln\,({}^cK^T_{ki})\right]\mathrm{d}\bar{E}_k \tag{23}$$

for the cyclic permutations

$$\begin{bmatrix} i \\ j \\ k \end{bmatrix} \equiv \begin{bmatrix} 1, & 2, & 3 \\ 2, & 3, & 1 \\ 3, & 1, & 2 \end{bmatrix}.$$

The second term in the square brackets requires comment. At first examination, since the integration is effected with respect to $\bar{E}_k$ and the limits of the integration are $\bar{E}_k = 0$ to $\bar{E}_k = 0$, it seems that this function is zero. This is not correct, however, since by definition

$$\bar{E}_i+\bar{E}_j+\bar{E}_k = 1, \quad \mathrm{d}\bar{E}_k = -\mathrm{d}\bar{E}_i-\mathrm{d}\bar{E}_j, \tag{24}$$

and therefore

$$\underset{\text{(any path)}}{\int_{1,0,0}^{0,1,0}} \ln\,({}^cK^T_{ki})\,\mathrm{d}\bar{E}_k = -\underset{\text{(any path)}}{\int_{1,0,0}^{0,1,0}} \ln\,({}^cK^T_{ki})\,\mathrm{d}\bar{E}_i - \underset{\text{(any path)}}{\int_{1,0,0}^{0,1,0}} \ln\,({}^cK^T_{ki})\,\mathrm{d}\bar{E}_j. \tag{25}$$

It is axiomatic that the evaluation of the function $K_{a,ij}$ in (23) be independent of the path of integration; with a limited quantity of data for the ternary system a numerical integration may be effected across the ${}^{c}K_{ij}^{T}$ and ${}^{c}K_{ki}^{T}$ surfaces between the appropriate limits. Figure 1 shows diagrammatically the numerical evaluation of the first integral in (23) with only a limited quantity of experimental data. Evaluation of the second integral in (22) involves excursions from the edge of the ${}^{c}K_{ki}^{T}$ surface (at which $\bar{E}_k = 0$ for all $\bar{E}_i$, $\bar{E}_j$) to values of $\bar{E}_i$, $\bar{E}_j$ for which experimental data for ${}^{c}K_{ki}^{T}$ are available.

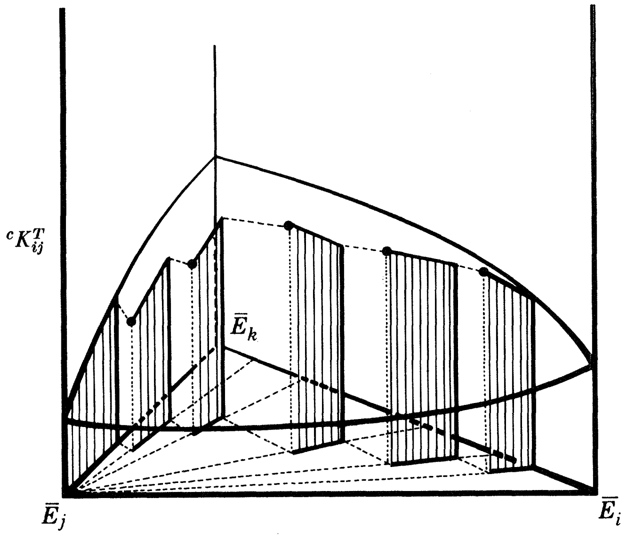

FIGURE 1. Diagrammatic representation of an evaluation by numerical integration of the first term in (23). The ternary composition of the system is depicted in triangular coordinates at the base of the perspective diagram, with the composition $\bar{E}_k = 1$ the vertex at the rear of the diagram. In the vertical direction are plotted values of ${}^{c}K_{ij}^{T}$ as a function of the ternary composition. The shaded areas give the value of the integral by one path across this ${}^{c}K_{ij}^{T}$ surface from $\bar{E}_i = 1$ to $\bar{E}_j = 1$.

The thermodynamic formulation of Fletcher & Townsend (1981*a–c*) takes into account also the water activity in the exchanger, although (see §2) in agreement with earlier studies on binary systems (Barrer & Klinowski 1974), the water activity corrections are not normally significant at low electrolyte concentrations in the external solution (Fletcher & Townsend 1981*b*). The general derivation begins from an opposite viewpoint to that of Chu & Sposito (1981), by directly defining ternary reaction equations and corresponding ternary equilibrium constants. Thus for three different exchanging cations $M_1^{z_1+}$, $M_2^{z_2+}$ and $M_3^{z_3+}$ the ternary exchange reactions are

$$2z_j z_k M_i^{z_i+} + z_i z_k \overline{M}_j^{z_j+} + z_i z_j \overline{M}_k^{z_k+} \rightleftharpoons 2z_j z_k \overline{M}_i^{z_i+} + z_i z_k M_j^{z_j+} + z_i z_j M_k^{z_k+}, \tag{26}$$

for the cyclic permutations

$$\begin{bmatrix} i \\ j \\ k \end{bmatrix} \equiv \begin{bmatrix} 1, & 2, & 3 \\ 2, & 3, & 1 \\ 3, & 1, & 2 \end{bmatrix}.$$

The general expression for the corresponding thermodynamic equilibrium constants is then

$${}^{\;i}_{j,k}K_a = (a_j^{z_i z_k} a_k^{z_i z_j} / a_i^{2z_j z_k})\ (\bar{E}_i \phi_i)^{2z_j z_k} / (\bar{E}_j \phi_j)^{z_i z_k} (\bar{E}_k \phi_k)^{z_i z_j}), \tag{27}$$

where ϕ_i, ϕ_j, ϕ_k are activity coefficients for the cations $M_i^{z_i+}$, etc. in the clay. Although the integration of the appropriate form of the Gibbs–Duhem equation between the prescribed limits can be by any path, Fletcher & Townsend (1981*b*) chose to specify particular paths, always in terms of two of the equivalent fractions only, namely $\bar{E}_1$ and $\bar{E}_2$. This simplifies the final equations, and therefore also the evaluation of both the K_a and ϕ values. The general expression for the thermodynamic equilibrium constant is

$$\ln ({}^{i}_{j,k}K_a) = z_j(z_k - z_i) + z_k(z_j - z_i) + \int_0^1 I_1 \ln k_{3/1} \, \mathrm{d}\bar{E}_1 + \int_0^1 I_2 \ln k_{3/2} \, \mathrm{d}\bar{E}_2, \qquad (28)$$

for the permutations

$$\begin{bmatrix} i \\ j \\ k \\ I_1 \\ I_2 \end{bmatrix} \equiv \begin{bmatrix} 1, & 2, & 3 \\ 2, & 3, & 1 \\ 3, & 1, & 2 \\ -2, & 1, & 1 \\ 1, & -2, & 1 \end{bmatrix}$$

and the activity coefficients are respectively

$$\ln \phi_1^{z_2 z_3} = \int_1^{\bar{E}_1} \ln \chi_{3/1} \, \mathrm{d}\bar{E}_1 + \int_0^{\bar{E}_2} \ln \chi_{3/2} \, \mathrm{d}\bar{E}_2 \qquad (29)$$

$$\ln \phi_2^{z_1 z_3} = \int_0^{\bar{E}_1} \ln \chi_{3/1} \, \mathrm{d}\bar{E}_1 + \int_1^{\bar{E}_2} \ln \chi_{3/2} \, \mathrm{d}\bar{E}_2 \qquad (30)$$

$$\ln \phi_3^{z_1 z_2} = \int_0^{\bar{E}_1} \ln \chi_{3/1} \, \mathrm{d}\bar{E}_1 + \int_0^{\bar{E}_2} \ln \chi_{3/2} \, \mathrm{d}\bar{E}_2 \qquad (31)$$

where

$$\left. \begin{aligned} k_{3/1} &= \bar{E}_3 a_1 / \bar{E}_1 a_3, \\ k_{3/2} &= \bar{E}_3 a_2 / \bar{E}_2 a_3, \end{aligned} \right\} \qquad (32)$$

$$\left. \begin{aligned} \chi_{3/1} &= (k_{3/1}/k^*_{3/1}) \exp\,[-z_2(z_3 - z_1)], \\ \chi_{3/2} &= (k_{3/2}/k^*_{3/2}) \exp\,[-z_1(z_3 - z_2)]; \end{aligned} \right\} \qquad (33)$$

$k^*_{3/1}$ and $k^*_{3/2}$ are the values of $k_{3/1}$, $k_{3/2}$ at the composition for which values of ϕ_1, ϕ_2 and ϕ_3 are required. Provided sufficient accurate experimental data on the ternary exchange equilibrium are available, it is comparatively easy to evaluate ϕ_1, ϕ_2 and ϕ_3 from (29)–(31). The dependence of $\ln \chi_{3/1}$ and of $\ln \chi_{3/2}$ on $\bar{E}_1$, $\bar{E}_2$ are expressed as polynomials:

$$\left. \begin{aligned} \ln \chi_{3/1} &= \sum_{a=0}^{e} \alpha_a (\bar{E}_1)^a + \sum_{b=1}^{f} \beta_b (\bar{E}_2)^b, \\ \ln \chi_{3/2} &= \sum_{c=0}^{g} \gamma_c (\bar{E}_1)^c + \sum_{d=1}^{h} \delta_d (\bar{E}_2)^d), \end{aligned} \right\} \qquad (34)$$

where α_a, β_b, γ_c, δ_d are appropriate coefficients of $\bar{E}_1$, $\bar{E}_2$. Then on taking (29) as an example,

$$\ln \phi_1^{z_2 z_3} = \sum_{a=0}^{e} \frac{\alpha_a}{a+1} (\bar{E}_1)^{(a+1)} + \sum_{b=1}^{f} \beta_b \bar{E}_1 (\bar{E}_2)^b + \sum_{c=0}^{g} \gamma_c \bar{E}_2 (\bar{E}_1)^c + \sum_{d=1}^{h} \frac{\delta_d}{d+1} (\bar{E}_2)^{(d+1)}. \qquad (35)$$

The integration procedures corresponding to (35) are shown in figure 2. Further details of these procedures, and examples of experimentally determined ϕ data, are given elsewhere (Fletcher *et al.* 1984; Franklin & Townsend 1984).

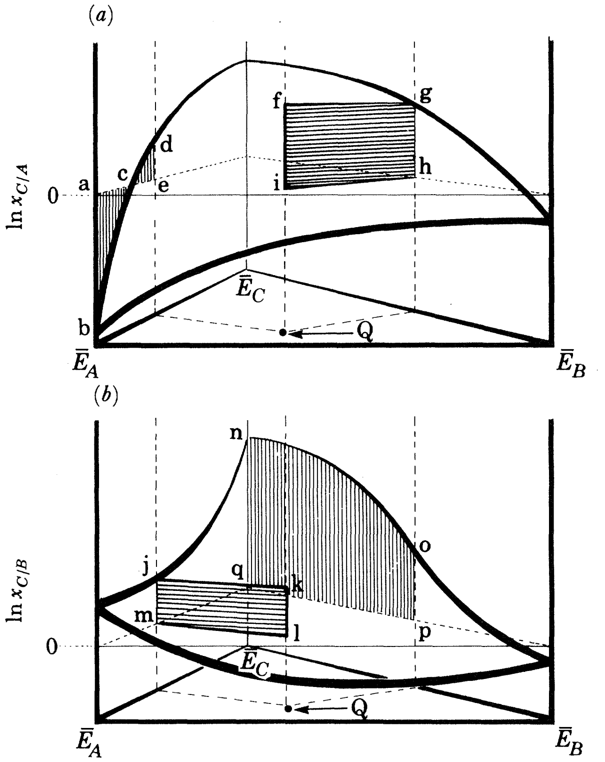

FIGURE 2. Representations with perspective diagrams of the integration procedures required to evaluate $z_2 z_3 \ln \phi_1$ at a composition Q by using (29) and (33). Figure 2*a* corresponds to the first integral in (29), or the first two summation terms in (35). Figure 2*b* corresponds to the second integral in (29) or the last two summations in (35). The value of $z_2 z_3 \ln \phi_1$ at the composition Q is seen to be equal to area [(cde) − (abc) + (fghi) + (jklm) + (nopq)].

(*c*) *Compatibility of different thermodynamic formulations for ternary ion exchange*

Thermodynamic rigour requires that the treatments of Chu & Sposito (1981) and Fletcher & Townsend (1981*a–c*) be fully compatible. The use of different concentration scales, and the choice of different integration paths makes a comprehensive proof of compatibility somewhat involved. However, for the case of exchanges involving univalent ions only $\bar{E}_i = \bar{X}_i$, etc., and if $\mathrm{M}_i = \mathrm{M}_1$, $\mathrm{M}_j = \mathrm{M}_2$, $\mathrm{M}_k = \mathrm{M}_3$ then (23) becomes

$$\ln K_{a,12} = \int_{\substack{\bar{E}_1=1,\,\bar{E}_2=0,\,\bar{E}_3=0\\ \text{(any path)}}}^{0,\,1,\,0} [\ln ({}^{c}K^{T}_{12})\, \mathrm{d}\bar{E}_2 - \ln ({}^{c}K^{T}_{31})\, \mathrm{d}\bar{E}_3]. \tag{36}$$

Applying the thermodynamic closure rule (Chu & Sposito 1981) together with (24) gives

$$\ln K_{23} + \ln K_{31} = \int_{\bar{E}_1=1,\,\bar{E}_2=0,\,\bar{E}_3=0}^{0,\,1,\,0} [\ln ({}^{c}K^{T}_{23})\, \mathrm{d}\bar{E}_2 - \ln ({}^{c}K^{T}_{31})\, \mathrm{d}\bar{E}_1]. \tag{37}$$

Also, from (22) and (27)

$$\tfrac{1}{3} \ln \{{}^{1}_{2,3}K_a / {}^{2}_{3,1}K_a\} = \ln K_{23} + \ln K_{31} \tag{38}$$

and from (28)

$$\tfrac{1}{3} \ln \{{}^{1}_{2,3}K_a / {}^{2}_{3,1}K_a\} = \int_0^1 \ln k_{3/2}\, \mathrm{d}\bar{E}_2 - \int_0^1 \ln k_{3/1}\, \mathrm{d}\bar{E}_1 \tag{39}$$

A comparison of (37), (38) and (39) shows that the right side of (37) and (39) should be the same if the treatments are compatible. From the definitions in (22) and (32)

$$\left.\begin{aligned} k_{\mathbf{3/1}} &= \bar{E}_3 a_1/\bar{E}_1 a_3 = {}^cK^T_{13} = ({}^cK^T_{31})^{-1}, \\ k_{\mathbf{3/2}} &= \bar{E}_3 a_2/\bar{E}_2 a_3 = {}^cK^T_{23}, \end{aligned}\right\} \tag{40}$$

and (37) and (39) are seen to be identical. The complicated relations between $\bar{X}_{i,j,k}$ and $\bar{E}_{i,j,k}$ when $z_i \neq z_j \neq z_k$ make proof of compatibility much more involved in these cases.

Two thermodynamically rigorous and mutually compatible procedures for determining thermodynamic functions are therefore available for ternary exchange studies in clays. These two formulations correspond in choice of scales of measurement with the Vanselow and Gaines & Thomas treatments for binary cation exchange.

4. SITE HETEROGENEITY IN CLAYS

(*a*) *Introduction*

Site heterogeneity in exchangers is a well-known phenomenon, which occurs not only in clays but also in resins (Soldatov & Bychkova 1971) and in zeolites (Barrer & Klinowski 1977, 1979; Fletcher *et al.* 1984). The nature of site heterogeneity in clays is, however, different from that found in the other most common forms of inorganic cation exchanger, the zeolites. In zeolites, the site heterogeneity arises because the exchanger normally contains several crystallographically distinct yet intimately mixed sets of sub-lattices for cations, the sites on which are at least partly occupied by exchange ions. In clays the heterogeneous cation sites are not necessarily intimately mixed. Thus in addition to those cation sites that are randomly spaced throughout the expansible interlayer spaces (Talibudeen 1981) and that are an *intrinsic* property of the clay, a significant quantity of sites (the number dependent on average particle size) may arise from faults, dislocations and exposed edges within the crystallites (Talibudeen 1981; Brouwer *et al.* 1983). pH-dependent site heterogeneity may be present also (Talibudeen 1981; Elprince *et al.* 1980).

(*b*) *Site heterogeneity and thermodynamic functions*

Site heterogeneity in an exchanger, if present, is indeed likely to manifest itself in the variation with the exchange composition of functions such as the differential enthalpy and entropy of exchange, or in the variation with composition of the corrected selectivity coefficient and associated activity coefficients. However, as emphasized in the introduction section, to reverse this 'cause and effect' phenomenon, and instead use thermodynamic measurements alone to infer details of a particular heterogeneous site model for the exchanger, is a highly questionable procedure. If other independent experimental measurements that provide information on the structure and site heterogeneity within the clay are also applied to the material (e.g. X-ray, electron microscopy, neutron diffraction, magic angle spinning n.m.r.), only then is it strictly permissible to interpret thermodynamic data in terms of site heterogeneity.

Site heterogeneity is undoubtedly responsible for the very complicated dependence on exchange composition that is often seen for activity coefficients and corrected selectivity coefficients, and is likely to be one reason why it is difficult to predict multicomponent equilibrium compositions from binary data alone. Failures of the 'sub-regular' model of Hardy

(1953) when it is applied to binary and ternary cation exchanges were attributed to site heterogeneity by Elprince *et al.* (1980) and Fletcher *et al.* (1984). The former case is an example where site heterogeneity appears to have arisen from the pH-dependent contribution to the cation exchange capacity of the clay. The authors emphasize rightly that while this is the likely cause for the failure 'the sub-regular model, being thermodynamic, neither assumes nor yields any information about the mechanism of cation exchange', and therefore 'the reasons for the failure of the model ... cannot be established precisely' (Elprince *et al.* 1980).

Sharp and large changes with composition in the corrected selectivity coefficient have also been interpreted in terms of site heterogeneity. Thus observed changes in K_G for a series of different exchanges in illite clay have been interpreted in terms of exchange into three kinds of sites within the clay (Brouwer *et al.* 1983). Earlier studies had indicated the presence of these three sets of sites (Bolt *et al.* 1963). In another recent study, Goulding & Talibudeen (1980) have shown that site heterogeneity can be used to characterize soils and clays and even to distinguish between materials having the same generic name. These characterizations are drawn from the behaviour with exchange composition of the differential enthalpy and entropy functions.

Concluding remarks

Thermodynamic formulations of ion exchange that are in current use today for all manner of ion exchange materials owe much to early studies on clays. The Gaines & Thomas (1953) convention for thermodynamic reference states in the exchanger phase has been almost universally adopted for thermodynamic studies on clays, yet two alternative scales of measurement for cation concentrations in the exchange are in common use. Despite recent criticism of the equivalent fraction scale, thermodynamic formulations based on either this or on the cationic mole fraction scale are equally acceptable and mutually compatible; the question of which scale to adopt is one of personal preference.

Recently, thermodynamic formulations have been developed independently by different workers to describe ternary or multicomponent exchanges. These treatments enable the direct measurement of activity coefficients for multicomponent cation systems within clays, and also the prediction of selectivity behaviour over a range of conditions. The different formulations are based on the same two scales of measurement which have been used for binary exchanges, and as in the binary case, the two treatments are both thermodynamically rigorous and mutually compatible. Direct measurement of activity coefficients for ternary systems is now possible, and is necessary owing to the failure of attempts to predict the values of these functions from binary data alone. A major cause of this failure must be due to the presence of site heterogeneity within clay exchangers, even though the nature and the degree of this heterogeneity is different to that found in zeolites and resins.

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