A MOLALITY-BASED BET EQUATION FOR MODELING THE ACTIVITY OF WATER SORBED ON CLAY MINERALS

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Abstract—The Brunauer-Emmett-Teller (BET) theory models the effective specific surface area and water content of solids as a function of the relative vapor pressure of water. A modified form of the BET equation has been used successfully to model water activity in concentrated electrolyte solutions as a function of electrolyte concentration. This modified form, referred to here as the Stokes-Robinson BET model, is based on the electrolyte molality rather than on the mass of solute sorbed. The present study evaluates the Stokes-Robinson form of the BET equation to model water-sorption data on two smectites with different layer charges. One smectite was saturated with Na^+ and another with Na^+, Ca^{2+}, or Mg^{2+}. These results are compared to the Stokes-Robinson BET results of aqueous electrolyte solutions. Given published data on cation exchange capacities and water-vapor sorption isotherms for various clays, the molality of the aqueous phase in contact with the clay surface is calculated and related to water activity. The Stokes-Robinson BET model was found to describe accurately the water activity as a function of cation molality below water activities of 0.5 for the smectites. Good relative agreement was obtained between the number of water binding sites predicted by the model and the experimental data reported in the literature for other smectites. Water molecules were found to have a significantly greater affinity for montmorillonite than electrolyte solutions with the same cation molality as the montmorillonite interlayer. This modified BET approach simplifies water-activity modeling in highly saline environments because the same equation can be used for both the liquid- and mineral-surface phases.

Key Words—BET model, Electrolyte Thermodynamics, Water Activity.

INTRODUCTION

The interaction of water molecules with the clay mineral surface is linked critically to essentially all chemical and physical aspects of clay science. Nearly all inorganic or organic solutes are attracted to, transformed on, or repelled from clay minerals in the presence of water (Johnston, 2010). Water activity at the mineral surface is responsible for the matric potential of unsaturated soils and the thermodynamic potential for evaporation (Hillel, 1982). Water activity impacts "negative anion adsorption" on clays (Dalton *et al.*, 1962; Edwards and Quirk, 1962; Polubesova and Borisover, 2009), swelling of clays (Posner and Quirk, 1964a, 1964b; Pashley and Quirk, 1984; Laird, 1996, 2006), and surface acidity of clay minerals (Mortland and Raman, 1968; Dontsova *et al.*, 2005). The impact of total electrolyte concentration on ion-exchange selectivity *via* the water activity has been known for many years (Laudelout *et al.*, 1971, 1972). The impact of mineral surfaces on water dynamics also needs to be understood in highly saline environments, such as evaporite deposits or below nuclear waste tank leaks (Zachara *et al.*, 2007).

The mechanisms of water sorption on soil materials is the subject of ongoing experimental and theoretical studies (Malikova *et al.*, 2007, 2010; Marry and Turq, 2003; Marry *et al.*, 2002).

In geotechnical areas, the presence of clay minerals is known to influence strongly the structural stability of soils and liquefaction. As clay minerals often represent a significant fraction of the hydrous mineral phases found in the Earth's mantle, they influence dynamic processes of water regulation and their presence in subduction zones are thought to play a role in triggering deep-focus earthquakes.

The fine particle size of expandable 2:1 phyllosilicate minerals, such as smectites, makes their impact in soil and sediment processes particularly important. The thickness of these fundamental particles is ~1 nm and the particles range in size from 100 to 1000 nm with specific surface areas that approach 800 m^2g^{-1} (Schoonheydt and Johnston, 2007; Środoń and McCarty, 2008). Montmorillonite is a typical expandable 2:1 phyllosilicate consisting of two silicon tetrahedral sheets that sandwich an aluminum octahedral sheet. During the formation of the clay, in the clay lattice isomorphous substitution occurred of Al^{3+} for Si^{4+} in the tetrahedral sheet, and of Fe^{2+}, Fe^{3+}, or Mg^{2+} for Al^{3+} in the octahedral sheet (Schoonheydt and Johnston, 2007). These substitutions impart an overall 'fixed' negative charge on the basal surface of the clay

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with the distance between negatively charged sites ranging from 0.9 to 1.4 nm. This negative charge is balanced by the presence of cations. The 'layer' of cations and attendant water molecules is denoted as the clay interlayer (see Figure 1). The amount of isomorphous substitution (and hence, layer charge of the sheets) depends on the genesis of the smectite. Although any cation or cationic species can occupy the interlayer between the layers, the most common ions associated with smectites in nature are Ca^{2+}, Mg^{2+}, K^+, Al^{3+}, and Na^+ (Borchardt, 1989). These cations are all characterized by relatively high enthalpies of hydration (Schoonheydt and Johnston, 2007). As a result, water is absorbed in the clay interlayer to satisfy, or partially satisfy, the hydration requirements of the cations. For certain cations on smectites with lower charge density, swelling can occur, resulting in *d* spacings that approach 10 nm (Figure 1) (Barshad, 1949; Pashley and Quirk, 1984; Laird, 1999; Johnston, 2010).

The mechanism of water sorption on 2:1 phyllosilicate clay minerals has been studied extensively (*e.g.* Schoonheydt and Johnston, 2011); water has been found to be bound predominantly to the interlayer cations when the water activity is $<\sim0.80$ (Cariati *et al.*, 1981; Xu *et al.* 2000; Schoonheydt and Johnston, 2011). As noted above, the clay interlayer resembles a unique type of concentrated electrolyte solution (Farmer and Russell, 1971). The amount of water sorbed by Na^+-, Ca^{2+}-, and

Mg^{2+}-saturated montmorillonites was measured by Cases *et al.* (1992, 1997). They found that roughly ten water molecules were sorbed to montmorillonite per Ca^{2+} ion at the limits of the crystalline swelling of the clay. This quantity of water may be representative of the maximum amount of water that the Ca^{2+} ions in the montmorillonite interlayer can adsorb. They found that Mg^{2+}-saturated montmorillonite can adsorb more than ten water molecules per ion and that Na^+-saturation results in less water sorption (Cases *et al.*, 1992, 1997).

In previous work, water:cation ratios as low as 4 H_2O per cation have been measured on montmorillonite (Xu *et al.*, 2000; Johnston *et al.*, 1992). This would correspond to roughly 13−14 molal electrolyte solution. What is unique about the clay interlayer is that the clay mineral surface functions as the negatively charged 'ligand' and generally no dissolved anionic species are present in the interlayer (Johnston, 2010). This phenomenon is frequently referred to as "negative anion adsorption" in the clay literature (*e.g.* Dalton *et al.*, 1962; Edwards and Quirk, 1962). Many studies of water activity in concentrated electrolyte solutions are available for comparison with clay minerals at a given water content (Lobo, 1989). As in clay minerals, the activity of water in highly concentrated electrolyte solutions is low, $\ll1$ (Lobo, 1989).

Stokes and Robinson (1948) envisioned that water molecules are "adsorbed" by electrolytes in highly
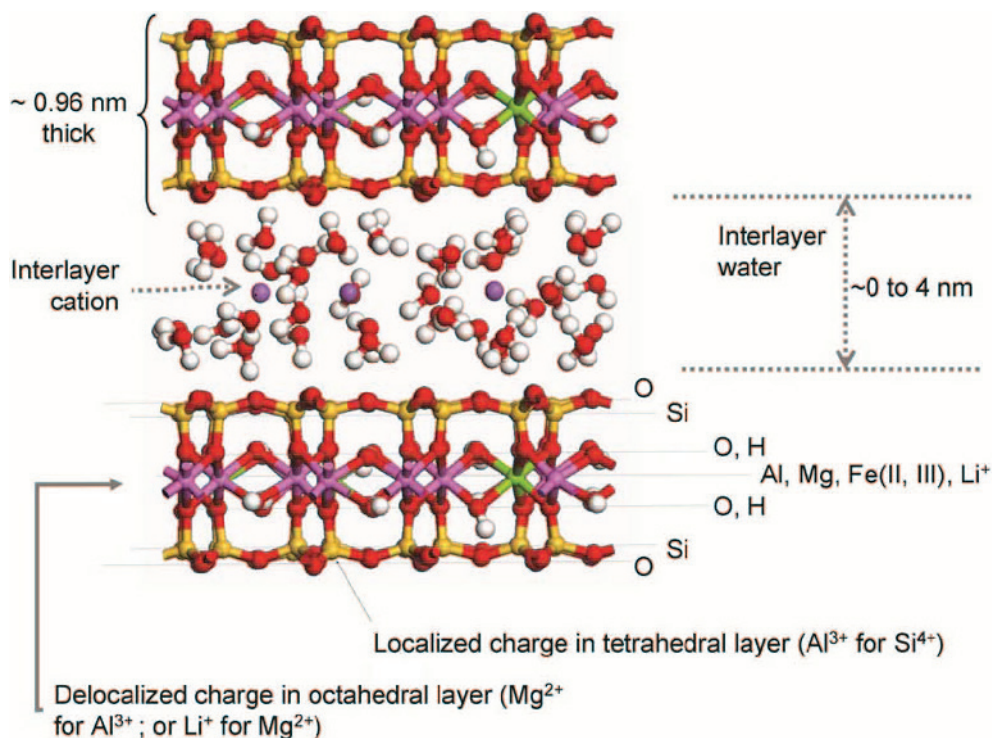

Figure 1. Structure of montmorillonite with interlayer cations (reproduced from Johnston, 2010, with the kind permission of the Mineralogical Society of Great Britain & Ireland).

concentrated solutions. Further, Stokes and Robinson (1948) envisioned that a second layer of water molecules could adsorb, resulting in a multi-layer adsorption phenomenon as the physical basis controlling water activity in highly concentrated electrolyte solutions. This physical model is identical to the multi-layer adsorption model of Brunauer *et al.* (1938), who developed the BET equation. Thus, Stokes and Robinson (1948) concluded that a modified form of the BET equation should be effective at describing water activity in highly concentrated electrolyte solutions. Their hypothesis has been validated for many concentrated electrolyte solutions (Marcus, 2005). Many researchers have studied the thermodynamics of water sorbed onto clay minerals from water vapor and electrolyte solutions. The Brunauer-Emmett-Teller (BET) model (Brunauer *et al.*, 1938) has been used successfully to model the thermodynamics of water sorption on clay minerals (Orchitson, 1955; Mooney *et al.*, 1952; Keren and Shainberg, 1975; Hatch *et al.*, 2012). Given the success of the traditional BET equation at modeling the thermodynamics of water sorption on clays, the Stokes-Robinson modified form was also predicted to be effective. Evaluating this hypothesis was the purpose of the present study.

In the Stokes-Robinson (1948) modification of the BET equation, shown in equation 1, m is the solution molality (moles/kg of water) and a_w is the water activity from vapor-pressure measurements. In the traditional BET model, the c coefficient represents the heat of adsorption when a monolayer is obtained whereas c is the energy of liquefication in the Stokes-Robinson modified form. In the traditional BET model, 'r' is regarded as the quantity of water in a monolayer whereas it is the number of water binding sites per mole of electrolyte in the Stokes-Robinson modification (Stokes and Robinson, 1948). A side-by-side comparison of the units in the regular and Stokes-Robinson BET equations is shown in Table 1. The coefficients 'c' and 'r' are normally determined empirically by fitting to water-activity measurements.

$$m\frac{a_w}{55.51(1-a_w)} = \frac{1}{cr} + \frac{(c-1)}{cr}a_w \qquad (1)$$

This Stokes-Robinson BET model (equation 1) has been employed in many studies of concentrated electrolyte solution thermodynamics. The c and r coefficients have been compiled by Marcus (2005) and are different for each electrolyte. c values of between 30 and 40 kJ/mol for Mg-bearing electrolytes and c values of between 10 and 42 kJ/mol for Ca-bearing electrolytes were reported by Marcus (2005). r values ranging between 4 and 8 waters per mole of electrolyte for both Mg- and Ca-bearing electrolytes were reported by Marcus (2005). The only Na-bearing electrolyte compiled by Marcus (2005) is NaOH, and the c and r values for NaOH reported are 19.3 kJ/mol and 3.2 waters per mole of electrolyte, respectively. The model is usually only applicable to electrolyte solutions when the water activity is <0.5, although some modifications extend the model's range of applicability (Stokes and Robinson, 1948). When the c and r coefficients are known, the water activity of a solution can be calculated at any molality within the range of validity using the quadratic equation.

While this form of the BET model was developed by Stokes and Robinson (1948) for electrolyte solutions, it embodies some of the same thought process that Woodruff and Revil (2011) used in the development of their own modified BET model for clay minerals. Woodruff and Revil (2011) assumed that the quantity of water in a monolayer on clay minerals was proportional to the cation exchange capacity (CEC) because the water sorbs to the interlayer cations. Thus, Woodruff and Revil (2011) modified the r term of the regular BET model to be proportional to the CEC.

Application of equation 1 to describe water sorption on smectite provides a common model that describes water activity for both mineral surfaces and concentrated electrolytes. This, in turn, simplifies algorithms that model water activity in many highly saline environments. In the present study, the Stokes-Robinson BET model was fitted to data on water sorption to montmorillonite saturated with Na^+, Ca^{2+}, or Mg^{2+} ions. The specific objective was to compare the experimental and modeled data directly with electrolyte solutions with the same cation molality (moles of cation per kg of water).

Table 1. Comparison of c and r parameters in traditional and Stokes-Robinson BET equations.

Model	r parameter	c parameter (kJ/mol)
Traditional BET Equation	Quantity of water in a monolayer (volume per mass of adsorbent)	Heat of adsorption in a monolayer
Stokes-Robinson BET equation	Number of binding sites per mole of electrolyte (waters per mole of electrolyte)	Energy of liquefaction

MODELING AND MODEL RESULTS

The present study incorporates previously reported water-vapor sorption data (Xu *et al.* 2000) for Na^+-, Ca^{2+}-, and Mg^{2+}-saturated homo-ionic montmorillonite. These data are particularly useful because both the water content and water-vapor pressure were measured with *in situ* infrared (IR) spectroscopy. This *in situ* measurement avoided any changes to the water content that might occur when the clay is removed from the equilibrium environment for water-content analysis. One of the smectites studied by Xu *et al.* (2000) was SAz-1 Cheto montmorillonite from Arizona. This is a 'high-charge' clay mineral with a CEC of 120 cmol/kg, saturated with Na^+, Ca^{2+}, or Mg^{2+}. Xu *et al.* (2000) also studied water sorption on Na^+-saturated SWy-1 Wyoming montmorillonite, a 'low-charge' clay mineral with a CEC of

80 cmol/kg. These CEC values were measured by Xu *et al.* (2000) and were in general agreement with values reported in the literature (Costanzo and Guggenheim, 2001; Środoń and McCarty, 2008).

One important difference between electrolyte solutions and clay minerals is that electrolyte solutions do not exhibit a water-vapor sorption hysteresis. Sposito and Prost (1982) noted the potential for non-equilibrium states for water sorption on montmorillonite, as shown by the hysteresis on water-sorption curves. Essentially no hysteresis in the Xu *et al.* (2000) data for the Ca^{2+}- and Mg^{2+}-saturated montmorillonites was observed, but some hysteresis was observed in the Na^+-saturated form. While the present authors cannot be certain that the data used here were truly at equilibrium, the data are sufficient to demonstrate that the modified Stokes-Robinson BET model can adequately fit sorption curves. Mooney *et al.*

Table 2. Water-sorption data (from Xu *et al.*, 2000).

——— Ca-SAz-1 montmorillonite ———			——— Mg-SAz-1 montmorillonite ———		
Water activity	kg H_2O/g clay	Ca molality	Water activity	kg H_2O/g clay	Mg molality
0.95	3.63E−04	1.65E+00	0.95	4.99E−04	1.20E+00
0.881	3.39E−04	1.77E+00	0.881	4.59E−04	1.31E+00
0.801	3.12E−04	1.92E+00	0.801	4.30E−04	1.40E+00
0.695	2.97E−04	2.02E+00	0.695	4.08E−04	1.47E+00
0.594	2.87E−04	2.09E+00	0.594	3.90E−04	1.54E+00
0.501	2.77E−04	2.17E+00	0.501	3.74E−04	1.60E+00
0.412	2.64E−04	2.27E+00	0.412	3.57E−04	1.68E+00
0.364	2.57E−04	2.33E+00	0.364	3.50E−04	1.71E+00
0.315	2.50E−04	2.40E+00	0.315	3.39E−04	1.77E+00
0.258	2.42E−04	2.48E+00	0.258	3.29E−04	1.82E+00
0.201	2.28E−04	2.63E+00	0.201	3.11E−04	1.93E+00
0.152	2.12E−04	2.83E+00	0.152	3.03E−04	1.98E+00
0.106	1.93E−04	3.11E+00	0.106	2.90E−04	2.07E+00
0.0602	1.69E−04	3.55E+00	0.0602	2.75E−04	2.18E+00
0.008	1.32E−04	4.55E+00	0.008	2.56E−04	2.34E+00

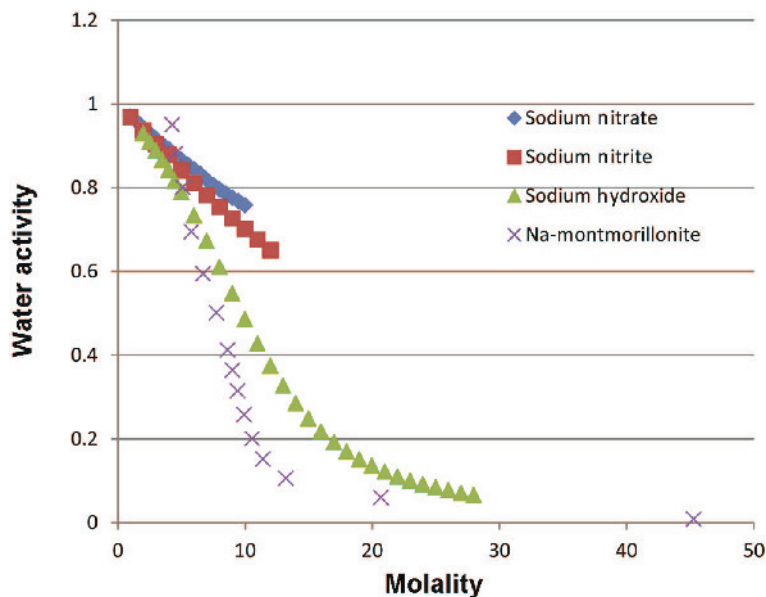| ——— Na-SWy-1 montmorillonite ———			——— Na-SAz-1 montmorillonite ———		
Water activity	kg H_2O/g clay	Na molality	Water activity	kg H_2O/g clay	Na molality
0.843	3.01E−04	2.66E+00	0.95	3.01E−04	4.30E+00
0.801	2.79E−04	2.86E+00	0.881	2.79E−04	4.53E+00
0.752	2.65E−04	3.02E+00	0.801	2.65E−04	5.11E+00
0.695	2.37E−04	3.37E+00	0.695	2.37E−04	5.80E+00
0.648	2.16E−04	3.70E+00	0.594	2.16E−04	6.71E+00
0.594	2.01E−04	3.99E+00	0.501	2.01E−04	7.77E+00
0.544	1.73E−04	4.63E+00	0.412	1.73E−04	8.65E+00
0.501	1.51E−04	5.30E+00	0.364	1.51E−04	9.02E+00
0.458	1.39E−04	5.77E+00	0.315	1.39E−04	9.43E+00
0.412	1.28E−04	6.26E+00	0.258	1.28E−04	9.95E+00
0.364	1.24E−04	6.46E+00	0.201	1.24E−04	1.06E+01
0.315	1.15E−04	6.98E+00	0.152	1.15E−04	1.14E+01
0.258	1.04E−04	7.66E+00	0.106	1.04E−04	1.32E+01
0.201	9.46E−05	8.46E+00	0.0602	9.46E−05	2.07E+01
0.152	8.02E−05	9.98E+00	0.008	8.02E−05	4.53E+01
0.106	6.37E−05	1.26E+01			
0.0602	4.91E−05	1.63E+01			
0.008	3.35E−05	2.39E+01			

Figure 2. Water activity *vs*. Na molality for Na^{+}-saturated SAz-1 montmorillonite.

(1952) determined that desorption curves are reproducible but that adsorption curves are not always reproducible. Therefore, the desorption data presented by Xu *et al.* (2000) were used in the present study for all three cations.

In order to use equation 1 in this study, the water contents from Xu *et al.* (2000) were converted to solution molalities (Table 2). Solution molality is defined as moles of electrolyte per kilogram of water. Thus, sorbed water weight percent along with the CEC of the clay minerals determined the molalities. Note that this approach defines the molality of the exchangeable cation sorbed in the interlayer (Figure 1). Thus, this electrolyte molality is equal to the corresponding solution electrolyte molality. This was done in order to facilitate comparison with aqueous electrolyte solutions.

A comparison between water activity in electrolyte solutions and in clay minerals as a function of cation molality can be made (Figures 2 through 4). The Na-bearing electrolytes in Figure 1 are the most prevalent electrolytes in nuclear waste at the Hanford, Washington, site (Hill *et al.*, 2011). This waste is extremely concentrated (Na molarities of >10), and some of this waste has leaked into the vadose zone below the tanks (Zachara *et al.*, 2007). Thus, the Hanford vadose zone is a potential application of the Stokes-Robinson BET equation. The Ca- and Mg-bearing electrolytes shown in Figures 3 and 4 are simply common electrolytes for which water activity data were readily available (Table 3) (Pearce, 1936; Staples and Nuttall, 1977; Goldberg and Nuttal, 1978).
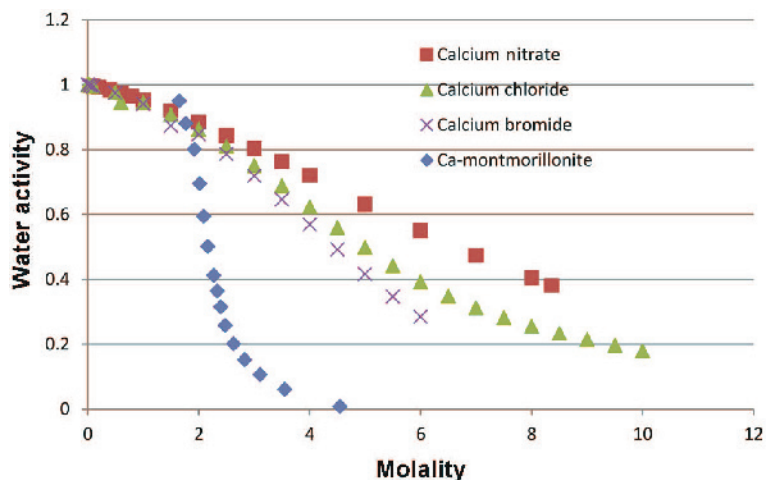

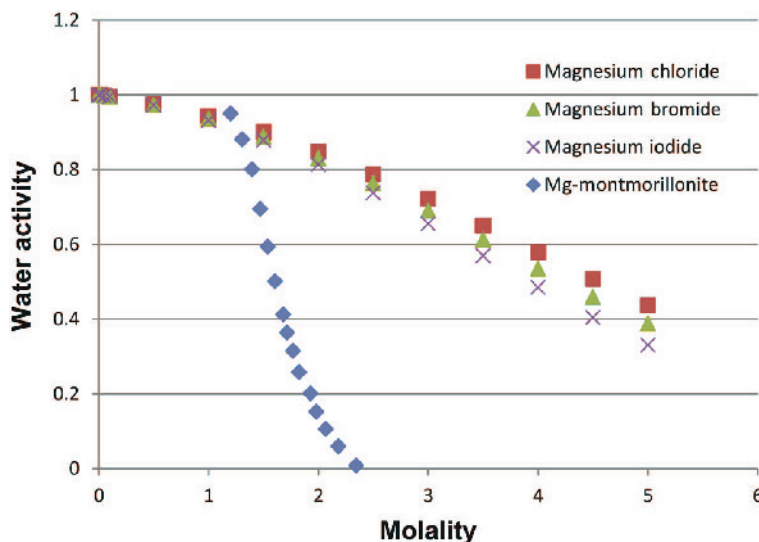Figure 3. Water activity *vs.* Ca molality for Ca^{2+}-saturated SAz-1 montmorillonite.

Figure 4. Water activity *vs.* Mg molality for Mg^{2+}-saturated SAz-1 montmorillonite.

The ability of the Stokes-Robinson BET model to fit the data can be evaluated graphically (Figures 5, 6) for Na^+-, Ca^{2+}-, and Mg^{2+}-saturated montmorillonites. The horizontal axis of these plots is the activity of water, and the vertical axis is the left hand side of equation 1. When the BET model is applicable to the data, the resulting plot should be linear (Ally and Braunstein, 1993). Equation 1 is most commonly applicable to electrolyte solutions when the activity of water is 0.5 or less, but can sometimes be effective for water activities as high as 0.75 (Marcus, 2005). For the mono-ionic clay minerals investigated in the present study, the plot was approximately linear when the water activity was <0.5 (Figures 5, 6) and deviated from linearity at larger water activities. The exception was for Na^+-SAz-1 montmorillonite, which was only linear at water activity values of <0.4. The linearity exhibited by these plots demonstrated that the Stokes-Robinson form of the BET equation is applicable to clay minerals and a molality-based model can be used to calculate the activity of water sorbed onto them.

The coefficients c and r in equation 1 were adjusted iteratively until the sum of the squared differences between the left-hand side of equation 1 (calculated from data) and the right-hand side (calculated from the coefficients) was minimized. This was performed using the *Solver*® function in a *Microsoft Excel*® spreadsheet, which employs the Newton method with quadratic projections. The coefficients for NaOH (Marcus, 2005) were used as the starting values in the iteration for the Na^+-saturated montmorillonites. The c and r coefficients for $CaBr_2$ and $MgBr_2$ (Marcus, 2005) were used for Ca^{2+}- and Mg^{2+}-saturated SAz-1 montmorillonite, respectively. The resulting c and r values determined by this regression (Table 4) and the model fits (Figures 5 and 6) reveal that the model fit is reasonable using the c and r values developed here.

DISCUSSION

At low water contents (and, hence, low water activities) the water sorbed on a clay mineral is bound predominantly to the cations in the clay interlayer rather than to the anionic phyllosilicate structure (Xu *et al.*, 2000; Cariati *et al.*, 1981; Sposito and Prost, 1982). Likewise, water is known to bind to cations more strongly than the anions in highly concentrated electrolyte solutions (Ohtaki, 2001), although certain anions such as hydroxide certainly bind water strongly (Stokes, 1945; Figure 2).

Table 3. References for electrolyte solution water activity data in Figures 2−4.

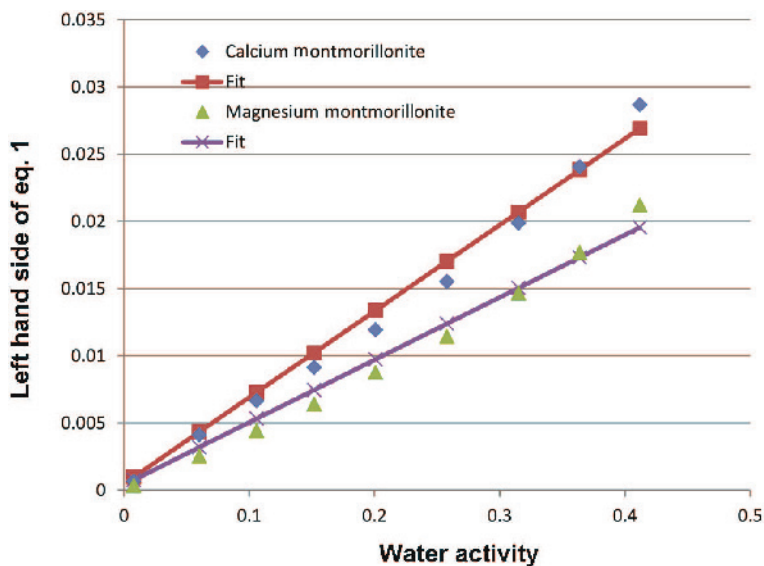| Electrolyte	Reference
$NaNO_3$	Shpigel and Mishchenko (1967)
$NaNO_2$	Staples (1981)
NaOH	Stokes (1945)
$CaNO_3$	Pearce (1936)
$CaCl_2$	Staples and Nuttall (1977)
$CaBr_2$, $MgCl_2$, $MgBr_2$, MgI_2	Goldberg and Nuttall (1978)

Figure 5. Model fit to Ca- and Mg-saturated montmorillonite data.

Water activity clearly decreases more quickly per mole of cation added as montmorillonite than for that same cation dissolved in an electrolyte solution (Figures 2−4). The difference between each cation in smectite *vs.* water must come from the direct impact of the anion on the water activity or from the anion's interference on the cation's ability to bind water. In the case of the clay mineral, the anion is the silicate structure. The plots (Figures 2−4) do not include all electrolyte solutions that could exist for each cation, but
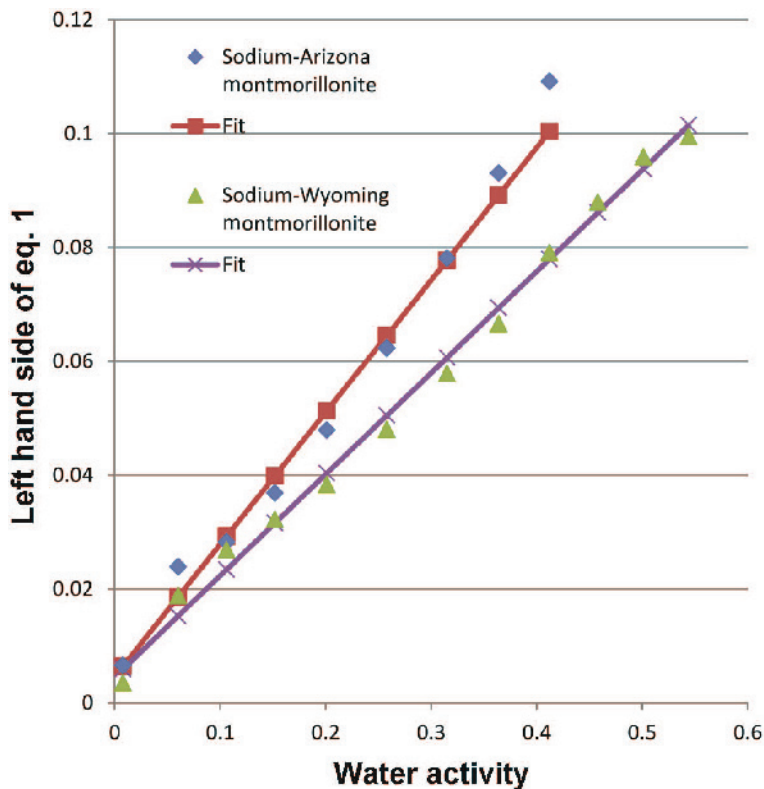

Figure 6. Model fit to Na-saturated montmorillonite data.

contain some common electrolyte solutions for which data are readily available. No conclusions can be made that the clay minerals decrease water activity more than ions dissolved in electrolyte solutions but they do bind the water molecules strongly.

Posner and Quirk (1964a, 1964b) showed that clay minerals sorbed water even from highly concentrated electrolyte solutions, consistent with the plots in Figures 2−4. Like the montmorillonites studied here, data from the literature indicate that the Stokes-Robinson form of the BET equation can accurately predict water activities as a function of molality when the water activity is <0.5 (Stokes and Robinson, 1948, Marcus, 2005). Water would have to exchange between the clay mineral and any adjacent electrolyte solution in order to maintain the system at equilibrium during perturbation. The BET equation could be used to calculate the molality of both the clay mineral and the electrolyte solution that equilibrates with a given measured water activity. Indeed, a major impetus for the present study was to develop a model that can be used to predict the distribution of water between clay minerals and highly concentrated electrolyte solutions. A common model that describes both the solid- and liquid-phase water activities (equation 1) would simplify calculations for those systems.

The water activity *vs.* Na molality is not the same for the two Na^+-saturated montmorillonites (Figure 6), even though the saturating cation is the same. This indicates that the *c* and *r* coefficients are only applicable to a specific montmorillonite. A major difference between these two montmorillonites is the layer charge (Xu *et al.*, 2000). Layer charge is well known to affect other properties of clay minerals such as swelling pressure (Laird, 1999) and ion-exchange selectivity (Onodera *et al.*, 1998). In turn, swelling pressure and ion-exchange selectivity are influenced by the thermodynamic properties of water (Barshad, 1949; Laudelout *et al.*, 1971, 1972; Laird, 1999). Thus, not surprisingly, two montmorillonites with differing layer charges will have differing thermodynamics of sorbed water. In this case, the Wyoming montmorillonite adsorbs more water per Na^+ ion than does the SAz-1 montmorillonite at a given water activity. Thus, a mole of Na^+ from Na^+-saturated Wyoming montmorillonite reduces the water activity more than a mole of Na^+ on the more highly charged

Arizona montmorillonite. This may be due to more ion−ion interactions occurring in the more highly charged interlayer. Xu *et al.* (2000) indicated that the Arizona montmorillonite has less hydrogen bonding at low water contents than the Wyoming montmorillonite, as indicated by the lower-frequency H−O−H stretching modes at the same water content.

The *r* value in equation 1 theoretically represents the number of water binding sites per mole of electrolyte (Stokes and Robinson, 1948). The *r* values determined by regression came to 4.3, 15.5, and 21.32 water binding sites for Na^+-, Ca^{2+}-, and Mg^{2+}-saturated SAz-1 montmorillonite, respectively (Table 4). Cases *et al.* (1992, 1997) studied the amount of water sorbed to Wyoming montmorillonite. They found the number of water molecules sorbed per mole of cation at the limits of crystalline swelling were <10, 10, and 20 for Na^+, Ca^{2+}, and Mg^{2+}, respectively. Hence, the water binding sites results for Wyoming montmorillonite reported by Cases *et al.* (1992, 1997) were consistent with the relative order of the binding site numbers determined by fitting equation 1 to vapor-adsorption data for SAz-1. Thus, these independent results for montmorillonite are consistent with the number of binding sites derived in Table 4. The relative order of these binding site numbers for Na^+, Ca^{2+}, and Mg^{2+} is also consistent with the data compiled by Marcus (2005) for electrolyte solutions bearing these same cations. The absolute value of *r* is greater than the value for dissolved electrolytes compiled by Marcus (2005). This is consistent with the larger decrease in water activity per mole of cation for montmorillonite compared to other common electrolytes observed earlier (Figures 2−4).

The position of the ~1630 cm^{-1} H−O−H bending band in the IR adsorption spectra of these clays as a function of the number of sorbed water molecules per cation was measured by Xu *et al.* (2000). The greater the wavenumber of this band, the more hydrogen bonded the sorbed water molecules are. The same authors found that the amount of hydrogen bonding between water molecules depended on the number of water molecules per cation. The number of water molecules per cation where they observed the greatest amount of hydrogen bonding corresponds roughly to the *r* value determined in the present study for these same montmorillonites.

Typical *c* values (binding energies) for electrolyte solutions at 25ºC reported by Marcus (2005) are between

Table 4. Coefficients for equation 1 for each montmorillonite.

Smectite	*r* (# of binding sites)	*c* (exp(kJ/mol))
Na^+-SWy-1 montmorillonite	5.471	40.61
Na^+-SAz-1 montmorillonite	4.298	938.6
Ca^{2+}-SAz-1 montmorillonite	15.47	135.6
Mg^{2+}-SAz-1 montmorillonite	21.32	120.0

1.7 and 62 exp(kJ/mol). During preliminary numerical analysis of the montmorillonite data, c values were highly sensitive to the precision used in the iterative procedure (precision is the number of decimal places carried in the sum of squared error). The sum of squares at higher precision was always improved by increasing the c value. Consequently, the c value returned was directly proportional to the precision requested of Solver®. Hence, the accuracy of the BET model at this single temperature is not very sensitive to the magnitude of the c value. Therefore, the reader is advised not to conclude anything about the significance of the magnitude of the c values for these montmorillonites reported in Table 4. Fortunately, the r values were insensitive to the precision requested of Solver®, as illustrated by plots for Ca-montmorillonite (Figure 7) of the changes in the sum of squares error (SSE) of the model as a function in the percent change in the c and r values from the value in Table 4 for Ca-Montmorillonite. Even a >700% change in the value of c has an insignificant effect on the quality of the model fit whereas a couple percent change in the value of r has an enormous effect. Thus, Figure 7 supports the conclusion that the value of c does not significantly affect the model result. The SSE for the fit in the units of the left-hand side of equation 1 were 6.35×10^{-5} (Na-Wyoming montmorillonite), 6.99×10^{-5} (Na-Arizona montmorillonite), 9.97×10^{-6} (Mg-Arizona montmorillonite), and 7.43×10^{-5} (Ca-Arizona montmorillonite).

The c value was suggested by Stokes and Robinson (1948) to be a function of temperature as described by equation 2, a relationship that has been verified for many electrolytes (Marcus, 2005).

$$c = \exp \left(\frac{\varepsilon}{\mathrm{R}T} \right) \qquad (2)$$

In equation 2, R is the Universal Gas Constant, T is the temperature in Kelvin, and ε is the difference between the molar liquefaction enthalpy of water and the molar enthalpy of water sorption on the montmorillonite or salt. The value of ε is determined empirically by fitting equation 1 to water-activity data at several temperatures. If water activity data were available at more than one temperature for the smectites studied here, the c value could be constrained by substituting equation 2 into equation 1 during the regression (Marcus, 2005).

The present study has shown that the Stokes-Robinson modification of the BET equation can adequately describe the water activity at clay mineral surfaces. Thus, this model is available as an alternative to other models applied to highly unsaturated soils. The type of environments where equation 1 is most likely to be applied by modelers, however, is in highly saline environments where the model can be applied to both the liquid phase and clay mineral phase. Use of equation 1 would simplify algorithms used for calculating water dynamics for these saline environments.

Given that the clay mineral interlayer resembles a concentrated electrolyte solution (minus the anions in the liquid phase; Figure 1), the distinction between solid and liquid phase within a mixture of montmorillonite and concentrated electrolyte solution is somewhat blurred. If the clay mineral interlayer is to be treated as a concentrated electrolyte solution, the impact of the clay mineral on the water activity in mixtures of the clay mineral and concentrated electrolytes will have to be determined in a similar way to mixtures of soluble electrolytes. Ally and Braunstein (1998) and Abraham and Abraham (2000) developed algorithms employing equation 1 for soluble electrolyte mixtures.
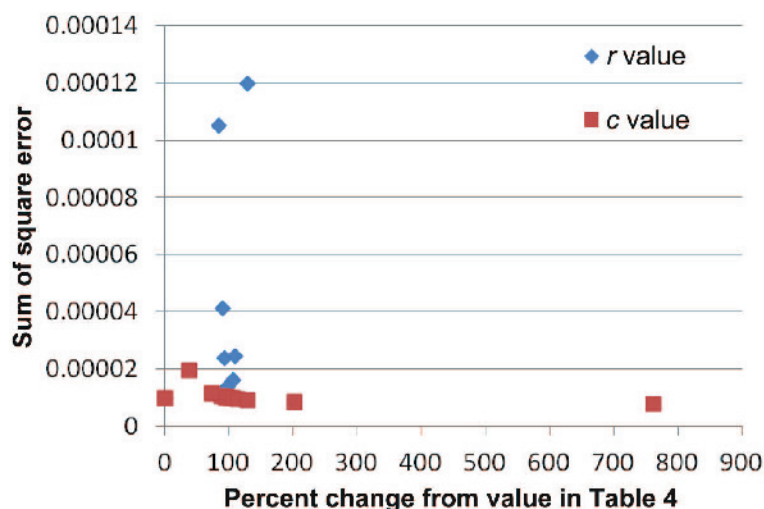

Figure 7. Change in the sum of squares error of the model fit to the Ca-montmorillonite data as a function of the percentage of the r or c values from those listed in Table 4.

Even though the clay interlayer resembles an electrolyte solution, thermodynamic methods exist to distinguish between the water in the clay mineral phase and an aqueous electrolyte solution in contact with the clay (Posner and Quirk, 1964b). Theoretically, the activity of water in the clay phase must equal the activity of water in the liquid phase, as long as some distinction between the clay and liquid phases can be made. Therefore, the activity of water in an electrolyte solution extracted from a clay-concentrated electrolyte solution mixture must be the same as the activity of water within that mixture, including the activity of water associated with the clay. This theoretical relationship has been confirmed by Olson and Robbins (1971). When the water activity is within the range where equation 1 is applicable to both clay-mineral and electrolyte solutions (water activity <0.5), equation 1 can be used to calculate the amount of water associated with the clay phase *via* the CEC and the exchanged-cation molality.

Clay minerals are well known to adsorb and desorb water from electrolyte solutions and the extent of the sorption depends on the relative affinity of the water for the clay mineral or the dissolved electrolyte (Denis, 1991; Posner and Quirk, 1964a, 1964b). This water adsorption from electrolyte solutions leads to what is commonly called "negative anion adsorption," where the concentration of an electrolyte in the bulk solution increases because of the repulsion of the electrolyte from the clay (Dalton *et al.*, 1962; Edwards and Quirk, 1962). Thus, clay affects the activity of water in bathing electrolyte solutions by sorbing (or desorbing) water from the bulk solution and, thereby, changing the concentration of the electrolyte in the bulk liquid phase. Hence, the activity of water in an electrolyte solution extracted from a clay mineral describes completely the activity of water in the system, but equation 1 can be used to calculate the distribution of water between the clay and liquid phases at that measured water activity.

CONCLUSION

The present study has shown that the Stokes-Robinson form of the BET model (Stokes and Robinson, 1948) is applicable to water sorbed to clay minerals. Furthermore, *r* values determined by regressing equation 1 are proportional to the stable layer hydrates observed in montmorillonites in the literature, as predicted by theory. Lastly, a mole of Na^+, Ca^{2+}, and Mg^{2+} in montmorillonite reduces the activity of water more than does a mole of these cations in many common aqueous electrolyte solutions. The Stokes-Robinson form of the BET equation is recommended for systems where it is valid for both the clay mineral and aqueous phases.

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