

HETEROGENEITY OF CHARGE DENSITY DISTRIBUTION IN MONTMORILLONITE AS INFERRED FROM COBALT ADSORPTION

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Abstract—A comparison is made of the ion exchange behavior, towards the cobalt ion, of five sodium montmorillonite clays. The selectivity for the bivalent ion at low cobalt loading is correlated with the average dimensions of the particles in the various clays, as characterized by several methods. The data are interpreted in terms of a higher selectivity of the bivalent ions for the broken bonds located at the edges of the clay crystals. Using a model comprising two areas of different charge densities, the experimental differences in behavior can be predicted reasonably well.

INTRODUCTION

The distribution of mono- and divalent cations between a clay and a mixed electrolyte solution is frequently described in terms of the double layer theory for planar charged surfaces (Bolt, 1955; Pratt *et al.* 1962; Shainberg and Kemper, 1966). Some years ago, it was shown by Bolt and Page (1965) that the simplified equation as derived by Eriksson (1952) is sufficiently accurate for so-called asymmetrical systems in which the mono- and divalent cations are not exactly matched by equal numbers of anions of the same valence. More recently, Laudelout *et al.* (1968) proposed a straightforward calculation of the coulombic contribution to the standard free energy of exchange at infinite dilution, eliminating thereby the symmetry problem altogether.

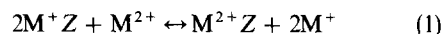
Although for most purposes the nature of the agreement with experimental data is satisfactory the theory has met with limited success in that the exergonic effect, resulting from the replacement of a monovalent cation such as sodium by a divalent one, exceeds theoretical predictions. In particular, we refer to the deplorable custom of multiplying the overall charge density as obtained experimentally with a factor of about 1.5–2 for the purpose of 'making it fit'. The easiest explanation for the discrepancy which is, however, difficult to test quantitatively, is to ascribe the extra free energy loss to non-coulombic forces. An alternative interpretation, proposed long ago (Pratt *et al.*, 1962) is that the surface charges may not be distributed uniformly but confined to areas of higher charge densities. Insofar as there is a choice, the second alternative seems more attractive,beit only because of the possibility of an experimental test.

This paper presents an analysis of the adsorption behavior of cobalt ions in sodium-montmorillonite in terms of a heterogeneous charge density distribution. In practical terms, an attempt is made to correlate quantitatively the overall selectivity coefficients for this

par of ions with the 'broken bonds' in the montmorillonite crystals.

THEORETICAL

The thermodynamic equilibrium constant, relating to the displacement of a monovalent cation M^+ from a solid phase Z by a divalent ion M^{2+} , as represented by:



is commonly defined by

$$K = K_c \frac{f_{M^{2+}}}{f_{M^+}^2}, \quad (2)$$

f represents the solid phase ion activity coefficients with reference to the homoionic exchangers and K_c is the selectivity coefficient, i.e. an experimental quantity to the extent that quantitative allowance can be made for the solution phase activity coefficients:

$$K_c = \frac{\bar{M}^{2+} a_{M^+}^2}{\bar{M}^{+2} a_{M^{2+}}} = K'_c \frac{\gamma_{M^+}^2}{\gamma_{M^{2+}}}. \quad (3)$$

In this equation, the bar refers to the equivalent fraction of the ions in the solid phase and a to the activities (on the molar scale) in solution; γ refers to the solution phase activity coefficients and K'_c is the experimental equilibrium quotient.

In thermodynamically ideal systems, the ratio of solid phase activity coefficients is constant and equal to 1/e, corresponding to a zero value for the excess free energy of mixing. The generally non-constant values of K_c for reactions of this kind are formally dealt with in terms of ion-ion interactions, as reflected in the solid phase activity coefficients which can be obtained from well-known procedures (Gaines and Thomas, 1953). Although formally, there is little objection to an extension of this approach to materials which manifestly exhibit site heterogeneity, such a procedure lacks

some rational basis in that the resulting mixing functions may have little bearing upon ion-ion interactions as such.

The theory for the very general case of a surface with various types of sites has recently been derived by Barner and Klinowski (1972). For the present purposes, it is sufficient to consider the most simple case of a mixture of two groups of sites which behave ideally and which exhibit a high (*H*) and a low (*L*) selectivity for one of the ions. In terms of the occupancies of the ions on the *H* and *L* sites, the overall selectivity coefficient can be defined as

$$K_c = \frac{H\bar{M}_H^{2+} + L\bar{M}_L^{2+} a_M^{2+}}{(H\bar{M}_H^+ L\bar{M}_L^+)^2 a_M^{2+}}, \quad (4)$$

in which the equivalent fractions of both types of sites are represented by *H* and *L*, the other symbols being self-explanatory.

MATERIALS AND METHODS

Five different montmorillonite clays have been used in this study: Camp Berteau (Morocco), Moosburg (GDR), Marnia (Algeria), a Greek montmorillonite and Wyoming bentonite. The symbols used for these clays throughout this paper are: CB, MO, MA, GM and WB. Using standard methods of centrifugation and sedimentation, the fraction <0.5 μm e.s.d. is separated and treated with 1 N NaCl at pH 3.5 for removing hydroxy-aluminum compounds which may have resulted from clay decomposition in the washing procedure. The clays are then brought in dialytic equilibrium with a 0.01 N NaCl solution (pH = 6) and stored at 5°C in the dark at a clay content of about 10 g/l. All clays were checked by X-ray powder diffraction and found to contain no other crystalline material.

The cation exchange capacity of the clays was measured at two different pH values by isotopic dilution methods using Na²². First, the CEC was measured at pH = 6 by equilibrating known amounts of clay suspension (10 g/l. and 0.01 N. NaCl) with a Na²² labelled 0.01 N NaCl solution. The CEC is directly obtainable from the change in radioactive content of the stock solutions and the equilibrium dialysates. A similar measurement is then carried out at a lower pH by equilibrating another sample of the clay with an acidified (pH = 3.5) 0.01 N. NaCl solution. The CEC at the resulting equilibrium pH is calculated from its value at pH 6 and the difference in radioactive content of the solution before and after equilibrium. All pH measurements were made using an expanded scale potentiometer.

Cobalt adsorption measurements were made at low cobalt occupancy by equilibrating the Na-clay with Co⁶⁰ labelled mixed solutions of 0.01 total normality. The adsorption measurements at lower pH were carried out in a similar fashion using mixed solutions which had been preacidified with a few drops of HCl. In all cases, the amount of cobalt adsorbed is obtained from the change in radioactive content of the solutions and expressed as equivalent fraction with respect to the CEC at the corresponding pH.

Table 1. Cation exchange capacities (in m-equiv./100 g) of five montmorillonite clays at two pH values, shown in parentheses

Clay	CEC (m-equiv./100 g)	
Marnia	103.9 (5.91)	92.7 (4.05)
Camp Berteau	105 (6.16)	91.5 (4.30)
Moosburg	96.5 (5.92)	84.6 (3.93)
Greek	97.5 (5.71)	89.0 (3.72)
Wyoming	91.1 (6.00)	77.1 (4.26)

The equilibrium dialysis procedure is as follows: membranes (Medicell Int., London) are soaked in distilled water, knotted at one end and dried prior to use. Known volumes, usually 10 ml, of clay suspension are pipetted into the dialysis bags and equilibrated with the solution in polyethylene tubes. Equilibrium is attained through a 24 hr shaking treatment in an end-over-end shaker at constant temperature (25°C). Radiometric assays are taken on 5 ml aliquots of the solutions, using a Packard single channel scintillation spectrometer. The Na²² and Co⁶⁰ radioisotopes, used in this work were obtained from the N.I.R. (Mol, Belgium).

RESULTS

The cation exchange capacities of the five clays as measured at 0.01 N NaCl are shown in Table 1, along with the corresponding pH, as measured on the equilibrium solutions. The data vary between 91 for WB and 105 m-equiv./100 g for CB at pH = 6. The CEC decrease at the lower pH corresponds to about 6 m-equiv./100 g per pH units.

Some typical examples of cobalt adsorption at low cobalt loading are shown in Fig. 1. The range covered by these measurements extends from about 0.02 to 0.07 in equivalent fraction of Co in the solid phase. The corresponding range of solution concentration is 1–7·10⁻⁶ N, i.e. equivalent fractions of the cobalt ion in solution up to 0.0007. The equivalent fraction of the cobalt ion in the clay at a given pH is expressed with respect to the CEC as obtained by linear interpolation of the data in Table 1. The error involved in such a procedure is small, perhaps 1–2 per cent, in view of the rather narrow pH range studied.

The equilibrium distribution data are summarized in Table 2 in terms of the averages of the experimental equilibrium quotients *K*'_c which are constant within about 2 per cent throughout the composition range studied. The pH values are given as averages and root mean square deviations. At pH = 6 *K*'_c values vary between 3.15 for MA and CB to 2.3 for GM and WB. In all clays, a rather significant decrease occurs in *K*'_c when lowering the pH, the effect being most important in the CB and MA clays. The differences in *K*'_c for the various clays vanish nearly completely at pH = 3.5 to 4, except for the WB clay which shows an anomalously low *K*'_c value at that pH.

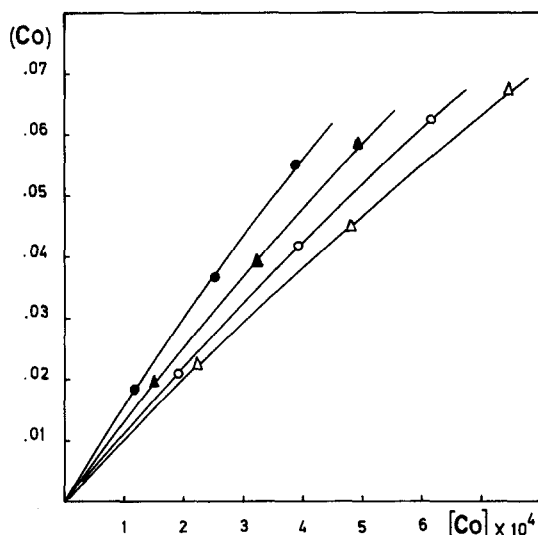


Fig. 1. Equivalent fraction of cobalt ions on the solid (Co) vs its equivalent fraction in the equilibrium solution $[Co]$ for two montmorillonite clays at $25^{\circ}C$ and 0.01 total normality: Marnia \bullet ($pH = 6.01$) and \circ ($pH = 3.67$); Moosburg \blacktriangle ($pH = 5.99$) and \triangle ($pH = 3.63$).

Table 2. Selectivity coefficients K'_c for five montmorillonite clays for the Co-Na pair at $25^{\circ}C$ and 0.001 total normality. The values are averages for three surface compositions up to a Co occupancy of 0.07

	K'_c	pH
Marnia	3.18 ± 0.03	6.01 ± 0.01
	2.77 ± 0.03	5.66 ± 0.04
	2.31 ± 0.01	3.67 ± 0.02
Camp Berteau	3.13 ± 0.02	6.29 ± 0.02
	3.09 ± 0.01	5.62 ± 0.08
	2.16 ± 0.03	3.88 ± 0.07
Moosburg	2.68 ± 0.05	5.99 ± 0.03
	2.47 ± 0.05	5.49 ± 0.13
	2.08 ± 0.02	3.63 ± 0.07
Greek	2.34 ± 0.05	6.13 ± 0.04
	2.60 ± 0.06	4.89 ± 0.15
	2.14 ± 0.02	3.50 ± 0.04
Wyoming bentonite	2.34 ± 0.08	6.12 ± 0.04
	2.27 ± 0.07	5.65 ± 0.03
	1.69 ± 0.03	3.78 ± 0.06

DISCUSSION OF RESULTS

Literature data indicate that the 'isomorphic' sites in montmorillonite exhibit either a slight preference for hydrogen (Gilbert and Laudelout, 1965) or sodium ions (Foscolos and Barshad, 1969), the equilibrium constants being but slightly different from unity. Consequently, a pH of 4 should have relatively little effect upon the sodium occupancy of the constant charge fraction of the overall exchange capacity of the sodium clays in a 0.01 N NaCl solution. Under such conditions, the equivalent fraction of hydrogen ions on the planar surfaces of the crystals is about 1 per cent at most and the decrease in CEC in the pH range studied

* Maes, A. and Cremers, A. Submitted for publication.

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is ascribed to the pH dependent charge fraction on the edges of the clay crystallites. Taking $50 \text{ m}^2/\text{g}$ as a rough estimate for the edge contribution to the surface, the pH effect would correspond to about $8 \mu\text{C}/\text{cm}^2/\text{pH}$ unit, a value which is but little different from that reported for silica surfaces in the same pH range. (Lykema, 1971).

The effect of pH upon the selectivity coefficient can be rationalized in terms of a varying contribution of the pH-dependent part to the overall exchange capacity. Whatever the exact proportion of the edges to the CEC, it is sufficiently evident from the data in Table 1 that the corresponding charge density at pH 6 is several times higher than that for the planar surfaces. On purely electrostatic grounds one should, therefore, expect that the selectivity of the divalent ions is significantly greater for sites on the crystal edges. It is important to stress that there is no ambiguity as to the nature of the reaction at low cobalt loading: this is exclusively a non-specific ion exchange reaction without any specific adsorption effects involving structural hydroxyl groups, as can be inferred from the perfectly reversible nature of the reaction.*

It may be argued that under acid conditions some release and preferential adsorption of lattice aluminum may occur either on the edges or the face surfaces, thereby affecting the ion exchange distribution. The upper limit of such an effect is of the order of 10 per cent of the capacity in varying the pH from 6-4 (keeping the NaCl concentration at 0.01 N). This can be inferred from the data in Table 1 which are obtained in conditions which are exactly identical to those used in the cobalt adsorption measurements. The fact remains that such a relatively small effect on the ion capacity results in the most significant decrease in the K'_c value for those clays which are characterized by the largest edge-to-face ratio.

The preferential adsorption of divalent cations at the sites of the broken bonds is confirmed by the relation between the selectivity coefficient (at pH 6) and the average dimensions of the crystallites in the various clays. A comparison of the particle shape factors, as obtained by three different methods,† shows quite clearly that the clays with a particle size distribution towards the smaller size exhibit the largest selectivity for the cobalt ion: the limiting viscosity numbers for WB and GM are about twice as large as for MA and CB while the value for MO is intermediate; the wavelength dependence of the optical density, which is a measure of the larger dimension of the particles, shows the same effect, although the differences are less pronounced; the average axial ratios of the particles for the WB and GM clays, as obtained from electrical conductivity, are about 3 times larger than for the other clays. Earlier data (Cremers and Laudelout, 1965) concerning particle shape in CB and WB are also consistent with the present results. The pH-dependency of the CEC in the clays shows a similar trend—except for the anomalously high value for WB—in that the GM montmorillonite is significantly less sensitive to pH changes.

Table 3. Theoretical overall K'_c values, assuming ideal behavior in the solid phase, for ${}^H K'_c = 10$ and ${}^L K'_c = 2$ at different proportions of the charge density regions

H	\overline{M}^{2-}		
	0.025	0.050	0.075
0.20	3.47	3.36	3.25
0.15	3.09	2.99	2.91
0.10	2.72	2.64	2.58

It can rightly be argued that particle shape factors, as obtained from such indirect measurements, may be a poor indication of the average shape of the individual crystallites. There are other and more direct data for CB and WB which show that the proportion of edge-to-planar surface is significantly larger in the CB clay. For instance, the amount of exchangeable aluminum in a freshly columnated H -clay is 0.15 m-equiv./g in CB and 0.07 to 0.08 m-equiv./g for WB (Eeckman and Laudelout, 1961; Banin and Ravikovitch, 1965). The fluoride adsorption data of Eeckman and Laudelout (1961), using the method of Weiss *et al.* (1956) for estimating the average diameter of the montmorillonite crystals, show the same tendency: the maximum fluoride adsorption in CB is nearly twice as large as in WB, a result which corresponds with a 50 per cent higher average particle radius in the case of WB.

Other literature data also show a higher selectivity of divalent cations for CB as compared to WB: Van Bladel and Menzel (1969) reported a K'_c value of 2.54 for the Sr–Na equilibrium in WB at low loading and at a total normality of 0.01 and 25°C; Gaviria, *et al.* (1969) found a value of 3.10–3.15* for the Ca–Na pair in CB under similar conditions. The very close similarity of these numbers with those in Table 1 is quite striking and indicates that the non-coulombic forces are apparently not very important.

The magnitude of the differences in K'_c at pH = 6 can also be predicted on theoretical grounds, using equation (4). Using $K'_c = 2$ for the low- and $K'_c = 10$ for the high charge density areas and using various combinations for the proportions produces the results shown in Table 3. The differences are similar to those found in the experimental data in Table 2. The K'_c values chosen for the high- and low-charge density areas correspond to a free energy difference of about 0.8 RT and are consistent with charge densities of 1 and $3 \cdot 10^{-7}$ m-equiv./cm², according to double layer theory. The neglect of the solution phase activity coefficients is justified since the ionic strength of all systems concerned is identical or very nearly so and since the purpose of these calculations is to predict differences rather than absolute values.

The interpretation of the differences of divalent ion adsorption in terms of varying contributions of the broken bonds finds additional support in the pH-dependency of K'_c for the various clays studied. It is im-

material at this stage whether we look upon the gradual, pH-induced elimination of edge sites as a direct or indirect effect, perhaps resulting from a blocking of these sites by aluminum released from the lattice. When plotting the K'_c values, shown in Table 2, as a function of pH, one finds a very distinct convergence towards a common value (except in the case of WB) of 2–2.1 at a pH value of about 2, which is the commonly known value for the zero point of charge for silica. Double layer calculations show these values of K'_c to be consistent with charge densities of 1.07–1.11 10^{-7} m-equiv./cm², which in fact correspond exactly to a CEC of 0.8 m-equiv./g if we take 750 m²/g for the specific surface of the planar faces.

CONCLUSIONS

The differences in ion exchange behavior of montmorillonite clays towards divalent cations can be quantitatively interpreted in terms of varying contributions from two regions of different charge densities. The first region is associated with the constant charge fraction of the ion capacity. Its exchange behaviour towards divalent cations in a 0.01 N NaCl solution is relatively insensitive to pH in mildly acid conditions, i.e. down to pH = 4, and can be characterized by a charge density of 10^{-7} m-equiv./cm². The second region, located at the edges of the montmorillonite crystals, is identified with broken bonds and its charge density is very much pH dependent. Assigning to it a value of $3 \cdot 10^{-7}$ m-equiv./cm² at pH 6, the overall adsorption affinity of divalent ions can be predicted reasonably well at low occupancies. The apparently smooth decrease in selectivity towards divalent ions at lower pH can be understood in terms of a gradual elimination of the broken-bond participation in the exchange reactions.

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* The numerical value of K'_c is obtained from actual experimental data, as supplied by Van Bladel.

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