

Thermodynamics of exchange in clays: Ion exchange equilibria of transition metals and sodium ions on illite

O P BANSAL

Chemical Laboratories, D S College, Aligarh 202 001, India

MS received 24 November 1981; revised 17 March 1983

Abstract. Ion exchange equilibria of bivalent transition metal ions have been studied at 20, 30 and 45°C on illite surface. The exchange isotherms and free energy changes indicate a higher preference of the illite surface for the metal ions. Cd^{2+} and Mn^{2+} ions were preferred throughout the entire range while reversal of behaviour occurred during Cu^{2+} , Zn^{2+} and Co^{2+} ions exchange on the illite surface. Enthalpy changes suggested a stronger preference of transition metal ions for the illite surface. Entropy changes indicated an increase in the order of system. The surface phase coefficients of the cations showed that with increasing metal ion saturation f_M continuously increases while f_{Na} decreases. The excess thermodynamic functions showed that the exchange reactions were non-ideal.

Keywords. Illite; ion exchange; thermodynamics; transition metals.

1. Introduction

Since plant nutrition and physico-chemical properties of soils are largely controlled by cation exchange between the surface of clay particles and the soil solution, an understanding of the equilibrium distribution of cations between these two phases is of fundamental importance in soil science. Although stoichiometry and reversibility of ion-exchange have been clearly established (Lamberg 1876), the mass action equations used to describe the exchange phenomenon apply only to a limited range of concentration of cations in the soil solution and on the exchange sites. Weigner (1931) followed by other workers broadened this concept.

Heavy metals such as Cu, Pb, Co, Zn, Mn and Cd are found only in traces in soils but may become concentrated under some circumstances. Their deficiency or excess can have considerable effect on plants, animals and human beings. The adsorption of heavy metals by clays moderates the partition of such metals between solid and aqueous phases in soils and controls their availability to plants and their concentration in aquifers.

In this paper the interactions of Cd^{2+} , Co^{2+} , Cu^{2+} , Zn^{2+} and Mn^{2+} with Na-illite suspension (pH = 6.4) at constant ionic strength have been studied with the help of thermodynamic parameters. The bases of the treatment are the thermodynamic models of earlier workers (Gaines and Thomas 1953; Deist and Talibudeen 1967; Singhal *et al* 1978; Udo 1978; Bansal 1981).

2. Experimental

The illite used was an American sample obtained from Morris, Illinois. The $< 2 \mu\text{m}$ fraction was purified by sedimentation and centrifugation. The suspension was then

converted into chloride-free Na-illite by Aldrich and Buchanan's (1958) method, and then into Cd-, Zn-saturated illites by the usual procedure. The concentration of the suspension used was 15 gl^{-1} . The base exchange capacity (BEC) of Na-illite used was 20.4 m.e./100 g as determined by Ganguli's (1951) method.

The exchange was carried out by taking 10 ml sample of Na-illite suspension (pH = 6.4) in glass stoppered tubes, and adding various amounts (0–15 ml) of 0.005 M transition metal solution. The ionic strength of each sample was then adjusted to a constant value 0.018 by adding 0.015 M NaNO_3 solution. The final volume was adjusted to 25 ml with distilled water. The tubes were shaken for 4 hr at 20 ± 0.1 , 30 ± 0.1 and $45 \pm 0.2^\circ\text{C}$. The mixtures were then centrifuged and the cations in the supernatant liquids estimated.

For the reverse reaction, 10 ml of transition metal ion saturated illite was treated with various amounts (0–15 ml) of 0.015 M NaNO_3 solution with ionic strength adjusted to 0.018 by adding 0.005 M transition metal solution. The tubes were shaken for 4 hr and then centrifuged.

The equilibrium concentration in the solid phase and in the solution phase was evaluated from the change of M^{2+} and Na^+ concentration relative to the initial concentrations of the solutions. The concentration of transition metals in the solution was determined by complexometric titrations (Reilley *et al* 1959) with EDTA. Sodium was estimated by flame photometry.

2.1 Theoretical aspects

The ion-exchange reactions of bivalent transition metal ions/ Na^+ exchange on illite can be represented as:



where bar refers to clay phase and M^{2+} is bivalent transition metal ions.

The selectivity coefficient K_C of the above reaction can be defined as (Marinsky 1966)

$$K_C = \frac{m_{\text{Na}^+}^2 \cdot \overline{X}_{\text{M}^{2+}} \cdot \gamma_{\text{Na}^+}^2}{m_{\text{M}^{2+}} \cdot \overline{X}_{\text{Na}^+}^2 \cdot \gamma_{\text{M}^{2+}}}, \quad (2)$$

where m_{Na^+} and $m_{\text{M}^{2+}}$ are the ionic activity coefficients of Na^+ and M^{2+} in solution. $\overline{X}_{\text{Na}^+}$ and $\overline{X}_{\text{M}^{2+}}$ are the equivalent fractions of the exchanging Na^+ and M^{2+} ions in illite phase.

The values of ionic activity coefficient ratio ($\gamma_{\text{Na}^+}^2/\gamma_{\text{M}^{2+}}$) in solution have been calculated using the following equation (Kraus and Randon 1959) as described elsewhere (Abe and Sudoh 1980)

$$\log \gamma_{\text{Na}^+}^2/\gamma_{\text{M}^{2+}} = \log \gamma_{\pm \text{NaNO}_3}^4/\gamma_{\pm \text{M(NO}_3)_2}^3 = 2S\sqrt{I}/1 + 1.5\sqrt{I} \quad (3)$$

and

$$S = 1.8252 \times 10^6 (\rho/\epsilon^3 T^3)^{\frac{1}{2}} \quad (4)$$

where ρ is the density of water, ϵ the dielectric constant of water and T the absolute temperature of the system.

The thermodynamic equilibrium constant (K) can be evaluated by using the simplified treatment of Gaines and Thomas (1953) equation, assuming that the change of water content in the clay and the entrance of anion from solution phase are

negligible:

$$\ln K = -(Z_M - Z_{Na}) + \int_0^1 \ln K_C d\bar{X}_M, \quad (5)$$

(where Z is the valence of cations and $M = Cd^{2+}, Mn^{2+}, Cu^{2+}, Zn^{2+}$ and Co^{2+}).

The change in the free energy of the ion-exchange reaction ΔG^0 , per cation equivalent was calculated as:

$$\Delta G^0 = -RT \ln K / Z_M \cdot Z_{Na}. \quad (6)$$

The change in the enthalpy (ΔH^0) and entropy was calculated as described elsewhere (Singhal *et al* 1978).

The surface phase coefficients of ions concerned were calculated from the expressions:

$$\ln f_M = -\bar{X}_{Na} - (\bar{X}_{Na} \ln K_C) + \int_{\bar{X}_M}^1 \ln K_C d\bar{X}_M \quad (7)$$

$$\ln f_{Na}^2 = \bar{X}_M + (\bar{X}_M \ln K_C) - \int_0^{\bar{X}_M} \ln K_C d\bar{X}_M. \quad (8)$$

The excess thermodynamic functions (ΔG_m^x , ΔH_m^x , ΔS_m^x) for the interactions were calculated as described elsewhere (Talibudeen 1971).

3. Results and discussion

Preliminary studies showed that equilibrium was attained within 3–5 hr. The relation between the adsorbed Cd^{2+}, Zn^{2+} ions on Na-illite and the amount of Cd^{2+} and Zn^{2+} ions liberated from Cd- and Zn-illite indicated stoichiometry for the ion-exchange reaction within experimental error. The ion-exchange isotherms for Cd-Na exchange at 20, 30 and 45°C is shown in figure 1. The ion-exchange isotherm for the systems Cd^{2+}/Na^+ , Mn^{2+}/Na^+ , Cu^{2+}/Na^+ , Zn^{2+}/Na^+ and Co^{2+}/Na^+ for the same temperatures was also plotted.

An examination of exchange isotherms showed that the ion-exchange isotherms can be classified into 2 types (a) selectivity for the entering cation over the entire range of exchanger composition *i.e.* for Cd^{2+}/Na^+ system and Mn^{2+}/Na^+ systems, (b) entering cations show a selectivity reversal with increasing equivalent fraction in the exchanger phase *i.e.* for Cu^{2+}/Na^+ , Zn^{2+}/Na^+ and Co^{2+}/Na^+ system. The affinity of transition metal ions (M^{2+}) decreases with rise in temperature. The results showed that the sequence of preference for illite was $Cd^{2+} > Mn^{2+} > Cu^{2+} > Zn^{2+} > Co^{2+}$.

The thermodynamic equilibrium constant K was evaluated from equations (2) and (5) and by plotting the curve between $\log K_C$ and \bar{X}_M . Figure 2 represents the curves for Cd-Na exchange. The values are given in table 1. The K values supported the inferences drawn from exchange isotherms for the affinity of cations on the illite surface at all the experimental temperatures.

Table 2. The surface phase activity coefficients, excess free energies, enthalpies of mixing for different Cd-Na compositions on illite surface at 20°C.

\bar{X}_M	f_M	f_{Na}^2	ΔG_m^* (J/eq)	ΔH_m^* (J/eq)	ΔS_m^* (J/eq-deg)
<i>Cd-Na</i>					
0.138	0.339	1.119	-64.2	0.0	0.22
0.261	0.386	1.196	-142.3	-98.2	0.15
0.365	0.436	1.341	-141.8	-97.1	0.15
0.434	0.485	1.441	-130.2	-92.0	0.13
0.515	0.541	1.540	-129.6	-90.2	0.13
0.563	0.581	1.544	-124.5	-87.7	0.12
0.691	0.682	1.658	-120.5	-82.8	0.12
0.756	0.772	1.653	-88.6	-65.5	0.11
0.807	0.842	1.522	-70.3	-55.8	0.05
0.829	0.880	1.499	-44.5	-51.7	-0.02
0.870	0.924	1.497	-20.4	-50.6	-0.10
0.925	0.981	1.337	-4.4	-45.3	-0.14
0.957	1.025	1.305	43.1	-23.7	-0.23

table 2. Surface phase activity coefficients have been interpreted in terms of relative freedom of movement of the adsorbed ions in clay systems (Deshpande and Marshall 1959; Gast 1962). The low f_M values (< 1) at low metal saturation indicate that metal ions mostly occupy the Stern layer. However, the increase in f_M with increasing metal ion saturation suggests that an increasing number of metal ions are distributed in Gouy-Chapman layer as metal ion saturation increases.

To examine the deviation of the heterogeneous system from ideality, excess thermodynamic functions for metal ions exchange reactions on Na-illite at 20, 30 and 45°C were calculated. The values at 20°C are given in table 2. The values of free energy of mixing were always negative, which means that with respect to pure forms, deviation from ideality occurred in mixed cation systems, which is more stable. The values of enthalpies of mixing were negative during metal ion exchange, while the entropies were positive. These results show that the mixture of sodium and metal ions are more strongly bound to the clay surface, and distribution of the mixture is more disordered on the heteroionic exchanger, as compared with the pure forms. The excess thermodynamic functions thus again supported the difference in the exchange equilibria involving sodium, cadmium, manganese, copper, zinc and cobalt ions on illite surface.

3.1 Interpretation of the selectivity at the infinitesimal concentration of the transition metals

The hypothetical thermodynamic data at infinitesimal concentration were calculated to interpret the selectivity of the microquantities of transition metals on illite surface. The values of $(\ln K_c)\bar{X}_M \rightarrow 0$ were obtained by extrapolating to zero-loading of transition metals. From these values (table 3) the hypothetical thermodynamic data were calculated by a similar treatment to that for the overall equilibrium constant.

The values of $(\Delta G^0)\bar{X}_M \rightarrow 0$ are negative for all systems studied, indicating that the transition metal ions can be exchanged preferably to the clay surface. The hypothetical

Table 3. Hypothetical thermodynamic data on zero loading of the ion-exchange reaction.

Cation	$(\ln K_C) \bar{X}_M \rightarrow 0$				$(\Delta G^0) \bar{X}_M \rightarrow 0$ (kJ/eq)			
	20°C	30°C	45°C	5°C	20°C	30°C	45°C	5°C
Cd ²⁺	5.66	5.43	5.13	5.13	-6.90	-6.84	-6.78	-6.78
Mn ²⁺	5.23	4.91	4.51	4.51	-6.37	-6.18	-5.96	-5.96
Cu ²⁺	5.34	5.00	4.61	4.61	-6.51	-6.30	-6.09	-6.09
Zn ²⁺	5.16	4.74	4.24	4.24	-6.28	-5.97	-5.60	-5.60
Co ²⁺	4.84	4.51	4.10	4.10	-5.89	-5.68	-5.42	-5.42
					$(\Delta H^0) \bar{X}_M \rightarrow 0$ (kJ/eq)	$(\Delta S^0) \bar{X}_M \rightarrow 0$ (J/deg-eq)	$(\Delta H_{ex}^0) \bar{X}_M \rightarrow 0$ (kJ/eq)	$(\Delta S_{ex}^0) \bar{X}_M \rightarrow 0$ (J/eq-deg)
					-8.16 ± 0.04	-4.33 ± 0.05	179.7	-9.77
					-11.21 ± 0.06	-16.54 ± 0.09	156.6	-36.41
					-11.59 ± 0.05	-17.36 ± 0.09	32.0	-40.79
					-14.29 ± 0.07	-27.37 ± 0.11	54.3	-52.26
					-11.59 ± 0.11	-19.45 ± 0.11	64.1	-55.85

thermodynamic selectivity series was found to be $\text{Cd}^{2+} > \text{Cu}^{2+} > \text{Mn}^{2+} > \text{Zn}^{2+} > \text{Co}^{2+}$, which is in accordance with the work of Abe and Kasai (1979). The numerical values of thermodynamic parameters (Δx^0) contribute to the difference in the thermodynamic function of hydration (Δx_{hydr}^0) of the ions in aqueous solution and that (Δx_{ex}^0) of the exchanged cations. The values of Δx_{hydr}^0 were obtained from Rosseinsky (1965) table. The calculated $(\Delta H_{\text{ex}}^0)\bar{X}_M \rightarrow 0$ were almost parallel to ΔH_{hydr}^0 in magnitude, indicating that the ion-exchange cations maintain the structure of the octahedral hydrated cations. The increased $(\Delta S_{\text{ex}}^0)\bar{X}_M \rightarrow 0$ for $\text{Cd}^{2+}/\text{Na}^+$ and $\text{Mn}^{2+}/\text{Na}^+$ exchange can be interpreted in terms of the entropy producing process by the net transfer of water molecules from clay phase to solution phase. The high selectivity coefficient of Cd^{2+} may be due to the contribution of a highly negative value of $(\Delta H^0)\bar{X}_M \rightarrow 0$ and a low value of $(\Delta S^0)\bar{X}_M \rightarrow 0$. It suggests a much stronger chemical bond between the Cd^{2+} ions and the clay than for the other transition metals.

Acknowledgement

Author is thankful to Dr S S Gupta, for facilities and encouragement. Thanks are also due to UGC (New Delhi) for financial assistance.

References

- Abe M and Kasai K 1979 *Sep. Sci. Technol.* **14** 895
 Abe M and Sudoh K 1980 *J. Inorg. Nucl. Chem.* **42** 1051
 Aldrich D G and Buchanan J R 1958 *Soil Sci. Soc. Am. Proc.* **22** 281
 Bansal O P 1981 *J. Inorg. Nucl. Chem.* **43** 1887
 Biggar J W and Cheung M W 1973 *Soil Sci. Soc. Am. Proc.* **37** 863
 Breeck D W 1974 *Zeolite molecular sieves, structure, chemistry and use* (New York: Wiley) p. 532
 Deist J and Talibudeen O 1967 *J. Soil Sci.* **18** 138
 Deshpande K B and Marshall C E 1959 *J. Phys. Chem.* **63** 1659
 Gaines G L and Thomas H C 1953 *J. Chem. Phys.* **21** 714
 Ganguli A K 1951 *J. Phys. Coll. Chem.* **55** 1417
 Gast R G 1962 *J. Coll. Sci.* **17** 492
 Gast R G and Klobe W D 1971 *Clays Clay Miner.* **19** 311
 Kraus K A and Randon R J 1959 *J. Phys. Chem.* **63** 1901
 Lamberg J 1876 *Z. Dent. Geol. Ges.* **28** 519
 Marinsky J A 1966 *Ion exchange. A series of Advances.* (New York: Marcel Dekker) Vol I, Chap. 7
 Reilley C N, Schmid R W and Sadek F S 1959 *J. Chem. Educ.* **36** 555
 Rosseinsky D R 1965 *Chem. Rev.* **65** 467
 Singhal J P, Khan S U and Bansal O P 1978 *J. Inorg. Nucl. Chem.* **40** 1591
 Talibudeen O 1971 *Int. Sym. Soil Fertility* (New Delhi) Vol I, p. 97
 Udo E J 1978 *Soil Sci. Soc. Am. J.* **42** 556
 Weigner G 1931 *J. Soc. Chem. Indian* **50** 657