

Studies on the Thermodynamics of Exchange in Clays: Part II—Zinc Exchange on Na- & Ca-Illites

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Zn-Na and Zn-Ca exchanges on Na- and Ca-illites have been studied with the help of adsorption isotherms and thermodynamic parameters. The isotherms and free energy changes are indicative of a lower preference of Zn ions for the illites as compared to the Na or Ca ions, i.e. the exchange is not spontaneous. Enthalpy effects point to a stronger binding of Na and a weaker binding of Ca as compared to Zn on the illite surface. These results find support from the entropy changes. A greater randomness and disorder seems to occur during Zn adsorption on Na-illite probably as a result of depletion of the hydration shell around Zn ions. A reverse effect is noticed during Zn adsorption on Ca-illite.

CLAY minerals occur widely as the colloidal constituent of soils. In spite of their being the most reactive fractions of soils, relatively little work has been done on the mechanism of exchange of cations in solution and the surface phase of these minerals. In view of the importance of zinc exchange in soils^{1,2}, it was considered useful to study the interaction of Zn(II) with the Na-illite and Ca-illite using exchange isotherms, thermodynamic parameters and surface phase activity coefficients. The basis of the treatment have been the thermodynamic formulations of previous workers³⁻⁷. It has been felt that such a study will throw considerable light on the mechanism of zinc adsorption and release by base saturated illites.

Materials and Methods

Illite used was an API sample obtained from Morris, Illinois, USA. It was dispersed after removal of organic matter in a normal NaCl solution and then centrifuged to give <2 micron suspension. The NaCl treatment was repeated and the suspension freed from chloride ions by repeated washings with deionized water. A part of the Na-illite suspension was converted into Ca-illite by saturating it with a normal solution of CaCl₂ and then washing it as above to remove the excess of the salt. The concentrations of the Na- and Ca-illite suspensions were 17.0 and 14.0 g per litre respectively.

For the exchange experiments the pH of the suspensions was adjusted to 4 with dil. HNO₃ to provide a buffering action and to eliminate hydroxide precipitation, if any. Ten ml each of the Na- and Ca-illite suspensions were taken in several glass stoppered tubes and treated with different amounts of 0.03N ZnSO₄ solution and the volume of the mixture adjusted to 25 ml with deionized water in each case. The mixtures were shaken for 6 hr at 30° ± 0.1° in the first set of experiments and at 60° ± 0.1° in the second set of experiments. The suspensions were then centrifuged and Na, Ca and Zn

contents determined in the supernatant liquids. Sodium was determined with a flame photometer and Ca and Zn by atomic absorptiometer. The ammonium acetate method of Jackson was followed to yield a value of 23 meq/100 g for the base exchange capacity (BEC) of illite⁸. The corresponding concentration of Na and Ca in the clay phase was obtained by difference (BEC minus the concentration of the cation in the supernatant liquid) and that for Zn from Zn added minus Zn in the supernatant liquid.

Results and Discussion

The reversible interaction between the zinc ions in solution and Na and Ca ions on the illite surface may be represented by Eqs. (1) and (2):



where \bar{C} represents the equivalent concentrations of the ions concerned in the illite phase and C_{Na} , C_{Ca} and C_{Zn} , the electrolyte concentration in the solution. The equivalent ionic fractions of Zn, Ca and Na in the clay phase and in the solution were calculated from the expressions

$$\bar{X}_{Zn} = \frac{\bar{C}_{Zn}}{\bar{C}}, X_{Zn} = \frac{C_{Zn}}{C}, \bar{X}_{Na} = \frac{\bar{C}_{Na}}{\bar{C}} \text{ etc.}$$

where \bar{C} is the total electrolyte concentration in the clay phase and C that in the solution ($\bar{C} = \bar{C}_{Zn} + \bar{C}_{Na}$ and $C = C_{Zn} + C_{Na}$, etc.).

The values obtained for the equivalent ionic fractions at 30° and 60° are given in Tables 1 and 2. The exchange isotherms are shown in Fig. 1 (curves 1-4). The deviation of the isotherms from the diagonal indicated a lower preference by illite for Zn ions as compared to Na or Ca ions in the entire range of concentration studied. It was also apparent that the preference of Ca-illite for Zn at 30° was higher than at 60°. No such correlation could be

TABLE 1 — VALUES OF EQUIVALENT IONIC FRACTIONS AND SELECTIVITY QUOTIENTS AT 30° AND 60° FOR THE Zn EXCHANGE ON Na-ILLITE

\bar{X}_{Zn}	X_{Zn}	\bar{X}_{Na}	X_{Na}	K_C	$\log K_C$
EXPERIMENTS AT 30°					
0.112	0.305	0.808	0.694	0.2246	-0.6486
0.159	0.524	0.841	0.467	0.0969	-1.0137
0.204	0.623	0.796	0.376	0.0728	-1.1379
0.242	0.695	0.757	0.305	0.0565	-1.2480
0.246	0.746	0.754	0.254	0.0371	-1.4306
0.249	0.779	0.751	0.221	0.0277	-1.5575
0.399	0.803	0.601	0.197	0.0536	-1.2708
0.427	0.866	0.573	0.134	0.0270	-1.5686
0.439	0.910	0.561	0.089	0.0122	-1.9136
0.482	0.924	0.518	0.075	0.0116	-1.9355
0.604	0.931	0.396	0.069	0.0206	-1.6861
0.600	0.946	0.400	0.054	0.0118	-1.9882
0.646	0.951	0.354	0.049	0.0108	-1.9666
EXPERIMENTS AT 60°					
0.066	0.324	0.934	0.676	0.1067	-0.9718
0.133	0.446	0.867	0.553	0.1213	-0.9162
0.133	0.573	0.867	0.426	0.0558	-1.2534
0.235	0.617	0.765	0.382	0.0950	-1.0223
0.319	0.646	0.680	0.354	0.1336	-0.8742
0.329	0.686	0.670	0.314	0.1046	-0.9805
0.402	0.738	0.598	0.262	0.1049	-0.9793
0.424	0.825	0.576	0.174	0.0464	-1.3335
0.458	0.893	0.542	0.107	0.0191	-1.7190
0.480	0.901	0.520	0.098	0.0197	-1.7055
0.528	0.911	0.471	0.088	0.0208	-1.6819
0.530	0.939	0.470	0.061	0.0102	-1.9914
0.590	0.945	0.410	0.055	0.0111	-1.9547

TABLE 2 — VALUES OF EQUIVALENT IONIC FRACTIONS AND SELECTIVITY QUOTIENTS AT 30° AND 60° FOR THE Zn EXCHANGE ON Ca-ILLITE

\bar{X}_{Zn}	X_{Zn}	\bar{X}_{Ca}	X_{Ca}	K_C	$\log K_C$
EXPERIMENTS AT 30°					
0.073	0.524	0.927	0.476	0.0715	-1.1457
0.191	0.595	0.809	0.405	0.1607	-0.7941
0.313	0.583	0.686	0.417	0.3263	-0.4864
0.422	0.576	0.578	0.424	0.5374	-0.2697
0.482	0.688	0.518	0.312	0.4219	-0.3748
0.554	0.735	0.446	0.264	0.4461	-0.3560
0.628	0.807	0.372	0.193	0.4037	-0.3939
0.737	0.822	0.262	0.177	0.6057	-0.2177
0.784	0.847	0.215	0.153	0.6586	-0.1814
0.820	0.789	0.180	0.121	0.6968	-0.1569
EXPERIMENTS AT 60°					
0.076	0.468	0.924	0.532	0.0934	-1.0297
0.157	0.588	0.843	0.412	0.1304	-0.8848
0.251	0.620	0.749	0.380	0.2053	-0.6898
0.396	0.600	0.604	0.400	0.4370	-0.3595
0.474	0.692	0.526	0.307	0.3997	-0.3982
0.471	0.754	0.529	0.246	0.2904	-0.5374
0.609	0.797	0.390	0.203	0.3977	-0.4004
0.748	0.807	0.252	0.192	0.7062	-0.1511
0.819	0.828	0.181	0.171	0.9344	-0.0295
0.864	0.846	0.136	0.154	1.1564	-0.0630

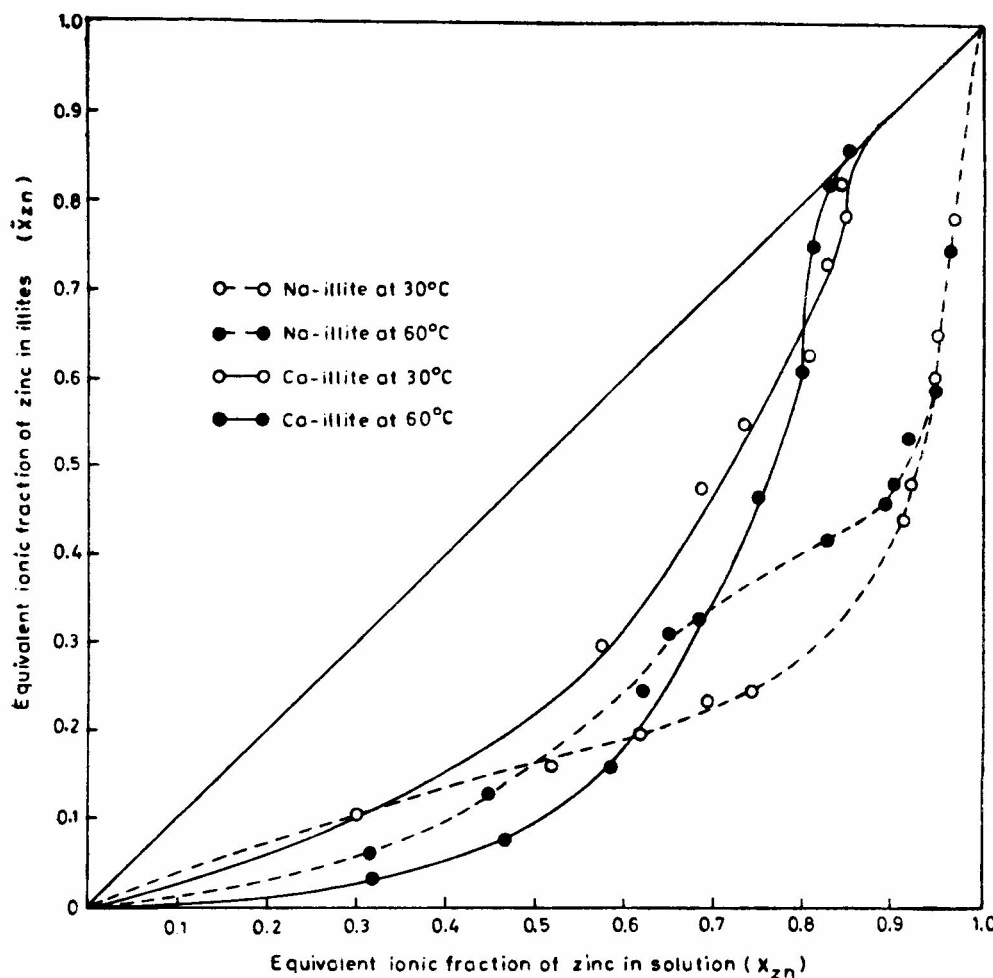


Fig. 1 — Plots of equivalent ionic fractions of zinc in illites against that in solution

observed in the case of Na-illite. From the isotherms it was also inferred that the illite clay had a higher preference for Na ions as compared with Ca ions at 30°. However, the effect at 60° was variable.

To examine the interaction in the liquid and illite phases the selectivity coefficients at 30° and 60° for different surface compositions of Zn were determined from the expressions^{9,10} (3 and 4) taking the ratio of activity coefficients as unity¹¹ in the dilute range studied

$$K_C = \frac{\bar{X}_{Zn} (X_{Na})^2}{(X_{Na})^2 \bar{X}_{Zn}} \text{ for the Na-Zn exchange} \quad \dots(3)$$

$$K_C = \frac{\bar{X}_{Zn} X_{Ca}}{\bar{X}_{Ca} \bar{X}_{Zn}} \text{ for the Ca-Zn exchange} \quad \dots(4)$$

The values for K_C (Tables 1 and 2) at different temperatures were plotted against \bar{X}_{Zn} (Fig. 2). An examination of the plots revealed that while the selectivity coefficients during the Ca-Zn exchange increased with an increase in the value of \bar{X}_{Zn} there was a continuous decrease with a small rise in between, in the values of selectivity coefficients during Na-Zn exchange. The pattern of behaviour was the same at both the temperatures in the two cases. Such a variation was in accordance with

the preference shown by Zn for the Ca-clay as compared to Na-illite (Fig. 1).

For a further study of the affinity the thermodynamic equilibrium constants K were calculated from the relationship proposed by Gaines and Thomas³.

$$\ln K = (Z_a - Z_b) \int_0^1 \ln K_C d\bar{X}_{Zn} \quad \dots(5)$$

where Z_a and Z_b represent the charges on the competing ions. The integrals were evaluated from the areas under the curves (Fig. 2) using the trapezoidal rule¹². Some uncertainty was involved in this evaluation. The isotherms were extrapolated at both the ends. Although justification^{12,13} for the extrapolation was available from an examination of the linearity and finite slope of the isotherms at large and small values of \bar{X}_{Zn} , the values of K obtained could not be classed as exact. In the discussion that follows, the values for the equilibrium constant and other thermodynamic parameters given in Table 3 have, therefore, been considered qualitatively only.

The values of the thermodynamic equilibrium constant (Table 3) were found to be lower at 30°

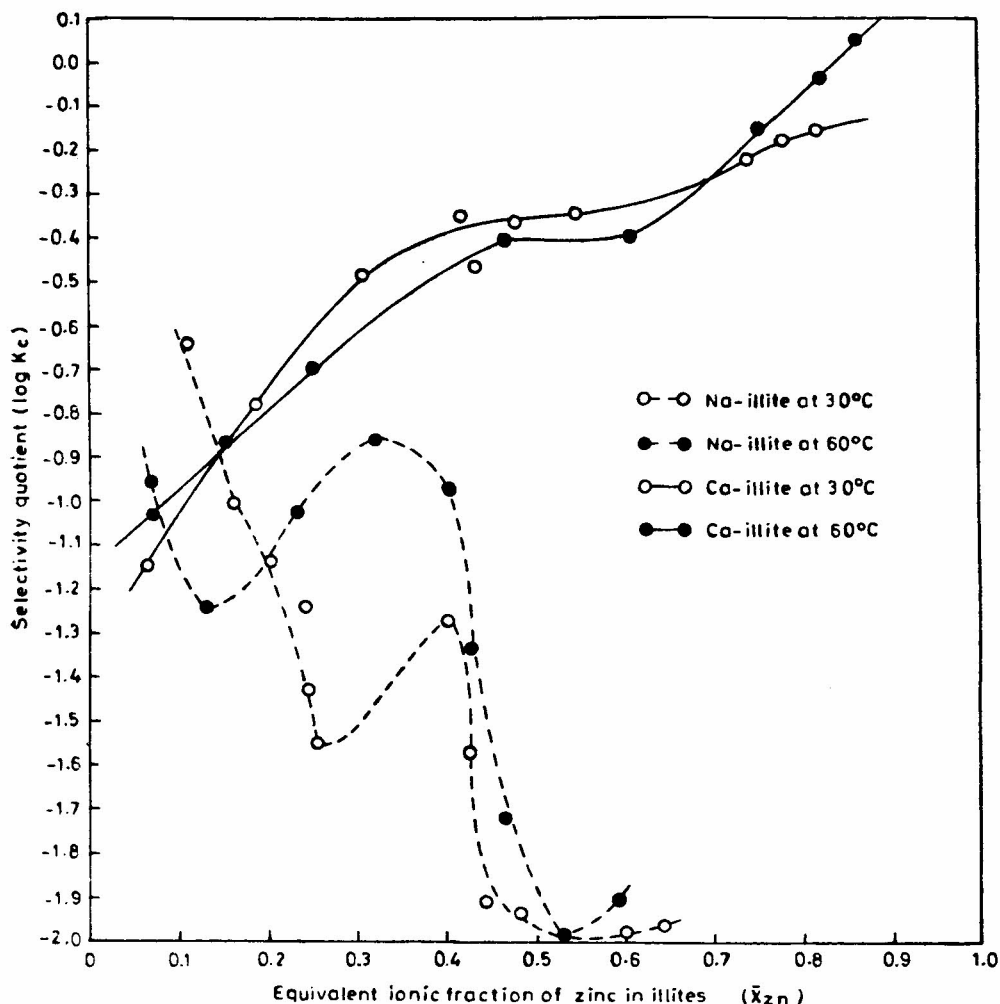


Fig. 2 — Plots of selectivity quotient ($\log K_C$) against equivalent ionic fractions of zinc in illites

TABLE 3 — THERMODYNAMIC PARAMETERS FOR THE ZN EXCHANGE ON Na- AND Ca-ILLITE AT 30° AND 60°

Thermodynamic parameter	Na-Zn system		Ca-Zn system	
	30°	60°	30°	60°
<i>K</i>	0.0498	0.0672	0.4404	0.4232
ΔG° (cal/mole)	+1820.85	+1775.95	+494.40	+569.90
ΔH° (cal/mole)		+2275.61		-267.72
ΔS° (cal/mole/deg)		1.50		-2.51

than at 60° in the Na-Zn system and higher at 30° than at 60° in the Ca-Zn system. These were indicative of the fact that the affinity of Na-illite for zinc increased with a rise in temperature while that of Ca-illite decreased. Also the higher values of *K* in the Ca-Zn system as compared to the Na-Zn system indicated that the affinity of Ca-illite for Zn was somewhat greater than that of Na-illite for Zn.

The positive ΔG values ($\Delta G^\circ = -RT \ln K$) (Table 3) for the interactions indicated that both at 30° and 60°, Na and Ca had a higher preference for illite than Zn and their replacement from illite by Zn could not be spontaneous.

The standard enthalpy changes ΔH° were calculated from the Van't Hoff isochore (6)

$$\ln \left(\frac{K_{T_2}}{K_{T_1}} \right) = \frac{-\Delta H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad \dots(6)$$

The values are given in Table 3. It may be mentioned that the values of enthalpy calculated above were not the enthalpies of exchange alone. They included the enthalpies of hydration, dilution, mixing and exchange. Also the method of determination by measuring equilibrium constants at two different temperatures involved an approximation to the extent of ± 1 to 2 kcal, although where a small temperature range was involved Eq. 6, gave reasonably satisfactory values.

A positive enthalpy effect during the Na-Zn exchange pointed to a stronger binding of Na as compared to Zn on the illite surface. A small negative enthalpy change during Ca-Zn exchange, however, pointed to a somewhat stronger binding of Zn as compared to Ca on the illite surface, which appeared to be contrary to the assumptions drawn from the adsorption isotherms.

The standard entropy changes ΔS° were calculated by the equation $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ and the values are given in Table 3.

The observation based on enthalpy found support from the entropy changes during the exchanges. The entropy changes arose from the randomness and disorder in the exchanger and solution phases as well as the hydration and dehydration¹⁴ of ions taking part in the exchange. Although a positive entropy effect during the

Na-Zn exchange may be in agreement with a higher preference on Na ions on the illite surface, yet it indicated a diffused and disordered arrangement of Zn ions in the Gouy layer and a more ordered arrangement of Na ions in the Stern layer. The greater disorder in the system appeared to be due to the depletion of the hydration shell around Zn ions caused by Na ions during the exchange reactions. On the other hand a negative entropy effect during the Ca-Zn exchange indicated that the hydration shell around Zn ions remained intact with Zn being bound at fixed, specific sites on the illite surface producing a greater order in the system. Valence, electrostatic considerations, the ion sizes and the nature of the diffused electrical double layer in the two exchanges justified these assumptions.

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