

CHEMISTRY

Chemical Thermodynamics

THERMODYNAMICS OF EXCHANGE IN CLAYS: NICKEL EXCHANGE ON Na- AND Mg- ILLITES

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The ion exchange equilibria of Ni-exchange with Na- and Mg-illites have been studied with the help of adsorption isotherms and thermodynamic parameters. The exchange at pH 5.0 and an equilibrium time 3 hrs. yielded isotherms, K , ΔG° values which were indicative of a spontaneity of reaction and a higher preference of Ni for the illite surface. Preference varied with temperature. Enthalpy and entropy effects suggested a stronger binding of Ni and changes in the hydration rates of Ni, Na and Mg with increase in order respectively. The surface phase activity coefficients and the excess thermodynamic functions were indicative of a non-ideal heterogenous exchange in which the mixture of ions on the illite surface was more stable and more tightly bound with significant differences in the hydration rates of the ions in the mixture with respect to the homo-ionic form.

Keywords: Adsorption; Isotherm; Thermodynamics of Exchange; Selectivity Coefficient; Illite; Nickel Chloride

INTRODUCTION

THE replacement of cations is one of the most important phenomena which controls the storage capacity of a soil for plant nutrient elements. The exchange is governed by several factors. A number of equations (Kerr, 1928; Vanselow, 1932; and Krishnamoorthy & Overstreet, 1949) have been proposed to give quantitative expression to the ion exchange. Gaines and Thomas (1953) introduced the conception of thermodynamics to ion exchange in clays. In the study of ion exchange, it has been noticed although two ions may exchange stoichiometrically, they would not in general be preferred or bound equally strongly on a surface.

The present work extends the studies already taken by the author on the ion exchange between nickel and Na- and Mg- illites with the help of thermodynamic models of Gaines and Thomas (1953), El-sayed *et al.* (1970), Singhal and Kumar (1977). Singhal and Singh (1973) and Singhal *et al.* (1976, 1978) Since nickel formulations are often used as pesticides and since soils are often illitic, it was considered that such a study will be of considerable significance in understanding the mechanism of nickel interaction with Na- and Mg- illites.

MATERIALS AND METHODS

The clay mineral used in these studies was illite from Morris, Illinois. It was dispersed, centrifuged and converted into chloride free Na- illite and then into

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Mg- and Ni- saturated illites by the usual procedure (Singhal *et al.*, 1976). The concentrations of the suspensions used was 10.2 to 14.3 gl^{-1} . The base exchange capacity (BEC) of Na-illite was determined by Ganguli's (1951) method, it yielded BEC value as equal to 27 meq per 100g clay. For the determination of the BEC of Mg-illite, a known volume of suspension was treated with a mixture consisting of 1 M NiCl_2 in 0.1M HCl. The amount of magnesium released was then estimated. It gave the BEC value as equal to 24 meq per 100g clay.

Since equilibrium is essential to the application of the theory of ion exchange, investigations were first made to determine the length of time required for the completion of interaction between exchangeable cations on the illite surface, at different concentrations. For this purpose 10ml of clay suspensions were taken in several glass stoppered test tubes and treated with 1.0, 5.0 and 15.0 ml of 0.005 M NiCl_2 . The ionic strength of each sample was then adjusted to a constant value of 0.018 by adding 14.0, 10.0 and 0.0 ml of 0.015 M NaCl or 0.005 M MgCl_2 as required. The final volume was adjusted to 25ml with distilled water. The samples were shaken for $\frac{1}{4}$, $\frac{1}{2}$, 1, 2, 3, 6, 9 and 12hr in a thermostatic water bath at 30° and then centrifuged. Nickel was estimated in the supernatants by titration with EDTA using copper-PAN (Reilley *et al.*, 1959) as indicator, sodium by flame photometer and magnesium with a standard solution of EDTA using eriochrome black T as indicator and 2 per cent NaCN solution as a masking agent. The amount of nickel adsorbed at different intervals of time was then obtained from the amount of nickel added minus remaining in the supernatants, the corresponding concentrations of Na and Mg in the illite phase were obtained by the difference (BEC—concentration of the cation in the supernatant liquid). The results are shown in Fig. 1.

To study the effect of pH, exchange experiments were carried out at pH values adjusted to 3, 4, 5, 6, 7, and 9, the pH adjustment having made with 0.1M HCl or 0.1M NaOH as required. For this purpose 10 ml of appropriate clay 1, 5 and 15 ml of 0.005 M NiCl_2 were taken in several glass stoppered tubes and their ionic strength was adjusted as described earlier. The tubes were then shaken for 3 hrs in a thermostatic water bath and the samples centrifuged. The amount of nickel in the supernatant liquids and clay phase were estimated as above. The results are shown in Fig. 2.

For an examination of reversibility, exchange experiments were carried out at constant ionic strength by taking 10 ml suspension of Mg-illite in several glass stoppered tubes, adding varying amount of NiCl_2 and then estimating the amount of nickel adsorbed. Similarly, reverse exchange was studied by taking 10ml suspension of Ni-clay in several glass stoppered tubes, adding varying amounts of MgCl_2 and then estimating the amount of nickel desorbed. The results are given in Figs. 3 and 4.

The exchange isotherms were determined at two different temperatures (30° and 60° C) for nickel exchange on Na- and Mg-illite with adjustment of total ionic strength at a pH value of 5.0 as described earlier (Singhal *et al.*, 1978) with a shaking time of 3hrs. The curves are given in Fig. 5.

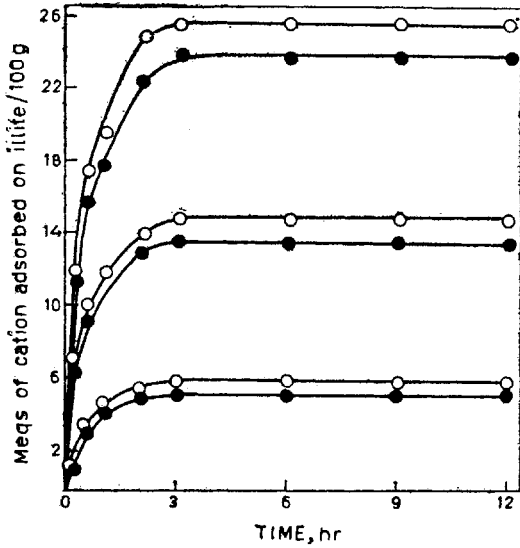


FIG. 1. Effect of time on the exchange, open circles (○) indicate nickel exchange on Na-illite and closed circles (●) indicate nickel exchange on Mg-illite.

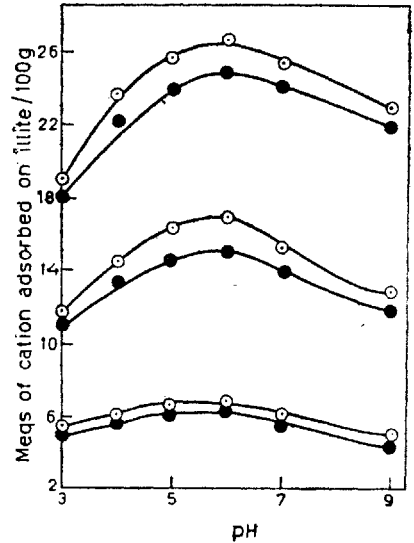


FIG. 2. Effect of pH on the exchange, open circles (○) indicate nickel exchange on Na-illite and closed circles (●) indicate nickel exchange on Mg-illite.

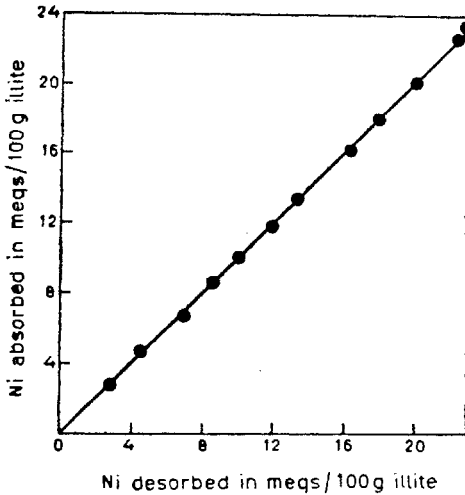


FIG. 3. Nickel desorbed in Magnesium exchange on Ni-illite vs nickel adsorbed in nickel exchange on Mg-illite.

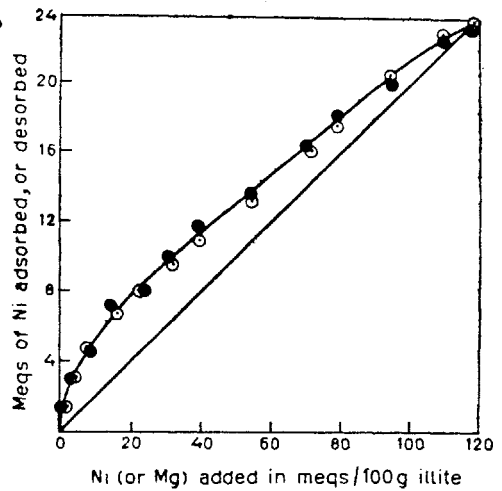


FIG. 4. Mg-Ni exchange on Illite at 30 °C in the forward and reverse direction. ●, Ni adsorbed on Mg-illite, ○, Ni desorbed from Ni-illite.

RESULTS AND DISCUSSION

An examination of Fig. 1 showed that exchange increased upto 3hrs for both the cations and thereafter reached equilibrium. Thus 3hrs were necessary for equilibrium to be attained and was used in further exchange experiments.

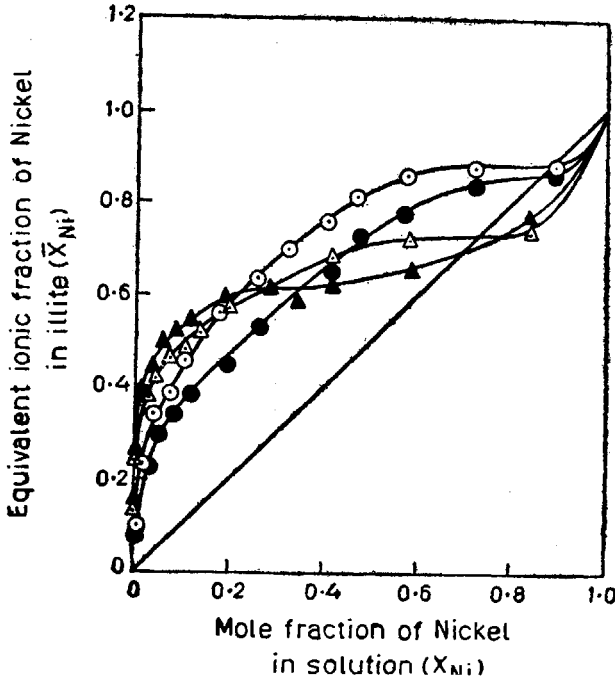


FIG. 5. Exchange isotherms involving nickel exchange on Na- (Δ , \blacktriangle) illites and Mg- (\circ , \bullet) illites at 30° and 60 °C.

From an examination of Fig. 2, it was seen that exchange increased upto a pH value 6 and then declined. At the highest concentration of exchangeable cation added, the exchange was in the neighbourhood of the BEC of the clay at a pH value of 5.0. This value of pH was, therefore selected for further examination of the exchange.

Figs. 3 and 4 showed the reversibility of exchange of nickel with Mg-illite.

The exchange equilibria between the Na- and Mg-illite and nickel may be represented by the equations :



where barred quantities refer to the equilibrium concentration of ion concerned in clay phase and unbarred that in solution phase.

The selectivity coefficient K_c for above reactions are calculated (Marinsky, 1966) as,

$$K_c = \frac{\bar{X}_{Ni} \cdot X_{Mg}}{\bar{X}_{Mg} X_{Ni}} \cdot \frac{\gamma_{CaCl_2}}{\gamma_{NiCl_2}} \quad \dots(3)$$

$$K_c = \frac{\bar{X}_{Ni} (X_{Na})^2}{(\bar{X}_{Na})^2 X_{Ni}} \cdot \frac{\gamma^2_{NaCl}}{\gamma_{NiCl_2}} \quad \dots(4)$$

where \bar{X} refers to the equivalent ionic fractions of counter ion in the exchanger phase, X to the mole fractions of counter ion in the solution phase (relative to the total molality of counter ions) and γ to the activity coefficients of the specified salt in the solution. The value of mean ionic activity coefficients in mixed solution were calculated as described by Laudelout *et al.* (1972). The values obtained for \bar{X}_{Ni} and X_{Ni} at both the temperatures for both the exchanges are represented in Fig. 5.

An examination of Fig. 5 revealed that the isotherms for the two systems at both the temperatures lie above the diagonal showing a strong preference for Ni by illite as compared to Na, or Mg ions throughout the range of concentration studied. With rise in temperature the affinity of Ni for Na-illite increase while for Mg-illite it decreased. From the results it was concluded that Ni was more preferred by Mg-illite than Na-illite, and the sequence of preference for illite was $Ni > Na > Mg$.

The values obtained for K_c and their variation with temperature and \bar{X}_{Ni} are shown in Fig. 6. During both the exchanges at both the temperatures the selectivity quotient (K_c) decreased as value of \bar{X}_{Ni} increase. Such trend indicated that the preference of Ni for illite generally decreased with a rise in its concentration in the solid phase.

For a further examination of the equilibrium, the thermodynamic equilibrium constant K was calculated from the simplified relationship of Gaines and Thomas (1953) :

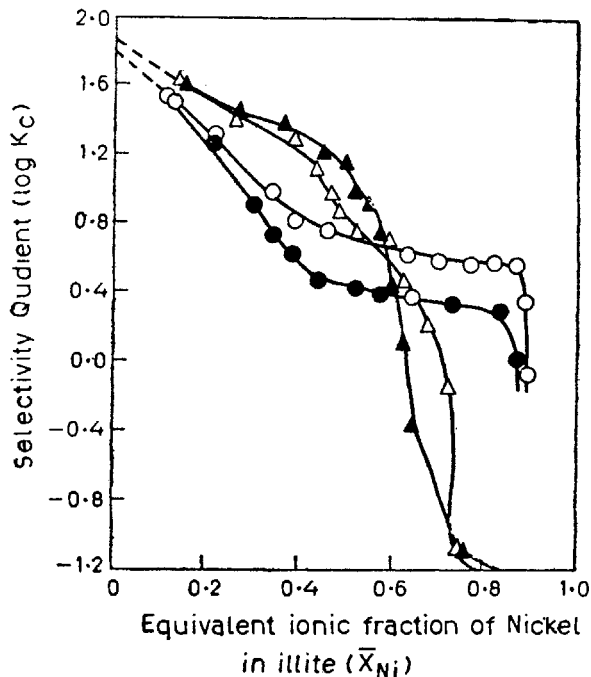


FIG. 6. Selectivity of nickel on nickel on Na (Δ , \blacktriangle) illite and Mg (\circ , \bullet) illite at 30° and 60 °C.

$$\ln K = (Z_B - Z_A) + \int_0^1 \ln K_c d\bar{X}_{Ni}$$

where Z_A was the valence of Na and Mg; and Z_B of Ni. For the derivation of the above simplified formula from Gaines and Thomas (1953) original relationship, it became necessary to assume that

$$\frac{Z_A}{\phi_B} (b) = \frac{Z_B}{\phi_A}$$

i.e., the activity of water was constant. That this was so borne out by the fact that the equilibria was carried out in dilute suspensions with a constant volume of water in the mixture.

The values of K were calculated by evaluating the integrals from the areas under the curves (Fig. 6) using the trapezoidal rule. The values are given in Table I. The values of K supported the inferences drawn from exchange isotherms for the affinity of the cations on the illites surface at both the temperatures.

TABLE I

Thermodynamic values of Na-Ni and Mg-Ni exchanges on illite at 30° and 60 °C.

Thermodynamic parameters	Na-Ni system		Mg-Ni system	
	30 °C	60 °C	30 °C	60 °C
K	1.17	1.28	7.74	4.93
ΔG° (k cal/mole)	- 0.10	- 0.16	- 1.24	- 1.06
ΔH° (k cal/mole)		0.58		- 3.02
ΔS° (cal/mole degree)		2.21		- 5.89

The values of overall change in, free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were calculated from the well-known equations (Singhal *et al.*, 1976) and are given in Table I. The values of ΔG° were negative in both the exchanges at both the temperatures and followed the order Mg > Na. With a rise in temperature the values decreased during Na-Ni exchanges while increased in Mg-Ni exchange. At both the temperatures both the exchanges were therefore spontaneous with a higher preference for Ni ion. Alternatively, it can be said that base exchange on illite surface followed the order Ni > Na > Mg, a result which is in accordance with the exchange isotherms. Values of ΔH° showed that the exchanges were temperature-dependent, the reaction being endothermic during the Ni exchange on Na-illite and exothermic during its exchange on Mg-illite. Such energy changes indicate that Ni was less tightly bound than Na and more strongly bound than Mg on illite surface. The exchanges were also ruled by entropy effects. The greater disorder in the Na-Ni system, indicated by the positive entropy change appears to arise from a process of dehydration of the hydration shell around the Ni ions caused by Na ions and an extended diffuse distribution of ions in the electrical

double layer. On the other hand the small negative entropy changes during Ni exchange on Mg-illite results from the binding of Ni to fixed specific site on the illite surface. The hydration shell around the Ni ions remains intact contributing to a greater order in the final state of exchanges. These facts are supported by evidences given by Gast and Klobe (1971); Biggar and Cheung (1973).

To check the validity and accuracy of thermodynamic parameters for the nickel exchange on Na- and Mg-illites, a comparison of these was made with those obtained from triangle rule. During Na-Ni and Mg-Ni exchanges the values of ΔG° at 30° and 60 °C showed differences of -48 cal/mole and -33 cal/mole; 83 cal/mole and 107 cal/mole respectively, while the values of ΔH° and ΔS° showed a difference of -66 cal/mole, -0.10 cal/mole; -186 cal/mole, -0.88 cal/mole respectively when compared with the values obtained indirectly from the values for (Na-Ca and Ca-Ni); (Mg-Na and Na-Ni) exchanges. The differences were within experimental error limits as reported by Gast (1969).

The surface phase coefficients of ions concerned were calculated from the expressions (Van Bladel & Menzel, 1969). The values obtained are given in Tables II and III. The values were indicative of a non ideal system resulting in an increase

TABLE II
Solid phase activity coefficients, free energies, enthalpies and entropies of mixing for different Na-Ni compositions on illite surface at 30° and 60 °C.

\bar{X}_{Ni}	f_{Na}^2	f_{Ni}	ΔG_m°	ΔH_m°	ΔS_m°
30 °C					
0.143	1.133	0.030	- 243.6	- 676	- 1.43
0.261	1.092	0.050	- 432.0	532.2	- 0.35
0.387	1.080	0.079	- 564.9	- 456.7	0.36
0.432	1.060	0.094	- 594.6	- 389.7	0.67
0.468	0.960	0.119	- 614.8	- 277.7	1.11
0.487	0.843	0.142	- 626.5	- 316.1	1.03
0.523	0.794	0.158	- 648.5	- 180.0	1.55
0.593	0.816	0.179	- 664.5	195.5	2.84
0.617	0.596	0.232	- 662.5	232.0	2.92
0.667	0.444	0.296	- 652.0	226.5	2.90
0.725	0.338	0.361	- 626.7	144.3	2.54
0.790	0.048	0.722	- 541.7	500.6	0.14
60 °C					
0.143	1.133	0.033	- 257.3	- 816.5	- 1.68
0.254	1.140	0.062	- 403.0	- 639.9	- 0.71
0.373	1.165	0.078	- 566.2	- 549.5	0.05
0.446	1.188	0.095	- 633.4	- 457.2	0.50
0.495	1.144	0.107	- 687.1	- 280.2	1.22
0.519	1.040	0.126	- 699.6	- 297.9	1.21
0.551	0.932	0.145	- 726.8	- 167.7	1.68
0.577	0.689	0.191	- 737.2	262.6	2.99
0.604	0.486	0.248	- 747.7	306.7	3.17
0.626	0.322	0.329	- 741.9	399.4	3.43
0.685	0.272	0.380	- 711.1	256.0	2.90
0.810	0.062	0.795	- 472.8	- 620.1	- 0.44

TABLE III

Solid phase activity coefficients, free energies, enthalpies and entropies of mixing for different Mg-Ni compositions on illite surface at 30° and 60 °C

\bar{X}_{Ni}	f_{Mg}	f_{Ni}	ΔG_m^x	ΔH_m^x	ΔS_m^x
30 °C					
0.109	0.980	0.009	- 326.7	0.0	1.07
0.228	0.898	0.026	- 555.9	0.0	1.83
0.343	0.740	0.082	- 633.1	- 749.1	- 0.38
0.383	0.606	0.142	- 638.1	- 822.2	- 0.60
0.459	0.590	0.190	- 634.0	- 719.8	- 0.61
0.568	0.555	0.295	- 597.9	- 403.8	0.64
0.636	0.505	0.385	- 513.4	- 456.7	- 0.19
0.700	0.490	0.480	- 436.9	- 191.8	0.81
0.760	0.472	0.591	- 349.7	29.2	1.25
0.811	0.495	0.679	- 270.4	73.1	1.13
0.856	0.452	0.768	- 204.6	228.4	1.43
0.867	0.292	0.845	- 185.9	- 208.3	- 0.07
0.876	0.118	0.980	- 172.0	- 340.9	- 0.56
60 °C					
0.109	0.980	0.009	- 359.2	0.0	1.07
0.228	0.898	0.026	- 611.0	0.0	1.83
0.306	0.720	0.125	- 572.6	- 922.4	- 1.05
0.346	0.619	0.196	- 583.1	- 913.6	- 1.00
0.385	0.562	0.259	- 580.4	- 670.8	- 0.27
0.442	0.490	0.368	- 561.1	- 176.5	1.16
0.523	0.488	0.449	- 508.2	- 412.6	0.29
0.574	0.449	0.524	- 472.5	- 72.8	1.20
0.694	0.449	0.605	- 410.0	- 93.6	1.52
0.721	0.436	0.688	- 322.7	182.5	1.55
0.771	0.483	0.730	- 274.1	224.0	1.49
0.833	0.380	0.844	- 200.6	- 320.0	- 0.36
0.868	0.190	0.960	- 169.6	- 439.1	- 0.81

in heterogeneity in the distribution of Na and Mg ions; and a decrease in heterogeneity in case of Ni ions on the solid surface. The results found support from the work of Diest and Talibudeen (1967).

To further examine the deviation of the heterogeneous system from ideality the excess thermodynamic functions for real exchange were calculated in the usual way (Gast & Klobe, 1971). The values of ΔG_m^x in both the exchanges at both the temperatures were negative which meant that with respect to the pure forms the heterogeneous surfaces were more stable than they would be if the mixing were ideal i.e., deviation from ideality occurred in the sense of a more stable mixture. The negative values of enthalpies of mixing (ΔH_m^x) during both the exchanges pointed to a more tightly bound mixtures of Ni and Mg ions; Ni and Na ions. The entropy of mixing for both the exchanges at both the temperatures pass from negative to positive values as the concentration of nickel increases, pointing to a

non ideal state of the mixture and a significant heterogeneity with more disordered distribution of ions on the surface. The difference in the hydration rates of the ions in the mixture resulted in a decrease in entropy with respect to the homoionic form. The excess thermodynamic functions thus again confirmed the differences in the exchange equilibria involving Ni, Na and Mg ions on the illite surface.

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