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Kinetics of Ion-exchange on Sodium-, Calcium-, and Magnesium Saturated Kaolinites

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The kinetics of Na^+, Ca^{2+}, Mg^{2+}, and Ni^{2+} ion-exchange reactions on kaolinite have been studied at four temperatures 16, 26, 36, and 46 °C. The mechanism of ion-exchange is a film diffusion as shown by interruption and ϕ tests. Kinetics parameters *e.g.* diffusion coefficients, half time of exchange, energies of activation have also been calculated and were used to predict the theoretical behaviour (mechanism) of Ni^{2+} exchange on the kaolinite surface.

The replacement of cations is one of the most important phenomenon which controls the storage capacity of a soil for plant nutrient elements. Thermodynamics is a powerful tool to study conditions at equilibrium but kinetics have an important role in the study of the mechanism of ion-exchange. A relatively little consideration has been given to the kinetics of ion-exchange. Various studies of the kinetics of ion-exchange on zeolites,[1] synthetic ion-exchangers[2—6] have been reported. Information in regard to kinetics of exchange in clays and soils is meagre.[7,8]

Nickel is an important trace element in plant nutrition and its formulation as $NiCl_2$ are often used as fungicide in soils. Kaolinite mineral is a 1:1 layer silicate, and occurs commonly in soils. It is a dioctahedral mineral with triclinic symmetry. The structure of the mineral involves hydrogen bonding between adjacent layers, which prevents the expansion of kaolinite beyond its basal spacing. Clay minerals constitute the most important reactive surface of soil providing reactive sites at the edges, corners, interlayer, and interlattice positions.[9—11] In the present report I have summarized my studies on the kinetics of exchange between Ni(II) and Na-, Ca-, Mg-kaolinites.

Experimental

Kaolinite used in these studies was a monomineralic standard from Bath, South Carolina. Less than 2 μm clay fraction was purified by sedimentation and centrifugation. It was converted into chloride free Na-kaolinite and then into Ca- and Mg-saturated kaolinites by ion exchange technique. The concentration of the mineral suspension ranged from 11.0 to 12.2 g dm^{-3}. The base exchange capacity (BEC) of the Na-kaolinite was 135 μequiv. g^{-1} clay, determined by Ganguli's method.[12] For the determination of the BEC of Ca- and Mg-kaolinite[13] a known volume of suspension was treated with a mixture consisting of 1 mol dm^{-3} $NiCl_2$ in 0.0001 mol dm^{-3} HCl (keeping in contact for 24 h) and the amount of calcium and magnesium released was estimated by titration with EDTA, giving the value 110 and 118 μequiv. g^{-1} clay respectively.

The ion-exchange reaction between Na-, Ca-, and Mg-kaolinites and Ni^{2+} can be represented as

$$2\overline{Na^+} + Ni^{2+} \rightleftharpoons \overline{Ni^{2+}} + 2Na^+, \tag{1}$$

$$\overline{M^{2+}} + Ni^{2+} \rightleftharpoons \overline{Ni^{2+}} + M^{2+}, \tag{2}$$

(where $M^{2+} = Ca^{2+}$ or Mg^{2+}).

Kinetic Measurement. Rates of exchange were measured by limited bath technique, for it, 10 cm^3 of appropriate clay suspensions were treated with 15 cm^3 of 0.002 mol dm^{-3} nickel solution. The solutions were kept in contact for appropriate time intervals (2—60 min) of time. The contents were then centrifuged and the concentration changes in the suspensions were determined by EDTA titrations in case of Ni^{2+}, Ca^{2+}, and Mg^{2+} ions and flame photometry in Na^+. The values of fractional attainment of equilibrium (F) at 16, 26, 36, and 46 °C were calculated using the expression:

$$F = \frac{\text{The amount of } Ni^{2+} \text{ exchange at time } t}{\text{The amount of exchange at infinite time (equilibrium)}}. \tag{3}$$

To perform the interruption test above procedure was applied for another set at two concentrations of Ni^{2+} and after a specified time intervals (10 and 30 min) the clay particles were removed and quickly separated from adhering solution by centrifugation. After 5 min they were re-immersed in their solutions and the experiment continued (Fig. 1). The concentration of Ni^{2+} at different time intervals at 16, 26, 36, and 46 °C was estimated before and after interruption.

The nature of the rate determining step was confirmed by calculating the value of function ϕ[14] as the values of are $\gg 1$ for film diffusion control and $\ll 1$ for particle diffusion. The values of ϕ are given by the following relation

$$\phi = \frac{X\overline{D}\delta}{CDr_o}(5 + 2\alpha_{\mathrm{B}}^{\mathrm{A}}), \tag{4}$$

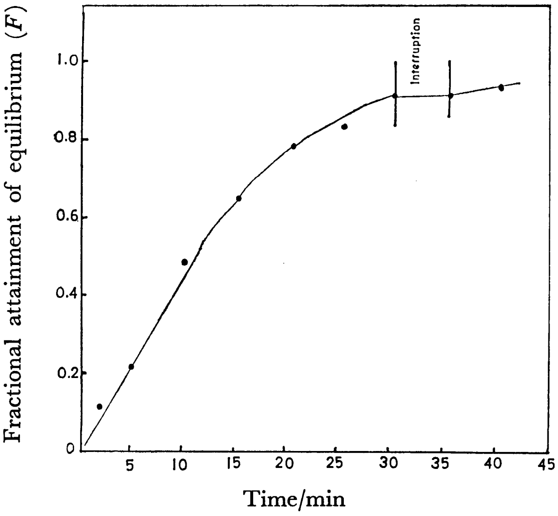

Fig. 1. The effect of interruption test on the rate of Ni^{2+} ion-exchange on Na-kaolinite at 16 °C after 30 min.

where X=concentration of fixed ionic groups taken as equivalent to a maximum exchange, C=concentration of counter ions in solution mequiv. cm^{-3}, $\bar{D}$=interdiffusion coefficient in the ion-exchanger, D=interdiffusion coefficient in the film, r_0=radius of clay particle (10^{-4} cm), δ=film thickness (10^{-2} cm in unstirred solution) and α_B^A the separation factor.

The separation factor α_B^A was calculated from the equivalent ionic fractions, using the equation

$$\alpha_{\mathrm{Na}}^{\mathrm{Ni}^{2+}} = \bar{X}_{\mathrm{Ni}}(X_{\mathrm{Na}})^2/X_{\mathrm{Ni}}(\bar{X}_{\mathrm{Na}})^2, \tag{5}$$

$$\alpha_{\mathrm{M}^{2+}}^{\mathrm{Ni}^{2+}} = \bar{X}_{\mathrm{Ni}}X_{\mathrm{M}}/\bar{X}_{\mathrm{M}}X_{\mathrm{Ni}}, \tag{6}$$

where $\bar{X}$=equivalent ionic fraction in clay phase and X= mole fraction in solution phase.

The values of $\bar{D}_i$ (effective diffusion coefficient in the clay phase) were calculated from the relationship:

$$\bar{D}_i = \mathrm{B}r_0{}^2/\pi^2. \tag{7}$$

The value of B was obtained from the plots of Bt vs. t (Fig. 2), the Bt values have been obtained from the suitable values of 'F' as tabulated by Reichenberg.[15] The values of D_i were calculated by Wheeler's[16] relation $\bar{D}_i = D_{i_\varepsilon}/2$ which has a resemblance (within ±15% error) with the values obtained by Mackie and Meares[17] relation $\bar{D}_i = D_i[\varepsilon/(2-\varepsilon)]^2$, where ε is pore volume of clay. The fractional pore volume of Na-, Ca-, and Mg-kaolinites were determined from bulk and particle densities.

The half time of exchanges ($t_{1/2}$) were calculated from the expression

$$t_{1/2} = 0.23\delta r_0 X/DC. \tag{8}$$

Since temperature effect has been very useful in providing an insight into the theory of all rate processes, the energetics of Ni^{2+} ion-exchange on clay were examined by temperature studies. The diffusion coefficient (D_i) can be related to temperature by the following expression[18]

$$D_i = D_0 \exp(-E_a/RT). \tag{9}$$

The activation energy (E_a) was calculated by the linear relationships of $\log D_i$ vs. $1/T$ and D_0 by extrapolation (Fig. 3). The values are given in Table 2.

The enthalpy (ΔH_a), entropy (ΔS_a) and free energy (ΔG_a) of activation were calculated using the expressions[19]

$$\Delta H_a = E_a - RT, \tag{10}$$

$$D_0 = 2.72d^2kT/h \exp(\Delta S_a/R), \tag{11}$$

$$\Delta G_a = \Delta H_a - T\Delta S_a,$$

where d=ionic jump distance (5×10^{-8} cm), k=Boltzmann constant, h=Planck constant, R=gas constant and T=ab-

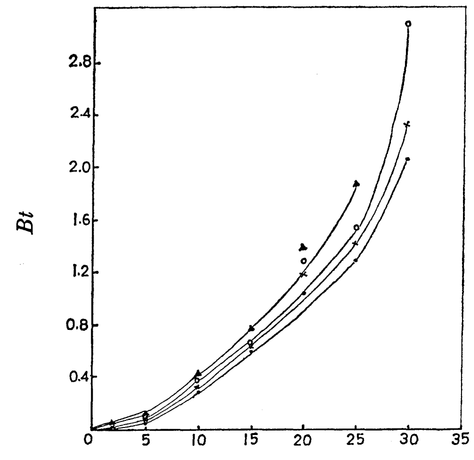

Fig. 2. A plot of Bt vs. t for Ni^{2+} ion-exchange on Na-kaolinites at 16 (●), 26 (×), 36 (○), and 46 °C (▲).

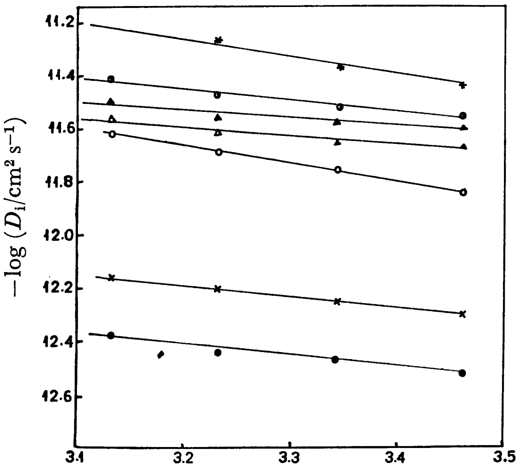

Fig. 3. A plot of $\log D_i$ vs. $1/T$ for Ni^{2+} ion-exchange on Na-kaolinite at 2 (●), 5 (×), 10 (○), 15 (△), 20 (▲), 25 (◑), and 30 (*) min time interval.

Table 1. Diffusion coefficients and ϕ values at different temperatures and time for Ni^{2+} ion-exchange on Na-, Ca-, and Mg-kaolinities

Temp / K	Time / min	Na-kaolinite					Ca-kaolinite					Mg-kaolinite				
		F	$\bar{D}_i\times10^{13}$ / cm^2 s^{-1}	$D_i\times10^{12}$ / cm^2 s^{-1}	ϕ	$t_{1/2}$ / h	F	$\bar{D}_i\times10^{13}$ / cm^2 s^{-1}	$D_i\times10^{12}$ / cm^2 s^{-1}	ϕ	$t_{1/2}$ / h	F	$\bar{D}_i\times10^{13}$ / cm^2 s^{-1}	$D_i\times10^{12}$ / cm^2 s^{-1}	ϕ	$t_{1/2}$ / h
289	2	0.108	0.93	0.30	153	41.7	0.094	0.71	0.23	148	42.1	0.080	0.52	0.17	141	43.1
	5	0.216	1.54	0.50	177	28.3	0.190	1.20	0.39	171	28.9	0.161	0.88	0.29	163	29.3
	10	0.487	4.78	1.54	199	14.2	0.450	3.95	1.30	193	14.6	0.440	3.77	1.26	186	15.4
	15	0.649	6.69	2.16	217	9.0	0.609	5.61	1.84	214	10.1	0.577	4.70	1.57	204	10.1
	20	0.781	7.94	2.56	239	7.5	0.750	6.51	2.14	230	7.8	0.645	5.08	1.70	226	8.0
	25	0.830	8.69	2.80	261	5.8	0.792	7.30	2.40	251	6.2	0.766	6.50	2.17	240	6.4
	30	0.922	11.44	3.70	277	4.1	0.872	8.75	2.87	263	4.4	0.861	8.30	2.77	250	4·9
319	2	0.129	1.29	0.42	130	34.7	0.116	1.10	0.36	126	37.0	0.100	0.77	0.26	120	38.2
	5	0.257	2.12	0.68	144	21.6	0.233	1.90	0.62	139	23.0	0.200	1.29	0.43	135	24.2
	10	0.582	7.43	2.40	162	9.0	0.514	5.55	1.82	158	10.0	0.540	5.69	1.90	150	10.7
	15	0.711	8.60	2.78	177	5.9	0.636	7.27	2.38	175	6.9	0.633	6.52	2.17	168	8.0
	20	0.849	10.48	3.38	190	4.7	0.812	8.75	2.87	186	6.2	0.766	7.61	2.54	179	6.4
	25	0.906	12.50	4.03	208	3.8	0.865	10.41	3.41	207	4.4	0.862	9.46	3.15	201	5.0
	30	1.000	—	—	—	—	0.960	15.60	5.11	216	3.0	0.933	12.40	4.13	209	3·5

Table 2. Energy parameters for Ni^{2+} ion-exchange on Na-, Ca-, and Mg-kaolinites at different temperatures (Time 2—30 min)

Nature of clay	Temp/K	E_a/kJ mol^{-1}	ΔH_a/kJ mol^{-1}	ΔS_a/J mol^{-1} deg^{-1}	ΔG_a/kJ mol^{-1}
Na-kaolinite	289	7.66 to 11.00	5.26 to 8.60	−210.2 to −187.8	59.5 to 69.3
	299		5.18 to 8.51	−210.6 to −188.2	61.5 to 71.5
	309		5.09 to 8.43	−211.0 to −188.6	63.4 to 73.6
	319		5.01 to 8.35	−211.4 to −189.0	65.3 to 75.8
Ca-kaolinite	289	8.61 to 12.92	6.20 to 10.52	−212.6 to −189.7	61.0 to 72.0
	299		6.13 to 10.43	−213.0 to −190.1	63.0 to 74.1
	309		6.04 to 10.35	−213.4 to −190.6	64.9 to 76.3
	319		5.96 to 10.27	−213.8 to −191.0	66.9 to 78.5
Mg-kaolinite	289	9.09 to 13.40	6.69 to 11.00	−214.9 to −191.3	62.0 to 73.1
	299		6.60 to 10.91	−215.4 to −191.8	63.9 to 75.3
	309		6.52 to 10.83	−215.8 to −192.2	65.9 to 77.5
	319		6.44 to 10.75	−216.3 to −192.7	67.9 to 79.7

solute temperature. The values obtained are recorded in Table 2.

Results and Discussion

To study the mechanism of ion-exchange both experimental and theoretical approach were used. The interruption test was applied as an experimental test to decide whether the kinetics are controlled by film diffusion or particle diffusion.[20] The results are presented in Fig. 1. These results showed no change in rate of exchange after 5 min interruption, indicate that the rate determining step is governed by film diffusion at all four temperatures studied. This is because that no concentration gradient was found to exist in the clay and the rate depended on the concentration differences across the film.

The values of ϕ calculated for the Na–Ni, Ca–Ni, and Mg–Ni exchanges at all four experimental temperatures were more than unity indicating that rate is controlled by film diffusion ($\phi \gg 1$) in all the case studied.[14] Table 1 also showed that order of exchange is Na->Ca->Mg-kaolinites as of ϕ values.

A plot of F (fractional attainment) *vs.* t (see Fig. 4) showed that Ni^{2+} exchange on Na-, Ca-, and Mg-kaolinites was characterized by a rapid initial exchange followed by subsequent falling in the rate as the concentration gradient diminished in the film. Rate of exchange also increases with rise in temperature from 16 to 46 °C, which may be due to the fact that mobility of Ni^{2+} increased with increase in temperature.

The values of half time of exchange ($t_{1/2}$) (Table 1) are in the order Mg>Ca>Na, and decreased with increase in time of contact, indicating that the rates of exchange as characterized by half time increased with time of contact (as half time decreases rate of exchange increases). With rise in temperature the $t_{1/2}$ values decreased, confirming the earlier inference.

An observation of Table 1 revealed that the rate of diffusion in the aqueous phase was much faster than in the clay phase at the all four temperatures in all the three exchanges studied and the order was Na->Ca->Mg-kaolinites. The diffusion coefficients increased with rise in temperature as well as with passage of time *i.e.* the rate of exchange of Ni^{2+} ion on Na-, Ca-, and Mg-kaolinites increased with time and temperature and the order of exchange was Na->Ca->Mg-kaolinite.

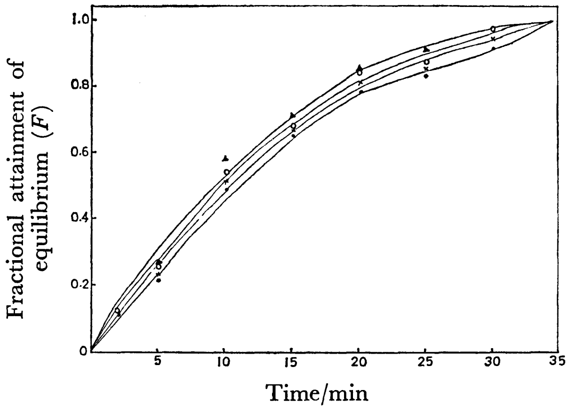

Fig. 4. A plot of fractional attainment of equilibrium (F) *vs.* t for Ni^{2+} ion-exchange on Na-kaolinite at 16 (●), 26 (×), 36 (○), and 46 °C (▲).

An examination of Table 2 showed an E_a range from 7.66 to 13.40 kJ/mol, and were in order Mg>Ca->Na-kaolinites. The magnitude of E_a showed that Ni^{2+} exchange is a film diffusion controlled process without steric hindrance.[21,22] The values of activation energies also confirm that order of exchange is Na->Ca->Mg-kaolinites. The low values of ΔH_a, support the physical type of adsorption involving ion-exchange process. The values of ΔH_a (see Table 2) decreased with rise in temperature or the rate of exchange of the Ni^{2+} increases as temperature of reaction went up, an inference in accordance with earlier conclusions. The negative values of ΔS_a (Table 2) pointed to a greater order produced during the activation process.[6,23] It may be due to formation of activated complex between Ni^{2+}, and Na-, Ca-, or Mg-kaolinites, resulting in a more orderly structure of Ni^{2+} ions on clay surface due to association or fixation and immobilisation of Ni^{2+} ions with consequent loss in the degrees of freedom of the system during the process. The free energy of activation (ΔG_a) (Table 2) for the exchange reaction had a tendency to increase with rise in temperature and were in order Na-<Ca-<Mg-kaolinites, indicating that the activated complexes of Ni^{2+} ions with Na-, Ca-, or Mg-kaolinites

were not very stable and probability of formation of activated complex further decreased with rise in temperature.[24] The increase in rate of exchange of Ni^{2+} with rise in temperature was due to large number of ions passing into an activated state with a less stable configuration.[23]

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