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SOME COLLOIDAL PROPERTIES OF BEIDELLITE: COMPARISON WITH LOW AND HIGH CHARGE MONTMORILLONITES

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Abstract—Recent evidence of the occurrence of beidellite in many soils around the world necessitates a better understanding of the role of charge location on the colloidal behavior of this smectite as compared to the more frequently studied montmorillonites. Clay suspension stability and sorption of an organic polymer, two properties sensitive to surface charge characteristics, were selected to examine the differences in colloidal behaviors of these smectites. The Otay montmorillonite was shown to have a higher charge than either the beidellite or the SWy-1 montmorillonite. Even though structural formulae resulted in a higher permanent charge for the beidellite as compared to the SWy-1, effective charge of these two smectites is the same. The pH dependency of the critical coagulation concentration of the smectites could not be explained based only on edge charge considerations, and it is proposed that tetrahedral charge location enhances the pH effect on the CCC. Decreased poly(vinyl) alcohol sorption with either increasing surface charge or tetrahedral charge location was observed. Both parameters affect the ease of replacement of water molecules by PVA on the surface of smectites.

Key Words—Beidellite, Charge location, Coagulation, Poly(vinyl) alcohol, Surface charge density.

INTRODUCTION

Particle-to-particle interaction of clays and the role of their associated electrical charge are critical in the formation of stable soil aggregates. The colloidal behavior of smectites has been examined extensively in order to elucidate the factors affecting the formation and stability of soil aggregates, but these studies have usually focused on the properties of montmorillonites (Swartzen-Allen and Matijevic, 1976; Burchill and Hayes, 1980; Goldberg and Glaubig, 1987). Recently, Wilson (1987) suggested that beidellites were more common in soils whereas montmorillonites were more typical of geologic materials. This postulate is supported by many recent mineralogical studies which suggest that beidellites may be quite widespread in soils (Lim and Jackson, 1984; Badraoui *et al.*, 1987; Badraoui and Bloom, 1990; Aragoneses and Garcia-Gonzales, 1991; Robert *et al.*, 1991). Therefore, in order to advance our understanding of soil processes, it is necessary to compare the colloidal behavior of a beidellite to that of montmorillonites. The criteria selected to examine the differences in the colloidal behavior of smectites are the critical coagulation concentrations and the ability to sorb a non-ionic aliphatic polymer. These two properties are sensitive to differences in clay surface charge characteristics that, in turn, may be important with respect to the formation and stability of soil aggregates.

The critical coagulation concentration (CCC) is the minimum electrolyte concentration that will cause the rapid flocculation of a suspension in a given time (van Olphen, 1977). Knowledge of the CCC of smectites is important since flocculation is believed to be a prerequisite to the formation of soil aggregates (Quirk, 1978). The CCCs of montmorillonites in various electrolytes or combination of electrolytes under different experimental conditions have been extensively investigated (Swartzen-Allen and Matijevic, 1976; Goldberg and Glaubig, 1987; Gu and Doner, 1990). These studies usually focused on the effects of electrolytes, surface species, or suspension pH on the CCCs. Comparison of layer silicates has usually been restricted to those with large structural differences. One study dealing with the stability of different smectite suspensions was carried out (Arora and Coleman, 1979), but the composition of these minerals is not well defined (see Kerr *et al.*, 1950) and, therefore, a discussion of the results in terms of surface charge characteristics is not possible. Few data are available on the stability of colloidal suspensions of beidellite. One such study (Frey and Lagaly, 1979) used the fine fraction of Unterrupsroth beidellite. This smectite is now believed to be of mixed mineralogy with a distinct montmorillonitic character in the finer fraction (Nadeau *et al.*, 1985).

The interactions between non-ionic aliphatic polymers and montmorillonites have also received much attention (Theng, 1979) in connection with flocculation and aggregation. Interest in these interactions stems from the potential use of these polymers as soil conditioners (de Boodt, 1990). One such polymer, poly(vinyl) alcohol, has been shown to improve the physical properties and the aggregate stability of clayey soils (Painuli and Pagliai, 1990). Two studies on the sorption of poly(vinyl) alcohol resulted in identical maximum sorption of PVA by montmorillonites (Greenland, 1963; Burchill and Hayes, 1980). Green-

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land (1963) stated that this maximum sorption was the same as that for another montmorillonite, but both clay specimens used were low charge montmorillonites. Burchill and Hayes (1980) showed decreased sorption of PVA on an illite as compared to a low charged montmorillonite. They postulated that this decreased sorption was due to a larger surface charge which increased the difficulty of water desorption by the PVA. Neither the effects of surface charge density or localization of charge deficiency in smectites were investigated by these researchers.

In view of the relative abundance of beidellite in soils compared to our understanding of its colloidal properties, the study of this smectite is very important. Both low and high charge montmorillonites are included in this study to separate the role of charge location from that of total surface charge density on the colloidal properties of smectites.

METHODS

The three smectites used in this study include a beidellite from DeLammar mine near Silver City, Idaho, a low-charge montmorillonite (SWy-1) from Crook County, Wyoming, and a high-charge montmorillonite from Otay, California. The <0.2 μm e.s.d. fractions were separated by centrifugation (Jackson, 1979). The smectites were prepared by washing in sodium perchlorate solutions following the method of Sposito and LeVesque (1985). This pretreatment is believed to remove surface contaminants from the clay.

The beidellite and Otay smectites were carefully analyzed to characterize their composition and ensure their origin. Total elemental analysis of the beidellite and Otay clays were performed by ICP-AES after lithium metaborate digestions (Suhr and Ingamells, 1966). The non-hydrated halloysite component of the beidellite sample was quantified by selective dissolution analysis (Jackson *et al.*, 1986). X-ray diffraction analysis of the smectites, after selected pretreatments (Whittig and Allardice, 1986), were performed using a Rigaku diffractometer with CuKα radiation at a scan rate of 2° 2θ mn^{-}. Locations of charge deficit in the structure were determined by the Greene-Kelly test (Greene-Kelly, 1953) following the method of Lim and Jackson (1984). Surface areas were measured using the Ca-EGME method (Carter *et al.*, 1986), except for the use of free liquid EGME (Eltantawy and Arnold, 1973). Free-standing EGME yields higher surface area than those calculated from crystallographic unit cell dimensions (Carter *et al.*, 1986), and the data were normalized to 800 $m^2\ g^{-1}$ for the SWy-1 montmorillonite.

Layer charge characteristics of the smectites were measured following a "rapid" alkylammonium ions method (Olis *et al.*, 1990). This method requires the measurement of the *c*-spacings of the smectites saturated with either a C12 or a C18 alkylammonium ion. The spacings were converted to permanent surface charge (σ_o) using the published regression lines. This method in conjunction with the Greene-Kelly test yields the percent charge originating from the tetrahedral sheet. Effective permanent layer charge (σ_o) was also estimated by a Cs adsorption method (Anderson and Sposito, 1991). This analysis is designed to measure permanent charge (σ_o), but can also be used to quantify the net proton surface charge density (σ_h) if chloride adsorption is also measured since $\sigma_o + \sigma_h = (q_+ - q_-)$ (Sposito, 1984). This was done at pH 7.

Critical coagulation concentrations of the smectites in various electrolyte solutions were measured following a method previously used in this laboratory (Gu and Doner, 1990). Briefly, a small volume of homocation saturated smectite is brought to a final suspension concentration of 0.1% (wt. vol.$^{-1}$) at a specific pH with solutions of varying concentrations of the same cation. The suspensions are then shaken for 15 s, allowed to stand for 24 hr, and the absorbance of the top 2 cm is measured at 615 nm. The absorbances are then normalized for that of the lowest electrolyte concentration to correct for different initial optical density of the three smectites. The CCC is hereafter defined as the minimum electrolyte concentration that results in the lowest absorbance of the suspension.

A 99–100% hydrolized poly(vinyl) alcohol of 11,000–31,000 relative molecular mass (Baker) was used for the polymer adsorption studies. A 0.1% wt. vol.$^{-1}$ smectite suspension was shaken with PVA at various concentrations for 24 hr. Differences between initial and final organic carbon concentrations, measured on a Xertex carbon analyzer, were used to determine the adsorption isotherms.

RESULTS AND DISCUSSION

Smectite analysis

Total elemental analysis of the beidellite (B) and the Otay (O) montmorillonite resulted in the following respective structural formulae:

$$Na_{0.79}K_{0.11}Ca_{0.03}(Si_{7.27}Al_{0.73})(Al_{3.67}Fe_{0.14}Mg_{0.17})\text{-}O_{20}(OH)_4(B)$$

$$Na_{1.33}K_{0.01}Ca_{0.01}(Si_{7.99}Al_{0.01})(Al_{2.55}Fe_{0.18}Mg_{1.23})\text{-}O_{20}(OH)_4(O).$$

The structural formula for the SWy^{-1} montmorillonite is (Weaver and Pollard, 1973):

$$Na_{0.62}(Si_{7.8}Al_{0.2})(Al_{3.28}Fe_{0.34}Mg_{0.38})O_{20}(OH)_4.$$

Total elemental analysis results for the beidellite were corrected for the measured 10% wt. wt.$^{-1}$ non-hydrated halloysite concentration prior to determination of the structural formula. The structural formula for the Otay montmorillonite is the same as that given by Schultz (1969) showing nearly all permanent charge originating

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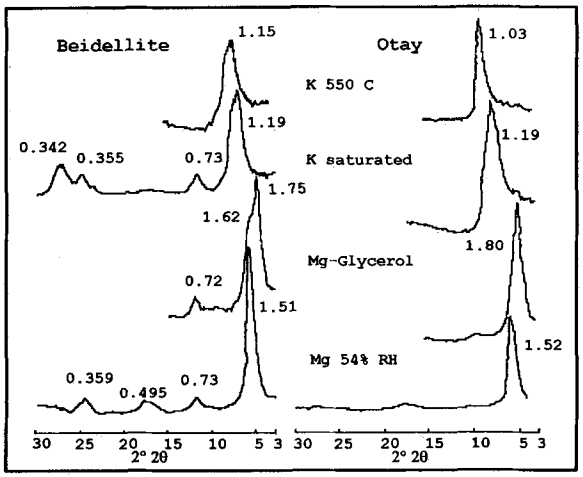


Figure 1. Diffraction tracings for the beidellite and Otay smectites after selected pretreatments. Peak locations are in nm.

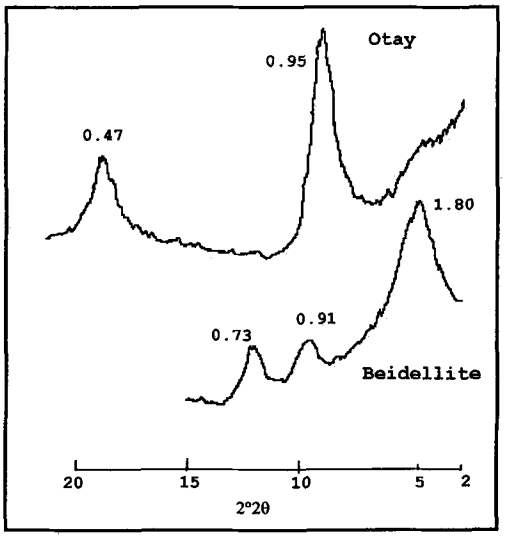


Figure 2. Diffraction tracings for the beidellite and Otay smectites after Li^+ saturation and heat treatment. Peak locations are in nm.

from the octahedral sheet. According to its structural formula, the beidellite is of intermediate charge between the two montmorillonites and has 80% of its charge originating in the tetrahedral sheet. The beidellite has a fraction of non-exchangeable K^+, which was not removed by the multiple sodium perchlorate washes. This concentration of K^+ yields a 6% illite concentration when calculated as 10% K_2O (wt. wt.$^{-1}$) (Jackson *et al.*, 1986).

The diffractograms for the beidellite and Otay montmorillonite are shown in Figures 1 and 2. Note that the beidellite does not collapse upon Li^+ saturation and heat treatment confirming the localization of charge in the tetrahedral sheet. Also, the beidellite rehydrates after K^+ saturation and heat treatment, where the Otay does not, which is more typical of vermiculites (Harward *et al.*, 1969).

Surface charge density

The results of the layer charge measurements by the alkylammonium ions and the Cs adsorption methods are given in Table 1. The effective permanent charge (σ_o), that is the surface charge as measured by a probe cation, for the SWy-1 montmorillonite is the same as that measured previously by the alkylammonium ions (Olis *et al.*, 1990) and the Cs adsorption method (Anderson and Sposito, 1991). For all three smectites, these two methods yield the same respective effective permanent charge. The effective permanent charge of the SWy-1 montmorillonite as measured by these two methods is no different than that obtained from the structural formula. This is not the case for the other two smectites, which exhibit lower effective charge than that deduced from the structural formula. Lower measured permanent charge for higher charged smectites by the alkylammonium ion method than from structural formulae has already been found (Senkayi *et al.*, 1985; Malla and Douglas, 1987). The lower values found for the Otay montmorillonite by Senkayi and co-workers (1985) both for structural formula and by

Table 1. Selected surface charge measurements of the smectites.[1]

	Anderson and Sposito[2]			Olis *et al.*[2]	S.F.[2]
	$q_{cs} = -\sigma_o$	$-\sigma_h$	$-(\sigma_o + \sigma_h)$	$-\sigma_o$	$-\sigma_o$
	mMol$_c$ Kg^{-1}				
Beidellite	690 (24)	68 (22)	759 (46)	706 (1–2)[3]	1130
Li Beidellite				564 (1–2)	
Otay	961 (18)	127 (4)	1088 (21)	972 (2–3)	1507
SWy-1	665 (23)	82 (7)	748 (25)	690 (1–2)	719

[1] All data are on a Cs saturated weight basis. Parentheses represent 1 S.D. (n = 3); σ_o = permanent structural surface charge density; σ_h = net proton surface charge density.

[2] Surface charge determined following the method of Anderson and Sposito (1991), Olis *et al.* (1990), and from the structural formulae (S.F.).

[3] Parentheses denote transition assumed for calculations.

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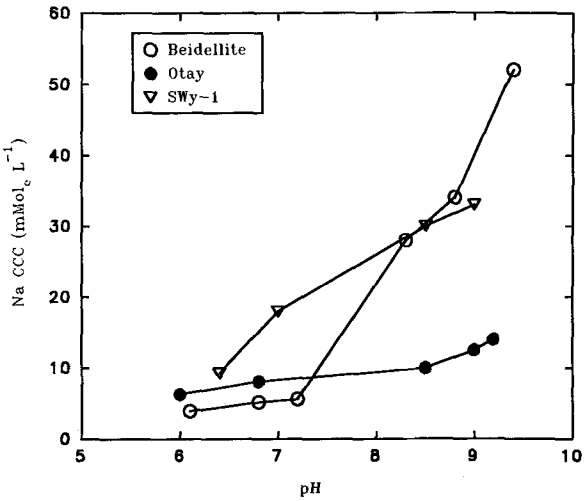


Figure 3. Critical coagulation concentrations for the three smectites in $Na^+(ClO_4^-)$ solutions as a function of suspension pH.

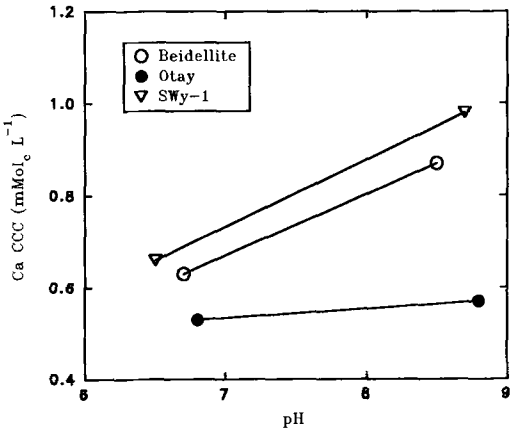


Figure 4. Critical coagulation concentrations for the three smectites in $Ca^{2+}(ClO_4^-)_2$ solutions as a function of suspension pH.

the alkylammonium ion method could be a result of the different particle sizes or sample preparation methods used. The alkylammonium ion method, in conjunction with the Greene-Kelly test, shows that 80% of the effective charge in this smectite originates from the tetrahedral sheet. This is in agreement with the results obtained from the structural formula.

The good agreement between the alkylammonium ion and the Cs adsorption methods indicates that the results found give a satisfactory estimate of the effective permanent charge of these smectites. These data show that the beidellite and the SWy-1 montmorillonite have the same effective permanent surface charge, whereas that of the Otay is much greater. The net proton surface charge is also the same for the beidellite and the SWy-1 montmorillonite, and that for the Otay is greater.

Critical coagulation concentrations

The results of the critical coagulation studies are shown in Figure 3 for the Na^+ electrolyte. In the acidic pH range, the beidellite coagulated at a lower electrolyte concentration than did the two montmorillonites. An increase in pH resulted in the greatest relative increase in the CCC for the Na^+ beidellite, and the smallest relative increase for the Na^+ Otay. The Na^+ SWy-1 showed an intermediary effect of pH on the CCC. A similar pH dependency of the CCC for the Ca^{2+} saturated smectites was found (Figure 4). Possible precipitation of $CaCO_3$ at the higher pH affects the absolute values of the Ca^{2+} CCC but still allows for a comparison of the effect of pH on the stability of colloidal suspensions of these Ca^{2+} smectites. The high CCC value in the basic pH range for the beidellite is not believed to be due to the presence of the 10% wt. wt.$^{-1}$ halloysite impurities. Previous work with a 50/50 mixture of kaolinite and montmorillonite showed that the CCC was controlled by the montmorillonite fraction (Goldberg and Glaubig, 1987). The pH dependency of the CCC for the beidellite is similar to that found for illite (Goldberg and Forster, 1990; Hesterberg and Page, 1990). Based on our results, the pH dependency of the CCC for Na^+ smectites cannot be completely attributed to the pH dependent charge (σ_h), as has been hypothesized for illite, since σ_h is smaller for the beidellite and the SWy-1 montmorillonite than for the Otay (Table 1) and for all three smectites σ_h is only a small component of total charge. Rather, the equivalent effective surface charge, both permanent and variable, of the beidellite and the SWy-1 montmorillonite indicate that the differences in colloidal behavior are due to the origin of charge deficiency within the smectite layers.

Many factors, such as particle size and shape, are believed to affect the CCC of clays, but based on these results the authors would like to advance the hypothesis that charge location is of primary importance in determining the extent of the effect of pH on the stability of smectite suspensions. The pH dependency of the CCC of the smectites can be explained using the hypothesis of van Olphen (1977), which suggests different structural arrangements of smectites in colloidal suspensions, edge-face (EF) at lower pH values, and edge-edge (EE) or face-face (FF) at higher pH. Edge to face interactions are believed to be involved in the flocculation of clays in the acid pH range (Hesterberg and Page, 1990; Gu and Doner, 1992). Based solely on coulombic interactions, EF attractions should be greatly enhanced by tetrahedral charge substitution as compared to octahedral charge due to the dependence of this energy on r^{-1}, the inverse of the charge separation distance. The strength of the EF interactions for beidellite in the acidic pH range would thus be greater

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Table 2. Ca CCC/Na CCC for the three smectites with the pH given in parentheses.

Beidellite	0.0606 (6.7)	0.0155 (8.5)
Otay	0.0327 (6.8)	0.0228 (8.9)
SWy-1	0.0355 (6.5)	0.0163 (8.5)

than that for the montmorillonites, resulting in greater particle-particle attraction. At the higher pH values, colloidal stability should be greatly enhanced for the beidellite over that of the montmorillonite due to greater repulsion of negative charge in either the FF or EE arrangements. EE interactions are by definition repulsive in both the acidic and basic pH range and can, therefore, be assumed not to influence the pH dependency of the CCC of smectites. The greater EF repulsion would require a larger electrolyte concentration in order to shield the surface charge and allow the beidellite particles to get close enough to coagulate. Charge consideration alone, therefore, predicts greater ease of formation of edge-face interactions at acid pH and greater repulsion of face-face arrangements at basic pH for smectites with tetrahedral charge deficiency as compared to those whose permanent negative charge originates in the octahedral sheet.

The effect of tetrahedral charge location on the pH dependence of particle-particle interactions can be shown differently. The relationship between cation valence and CCC is expected to follow that described by the Schulze-Hardy rule for which the DLVO theory predicts a $CCC(Ca^{2+})/CCC(Na^{+})$ ratio of 0.0156 (Sposito, 1984). Yet, the experimental results at the lower pH deviate from the expected (Table 2). This is especially significant for the beidellite. In the basic pH range, all of the CCC ratios conformed more closely to the DLVO predicted ratio. This trend in the ratio of the CCCs supports the role of charge location in determining the CCC of smectites. Edge-face interactions should lower the CCC for Na^{+} more than for Ca^{2+} due to the different valences of these two cations; and at a higher pH, the loss of edge-face associations should result in a better fit to the DLVO model as was found.

Unlike the data for illite (Hesterberg and Page, 1990), the CCCs in a K^{+} perchlorate electrolyte solution were the same or higher than those for Na^{+}, for the three smectites (Table 3). This implies that K^{+} does not form inner-sphere complexes as easily with smectites as with illites in suspensions. No differences were found in the stability of Ca^{2+} and Mg^{2+} smectites suspension (Table 3 and Figure 4).

Table 3. Critical coagulation concentrations of the smectites in various perchlorate electrolyte solutions.

	K	Mg
	mMol$_c$ liter^{-1}	
Beidellite	4.0 (6.4)	0.45 (6.5)
Otay	11 (6.5)	0.65 (6.8)
SWy-1	10 (6.4)	0.65 (6.5)

Numbers in parentheses denote pH of measurement.

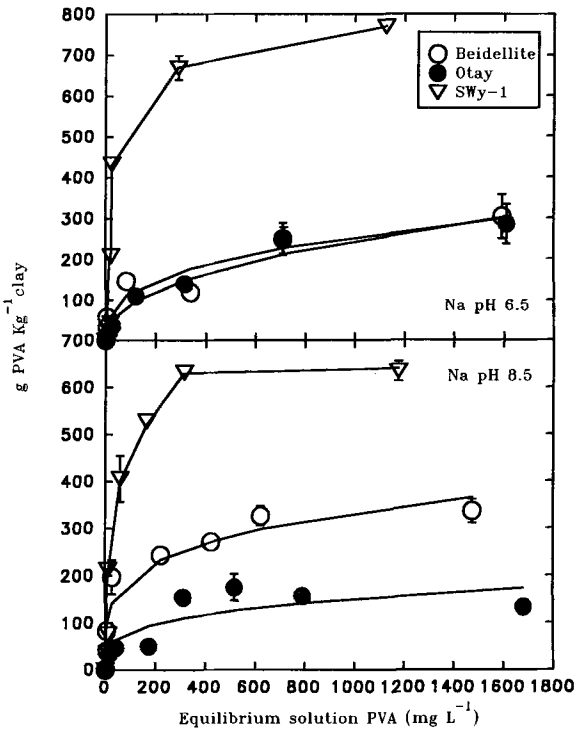


Figure 5. Adsorption isotherms for poly(vinyl) alcohol by the three smectites at two pH values.

Poly(vinyl) alcohol sorption

The sorption isotherms of poly(vinyl) alcohol by the three Na^{+} saturated smectites at two pH values are shown in Figure 5. The maximum sorption (~800 mg PVA g^{-1} clay) of PVA by the SWy-1 montmorillonite at pH 6.5 is equivalent to that found in two previous studies for another low charge montmorillonite (Greenland, 1963; Burchill and Hayes, 1980). Greenland (1963) states that no differences in PVA adsorption were found between the montmorillonite used in the study and that from Upton (Wyoming), but both are low-charge montmorillonites. The other two Na^{+} smectites sorbed significantly less PVA (300 mg g^{-1}) at pH 6.5. Lower PVA adsorption at pH 8.5 was found for the two montmorillonites but not for the beidellite. Positive edge charge must therefore take part in the sorption of PVA by montmorillonites. That this effect was not seen for beidellite can be explained using the same coulombic arguments as for the CCC data. The EF interaction in acidic conditions between positive edge charge and tetrahedral permanent charge may be strong enough that PVA cannot compete for these pH-dependent adsorption sites.

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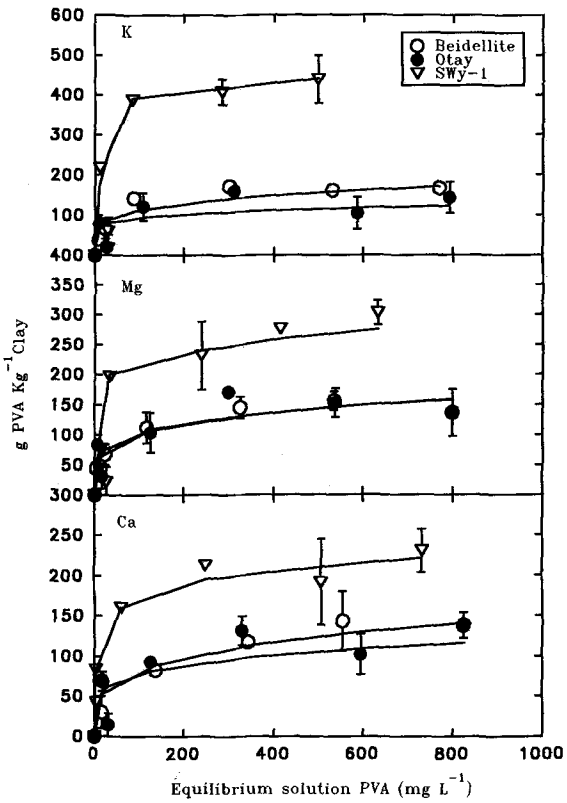


Figure 6. Adsorption isotherms for poly(vinyl) alcohol by the three smectites saturated with different cations at pH 7.

Potassium, calcium and magnesium saturation resulted in a decreased PVA sorption on all three smectites as compared to Na^+ (Figure 5). This decreased PVA adsorption is likely to be due to decreased interlayer distances when saturated with K^+, Ca^{2+}, and Mg^{2+} (Suquet *et al.*, 1975). Ca^{2+} and Mg^{2+} saturated smectites had similar adsorption maxima for each smectite which again is likely to be related to the equivalent interlayer distance in solution.

Surface area accessibility is not believed to be a factor in determining the differences in the maximum adsorption of PVA by the three smectites. For the Na^+ saturated SWy-1 and Otay montmorillonites, interlayer distance can be greater than 40 Å (Norrish, 1973; Suquet *et al.*, 1975). Beidellites may also be capable of such swelling when Na^+ saturated, but it is not known whether the one used in this study shows that phenomenon. Therefore, a surface accessibility argument could be brought forth to explain the PVA sorption data on the Na^+ saturated smectites. Similar order of maximum PVA sorption by the smectites saturated by the other three cations contradicts this argument. Interlayer distances in aqueous solution for smectites are similar when Ca^{2+} or Mg^{2+} saturated (Suquet *et al.*, 1975) indicating equivalent accessibility of interlayer surfaces for PVA uptake. Also, surface areas (Table 4) do not correlate with maximum PVA sorption. That is, the surface available for EGME uptake in the Ca^{2+} saturated smectites is not related to that available to PVA. Using 0.152 nm^2 as the area occupied by one ($CHOH\text{-}CH_2$) (Greenland, 1963) and the EGME surface area (Table 4), the surface coverage is calculated as 61%, 34%, and 47% for the Ca^{2+} saturated SWy-1, Otay, and beidellite clays respectively. The equivalent effective layer charge of the beidellite and SWy-1 montmorillonite demonstrates that tetrahedral charge location in itself leads to a reduced sorption of PVA and lower surface coverage by PVA. Increased effective surface charge, as with the Otay montmorillonite, also reduces PVA sorption and surface coverage.

Table 4. Specific surface area in m^2 g^{-1} of the <0.2 μm fraction of the three smectites.

Beidellite	597 (1)
Otay	825 (15)
SWy-1	800 (28)

Parentheses represent 1 S.D. (n = 3).

Lower sorption of PVA by an illite as compared to montmorillonite was thought to arise from the relative ease of desorption of water molecules on the clay "surfaces" by the polymer (Burchill and Hayes, 1980). This decreased sorption with increasing surface charge is the case for the Otay montmorillonite as compared to the SWy-1 montmorillonites. From these data, it is evident that distance of charge deficiency from the surface also affects the sorption properties of smectites. As with the CCC, these results are consistent with a coulombic argument. That is, as with increased surface charge, tetrahedral charge impedes the replacement of water molecules on the smectite surfaces by PVA. This supports results previously reported by Doner and Mortland (1971) concerning the role of charge location as a factor in dehydration of 2:1 layered clay minerals.

CONCLUSIONS

Effective permanent surface charge is lower for the high charge montmorillonite and beidellite than that calculated from the structural formula. For the low charge montmorillonite, structural formula was a good indicator of effective permanent surface charge. The "rapid" alkylammonium ion and Cs adsorption methods showed similar effective permanent charge for the three smectites. The CCC and the pH dependency of the CCC of smectites cannot be solely explained by the presence of pH dependent edge charge. It is hypothesized that tetrahedral charge location is a crucial factor in determining the effect of pH on the CCC. Increase in either total effective surface charge or tetrahedral charge deficiency results in a decreased surface coverage and adsorption maxima of PVA.

These data show that understanding the effects of smectites on soil properties such as the formation of

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stable aggregates based on results of a reference specimen is not enough to predict behavior of all smectites. Also, the extrapolation of data such as surface charge density, whether effective or derived from structural formulae, to predict the colloid properties of smectites will be erroneous unless the localization of permanent charge is taken into account.

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