

# Ca-K-H Exchange on Silt-, Clay- and Silt + Clay-size Soil Separates

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Two approaches to predicting selectivity coefficients for heterogeneous ion-exchanger mixtures have been tested for a ternary ion-exchange system: weighted arithmetic mean and weighted geometric mean. If changes in mixture-component selectivity coefficients were estimated, following either approach yielded accurate selectivity coefficient predictions. The weighted geometric mean approach is far easier to apply when modelling multi-component ion-exchange systems.

Ion-exchange reactions often affect, and sometimes dominate, the ionic chemical equilibria of natural aquatic systems. To model ion-exchange equilibria in these systems, the appropriate ion-exchange selectivity coefficients must be determined. Unfortunately, selectivity coefficients of natural ion exchangers, for example soils, aquatic sediments and aquifer materials, vary greatly in the environment. These differences in selectivity coefficients are often attributable to differences in their composition.

Natural ion-exchangers have two types of reactive heterogeneity, which can be termed compositional and structural. *Compositional heterogeneity* arises from the fact that natural ion-exchangers are heterogeneous mixtures of distinct, and in principle, separable, materials. Several distinct minerals and organic materials can be distinguished typically in many natural ion-exchangers. If these were separated physically, each would have its own measurable selectivity coefficient and exchange equilibrium constant. On the other hand, *structural heterogeneity* arises from the fact that pure mineral or organic materials have several identifiable surface functional groups. Each of these surface functional groups has a different affinity for ions in solution, but they cannot be separated physically for chemical evaluation. Talibudeen and Goulding,<sup>1,2</sup> for example, identified six types of ion-exchange reactive sites each in smectite and kaolinite clays.

To predict accurately chemical equilibria of a natural ion-exchanger, one is forced to measure its ion-exchange properties, often a time-consuming task. If reliable formulae could be developed which relate the exchange properties of a heterogeneous mixture to those of its components, the work involved in predicting accurately chemical equilibria for natural ion-exchangers would be reduced substantially. Because properties of individual components can be measured unambiguously, chemical thermodynamics techniques can be applied directly to the problems of compositional heterogeneity. Because the individual surface-functional groups cannot be isolated, it can be assumed, though never demonstrated, that formulae developed from experiments investigating compositional heterogeneity can be applied to problems of structural heterogeneity. We report here an ion-exchange study of compositional heterogeneity. It is hoped that conclusions made here are valid also for problems of structural heterogeneity.

Two general approaches to predicting the chemical properties of ion-exchanger mixtures, both due to Barrer and his co-workers,<sup>3,4</sup> were investigated. For simplicity, these approaches were designated weighted arithmetic mean and weighted geometric mean. The *weighted arithmetic mean* states that, for an ion-exchanger mixture, the equivalent frac-

tion of exchangeable ion A is

$$E_A^m = \sum_{i=1}^n \phi_i E_A^i \quad (1)$$

Eqn. (1) is not hypothetical, but an algebraic identity coming directly from the partitioning of exchangeable ions between ion-exchanger components in a mixture. Any errors that may arise from using eqn. (1) would occur because the individual  $\phi_i$  or  $E_A^i$  values were not determined accurately.

The *weighted geometric mean* comes from an ion-exchanger mixture's standard reaction Gibbs energy

$$\Delta_r \bar{G}_{A/B}^{\ominus; m} = \sum_{i=1}^n \phi_i \Delta_r \bar{G}_{A/B}^{\ominus; i} \quad (2)$$

For both the Vanselow and Gapon selectivity coefficients,<sup>5,6</sup> a component's corrected selectivity coefficient ( $k_{A/B}^{a; i}$ ) is approximately equal to the corresponding exchange equilibrium constant ( $K_{A/B}^{ex; i}$ )

$$\ln k_{A/B}^{a; i} \approx \ln K_{A/B}^{ex; i} \equiv -\frac{\Delta_r \bar{G}_{A/B}^{\ominus; i}}{RT} \quad (3)$$

The approximate relation for the Gaines-Thomas selectivity coefficient<sup>7</sup> is

$$\ln k_{(GT)A/B}^{a; i} \approx (z_B - z_A) + \ln K_{(GT)A/B}^{ex; i} \quad (4)$$

The weighted geometric mean for all three corrected selectivity coefficients may be defined by

$$k_{A/B}^{a; m} \approx \prod_{i=1}^n (k_{A/B}^{a; i})^{\phi_i} \quad (5)$$

We compared selectivity coefficient predictions made with eqn. (1) and (5) for ternary, heterovalent cation-exchange reactions on a binary cation-exchanger mixture of silt- and clay-size soil separates.

## Experimental

Particle-size separates of a Nordya sandy loam (a typical Rhodoxeralf<sup>8</sup>) surface horizon were studied. By X-ray diffraction analysis, the approximate mineralogy of the clay-size fraction was found to be: 43% kaolinite, 5% chloritized vermiculite, 10% mica, 51% complex randomly interstratified 2:1 mineral with a large smectite component, and traces of quartz and calcite. The soil was ground to pass through a no. 20 sieve (0.85 mm opening). The soil was tested for the presence of carbonates and gypsum;<sup>9</sup> gypsum was not found. Carbonates were removed by repeated washing with 0.5 mol dm<sup>-3</sup> sodium acetate adjusted to pH 5. The sodium acetate supernatant solution was screened to remove floating organic debris from the suspension. After effervescence of the suspension ceased, the suspension was equilibrated five times with 0.02 mol dm<sup>-3</sup> NaClO<sub>4</sub> solutions. Sand-size minerals were

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separated from finer soil separates by repeated gravitational separation in a beaker. The remaining silt + clay-size separate was divided into two samples; one was set aside, the other was further separated into silt- and clay-size separates by centrifugation. (The separates were found to have the following organic C contents:<sup>10</sup> clay-size separate, 1.4%; silt-size separate, 4.7% and silt + clay-size separate, 1.7%.) Each of the three separates was then divided into two portions; each was washed five times with CaCl<sub>2</sub> or KCl solutions having Cl concentrations of 1.0 mol dm<sup>-3</sup>. The soil separates were washed initially with chloride, rather than perchlorate, salts to reduce costs. The separates were then washed five times with Ca(ClO<sub>4</sub>)<sub>2</sub> or KClO<sub>4</sub> solutions with ClO<sub>4</sub> molalities of 0.02 mol kg<sup>-1</sup>. Varying amounts of the Ca- and K-saturated soil-separate suspensions were mixed with Ca(ClO<sub>4</sub>)<sub>2</sub> and KClO<sub>4</sub> solutions with ClO<sub>4</sub> molalities of 0.02 mol kg<sup>-1</sup> to yield suspensions of ca. 40 cm<sup>3</sup> volume and ca. 1 g colloid in tared, 50 cm<sup>3</sup> Pyrex centrifuge tubes. The respective proportions of each suspension and each electrolyte solution which were combined were calculated beforehand with the intention of yielding cation-exchange equilibria at evenly spaced increments of exchangeable Ca or K mole fractions. The centrifuge tubes were then stoppered and equilibrated statically for 7 days at 25 °C. The pH of the supernatant solution was measured and the supernatant solution was then drawn off with a siphon. The tubes were weighed, dried in an oven at 104 °C until a stable weight was achieved, allowed to cool over CaSO<sub>4</sub>, then weighed again. The soil separate in the tube was washed eight times with 30 cm<sup>3</sup> 1.0 mol dm<sup>-3</sup> ammonium acetate solution adjusted to pH 7. Ca and K were determined in the equilibrating and extractant solutions by atomic absorption spectrometry. The mass of the salts in the entrained solution was estimated from the concentrations of the cations in the equilibrating solutions.

### Results and Discussion

Table 1 presents the equilibrating solution pH and Ca and K concentrations and exchangeable Ca and K contents for the clay-, silt- and silt + clay-size separates. Fig. 1 shows the change with exchangeable-cation composition in the charge borne by the exchangeable Ca and K. It was assumed that the c.e.c. of the material was equal to the maximum measured charge of exchangeable Ca and K. These values were estimated to be: clay, 1.011 mol (K<sup>+</sup> + 2Ca<sup>2+</sup>) kg<sup>-1</sup>; silt, 0.1998 mol (K<sup>+</sup> + 2Ca<sup>2+</sup>) kg<sup>-1</sup>; silt + clay, 0.672 mol (K<sup>+</sup> + 2Ca<sup>2+</sup>) kg<sup>-1</sup>. Based on these values, the c.e.c. of the silt + clay separate was estimated to be partitioned according to  $\phi_{\text{clay}} = 0.58$  and  $\phi_{\text{silt}} = 0.42$ . An estimate was made of the 'non-exchangeable' K in clay- and silt-size separate residues following the cation-exchange experiment. The residues were

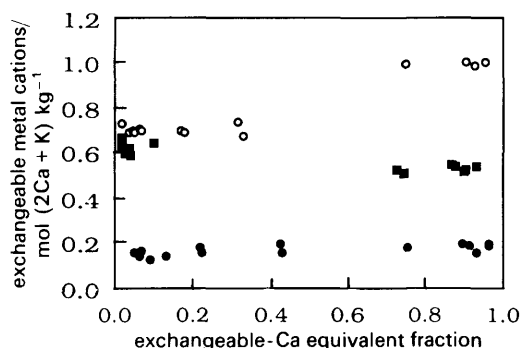


Fig. 1 Change in total charge of exchangeable metal-cations with exchangeable-Ca equivalent fraction of silt- (●), clay- (○), and silt + clay-size (■) soil separates

Table 1 Equilibrating-solution composition and corresponding exchangeable metal-cation concentrations on carbonate-free clay-, silt-, and silt + clay separates of a Nordya sandy surface horizon

pH	molality/mmol kg <sup>-1</sup>		specific surface excess/mol kg <sup>-1</sup>	
	aqueous Ca	aqueous K	Ca	K
clay-size soil separate				
7.72	5.508	9.187	0.373 63	0.249 95
7.70	8.623	3.060	0.455 09	0.095 52
7.99	9.169	2.099	0.458 00	0.070 27
7.82	9.477	1.043	0.478 24	0.046 87
7.71	9.476	1.010	0.478 59	0.047 37
6.72	0.025	22.123	0.006 38	0.714 80
6.47	0.027	21.641	0.013 06	0.667 13
6.41	0.053	21.939	0.016 69	0.657 65
6.60	0.041	21.518	0.016 52	0.668 71
6.16	0.072	21.369	0.023 44	0.648 73
6.20	0.068	21.379	0.023 24	0.661 75
6.01	0.971	20.652	0.059 28	0.581 88
6.29	0.976	20.766	0.060 91	0.570 64
5.84	3.260	17.687	0.110 46	0.453 06
6.10	3.283	17.776	0.116 15	0.505 18
silt-size soil separate				
<sup>a</sup>	4.389	11.166	0.068 42	0.045 14
<sup>a</sup>	7.620	3.836	0.087 54	0.016 88
<sup>a</sup>	7.671	3.761	0.088 54	0.020 47
<sup>a</sup>	8.341	2.569	0.074 33	0.010 79
<sup>a</sup>	8.949	1.310	0.095 51	0.007 14
<sup>a</sup>	8.877	1.348	0.090 48	0.006 56
<sup>a</sup>	0.017	19.521	0.003 94	0.145 29
<sup>a</sup>	0.017	18.431	0.003 99	0.149 41
<sup>a</sup>	0.031	18.856	0.005 66	0.151 42
<sup>a</sup>	0.028	19.225	0.004 62	0.131 06
<sup>a</sup>	0.037	18.058	0.005 81	0.113 05
5.90	0.172	22.584	0.009 49	0.124 64
6.18	0.136	19.202	0.017 51	0.121 93
6.18	0.133	19.155	0.020 01	0.141 63
5.22	0.716	16.889	0.032 95	0.088 38
5.13	0.787	16.561	0.041 12	0.111 89
silt + clay-size soil separate				
5.49	5.570	9.526	0.191 42	0.144 78
5.74	5.644	9.707	0.188 44	0.130 61
5.49	8.263	4.107	0.238 29	0.066 34
5.46	8.402	3.978	0.238 17	0.072 47
5.49	8.675	2.996	0.232 23	0.051 68
5.77	8.809	2.892	0.238 95	0.050 71
5.78	9.353	1.819	0.250 55	0.037 77
6.66	0.006	21.940	0.005 79	0.657 02
6.68	0.003	21.725	0.005 75	0.617 36
6.57	0.004	21.570	0.007 96	0.602 00
6.62	0.006	22.321	0.008 70	0.575 52
6.13	0.009	22.008	0.011 68	0.593 46
6.50	0.010	21.847	0.011 54	0.562 10
6.59	0.135	31.668	0.032 01	0.595 56
6.52	0.113	21.454	0.032 75	0.581 22
6.30	3.260	20.282	0.102 54	0.420 51

<sup>a</sup> Not measured; assumed to be 5.49.

extracted for 15 min in boiling 1.0 mol kg<sup>-1</sup> nitric acid.<sup>11</sup> This procedure extracted 0.046 55 and 0.016 11 mol kg<sup>-1</sup> from the clay- and silt-size separates, respectively.

For each separate, the quantity of exchangeable hydrogen was assumed to be

$$n_{\text{H}}^{\text{e}}/m = \text{c.e.c.} - 2n_{\text{Ca}}^{\text{e}}/m - n_{\text{K}}^{\text{e}}/m \quad (6)$$

Table 2 presents the exchangeable Ca, H and K mole fractions along with the corresponding Vanselow and Gaines-Thomas selectivity coefficients ( $k_{\text{(V)A/B}}^{\text{e}}$  and  $k_{\text{(GT)A/B}}^{\text{e}}$ , respectively). In this study, these corrected selectivity coeffi-

**Table 2** Exchangeable-cation mole fractions and corresponding Vanselow and Gaines–Thomas selectivity coefficients for Ca–H–K exchange on carbonate-free clay-, silt-, and silt + clay-size separates from a Nordya sandy-loam surface-horizon sample

$x_{Ca}$	$x_H$	$x_K$	$\ln k_{(V)Ca/H}^a$	$\ln k_{(V)H/K}^a$	$\ln k_{(V)Ca/K}^a$	$\ln k_{(GT)Ca/H}^a$	$\ln k_{(GT)H/K}^a$	$\ln k_{(GT)Ca/K}^a$
clay-size soil separate								
0.5865	0.0212	0.3923	-22.900	9.979	-2.943	-21.746	9.979	-1.788
0.8191	0.0090	0.1719	-21.199	8.791	-3.618	-19.908	8.791	-2.327
0.8287	0.0442	0.1271	-25.766	10.972	-3.821	-24.469	10.972	-2.525
0.8982	0.0138	0.0880	-22.606	9.084	-4.437	-21.272	9.084	-3.103
0.8994	0.0116	0.0890	-21.744	8.612	-4.521	-20.410	8.612	-3.187
0.0063	0.2819	0.7117	-22.595	10.561	-1.472	-21.896	10.561	-0.773
0.0131	0.3182	0.6687	-21.067	10.149	-0.769	-20.361	10.149	-0.063
0.0168	0.3216	0.6616	-21.229	10.044	-1.141	-20.519	10.044	-0.431
0.0166	0.3107	0.6726	-21.784	10.413	-0.957	-21.074	10.413	-0.247
0.0237	0.3192	0.6571	-20.019	9.444	-1.132	-19.303	9.444	-0.416
0.0235	0.3063	0.6701	-20.080	9.475	-1.129	-19.364	9.475	-0.413
0.0623	0.3261	0.6116	-21.007	9.149	-2.708	-20.254	9.149	-1.955
0.0641	0.3351	0.6008	-22.327	9.844	-2.639	-21.571	9.844	-1.883
0.1227	0.3740	0.5033	-21.018	8.921	-3.177	-20.209	8.921	-2.368
0.1298	0.3054	0.5647	-21.761	9.206	-3.349	-20.945	9.206	-2.534
silt-size soil separate								
0.5207	0.1357	0.3436	-16.261	7.044	-2.173	-15.149	7.044	1.061
0.7798	0.0698	0.1504	-15.071	6.128	-2.815	-13.802	6.128	1.546
0.7959	0.0202	0.1840	-12.573	4.664	-3.244	-11.294	4.664	1.966
0.5924	0.3216	0.0860	-18.489	7.810	-2.868	-17.330	7.810	1.710
0.9158	0.0158	0.0685	-12.089	4.347	-3.396	-10.746	4.347	2.053
0.8277	0.1123	0.0600	-16.112	6.473	-3.166	-14.816	6.473	1.870
0.0201	0.2381	0.7418	-15.132	7.414	-0.304	-14.419	7.414	-0.409
0.0204	0.2166	0.7631	-14.884	7.239	-0.407	-14.171	7.239	-0.306
0.0291	0.1909	0.7800	-14.893	7.111	-0.670	-14.171	7.111	-0.052
0.0237	0.3048	0.6715	-15.946	7.747	-0.452	-15.229	7.747	-0.265
0.0300	0.3873	0.5828	-16.463	8.070	-0.322	-15.740	8.070	-0.400
0.0499	0.2952	0.6549	-18.794	8.819	-1.155	-18.052	8.819	0.414
0.0961	0.2350	0.6689	-18.749	9.067	-0.615	-17.964	9.067	-0.170
0.1113	0.1010	0.7878	-16.889	8.056	-0.776	-16.090	8.056	-0.023
0.1975	0.2728	0.5297	-15.572	7.113	-1.346	-14.698	7.113	0.472
0.2591	0.0357	0.7051	-10.913	4.568	-1.778	-9.990	4.568	0.855
silt + clay-size soil separate								
0.3981	0.3008	0.3011	-18.334	7.796	-2.742	-17.306	7.796	-1.713
0.3895	0.3406	0.2699	-19.767	8.623	-2.522	-18.745	8.623	-1.500
0.5491	0.2981	0.1529	-18.380	7.614	-3.152	-17.249	7.614	-2.021
0.5486	0.2844	0.1669	-18.164	7.377	-3.411	-17.034	7.377	-2.280
0.5277	0.3548	0.1174	-18.816	7.736	-3.344	-17.699	7.736	-2.227
0.5514	0.3316	0.1170	-19.941	8.280	-3.380	-18.808	8.280	-2.248
0.5941	0.3164	0.0896	-19.876	8.058	-3.760	-18.717	8.058	-2.601
0.0087	0.0056	0.9858	-12.804	6.164	-0.477	-12.102	6.164	0.225
0.0086	0.0642	0.9262	-17.078	8.725	0.372	-16.376	8.725	1.074
0.0120	0.0818	0.9062	-17.067	8.715	0.362	-16.362	8.715	1.068
0.0131	0.1196	0.8673	-18.345	9.285	0.224	-17.639	9.285	0.930
0.0177	0.0840	0.8983	-15.436	7.754	0.073	-14.725	7.754	0.784
0.0175	0.1319	0.8507	-18.193	9.105	0.017	-17.483	9.105	0.728
0.0500	0.0199	0.9301	-16.302	7.665	-0.972	-15.560	7.665	-0.230
0.0512	0.0400	0.9088	-17.212	7.874	-1.464	-16.469	7.874	-0.721
0.1800	0.0820	0.7381	-19.710	8.207	-3.297	-18.851	8.207	-2.438

coefficients are defined by

$$k_{(V)A/B}^a \stackrel{\text{def}}{=} \frac{(a_{\pm B(\text{ClO}_4)_z}(\text{aq})^{z_A} x_A^{z_B})}{(a_{\pm A(\text{ClO}_4)_z}(\text{aq})^{z_B} x_B^{z_A})} \quad (7)$$

and

$$k_{(GT)A/B}^a \stackrel{\text{def}}{=} \frac{(a_{\pm B(\text{ClO}_4)_z}(\text{aq})^{z_A} E_A^{z_B})}{(a_{\pm A(\text{ClO}_4)_z}(\text{aq})^{z_B} E_B^{z_A})} \quad (8)$$

The mean ionic activities of the perchlorate salts were estimated by<sup>12</sup>

$$a_{\pm A(\text{ClO}_4)_z}(\text{aq}) = \frac{m_{\pm A(\text{ClO}_4)_z}(\text{aq})^{\gamma_{\pm A(\text{ClO}_4)_z}}}{m_{A(\text{ClO}_4)_z}^{\ominus}(\text{aq})} \quad (9)$$

The mean-ionic activity coefficients for  $\text{KClO}_4$  were estimated by the parameters to Guggenheim's equation presented in ref. 13. The mean ionic activity coefficients for  $\text{Ca}(\text{ClO}_4)_2$  were estimated using the data of Nicholson and Felsing<sup>14</sup> and Robinson *et al.*<sup>15</sup>

The exchange equilibrium constant  $K_{(V)Ca/K}^{\text{ex}}$  was calculated for each separate using the method developed by Sposito *et al.*<sup>16</sup> for ternary ion-exchange systems. The  $\ln K_{(V)Ca/K}^{\text{ex}}$  values for the three separates were calculated to be: silt + clay, -2.14; clay, -3.11 and silt, -1.88. The value of  $\ln K_{(V)Ca/K}^{\text{ex}}$  predicted by eqn. (5), wherein  $K_{(V)Ca/K}^{\text{ex}}$  replaced  $k_{A/B}^a$ , was -2.59.

To test eqn. (1) and (5), regression equations were fitted to predict the ion-exchange properties of the silt- and clay-size components of the silt + clay-size separate. For the clay and

silt systems, the equations

$$\begin{aligned} \ln k_{(V)Ca/K}^a = & \beta_0 + \beta_1 E_{K(aq)} \\ & + \beta_2 E_{K(aq)}^2 + \beta_3 E_{K(aq)}^3 \\ & + \beta_4 E_{K(aq)}^4 + \beta_5 E_{K(aq)}^5 \end{aligned} \quad (10)$$

and

$$\begin{aligned} \ln k_{(GT)Ca/K}^a = & \beta_0 + \beta_1 E_{K(aq)} \\ & + \beta_2 E_{K(aq)}^2 + \beta_3 E_{K(aq)}^3 \\ & + \beta_4 E_{K(aq)}^4 + \beta_5 E_{K(aq)}^5 \end{aligned} \quad (11)$$

The smallest coefficient of determination ( $R^2$ ) for these equations with the two separates was 0.96. The agreement of eqn. (10) with the measured data from the clay- and silt-size separates is shown in Fig. 2. This figure also shows that the  $\ln k_{(V)Ca/K}^a$  values were distinct in the silt- and clay-size separates and that the relationship between  $\ln k_{(V)Ca/K}^a$  and  $E_{K(aq)}$  broke down as  $E_{K(aq)}$  approached 1.0. Agreement of eqn. (11) with measured data were equally good. Similar regressions were attempted with  $\ln k_{(V)H/K}^a$  and  $\ln k_{(GT)H/K}^a$  as dependent variables. These regressions were not significant, therefore values of  $\ln k_{(V)H/K}^a$  and  $\ln k_{(GT)H/K}^a$  for the silt + clay-size separate were predicted from their mean values for the silt- and clay-size separates. For the silt + clay-size separate equilibrating solutions, the equation

$$E_{H(aq)} = \beta_0 + \beta_1 E_{K(aq)} + \beta_2 E_{K(aq)}^2 \quad (12)$$

was fitted by regression. A plot of eqn. (12) ( $R^2 = 0.83$ ) is presented in Fig. 3. The aqueous molalities of Ca and H in the silt + clay-size separate equilibrating solutions as functions of  $E_{K(aq)}$  were estimated by eqn. (12) assuming that the sum of cationic charge in the silt + clay-size separate equilibrating solutions was  $0.02122 \text{ mol kg}^{-1}$ . Mean-ionic activities were calculated using eqn. (9).

Predictions using eqn. (1) for which the mixture component exchangeable-ion equivalent fractions were estimated accurately were considered the standard with which other prediction techniques should be compared. Vanselow selectivity

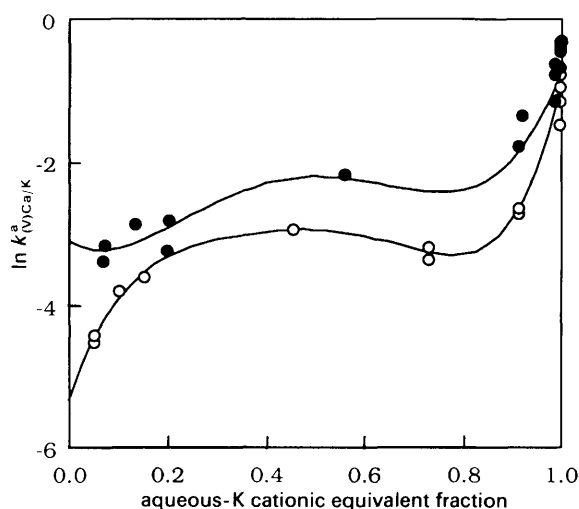


Fig. 2 Values of  $\ln k_{(V)Ca/K}^a$  measured on silt- (●) and clay-size (○) soil separates plotted with lines predicted by eqn. (10) fitted by regression

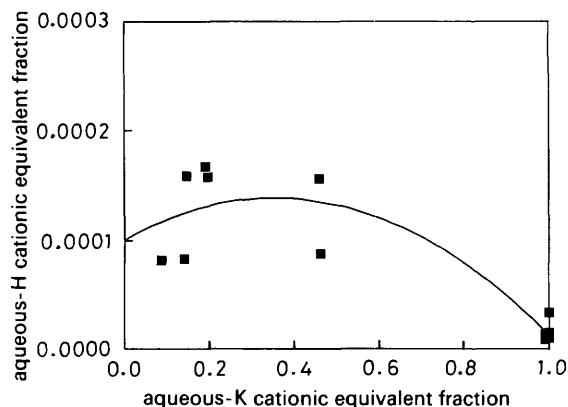


Fig. 3 Relation between aqueous  $H^+$  and  $K^+$  equivalent fractions in the silt + clay-size soil separate equilibrating solutions and a plot of eqn. (12) fitted by regression

coefficients for the silt + clay-size separate were calculated from exchangeable-cation compositions estimated using eqn. (1). The exchangeable-cation composition of the clay- and silt-size separates was estimated by

$$\begin{aligned} x_H = & \frac{1}{2} \left[ \left( \frac{k_{(V)H/K}^a a_{\pm HClO_4(aq)} (k_{(V)H/K}^a a_{\pm HClO_4(aq)} + a_{\pm KClO_4(aq)})^2}{k_{(V)Ca/K}^a a_{\pm Ca(ClO_4)_2(aq)}} \right)^2 \right. \\ & + \left. \left( \frac{4(k_{(V)H/K}^a a_{\pm HClO_4(aq)})^2}{k_{(V)Ca/K}^a a_{\pm Ca(ClO_4)_2(aq)}} \right)^{1/2} \right. \\ & \left. - \frac{k_{(V)H/K}^a a_{\pm HClO_4(aq)} (k_{(V)H/K}^a a_{\pm HClO_4(aq)} + a_{\pm KClO_4(aq)})}{k_{(V)Ca/K}^a a_{\pm Ca(ClO_4)_2(aq)}} \right] \end{aligned} \quad (13)$$

$$\begin{aligned} x_K = & \frac{1}{2} \left[ \left( \frac{a_{\pm KClO_4(aq)} (k_{(V)H/K}^a a_{\pm HClO_4(aq)} + a_{\pm KClO_4(aq)})^2}{k_{(V)Ca/K}^a a_{\pm Ca(ClO_4)_2(aq)}} \right)^2 \right. \\ & + \left. \left( \frac{4(a_{\pm KClO_4(aq)})^2}{k_{(V)Ca/K}^a a_{\pm Ca(ClO_4)_2(aq)}} \right)^{1/2} \right. \\ & \left. - \frac{a_{\pm KClO_4(aq)} (k_{(V)H/K}^a a_{\pm HClO_4(aq)} + a_{\pm KClO_4(aq)})}{k_{(V)Ca/K}^a a_{\pm Ca(ClO_4)_2(aq)}} \right] \end{aligned} \quad (14)$$

and

$$x_{Ca} + x_H + x_K = 1 \quad (15)$$

Eqn. (13) and (14) were derived using *Mathematica*.<sup>17</sup> Once the exchangeable-cation compositions of the silt- and clay-size separates were estimated as a function of  $E_{K(aq)}$ , the exchangeable-cation composition of the silt + clay-size separate was calculated with eqn. (1). The  $\ln k_{(V)Ca/K}^a$  values for the silt + clay-size separate were then determined from the predicted exchangeable-cation composition. These calculated  $\ln k_{(V)Ca/K}^a$  values showed excellent agreement with the measured values, as shown in Fig. 4. This agreement failed somewhat at  $E_{K(aq)}$  values near 1, where  $\ln k_{(V)Ca/K}^a$  values for all separates were changing rapidly with increasing values of  $E_{K(aq)}$ . The same procedure was attempted, but with exchange equilibrium constants in eqn. (13) and (14) replacing the Vanselow selectivity coefficients. As can be seen in Fig. 5,  $\ln k_{(V)Ca/K}^a$  values so predicted showed poor agreement with experimental data. Accordingly, we concluded that eqn. (1)

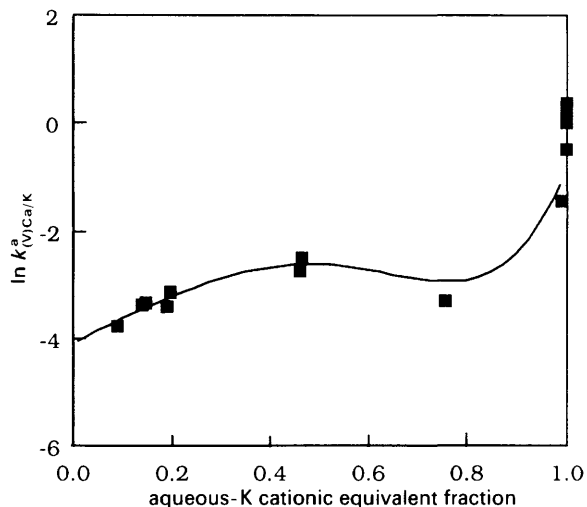


Fig. 4 Values of  $\ln k_{(V)Ca/K}^a$  measured on silt + clay-size soil separate and those predicted by the weighted arithmetic mean approach and variable selectivity coefficients

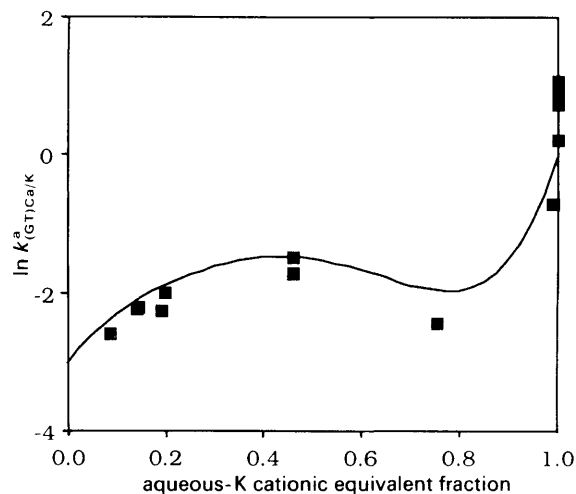


Fig. 7 Values of  $\ln k_{(GT)Ca/K}^a$  measured on silt + clay-size soil separate and those predicted by the weighted geometric mean approach

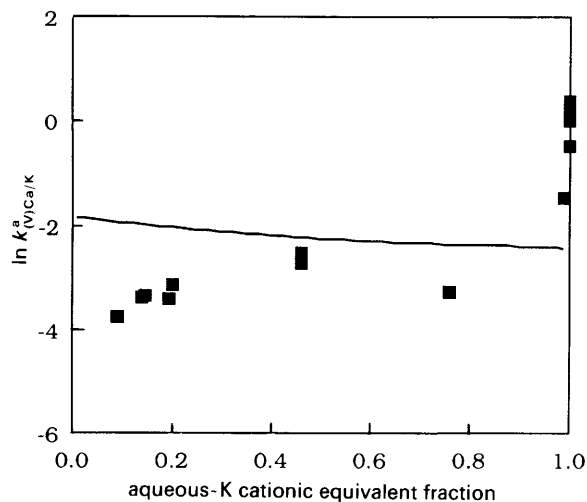


Fig. 5 Values of  $\ln k_{(V)Ca/K}^a$  measured on silt + clay-size soil separate and those predicted by the weighted arithmetic mean approach and the exchange equilibrium constant

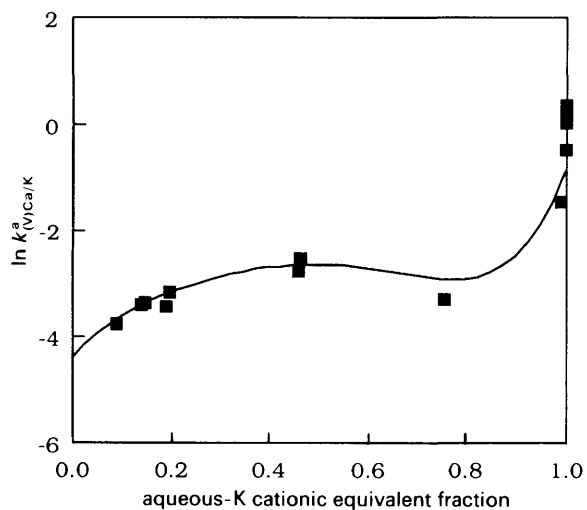


Fig. 6 Values of  $\ln k_{(V)Ca/K}^a$  measured on silt + clay-size soil separate and those predicted by the weighted geometric mean approach

should not be applied using fixed selectivity coefficients to systems with compositional heterogeneity unless mixture-component selectivity coefficients are indeed constant. Since each of the soil separates investigated here had significant compositional heterogeneity, we doubt that this conclusion can be applied confidently to problems of structural heterogeneity. We think that experiments similar to this one, but with mixture-component exchangers with little compositional or structural heterogeneity, should be carried out to ascertain if this conclusion is valid when applying eqn. (1) to problems of structural heterogeneity.

The applicability of eqn. (5) for predicting selectivity coefficients of ion-exchanger mixtures was tested with two selectivity coefficients: the Vanselow and the Gaines-Thomas coefficients. The variation of measured and predicted  $\ln k_{(V)Ca/K}^a$  and  $\ln k_{(GT)Ca/K}^a$  with  $E_{K(aq)}$  are presented in Fig. 6 and 7. Estimation of the corrected selectivity coefficients using eqn. (5) was surprisingly accurate, although in this exercise, using the Vanselow selectivity coefficients gave slightly better results than the Gaines-Thomas selectivity coefficient. More experiments of this type need to be conducted before these results could be taken to be conclusive. We hypothesize that eqn. (5) estimates accurately selectivity coefficients of systems with compositional and structural heterogeneity.

### Conclusions

Provided ion-exchanger mixture-component selectivity coefficients were modelled adequately, selectivity coefficients of a binary ion-exchanger mixture in ternary ion-exchange systems could be predicted accurately either by the weighted arithmetic mean [eqn. (1)] or the weighted geometric mean [eqn. (5)]. Since the weighted geometric mean approach requires substantially fewer calculations to implement when modelling multicomponent ion-exchange equilibria it is recommended for modelling natural ion-exchanger mixtures.

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## Glossary

(1) after a symbol's description indicates that the quantity is dimensionless.

$a_{\pm A(\text{ClO}_4)_z A(\text{aq})}$	mean-ionic activity of the perchlorate salt of cation A (1)
c.e.c.	cation exchange capacity ( $\text{mol kg}^{-1}$ )
$E_A$	exchangeable-cation A equivalent fraction (1)
$E_{A(\text{aq})}$	aqueous-cation A equivalent fraction (1)
$E_A^i$	equivalent fraction of exchangeable ion A for ion-exchanger mixture-component $i$ (1)
$E_A^m$	equivalent fraction of exchangeable ion A for an ion-exchanger mixture (1)
$k_{A/B}^{a:i}$	corrected selectivity coefficient of ion-exchanger mixture-component $i$ (1)
$k_{A/B}^{a:m}$	corrected selectivity coefficient of an ion-exchanger mixture (1)
$k_{(\text{GT})A/B}^a$	Gaines-Thomas selectivity coefficient (1)
$k_{(V)A/B}^a$	Vanselow selectivity coefficient (1)
$K_{A/B}^{\text{ex}}$	exchange equilibrium constant (1)
$K_{A/B}^{\text{ex};i}$	exchange equilibrium constant for mixture-component $i$ (1)
$K_{(\text{GT})A/B}^{\text{ex};i}$	exchange equilibrium constant (Gaines-Thomas reaction stoichiometry) for mixture-component $i$ (1)
$K_{(V)A/B}^{\text{ex}}$	exchange equilibrium constant (Vanselow reaction stoichiometry)
$m_{\pm A(\text{ClO}_4)_z A(\text{aq})}$	mean-ionic molality of the perchlorate salt of cation A ( $\text{mol kg}^{-1}$ )
$m_{A(\text{ClO}_4)_z A(\text{aq})}^\ominus$	standard-state molality of the perchlorate salt of cation A ( $\text{mol kg}^{-1}$ )
$n$	number of components in an ion-exchanger mixture (1)
$n_A^z/m$	specific surface excess of exchangeable-cation A ( $\text{mol kg}^{-1}$ )
$R$	gas constant ( $\text{J mol}^{-1} \text{K}^{-1}$ )
$T$	temperature (K)
$x_A$	mole fraction of exchangeable cation A (1)
$z_A$	charge number of cation A (1)
$\beta_0 - \beta_5$	regression-equation coefficients (1)
$\gamma_{\pm A(\text{ClO}_4)_z A}$	mean ionic activity coefficient of the perchlorate salt of cation A (1)

$\Delta_r \bar{G}_{A/B}^{\ominus:m}$	standard reaction Gibbs energy for an ion-exchanger mixture ( $\text{J mol}^{-1}$ )
$\Delta_r \bar{G}_{A/B}^{\ominus:i}$	standard reaction Gibbs energy for ion-exchanger mixture component $i$ ( $\text{J mol}^{-1}$ )
$\phi_i$	fraction of the mixture's exchange capacity carried by ion-exchanger component $i$ (1)

## References

- O. Talibudeen and K. W. T. Goulding, *Clays Clay Miner.*, 1983, **31**, 37.
- O. Talibudeen and K. W. T. Goulding, *Clays Clay Miner.*, 1983, **31**, 137.
- R. M. Barrer and K. Klinowski, *J. Chem. Soc., Faraday Trans. 1*, 1972, **68**, 73.
- R. M. Barrer, *Zeolites*, 1984, **4**, 361.
- A. P. Vanselow, *Soil Sci.*, 1932, **33**, 95.
- E. N. Gapon, *J. Gen. Chem. U.S.S.R.*, 1933, **3**, 144.
- G. L. Gaines Jr. and H. C. Thomas, *J. Chem. Phys.*, 1953, **21**, 714.
- Soil Survey Staff, *Soil Taxonomy: A Basic System of Soil Classification for Making and Interpreting Soil Surveys*, U.S. Government Printing Office, Washington, DC, 1975.
- G. W. Kunze and J. B. Brown, in *Methods of Soil Analysis*, ed. A. L. Page, R. H. Miller and D. R. Keeney, American Society of Agronomy, Madison, WI, 2nd edn., 1982, part 1, p. 91.
- A. Walkley and I. A. Black, *Soil Sci.*, 1934, **37**, 29.
- D. Knudsen, G. A. Peterson and P. F. Pratt, in *Methods of Soil Analysis*, ed. A. L. Page, R. H. Miller and D. R. Keeney, American Society of Agronomy, Madison, WI, 2nd edn., 1982, part 2, p. 225.
- I. M. Mills, *Quantities, Units and Symbols in Physical Chemistry*, Blackwell Scientific Publications for IUPAC, Oxford, 1988, p. 51.
- H. S. Harned and B. B. Owen, *The Physical Chemistry of Electrolytic Solutions*, Reinhold Publishing Corporation, New York, 3rd edn., 1958.
- D. E. Nicholson and W. A. Felsing, *J. Am. Chem. Soc.*, 1951, **73**, 3520.
- R. A. Robinson, C. K. Lim and K. P. Ang, *J. Am. Chem. Soc.*, 1953, **75**, 5130.
- G. Sposito, C. Jouany, K. M. Holtzclaw and C. S. LeVesque, *Soil Sci. Soc. Am. J.*, 1983, **47**, 1081.
- S. A. Wolfram, *Mathematica: A System for Doing Mathematics by Computer*, Addison-Wesley Publishing Company, Inc., Redwood City, CA, 1988.

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