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Thermodynamics of Sr–Mg vermiculite exchange and the effect of PVA on Mg release

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Abstract

The aim of this work is to study the thermodynamics of Sr–Mg vermiculite exchange and the effect of polyvinyl alcohol (PVA) on the interlayer magnesium release from the clay surface. The results indicated that the affinity of adsorption decreases as the unhydrated ionic radius increases. Also it was found that the surface of vermiculite exhibits more selectivity for Sr by treating Mg-vermiculite with PVA than in its absence. With increasing temperature the exchange of Mg by Sr increases. The enthalpy value (ΔH) was positive, i.e. the exchange reaction is endothermic. X-ray diffraction of the clay indicates that the *c*-spacing of vermiculite increases gradually as the adsorbed amount of Sr ion increases on the vermiculite surface. The activity coefficient ratio of f_{Sr}/f_{Mg} varies at 20°C from 0.042 at 10% Sr saturation to 0.364 at 90% Sr saturation, i.e. the ratio increased with increasing Sr saturation. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Thermodynamic; Vermiculite; Exchange; Polyvinyl alcohol; Adsorption

1. Introduction

The interaction of clay minerals with polymers has received a considerable amount of attention because of their great potential as conditioning and stabilizing agents in many applications. Although some of the contributions to this attention have helped to clarify the conformation, adsorption affinity, segment density distribution of the polymer on clay surfaces, a complete satisfactory understanding of the effect of polymer on the cation exchange reactions at the clay surfaces is not available.

The purpose of the present work is to study the effect of adsorption of polyvinyl alcohol on Sr–Mg exchange reaction (interlayer magnesium release from the clay structure) [1].

2. Experimental

2.1. Materials and methods

2.1.1. Clay preparation

Russian vermiculite was used in this study. Particles less than 5 μm were separated by sedimentation from the clay sample. The clay was then converted to the Mg-form by treating it five times with 0.5 M $MgCl_2$. The Mg-clay was washed several times to remove the excess electrolyte by centrifugation and then freeze-dried.

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2.1.2. Equilibration of strontium ions with Mg-clay

The reaction was carried out at two different temperatures (20°C and 40°C) in a thermostated shaker. Powder samples (40 mg) were placed in 50 ml centrifuge tubes. To each of these a 20 ml aliquot of $SrCl_2$ solution was added to give the following initial molar concentration of Sr ion ($\times 10^{-4}$): 0, 5, 10, 20, 30, 40, 50, 60, 70, 80, 100, 150 and 200.

These suspensions were shaken for 24 h and then centrifuged. The supernatants were analyzed for Sr and Mg by atomic absorption spectrophotometry (Perkin–Elmer 403).

To study the effect of polyvinyl alcohol (PVA) [Merck, M.wt=72 000, 98% hydrolyzed], on the interlayer magnesium release from the clay structure, 40 mg samples of Mg-clay were firstly suspended in 10 ml of 5000 ppm of PVA solution. The suspensions were shaken for 48 h at 20°C, then l0 ml of $SrCl_2$ was added to each of these samples to give the same level of $SrCl_2$ concentrations as in the first experiment. The suspensions were again shaken for 24 h and centrifuged. The supernatants were analyzed for Sr and Mg ions.

Thin films of the unmodified and the modified vermiculite at different $SrCl_2$ concentrations were examined as thin, oriend clay layers on glass slides by X-ray diffraction analysis (XRD) using a Phillips Norelco diffractometer (Ni-filtered CuKα radiation and 1°2θ/min recording rate).

2.1.3. Cation-exchange capacity

Duplicate 1 g samples of Mg-vermiculite were washed five times with 0.5 M $BaCl_2$ solution. The supernatant was analyzed for magnesium. The cation-exchange capacity (CEC) value obtained was 1.041 meq/g.

3. Results and discussion

Applying the law of mass action to the exchange reaction,

$$\overline{C}_{Mg} + C_{Sr} \rightarrow \overline{C}_{Sr} + C_{Mg}. \qquad (1)$$

From the equilibrium results, $\overline{X}_{Sr}$ and X_{Sr} are obtained and isotherms are constructed for strontium adsorption on Mg-vermiculite, where $\overline{X}_{Sr}$ and X_{Sr} are the equivalent cation ratios of Sr in clay and in solution respectively, and are given by

$$\overline{X}_{Sr} = \overline{C}_{Sr}/\overline{C}_0 \quad \text{and} \quad X_{Sr} = C_{Sr}/C_0,$$

where C_{Sr} and C_0 are the equivalent concentration of Sr in solution and the total electrolyte concentration respectively. $\overline{C}_{Sr}$ and $\overline{C}_0$ are the corresponding parameters on vermiculite. Similar notation is applied to magnesium [2,3].

3.1. Strontium–magnesium exchange isotherms

Fig. 1 shows the strontium–magnesium isotherm at 20°C in the presence and absence of PVA. The results indicated that the affinity decreases as the unhydrated ionic radius increases, i.e. Mg much more selective than Sr ion. This is the reverse of what is found in organic resins and most other clay minerals [4–6] in which the radii of the fully hydrated ions determine the distance of approach of the cations to the negatively charged surface. This unusual behavior was obtained because the strong attraction forces between the vermiculite sheets prevent the full hydration of the interlayer ions.

Fig. 1 also shows the effect of PVA adsorption on the Mg–Sr exchange. It was found that the surface of vermiculite exhibits more selectivity for Sr by treating the Mg-vermiculite with PVA than in its absence. The difference between these two conditions of exchange

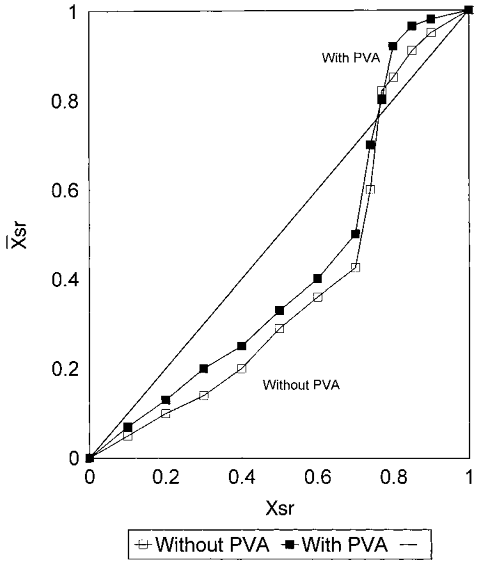

Fig. 1. Strontium–magnesium exchange isotherms at 20°C.

is not relatively high, and it may have been due to that the Mg-vermiculite particles swelled during their treatment with PVA causing condition for Mg ions to leave the surface and to diffuse out of the interlayer and Sr will be adsorbed instead.

3.2. Thermodynamic parameters of the Mg–Sr exchange

From reaction (1) the uncorrected selectivity coefficient is readily calculated from Eq. (2)

$$\bar{K}_c = (\bar{X}_{Sr}/\bar{X}_{Mg})(X_{Mg}/X_{Sr}). \tag{2}$$

The corrected selectivity coefficient K_c for the preferences of the solution phase can be obtained by means of the solution ion activity coefficient (γ),

$$K_c = \bar{K}_c(\gamma_{Mg}/\gamma_{Sr}). \tag{3}$$

Figs. 2 and 3 show the experimental value of log K_c and the equivalent fraction ($\bar{X}$) of strontium ion in clay at 20°C and 40°C, respectively.

The integration indicated in Eq. (4) for evaluating the thermodynamic equilibrium constant, K, is performed by measuring the area under the curves of Figs. 2 and 3.

$$\begin{aligned}\ln K &= -(Z_{Sr} - Z_{Mg}) + \int_0^1 \ln K_c \, d\bar{X}_{Sr} \\ &= \int_0^1 \ln K_c \, d\bar{X}_{Sr},\end{aligned} \tag{4}$$

where Z is the valence of ions.

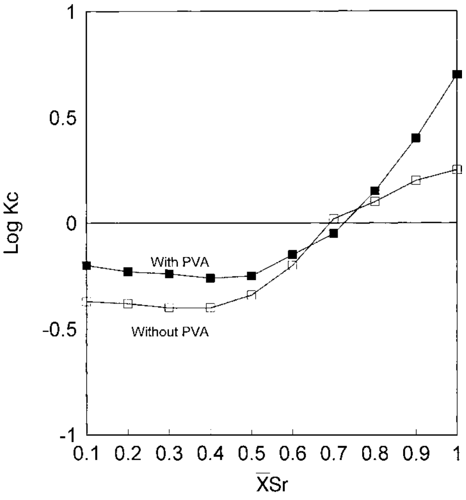

Fig. 2. Strontium selectivity as a function of Sr in clay at 20°C.

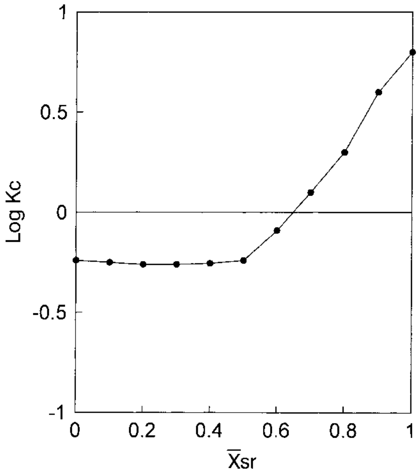

Fig. 3. Strontium selectivity as a function of Sr in clay at 40°C.

The standard free energy of reaction (1) is calculated from

$$\Delta G^\circ = -RT \ln K. \tag{5}$$

The standard enthalpy, ΔH° is determined using Van't Hoff relationship,

$$\ln(K_{40}/K_{20}) = -\Delta H^\circ/R(1/T_{40} - 1/T_{20}) \tag{6}$$

and the standard entropy ΔS°, is calculated by using the relationship

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ. \tag{7}$$

Fig. 4 shows the strontium–magnesium exchange isotherm at 40°C. From Figs. 1 and 4 it was found that on increasing the temperature, the preference for Sr ions increased. Table 1 gives the thermodynamic parameter of the Mg–Sr exchange reaction. The value of the enthalpy, ΔH°, indicates that the exchange reaction is endothermic in the direction of forming Sr-vermiculite. This suggests that the enthalpy gain may be due to an expansion of the interlamellar space to accommodate the larger Sr^{+2} ions. The same behavior was obtained by Keay and Wild [7] and Wild and Keay [8].

The preference for Mg shown by the isotherms could be caused by entropy changes. ΔS° obtained from Eq. (7) and given in Table 1 is the algebraic sum of all entropy changes in the system of reaction (1). This may be written formally, as was given by Diest

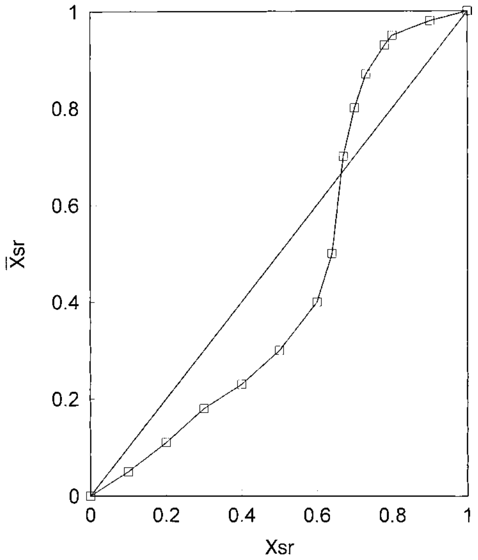

Fig. 4. Strontium–magnesium exchange isotherms at 40°C.

and Talibuden [9]:

$$\Delta S^\circ = (\bar{S}^\circ_{\mathrm{Sr}} - \bar{S}^\circ_{\mathrm{Mg}})_{\mathrm{clay}} - (S^\circ_{\mathrm{Sr}} - S^\circ_{\mathrm{Mg}})_{\mathrm{solution}}. \quad (8)$$

This equation demonstrates the importance of the entropy changes in the solution phase. On substituting values obtained by Horne [10] for S°_{Mg} (−28.2 cal/mol-degree) and S°_{Sr} (−9.4 cal/mol-degree) at 20°C in aqueous solution, $\Delta S^\circ_{\mathrm{clay}}$ becomes even more positive (Table 1) indicating that the entropy increases due to the clay component in reaction (1) was more than that experimentally obtained for the overall reaction. Thus, this increase points to a more orderly structure with Mg ions on the surface than that with Sr ions. That is because the first bracket of the right-hand side of Eq. (8) represents the change of the surface entropy due to the exchange reaction (1), and it reflects the ordering of the ions on the surface, while the second bracket represents the entropy change in solution.

Since the entropy of a system is related to the number of arrangements that it can assume, the higher degree of order of Mg-vermiculite as compared to Sr-vermiculite, could be attributed again to their greater proximity to the surface. This restricts their freedom in such a way as to decrease the number of arrangements which they may assume causing entropy loss for Mg-vermiculite and entropy gain, as was obtained from reaction (1) for Sr-vermiculite [11].

4. X-ray

Table 2 shows the *c*-spacing of Mg–Sr clay systems with and without PVA. The X-ray data were obtained for samples which had been air dried, where the PVA conformations are likely to be very different from the wet state [12]. From Table 2, the *c*-spacing of Mg–PVA-vermiculite has the same value as for Mg-vermiculite without PVA. By increasing the Sr ion concentration in solution, the *c*-spacing becomes larger for the treated PVA-vermiculite than the untreated. This would suggest that as Sr adsorption continued, fewer segments of the polymer found spaces to be adsorbed on the surfaces and the PVA coil dimensions provided by Garvey et al. [13] would suggest that the polymer undergoes considerable flattening in order to enter between the layers. Also the *c*-spacing is affected by the crystallographic rather than hydrated radius of the ion [11]. Keay and Wild [7] stated that, in vermiculite the number of water molecules per cation is almost constant, and then the distance between the two silicate faces increases with the diameter of the cation.

Table 2 also gives the *c*-spacing of Mg-vermiculite at different levels of Sr saturation. The results indicate that the *c*-spacing of vermiculite increases gradually

Table 1
Thermodynamic quantities for Sr ion exchange with Mg-vermiculite

Thermodynamic parameter	20°C (without PVA[a])	20°C (with PVA)	40°C (without PVA[a])
K	0.713	0.840	0.912
ΔG° (cal/mol)	+198.2	+101.9	+57.7
ΔH° (cal/mol)		+22.57[a]	
ΔS° (cal/degree-mol)		+6.790[a]	
$\Delta S^\circ_{\mathrm{clay}}$ (cal/degree-mol)		+25.60[a]	

[a] The values obtained by using the data of ΔG° in the absence of PVA.

Table 2
c-spacing of Mg-vermiculite at different levels of Sr saturation, with and without PVA treatment

Symmetry value of Sr to Mg-vermiculite	*c*-spacing (A°)	
	Without PVA	With PVA
0	13.81	13.81
0.2	13.81	14.49
0.4	14.03	14.49
0.8	14.03	14.73
0.2	14.03	14.73
1.6	14.25	14.49
2.0	14.25	14.49
3.0	14.61	14.61
4.0	14.49	14.61
6.0	14.73	14.98
7.5	14.85	14.98
10.0	14.85	14.98

as the adsorbed amount of Sr ions increases in the vermiculite surface. Under this condition, the activity coefficient of the exchangeable Mg changes continuously reflecting the decrease in the electrical attraction between the Mg ion and the charged surface as will be discussed later. The isotherms of our experiments lend support to that conclusion. These isotherms follow paths showing preference for magnesium even at the higher levels of X_{Sr}, but at about $X_{\mathrm{Sr}}=0.8$, strontium was preferred than magnesium. This selectivity reversal is characteristic of heterogeneous surfaces or rather surfaces with different sites having different affinities for the ion. Helfferich [14] attributed it to the presence of so-called "islands" of high charge density in the structure of the exchanger imbedded in regions of much lower density. It might be expected that a stronger binding of Mg, presumably due to fewer layers of hydration water, a condition that results in a closer proximity to the surface than strontium.

4.1. *Activity coefficients of the surface Sr^{+2} and Mg^{+2}*

The change in the selectivity coefficient with Sr saturation is an indication of the change in the interactions of the counterions as their amount changes. This change in the interactions is reflected in the activity coefficient ratios of the exchangeable cations.

The activity coefficients of the surface Sr^{2+} and Mg^{2+} were calculated from Eqs. (9) and (10), derived by Grains and Thomas [15]:

$$\ln \bar{f}_{\mathrm{Sr}} = (\bar{X}_{\mathrm{Sr}} - 1)\ln K_{\mathrm{c}} + \int_{\bar{X}_{\mathrm{Sr}}}^{1} \ln K \, \mathrm{d}\bar{X}_{\mathrm{Sr}}, \qquad (9)$$

$$\ln \bar{f}_{\mathrm{Mg}} = \bar{X}_{\mathrm{Sr}} \ln K_{\mathrm{c}} - \int_{0}^{\bar{X}_{\mathrm{Sr}}} \ln K_{\mathrm{c}} \mathrm{d}\bar{X}_{\mathrm{Sr}}. \qquad (10)$$

The calculated activity coefficients of exchangeable Sr and Mg in vermiculite are given in Table 3 at 20°C and 40°C. The ratio of the activity coefficients as a function of Sr saturation is also listed in Table 3. From Table 3, the activity coefficient ratio of $\bar{f}_{\mathrm{Sr}}/\bar{f}_{\mathrm{Mg}}$ varies; at 20°C, from 0.042 at 10% Sr saturation to 0.364 at 90% Sr saturation, i.e. the ratio increased about 10 times throughout the isotherm, as the Sr saturation increases. This phenomenon can be explained by the fact that at the high Mg saturation the *c*-spacing contracts, so that the larger ion, Sr, cannot easily

Table 3
Activity and activity ratios of Sr and Mg in vermiculite at different equivalent cation ratios

$X_{\mathrm{Sr}}^{\mathrm{a}}$	20°C (without PVA)			20°C (with PVA)			40°C (without PVA)		
	$\bar{f}_{\mathrm{Sr}}$	$\bar{f}_{\mathrm{Mg}}$	$\bar{f}_{\mathrm{Sr}}/\bar{f}_{\mathrm{Mg}}$	$\bar{f}_{\mathrm{Sr}}$	$\bar{f}_{\mathrm{Mg}}$	$\bar{f}_{\mathrm{Sr}}/\bar{f}_{\mathrm{Mg}}$	$\bar{f}_{\mathrm{Sr}}$	$\bar{f}_{\mathrm{Mg}}$	$\bar{f}_{\mathrm{Sr}}/\bar{f}_{\mathrm{Mg}}$
0.1	0.333	7.909	0.042	0.22	8.10	0.027	0.22	7.83	0.028
0.2	0.370	4.310	0.042	0.27	6.31	0.042	0.25	6.19	0.040
0.3	0.389	3.558	0.109	0.30	5.03	0.060	0.29	4.87	0.060
0.4	0.415	2.836	0.146	0.34	4.01	0.085	0.34	3.77	0.090
0.5	0.419	2.386	0.176	0.35	3.40	0.103	0.33	3.32	0.099
0.6	0.407	2.303	0.177	0.38	3.98	0.095	0.34	3.10	0.110
0.7	0.444	2.326	0.191	0.42	2.70	0.156	0.38	3.21	0.118
0.8	0.562	2.018	0.278	0.48	3.09	0.155	0.48	3.38	0.142
0.9	0.737	2.020	0.364	0.63	4.49	0.140	0.66	4.35	0.152

[a] Mole fraction of the exchangeable ions in solution.

penetrate, and the ratio is lower but as the Mg saturation decreases, the *c*-spacing increases (Table 2) and the smaller ion, Mg, will be more loosely held and under this condition the activity coefficient of Sr ion increased while the $\bar{f}_{\mathrm{Mg}}$ decreased. Also the ratios of $\bar{f}_{\mathrm{Sr}}/\bar{f}_{\mathrm{Mg}}$ increased (Table 3) by increasing Sr saturation.

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