

EFFECT OF COSOLVENTS ON Ca-Na EXCHANGE ONTO WYOMING BENTONITE

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Abstract—Calcium-sodium exchange on Wyoming bentonite in methanol, ethanol and acetone-water systems were investigated at 0.03 N Cl and at room temperature. Calcium-sodium exchange isotherms were plotted at cosolvent concentrations ranging from 0 to 70% wt./wt. using Ca and Na ionic activities before and after correction for CaCl⁺ formation. In both cases and in all treatments, a greater selectivity of bentonite surfaces for Ca ions was observed. When compared to water, different trends were observed among and within cosolvents. These trends varied depending on whether or not CaCl⁺ formation was accounted for. Ignoring the formation of CaCl⁺, the preference of bentonite for Ca increased in methanol-water systems with increased percent methanol at low equivalent Ca fraction (<0.2). At higher Ca fractions, this preference matched that of water. In ethanol-water, no increased preference of the surface for Ca was observed. In acetone-water, increasing cosolvent concentration decreased the preference of the surface for Ca. The magnitude of this decrease was larger at low equivalent Ca fraction (<0.2). After correction for CaCl⁺, both in solution and on the surface, the preference of bentonite for Ca²⁺ was larger in methanol- and ethanol-water systems. In acetone-water, increased surface preference for Ca was only apparent at low acetone fractions (<50%). At higher acetone fractions, there was evidence of increased Na loading but no increase in Ca²⁺ selectivity. Clearly, ion-pair formation and its effects on Ca-Na exchange reactions cannot be ignored in mixtures of aqueous-organic solvents. After accounting for this effect, Ca-Na exchange in the studied solvents appears to be more of a surface- than a solution-controlled phenomenon that involves both electrostatic and specific solvent-surface types of interactions that have not been elucidated.

Key Words—Binary Exchange, Cation Exchange Capacity (CEC), Cosolvents, Dielectric Constant, Fractional Isotherms, Pairing, Wyoming Bentonite.

INTRODUCTION

The study of soil-contaminant interactions in non-aqueous and in mixtures of aqueous and organic solvents presents a growing field of interest especially from an environmental point of view (Artiola-Fortuny and Fuller, 1982; Bedient *et al.*, 1983). Understanding these processes can have practical implications for the selection of remediation techniques, particularly in sites where co-contamination with solvents is very likely (Sawhney and Kozloski, 1984; Riley and Zachara, 1992).

To understand the behavior of inorganic contaminants in non-aqueous and in mixtures of aqueous and organic solvents where both increased and decreased transport have been reported (Sheets and Fuller, 1986; Miller *et al.*, 1992), it is essential to consider, from a theoretical aspect, both the separate and the combined effects of solvents on the solution and the surface physicochemical properties.

The single ion activity, $\{i\}$, describes the behavior of a particular chemical species in solution,

$$\{i\} = \gamma_i c_i \quad (1)$$

where γ_i denotes the single-ion activity coefficient and c_i the molar concentration of the chemical species. In ideal dilute aqueous solutions, $\gamma_i = 1$ and the ionic activity equals the molar concentration. In concentrated aqueous solutions and in complex non-aqueous solutions, γ_i decreases, as predicted by the Debye-Hückel equation

$$\log \gamma_i = - \frac{Az_i^2 I^{0.5}}{1 + Ba_i I^{0.5}} \quad (2)$$

where z_i is the ionic charge, a_i is the ion-size parameter and A and B are two parameters related to the solvent properties and the temperature of the solution

$$A = (2\pi N_A \rho)^{0.5} \left[\frac{e_0^2}{4\pi \epsilon_r \epsilon_0 kT} \right]^{1.5} \quad (3)$$

$$B = e_0 \left(\frac{2N_A \rho}{\epsilon_r \epsilon_0 kT} \right)^{0.5} \quad (4)$$

where N_A is Avogadro's number, ρ is the solvent bulk density, e_0 is the electronic charge, ϵ_r is the solvent dielectric constant, ϵ_0 is the permittivity of vacuum, k is Boltzmann's constant, and T is the absolute temperature. If all variables are kept constant, equations 2–4 predict that a decrease in ϵ_r would decrease the single ion activity coefficient and, hence, reduce its activity (equation 1). However, the effect of ϵ_r on the ion-solvent interactions may be more pronounced than is

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predicted by the Debye-Hückel theory because specific ion pairing may be responsible for a greater departure from ideality than non-specific electrostatic interactions. As predicted by Coulomb's law, a decrease in ϵ_r will increase the forces of attraction between oppositely charged ions as a result of the decreased shielding of charges by the surrounding molecules. This increased attraction is manifested by an increase in the magnitude of ion pairing between these charges and the formation of new pairs such as triple-ion pairs (Izutsu, 2002) that would not otherwise form in aqueous solvents. Experimental data on ion pairing and complexation in non-aqueous and mixed aqueous organic solvents further support this hypothesis (Evers and Knox, 1951; Mui and McBride, 1974; Gaizer *et al.*, 1985; Doe *et al.*, 1987; Doe *et al.*, 1990; Xue and Traina, 1996b).

The effect of solvents on the surface properties of clay minerals can be best described by examining the effect of the solvent dielectric constant on the forces governing clay flocculation and dispersion, most importantly the attractive van der Waals, Φ_{vdW} , (equation 5) and the repulsive electrostatic or diffuse double layer, (equation 6) forces

$$\Phi_{vdW} = -\frac{1}{(4\pi\epsilon_r)^2} \left[1\alpha\mu^2 + \frac{2}{3} \frac{\mu^4}{kT} + \frac{3}{4} h\nu\alpha \right] x^{-6} \quad (5)$$

$$\psi_x = \psi_0 e^{-Kx} \quad (6)$$

where

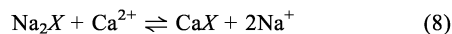
$$K = \sqrt{\frac{(8\pi e \sum n_i z_i^2)}{(\epsilon_r kT)}} \quad (7)$$

α is the polarizability (always negative), μ is the dipole moment, ν is the vibrational frequency of electrons (always negative), ψ_x is the potential at distance x from the clay particle, h is Planck's constant, n_i is the number of moles of species i and ψ_0 is the potential at the surface of the clay particle. If all chemical variables are held constant, decreasing ϵ_r will increase the net Van der Waals (equation 5) attractive forces, reduce the repulsive diffuse double-layer forces (equation 6), decrease the thickness of the diffuse double layer (K^{-1} , equation 7), and hence promote flocculation. Several authors have examined the effect of solvent physicochemical properties on the thickness of the diffuse double layer by studying the intracrystalline swelling of clay minerals (mostly montmorillonite) in non-aqueous (Barshad, 1952; Olejnik *et al.*, 1974; Murray and Quirk, 1982; Anderson *et al.*, 1985) and mixtures of aqueous and organic solvents (Brindley *et al.*, 1969). Generally, decreased intracrystalline swelling is observed in solvents with low dielectric constants (Barshad, 1952). Brindley *et al.* (1969) reported that the intracrystalline swelling of Ca-montmorillonite increases with an increase in the fraction of organic solvent (f_c) up to a

certain threshold dictated by the solvent molecule size and the medium dielectric constant, after which collapse of the interlayer spacing occurs. They explained this observed phenomenon through the effects of solvents on the cation hydration whereby expansion occurred as a result of water molecules being replaced by those of the solvent.

In soils and waste-contaminated sites, net solvent effects on inorganic contaminant behavior will result from the combined effects on the solution and the surface properties. Solvent effects on the physical properties of soils and clays have been reported (Brown and Thomas, 1987; Fernandez and Qigley, 1985), but there has been little work on solvent effects on metal-surface reactions (Kosmulski, 1994; Miller *et al.*, 1992) and none on clay minerals. Studying Ca-Na exchange reactions on Wyoming bentonite in mixed aqueous organic solvents offers many advantages. This system is well studied in aqueous solvents (Van Bladel and Gheyi, 1980; Sposito *et al.*, 1983; Amrhein and Suarez, 1991; Zhang and Sparks, 1996) and it has been established that, in the absence of significant ion pairing and complexation, the long-range electrostatic attraction of cations to the surface favor the adsorption of Ca^{2+} as opposed to Na^+ ions. As ion-pairing increases, this selectivity tends to decrease (Sposito *et al.*, 1983). Both Ca and Na are hard Lewis acids and both tend to form outer-sphere surface complexes with the hard Lewis base Wyoming bentonite.

For the exchange reaction



The Vanselow selectivity coefficient is defined as:

$$K_v = \frac{\{\text{Na}^+\}^2 N_{\text{Ca}}}{\{\text{Ca}^{2+}\} N_{\text{Na}}^2} = \frac{[\text{Na}^+]^2}{[\text{Ca}^{2+}]} \times \frac{\gamma_{\text{Na}^+}^2}{\gamma_{\text{Ca}^{2+}}} \times \frac{N_{\text{Ca}}}{N_{\text{Na}}^2} \quad (9)$$

where X indicates a solid phase exchanging surface with a charge of -2 , $\{ \}$ refers to the activity of the specific cation, and N_{Ca} and N_{Na} are the mole fractions of Ca and Na on the exchanger sites, respectively. Because changes in $N_{\text{Ca}}/N_{\text{Na}}^2$ would result in shifts in data point positions on a Ca-Na exchange isotherm or changes in the isotherm position, it is easier to relate these changes, if any, to the effects of cosolvents on solution properties (ionic activities or $\gamma_{\text{Ca}^{2+}}/\gamma_{\text{Na}^+}^2$) or surface properties (K_v) or both if equation 9 is rearranged as

$$\frac{N_{\text{Ca}}}{N_{\text{Na}}^2} = K_v \times \frac{[\text{Ca}^{2+}]}{[\text{Na}]^2} \times \frac{\gamma_{\text{Ca}^{2+}}}{\gamma_{\text{Na}^+}^2} \quad (10)$$

Increasing cosolvent fraction will decrease $\gamma_{\text{Ca}^{2+}}/\gamma_{\text{Na}^+}^2$ (Figure 1) and decrease (Ca^{2+}) due to increased ion-pairing (more pronounced for divalent Ca^{2+} than the monovalent Na^+). Assuming no changes in the exchanger activity coefficients or in K_v , this should decrease $N_{\text{Ca}}/N_{\text{Na}}^2$ (increase Na loading). This should shift the

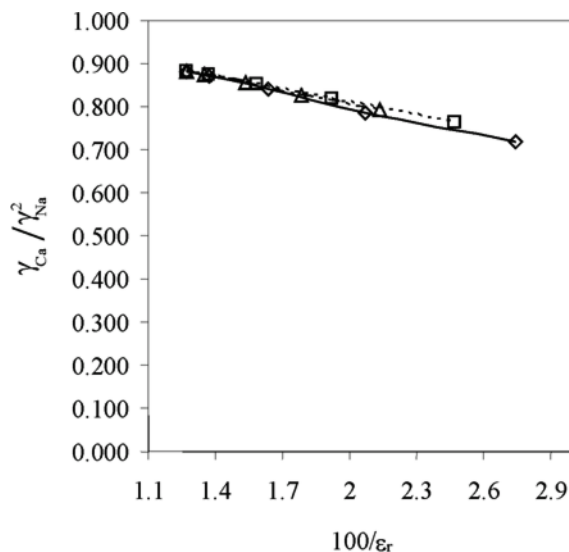


Figure 1. Changes in the single ion activity ratio (as predicted by the Debye-Hückel equation) as a function of $100/\epsilon_r$ in \triangle methanol, \square ethanol and \diamond acetone (calculated using equations 2–4).

position of data points along the isotherm towards the Na-rich end. Other shifts in data point positions on the isotherm or changes in isotherm shape with cosolvent fraction, after correction for changes in the solution phase metal activity, may indicate changes in exchanger activity coefficients, K_v , or some other solvent-specific interactions.

It is the objective of this study to determine the net effect of cosolvents on the changes in the selectivity of Wyoming bentonite for Ca/Na ions by examining the effect of the solvent dielectric constant on both the surface and the solution properties. Given the inherent difficulty in measuring the activities of ions in the solid phase, only the activities of ions in solution will be corrected for both changes in single-ion activity coefficient (Debye-Hückel equation) and free metal concentration (ion pairing).

MATERIAL AND METHODS

Na-montmorillonite

Wyoming bentonite was obtained from the American Colloid Company at their Upton, Wyoming plant. Before clay separation, soluble and insoluble salts, organic matter and Fe oxides were removed according to standard procedures (Kunze and Dixon, 1986). The $<2.0\ \mu\text{m}$ clay fraction was separated by repeated washing and centrifugation and Na-saturated clays were prepared by repeated equilibration with 1 M NaCl. Excess salts were removed by dialysis against distilled water until an AgNO_3 test indicated that the equilibrium solution was free of chloride ions. The salt-free gel was freeze dried and stored for further analysis.

Cosolvents

The solvents used in this study were deionized water, HPLC-grade methanol, HPLC-grade acetone, and reagent-grade ethanol. All solvents were used without further purification. Cosolvent fractions (0, 10, 30, 50 and 70%) were prepared on a weight basis for methanol and acetone. For ethanol, volume fractions were used. For ease of comparison, these volume fractions were converted to weight percentages using density data (Table 1).

Sodium-calcium exchange experiments

In the methanol and acetone experiments, 0.1 M of NaCl and CaCl_2 stock solutions were prepared by adding appropriate amounts of oven-dried (105°C overnight) anhydrous CaCl_2 and NaCl salts to 50 mL of cosolvent solution. The stock solutions were then used to prepare a series of mixed $\text{CaCl}_2/\text{NaCl}$ solutions with a constant total chloride concentration of 0.03 N Cl and different fractions of soluble calcium, X_{Ca} . The solution compositions were 0.05, 0.1, 0.2, 0.4, 0.6 and 0.8 X_{Ca} . Approximately 0.05g of Na-montmorillonite were added to tared 15 mL polyethylene centrifuge tubes and reacted with 10 mL of methanol-water and acetone-water mixtures.

For the ethanol experiments, concentrated stock solutions with various X_{Ca} values, but a constant total chloride concentration of 0.03 N Cl were prepared in distilled water. Appropriate volumes of water and ethanol were added to 15 mL tared polyethylene tubes

Table 1. Physical properties of cosolvents at 25°C .

Solvent	Wt. %	ϵ_r	ρ (kg/m^3)
Water ^a	0	78.48	997.1
Methanol ^b	10	74.21	981.6
	30	65.19 ^c	951.4
	50	56.05	915.6
	70	46.90 ^c	871.5
	Ethanol ^c	8.6	73.08 ^c
Acetone ^d	10	72.29 ^c	981.9
	26.6	63.01 ^e	947.2
	30	61.11 ^e	953.9
	46.3	51.99 ^e	907.3
	50	49.92 ^c	913.9
	67	40.41 ^e	877.4
	70	36.42	886.7

^a ϵ_r and ρ were obtained from Janz and Tomkins (1973)

^b ϵ_r was obtained From Janz and Tomkins (1973), ρ from the *Handbook of Chemistry and Physics* (2003–2004)

^c ϵ_r was obtained From Timmermans (1960), ρ from

Handbook of Chemistry and Physics (2003–2004)

^d ϵ_r was obtained From Timmermans (1960), ρ from Janz and Tomkins (1973)

^e Interpolated values

containing 0.05 g of Na-montmorillonite to yield 10%, 30%, 50% and 70% (v/v) solvent concentrations. Exactly 0.1 mL of each stock solution were then added to make a series of samples with varied composition, but all having a constant total chloride concentration of 0.03 N Cl. Two replicates were used for each cosolvent fraction.

Clays were uniformly dispersed using a vortex mixer and centrifuge tubes were equilibrated by rotating end-over-end in a rock tumbler for 12 h. After equilibration, tubes were centrifuged at 5000 rpm for 20 min, and the supernatant solutions were collected for Ca and Na determination. Exactly 1 mL of supernatant liquid was removed and evaporated to dryness in Pyrex tubes in a digestion block at 130°C. The evaporated salts were re-dissolved in acidified lanthanum oxide solution and Na and Ca were determined by atomic absorption and emission spectrophotometry, respectively, using a Perkin Elmer, AAnalyst 100. These measured values of Ca and Na were used to calculate the equilibrium concentrations of Ca^{2+} and Na^+ ions in the supernatant solution of the Na-Ca exchange reaction. The centrifuge tubes were weighed to determine the mass of the entrained solution in each clay sample. The volume of entrained solution was calculated using appropriate cosolvent density values (Table 1).

The clays were then extracted twice with 10 mL of 1 M and 0.1 M concentrated MgCl_2 by shaking, centrifuging and decanting. Extracting solutions of 1 M MgCl_2 were prepared in corresponding cosolvent solution fractions except for 50% and 70% acetone, where 0.1 M MgCl_2 was used. The supernatant solution from each clay sample was collected and Na and Ca concentrations were determined as described above.

DATA ANALYSIS

To calculate single-ion activity coefficients, the parameters A and B (equations 3 and 4) were calculated for each cosolvent fraction by replacing ϵ_r and ρ with their corresponding values (Table 1). The ion-size parameters for Na, Ca and CaCl^+ were taken as equal to their values in water, *i.e.* 4.0, 6.0 and 5.1 Å, respectively (Kielland, 1937). The charges of adsorbed Na and Ca on the exchangers were calculated as follows:

$$q_{\text{Na}} = n_{\text{Na}} - \frac{C_{\text{Na}} V_e}{M_{\text{clay}}} \quad (11)$$

$$q_{\text{Ca}} = 2(n_{\text{Ca}} - \frac{C_{\text{Ca}} V_e}{M_{\text{clay}}}) \quad (12)$$

where n is the number of moles of Ca or Na per kg of clay extracted by MgCl_2 solutions, C is the molar concentration of Ca and Na ions in the equilibrium supernatant solution, V_e is the volume in liters of the entrained solution and M_{clay} is the mass of clay in kg. The total charge of adsorbed metals, Q , is given by the equation

$$Q = q_{\text{Na}} + q_{\text{Ca}} \quad (13)$$

where q_{Na} and q_{Ca} are defined in equation 11 and 12.

The non-preference isotherm for Na-Ca exchange (Sposito, 1981) was,

$$E_{\text{Ca}} = 1 - \left[1 + 2 \frac{\gamma_{\text{Ca}}}{(TN)\gamma_{\text{Na}}^2} \left(\frac{1}{(1 - E'_{\text{Ca}})^2} - \frac{1}{E'_{\text{Ca}}} \right) \right]^{-0.5} \quad (14)$$

where

$$E'_{\text{Ca}} = \frac{2\{\text{Ca}\}}{2\{\text{Ca}\} + \{\text{Na}\}} \quad (15)$$

E'_{Ca} is the charge fraction of Ca in solution; E_{Ca} is the equivalent fraction of Ca on the exchanger.

The adsorbed Ca^{2+} charge fraction was corrected for CaCl^+ by adopting the method developed by Sposito *et al.* (1983). The total adsorbed metal charge, Q_0 , is calculated as follows

$$Q_0 = q_{\text{Na}^+} + q_{\text{Ca}^{2+}} + q_{\text{CaCl}^+} \quad (16)$$

and q_{CaCl^+} was calculated as follows

$$q_{\text{CaCl}^+} = Q - Q_0 \quad (17)$$

In order to isolate the effect of solvents on the selectivity of bentonite surfaces for Ca and Na ions, it was important to correct for ion-pair formation in solution and surface adsorption. In this context, the CaCl^+ association constants, K_{1A} , were determined experimentally (Srouf, 2004) using conductometric methods for each cosolvent concentration (Fuoss and Edelson, 1951). In this approach, the formation of CaCl_2^0 pairs was assumed to be negligible.

The adsorbed fraction of CaCl^+ on the exchanger, q_{CaCl^+} , was calculated using equation 17. The value of Q_0 can be measured by determining Q (equation 13) in an exchange experiment in a medium where no ion-pair formation is expected (*e.g.* perchlorate) or it can be extrapolated from Q measured in an exchange experiment using chloride background with Ca concentrations decreased until q_{Ca} approaches zero. In cosolvent systems where ion-pair formation is significant, even with ligands such as perchlorates (Doe *et al.*, 1984), that do not readily form ion pairs, the second option by extrapolation from Q seemed more appropriate to calculate Q_0 . Therefore, in every treatment and at every cosolvent fraction, Q was plotted as a function of the equivalent fraction of Ca in solution and Q_0 was taken to be equal to the cubic polynomial regression estimate of Q when the clay was Na saturated.

RESULTS

Solution and exchanger-phase composition

The equilibrium solution and exchanger compositions for Ca-Na exchange reactions onto bentonite clays are

Table 2. Ionic association constants, K_{1A} for CaCl_2 at 25°C .

Solvent	Wt. %	K_{1A}
	0	2.63*
Methanol	10	27.38±0.05
	30	31.52±0.28
	50	43.01±0.10
	70	61.41±2.25
Ethanol	10	28.69±0.73
	30	55.95±0.06
	50	58.90±0.35
	70	84.56±0.70
Acetone	10	38.23±1.84
	30	149.96±0.38
	50	219.43±1.92
	70	487.48±13.60

* Values of K_{1A} for water were obtained from Smith and Martell (1976).

summarized in Tables 3–5. In each table, the fourth and the fifth columns represent the equilibrium activity of Ca and Na, respectively. Within a treatment, greater Ca and Na concentrations resulted in larger decreases in effective molar concentration (*i.e.* activity) that were more prominent for Ca than Na. Acetone had a larger effect on ion activities than did ethanol, which in turn had a larger effect than methanol. As the solvent dielectric constant decreases, the activity of the ions is expected to decrease due to a decreased single-ion activity coefficient (equations 2–4) and increased ion-pairing (Coulomb's Law).

In methanol-water treatment (Table 3), the seventh column presents the adsorbed Ca charge in $\text{mol}_c \text{ kg}^{-1}$, q_{Ca} , on Wyoming bentonite surfaces. Within a cosolvent treatment, q_{Ca} increased as X_{Ca} and percent cosolvent increased. At first sight, this trend, coupled with decreased Ca activity in solution, might indicate greater

Table 3. Experimental data for Ca-Na exchange on Wyoming bentonite in methanol-water mixtures at 0.03 N Cl at room temperature.

X_{Ca}	C_{Na} — mol L ⁻¹ —	C_{Ca}	(Na)	(Ca)	q_{Na}	q_{Ca} mol _c kg ⁻¹	Q
Water							
0.05	2.92E-02	5.59E-04	2.45E-02	2.94E-04	0.404±0.027	0.508±0.020	0.912±0.029
0.1	2.80E-02	1.29E-03	2.34E-02	6.81E-04	0.238±0.040	0.715±0.059	0.953±0.048
0.2	2.39E-02	3.24E-03	2.00E-02	1.70E-03	0.122±0.021	0.932±0.036	1.054±0.024
0.4	1.72E-02	6.65E-03	1.44E-02	3.50E-03	0.042±0.012	1.004±0.029	1.046±0.023
0.6	1.29E-02	8.83E-03	1.08E-02	4.64E-03	0.014±0.003	1.041±0.034	1.055±0.034
0.8	7.48E-03	1.16E-02	6.26E-03	6.08E-03	0.003±0.001	1.089±0.048	1.092±0.049
10% (wt./wt.) methanol							
0.05	2.95E-02	5.53E-04	2.46E-02	2.86E-04	0.580±0.026	0.689±0.005	1.268±0.031
0.1	2.72E-02	1.17E-03	2.27E-02	6.06E-04	0.278±0.001	0.928±0.008	1.205±0.007
0.2	2.36E-02	3.07E-03	1.96E-02	1.57E-03	0.130±0.006	1.121±0.003	1.251±0.002
0.4	1.73E-02	6.66E-03	1.43E-02	3.30E-03	0.057±0.008	1.175±0.016	1.231±0.025
0.6	1.24E-02	9.22E-03	1.02E-02	4.48E-03	0.037±0.011	1.201±0.015	1.238±0.004
0.8	8.43E-03	1.14E-02	6.88E-03	5.45E-03	0.025±0.002	1.228±0.005	1.253±0.003
30% (wt./wt.) methanol							
0.05	2.70E-02	4.00E-04	2.20E-02	1.90E-04	0.501±0.010	0.708±0.010	1.209±0.000
0.1	2.67E-02	1.23E-03	2.17E-02	5.73E-04	0.263±0.006	0.979±0.003	1.241±0.003
0.2	2.28E-02	3.48E-03	1.84E-02	1.58E-03	0.122±0.005	1.161±0.025	1.283±0.030
0.4	1.65E-02	7.27E-03	1.31E-02	3.17E-03	0.067±0.020	1.220±0.001	1.287±0.021
0.6	1.21E-02	1.02E-02	9.51E-03	4.30E-03	0.032±0.004	1.238±0.007	1.270±0.003
0.8	7.96E-03	1.29E-02	6.05E-03	4.88E-03	0.028±0.003	1.260±0.000	1.288±0.004
50% (wt./wt.) methanol							
0.05	2.79E-02	4.23E-04	2.17E-02	1.71E-04	0.520±0.007	0.819±0.019	1.340±0.026
0.1	2.66E-02	1.27E-03	2.06E-02	5.07E-04	0.255±0.090	1.054±0.010	1.309±0.100
0.2	2.34E-02	3.58E-03	1.80E-02	1.37E-03	0.148±0.009	1.215±0.027	1.362±0.018
0.4	1.75E-02	7.58E-03	1.32E-02	2.75E-03	0.079±0.003	1.289±0.035	1.368±0.038
0.6	1.22E-02	1.07E-02	9.09E-03	3.75E-03	0.053±0.014	1.334±0.004	1.387±0.017
0.8	8.26E-03	1.34E-02	6.10E-03	4.55E-03	0.033±0.002	1.316±0.012	1.350±0.010
70% (wt./wt.) methanol							
0.05	2.83E-02	3.44E-04	2.07E-02	1.11E-04	0.515±0.007	0.869±0.010	1.384±0.003
0.1	2.72E-02	1.09E-03	1.98E-02	3.46E-04	0.267±0.020	1.128±0.025	1.396±0.005
0.2	2.32E-02	3.44E-03	1.67E-02	1.06E-03	0.144±0.009	1.254±0.008	1.398±0.001
0.4	1.73E-02	7.56E-03	1.22E-02	2.16E-03	0.081±0.012	1.334±0.014	1.415±0.026
0.6	1.21E-02	1.07E-02	8.38E-03	2.92E-03	0.056±0.001	1.379±0.002	1.435±0.003
0.8	8.30E-03	1.30E-02	5.70E-03	3.45E-03	0.043±0.003	1.429±0.065	1.471±0.062

Table 4. Experimental data for Ca-Na exchange on Wyoming bentonite in ethanol-water mixtures at 0.03 N Cl at room temperature.

X_{Ca}	C_{Na} — mol L ⁻¹ —	C_{Ca}	(Na)	(Ca)	q_{Na}	q_{Ca} mol _c kg ⁻¹	Q
8.6% (wt./wt.) ethanol							
0.05	2.69E-02	3.87E-04	2.26E-02	2.03E-04	0.552±0.043	0.449±0.028	1.001±0.071
0.1	2.65E-02	1.30E-03	2.21E-02	6.68E-04	0.336±0.065	0.684±0.03	1.020±0.035
0.2	2.36E-02	3.38E-03	1.95E-02	1.70E-03	0.130±0.016	0.932±0.07	1.062±0.086
0.4	1.66E-02	6.65E-03	1.36E-02	3.27E-03	0.040±0.004	0.971±0.032	1.010±0.036
0.6	1.18E-02	9.38E-03	9.67E-03	4.51E-03	0.019±0.001	1.084±0.061	1.103±0.062
0.8	8.20E-03	1.16E-02	6.66E-03	5.48E-03	0.002±0.001	0.994±0.008	0.995±0.008
26.6% (wt./wt.) ethanol							
0.05	2.80E-02	3.72E-04	2.26E-02	1.69E-04	0.486±0.009	0.460±0.038	0.946±0.028
0.1	2.66E-02	1.06E-03	2.14E-02	4.79E-04	0.258±0.027	0.673±0.04	0.931±0.068
0.2	2.40E-02	3.14E-03	1.91E-02	1.37E-03	0.111±0.002	0.891±0.004	1.001±0.006
0.4	1.74E-02	6.85E-03	1.37E-02	2.88E-03	0.042±0.004	1.067±0.019	1.109±0.015
0.6	1.22E-02	9.50E-03	9.50E-03	3.91E-03	0.019±0.014	1.062±0.022	1.081±0.037
0.8	8.23E-03	1.19E-02	6.38E-03	4.78E-03	0.002±0.001	1.056±0.025	1.058±0.023
46.3% (wt./wt.) ethanol							
0.05	2.78E-02	3.32E-04	2.11E-02	1.22E-04	0.535±0.003	0.462±0.011	0.997±0.015
0.1	2.67E-02	1.09E-03	2.02E-02	3.97E-04	0.305±0.017	0.737±0.038	1.042±0.055
0.2	2.36E-02	3.19E-03	1.77E-02	1.12E-03	0.133±0.007	0.926±0.023	1.059±0.03
0.4	1.65E-02	6.57E-03	1.22E-02	2.23E-03	0.050±0.006	1.058±0.063	1.108±0.068
0.6	1.18E-02	9.59E-03	8.63E-03	3.12E-03	0.017±0.009	1.135±0.137	1.153±0.147
0.8	7.98E-03	1.16E-02	5.78E-03	3.70E-03	0.003±0.001	1.097±0.047	1.099±0.048
67% (wt./wt.) ethanol							
0.05	2.61E-02	3.22E-04	1.79E-02	8.36E-05	0.563±0.007	0.456±0.02	1.019±0.027
0.1	2.51E-02	1.03E-03	1.71E-02	2.64E-04	0.326±0.004	0.716±0.03	1.041±0.034
0.2	2.29E-02	3.11E-03	1.53E-02	7.44E-04	0.172±0.003	0.957±0.019	1.129±0.016
0.4	1.56E-02	6.24E-03	1.04E-02	1.45E-03	0.065±0.007	1.031±0.028	1.096±0.035
0.6	1.14E-02	9.16E-03	7.38E-03	2.00E-03	0.022±0.001	1.182±0.016	1.204±0.017
0.8	7.79E-03	1.15E-02	4.99E-03	2.41E-03	0.006±0.001	1.153±0.071	1.158±0.073

preference of the exchanging surface for Ca ions as the values of X_{Ca} and percent cosolvent were increased. In ethanol and acetone-water systems (Tables 4 and 5) and within each wt.% cosolvent, q_{Ca} increased with increased X_{Ca} . Across treatments, q_{Ca} was rather constant.

The values of the total adsorbed metal charge in mol_c kg⁻¹, Q , are reported in column 8 in Tables 3–5. Within a cosolvent treatment, the values of Q generally increased as the exchangeable fraction of Ca increased. This increase in Q can be attributed to assigning all of the adsorbed Ca(II) species a +2 valence when in fact one of the adsorbed species is the monovalent complex, CaCl⁺ (Sposito *et al.*, 1983). Among various cosolvents, different trends were observed. In methanol-water treatments and for constant X_{Ca} (Table 3), Q increased with increased percent methanol especially at 50% and 70%. In ethanol and acetone-water treatments, Q was fairly constant. The observed increase in the total adsorbed metal charge, Q , in methanol-water systems, at higher cosolvent wt.%, may be explained by an increase in the apparent number of available adsorption sites or some specific surface-solvent interactions. An increase in the number of apparent surface charges, as a

result of Gran titrations of a goethite suspension has been reported by Xue and Traina (1996a) in acetone and methanol-water mixtures. In their work, this increase was mainly attributed to the increased strength of some originally weak Fe oxide and Fe hydroxide bonds in water because of the increased long-range electrostatic bonds. In addition, the low-dielectric constant observed at high cosolvent fractions decreased the solubility of H⁺ ions and reduced the solvation forces that usually compete with H⁺ for the protonation of surface sites. In this experiment, an increase in the apparent number of available adsorption sites with increased cosolvent fraction as a result of the activation of pH-dependent charges is impossible to detect as no account was taken of the separate contributions of permanent and pH-dependent charges to the total adsorbed metal charge and the effect of cosolvents on each. Specific solvent-surface interactions are more likely to be involved.

Ca-Na fractional isotherms

Figure 2 presents the fractional isotherms for Ca-Na exchange on Wyoming bentonite. In these plots, the equivalent fraction of Ca in solution was corrected for single-ion activity coefficients, but not for the formation

Table 5. Experimental data for Ca-Na exchange on Wyoming bentonite in acetone-water mixtures at 0.03 N Cl at room temperature.

X_{Ca}	C_{Na} — mol L ⁻¹ —	C_{Ca}	(Na)	(Ca)	q_{Na}	q_{Ca} mol _c kg ⁻¹	Q
10% (wt./wt.) acetone							
0.05	3.11E-02	6.01E-04	2.57E-02	3.03E-04	0.341±0.020	0.370±0.013	0.711±0.006
0.1	2.95E-02	1.68E-03	2.43E-02	8.36E-04	0.233±0.060	0.527±0.044	0.760±0.103
0.2	2.42E-02	3.42E-03	1.99E-02	1.70E-03	0.141±0.004	0.606±0.003	0.747±0.007
0.4	1.83E-02	6.76E-03	1.50E-02	3.27E-03	0.067±0.013	0.697±0.01	0.763±0.024
0.6	1.17E-02	9.88E-03	9.55E-03	4.69E-03	0.046±0.004	0.762±0.037	0.808±0.041
0.08	6.98E-03	1.15E-02	5.68E-03	5.44E-03	0.025±0.006	0.805±0.019	0.829±0.025
30% (wt./wt.) acetone							
0.05	3.23E-02	4.58E-04	2.54E-02	1.92E-04	0.373±0.038	0.407±0.001	0.781±0.037
0.1	2.97E-02	1.51E-03	2.33E-02	6.30E-04	0.257±0.013	0.586±0.013	0.843±0.001
0.2	2.48E-02	3.69E-03	1.94E-02	1.52E-03	0.133±0.009	0.708±0.001	0.841±0.007
0.4	1.80E-02	7.23E-03	1.39E-02	2.88E-03	0.069±0.011	0.758±0.007	0.827±0.019
0.6	1.21E-02	1.03E-02	9.28E-03	3.99E-03	0.038±0.005	0.805±0.021	0.843±0.016
0.08	7.22E-03	1.25E-02	5.52E-03	4.78E-03	0.015±0.007	0.848±0.003	0.863±0.004
50% (wt./wt.) acetone							
0.05	3.00E-02	7.20E-04	2.17E-02	2.27E-04	0.392±0.021	0.256±0.006	0.648±0.027
0.1	2.87E-02	1.77E-03	2.06E-02	5.47E-04	0.253±0.011	0.426±0.009	0.678±0.002
0.2	2.35E-02	3.96E-03	1.68E-02	1.20E-03	0.151±0.013	0.547±0.022	0.698±0.009
0.4	1.53E-02	7.84E-03	1.09E-02	2.29E-03	0.079±0.005	0.640±0.001	0.719±0.005
0.6	1.12E-02	1.03E-02	7.84E-03	2.92E-03	0.035±0.001	0.676±0.013	0.712±0.014
0.08	6.85E-03	1.29E-02	4.75E-03	3.52E-03	0.024±0.001	0.663±0.026	0.687±0.027
70% (wt./wt.) acetone							
0.05	3.27E-02	8.43E-04	2.02E-02	1.54E-04	0.491±0.042	0.260±0.005	0.750±0.036
0.1	3.06E-02	1.89E-03	1.88E-02	3.39E-04	0.348±0.002	0.430±0.013	0.778±0.015
0.2	2.51E-02	3.97E-03	1.54E-02	7.05E-04	0.240±0.007	0.528±0.010	0.769±0.002
0.4	1.69E-02	7.62E-03	1.02E-02	1.30E-03	0.147±0.006	0.648±0.005	0.795±0.001
0.6	1.18E-02	1.02E-02	7.05E-03	1.68E-03	0.078±0.001	0.682±0.023	0.760±0.023
0.08	6.91E-03	1.22E-02	4.11E-03	1.98E-03	0.053±0.001	0.754±0.019	0.807±0.019

of CaCl⁺ pairs. All isotherms were above the non-preference isotherm, indicating a greater selectivity of the surface for Ca ions. As the percent of methanol was increased, a shift in the isotherms towards greater Ca preference (as indicated by the dotted-line arrow) is observed at low equivalent Ca fraction (<0.2). At higher Ca fractions, the E_{Ca}/Q values in all isotherms converged to 1.0, but tended towards decreased E'_{Ca} as the percent of methanol was increased. This was shown by a shift of individual points towards the Na-rich end as the methanol concentration increased along the solid-line arrow direction. In ethanol-water mixtures, no increased preference for Ca was shown (only a shift in the individual points along the water isotherm towards increased Na loading). In acetone-water mixtures, increasing cosolvent concentration decreased the preference of the surface for Ca ions. There was a complete shift in the isotherms as we moved from water to higher acetone-water fractions. At the Ca-rich end of the isotherm, increased cosolvent concentrations increased Na loading in methanol, ethanol and to a lesser extent in acetone. This observation is consistent with the increased CaCl⁺ ion-pair formation in low- ϵ_r solutions.

In methanol, the increased Ca loading at the Na-rich end of the isotherm with increased cosolvent concentration may indicate a methanol-specific effect on metal ion activity coefficients in solution and on the surface.

Q_0 and ion-pair formation

Table 6 presents the calculated values of Q_0 in various cosolvents. In methanol-water and ethanol-water systems, Q_0 initially increased from 0.865 in water to 1.247 in 10% methanol and 1.012 in 8.6% ethanol. This was followed by a 10–30% decrease of Q_0 as the cosolvent fraction was increased until a cosolvent fraction of 30% was reached. At cosolvent fractions above 30%, Q_0 increased. In acetone-water, the values of Q_0 increased as the cosolvent fraction increased except at 30% and 50% acetone. When the values of Q_0 were averaged for each solvent type, a decrease in the order methanol > ethanol > acetone was observed (Q_0 for water = 0.865; Q_0 for methanol = 1.287; Q_0 for ethanol = 0.989; and Q_0 for acetone = 0.720). This observation should be interpreted carefully as it might be the result of a simple heterogeneity in the surface charge density of bentonite clay samples rather than some direct solvent

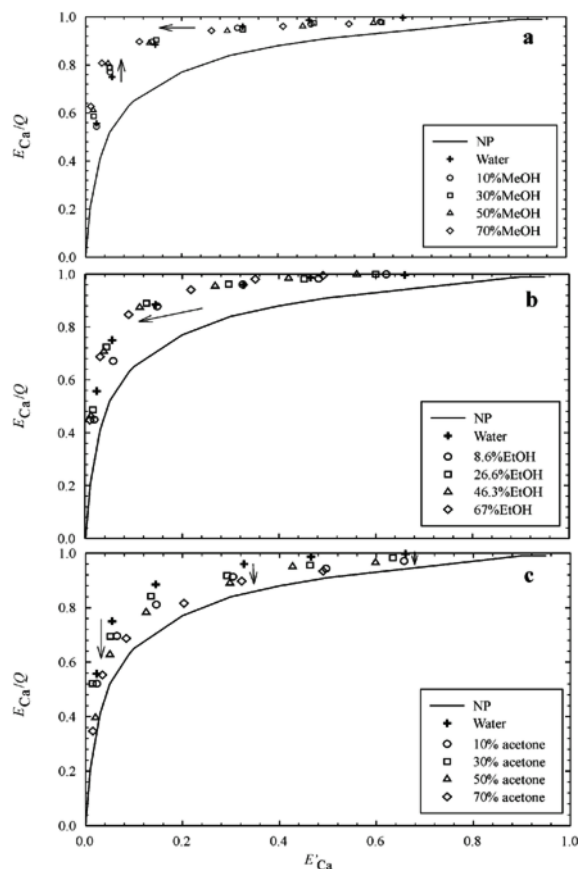


Figure 2. Ca-Na exchange isotherms on Wyoming Bentonite at 0.03 N Cl in methanol-water (a), ethanol-water (b) and acetone-water (c) systems. (Arrows indicate changes in position of individual data points within and between isotherms.)

effect of clay physicochemical structure. After the determination of Q_0 , the exchange isotherms in Figure 2 were corrected for CaCl^+ formation both in solution (Table 2) and on the surface (Figures 3, 4, and 5 for methanol, ethanol and acetone-water treatment, respectively). The value of the $\log K_{1A}$ for CaCl^+ in water (Table 2) was taken from the literature (Smith and Martell, 1976). Other values were reported elsewhere. Lindsay (1979) reported a value of -1 for the thermodynamic stability constant.

In Figures 3–5, each cosolvent-water mixture was plotted separately for ease of comparison. In all treatments, the fraction of CaCl^+ on the surface generally increased as the equivalent fraction of CaCl^+ in solution increased. There were some distinct trends among and within cosolvents that indicated that Ca-Na exchange on Wyoming bentonite in a chloride background involves the ternary exchange system Ca-Na-CaCl^+ . In 10% methanol, though E'_{CaCl^+} increased with E'_{CaCl^+} , the magnitude of increase was small (Figure 3). For all other cosolvent concentrations, adsorption of CaCl^+ was significant. In acetone-water treatments (Figure 5), the preference of the surface for CaCl^+

Table 6. Values of Q_0 in cosolvent solutions as determined by a cubic polynomial regression of Q vs. equivalent fraction of Ca in solution.

Solvent	Wt. %	Q_0	Standard error of Q_0
Methanol	0	0.865	0.020
	10	1.247	0.041
	30	1.191	0.003
	50	1.328	0.026
Ethanol	70	1.384	0.005
	8.6	1.012	0.065
	26.6	0.919	0.030
	46.3	1.008	0.024
Acetone	67	1.018	0.055
	10	0.719	0.028
	30	0.785	0.027
	50	0.640	0.009
	70	0.738	0.025

increases almost linearly with E'_{CaCl^+} for all acetone-water solutions. In the water treatment, our results are in good agreement with those described by Sposito *et al.* (1983). Others (Amrhein and Suarez, 1991; Zhang and Sparks, 1996) have reported no evidence for the adsorption of CaCl^+ ions in water. Demonstrating whether CaCl^+ adsorption is significant or not was not the objective of this study. It is rather the identification of the major processes that control the selectivity of bentonite for a specific cation in cosolvents where the magnitude of pairing is significant. This would not be possible unless an allowance is made for CaCl^+ formation both in solution and on the surface (Figure 4). An exact explanation for these differences in behavior among and within cosolvents is currently unavailable. However, increased solution stability rather than surface stability of CaCl^+ or decreased bentonite surface-affinity for CaCl^+ is suggested. Greater competition between Na^+ and CaCl^+ for external sites at the Carich end (Sposito *et al.*, 1983) might occur in media with a lower dielectric constant than water. This might explain why the affinities of bentonite for CaCl^+ in all treatments were less than that in water.

In this experiment, only the formation of CaCl^+ pairs was considered significant. At 0.03 N Cl and for the studied range of dielectric constants ($36.42 < \epsilon_r < 78.48$), the magnitude of NaCl pairs was assumed to be small and, hence, were not included in the ion-activity calculations. This assumption was based on a study conducted by Spivey and Shedlovsky (1967) for NaCl^0 determination in ethanol-water mixtures using conductometric measurements. In their work, no significant ion association ($K_A < 10$) was indicated below 80% ethanol ($\epsilon_r > 41.45$). In our study, we also suggested that there was no significant ion association for NaCl pairs in methanol-water and acetone-water because the dielectric

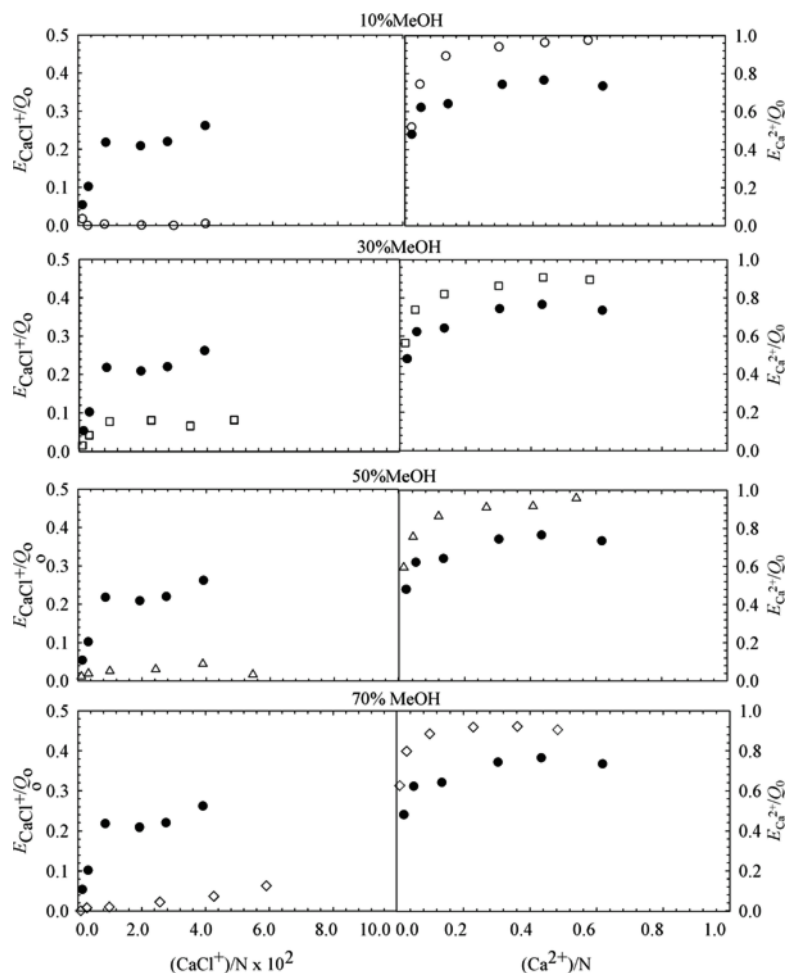


Figure 3. Exchange isotherms for CaCl^+ (left-hand side) and Ca^{2+} (right-hand side) on Wyoming bentonite at 0.03 N Cl in methanol-water systems, corrected for CaCl^+ . Filled symbols: water; open symbols: cosolvent. On the horizontal axis, N refers to the total normality of the system.

constants of these mixtures were greater than 41.45 except for 70% acetone ($\epsilon_r = 36.4$). This assumption is valid if no specific ion-solvent interactions are affecting the formation of NaCl pairs. To test for the possible effects of NaCl pairs on the selectivity of bentonite for Ca^{2+} at 0.03 M Cl in ethanol-water systems, the activities of Na ions in solution and subsequently the values of E'_{Ca} were corrected, assuming a maximum value of K_A equal to 10 (Spivey and Shedlovsky, 1967). When plotting the Ca^{2+} -Na exchange isotherms, a shift in E'_{Ca} towards higher values occurred at the Ca-rich end of the isotherm (data not reported). This shift in data points along the same isotherm does not affect the overall interpretation of our data which is based on comparing the positions of the cosolvent fractional isotherms relative to water before and after correction for CaCl^+ . For cosolvents with lower ϵ_r and for exchange reactions conducted at a higher total chloride concentration, the formation of NaCl pairs may need to be considered.

DISCUSSION

Prior to CaCl^+ correction, our results (Tables 3–5, Figure 2) indicate a preference of bentonite surfaces for Ca^{2+} ions in all solvents as indicated by the positions of the cosolvent fractional isotherms relative to the non-preference isotherms. In comparison to the water isotherm, various trends were distinguished among and within cosolvents. The change in the position of the fractional isotherms, especially for acetone-water mixtures and methanol-water mixtures at low equivalent Ca fraction (<0.2) indicate that bentonite selectivity for Ca ions in cosolvents is a surface-controlled phenomenon essentially driven by solvent-surface interactions. In ethanol, the Ca surface preference seems to be driven by water-ethanol interactions.

Effect of pairing

The predicted increase in K_v in response to increased cosolvent concentration was apparent in methanol and

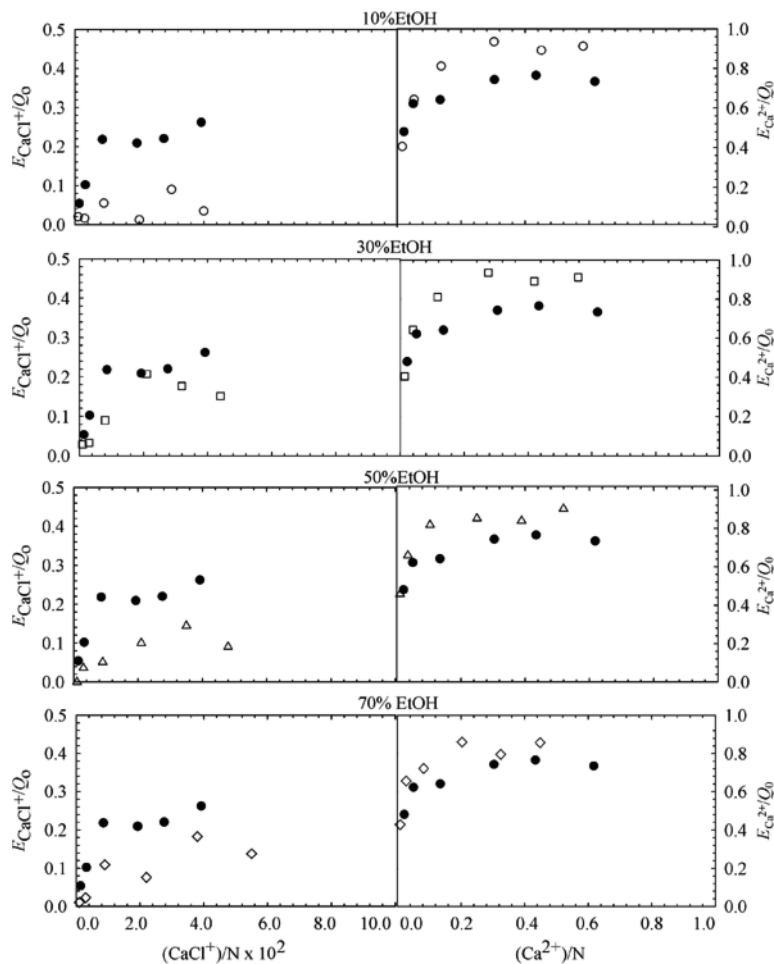


Figure 4. Exchange isotherms for CaCl^+ (left-hand side) and Ca^{2+} (right-hand side) on Wyoming bentonite at 0.03 N Cl in ethanol-water systems, corrected for CaCl^+ . Filled symbols: water; open symbols: cosolvent. On the horizontal axis, N refers to the total normality of the system.

ethanol only after correcting for formation of CaCl^+ . In acetone-water, there was evidence of increased Na loading with larger acetone fractions (Figure 5), but no increase in Ca^{2+} selectivity. In methanol- and ethanol-water mixtures, the observed increase in the preference of bentonite clays for Ca^{2+} after CaCl^+ correction can be explained by increased attraction between bentonite surface and Ca^{2+} ions as a result of decreased solvent dielectric constant. In acetone-water, specific surface-cosolvent effects seem to be involved. These effects become more apparent when the three cosolvents are compared. This is indicated by gradual decreases in Ca^{2+} surface preference when changing from methanol-water to ethanol-water to acetone-water systems that were corrected for both ion-pairing and single-ion activity coefficients. These decreases were indicated by numerical differences in Ca^{2+} surface preference between water and cosolvent-water isotherms. If only enhanced Coulombic attractions between the surface and the divalent cation as a result of decreased solvent dielectric constant were involved, then the magnitude of the Ca^{2+}

preference should decrease in the order acetone > ethanol > methanol. Dielectric saturation of the bentonite surfaces may be larger in methanol than in ethanol and acetone.

Effect of cosolvents on the total adsorbed metal charge

When the total adsorbed metal charge, Q was corrected for CaCl^+ adsorption, the values of Q_0 varied among and within cosolvents (Table 6). The change in the values of Q_0 with percent cosolvent is not clearly understood. It might be the result of clay surface heterogeneity or might imply a direct effect of cosolvents on the intracrystalline layer spacing of bentonite clays (Brindley *et al.*, 1969) or some specific solvent-surface interactions. In this study, cosolvent effects on Na-bentonite intracrystalline swelling were not experimentally determined. However, visual observations of clays during the exchange experiments indicated that flocculation was much greater in solutions where the percent cosolvent exceeded 50%. Enhanced clay flocculation with decreased ϵ_r might explain the

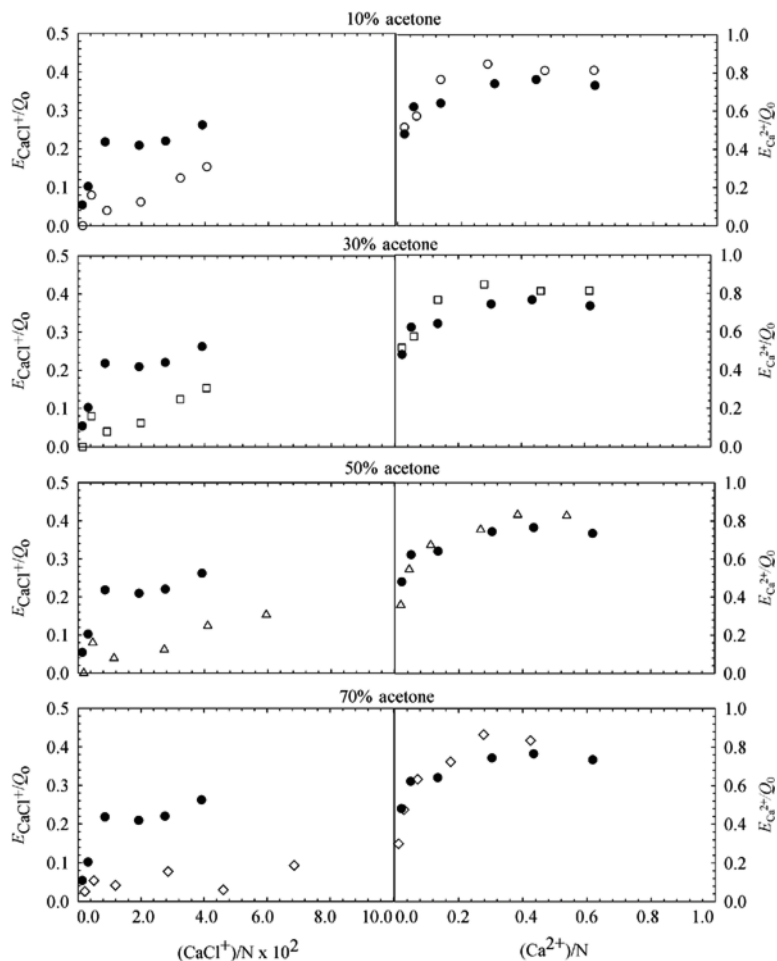


Figure 5. Exchange isotherms for CaCl^+ (left-hand side) and Ca^{2+} (right-hand side) on Wyoming bentonite at 0.03 N Cl in acetone-water systems, corrected for CaCl^+ . Filled symbols: water; open symbols: cosolvent. On the horizontal axis, N refers to the total normality of the system.

decrease in Q_0 at a specific threshold cosolvent fraction but does not explain the subsequent increase in the values of Q_0 after this threshold value is reached. More work is needed to identify the effect of exchanger composition and cosolvent concentration on the physical structure of clays and its relation to their surface reactivity.

When the values of Q_0 were averaged for each solvent system, a decrease in Q_0 in the order methanol > ethanol > acetone was observed. This decrease followed the same order of decreased surface preference for Ca^{2+} ions and further supports the occurrence of some systematic specific solvent-surface interactions.

SUMMARY AND CONCLUSIONS

In this study, the affinity of Wyoming bentonite (chloride background) for Ca^{2+} , after correction for CaCl^+ formation on the surface and in solution, was larger than that of Na^+ , with the magnitude of preference decreasing in the order methanol > ethanol > acetone.

The average values of surface charge density, Q_0 , also decreased in the order methanol > ethanol > acetone. This implies that specific surface-cosolvent interactions are involved in determining the selectivity of the surface for a specific cation in mixtures of aqueous-organic solvents. This increased selectivity of bentonite clays for Ca^{2+} may result in enhanced flocculation of clays in landfill liners and a subsequent increase in hydraulic conductivity. This suggests that these clay liners, in the presence of cosolvents, are at greater risk of failing and releasing contaminants than is predicted by studies conducted in aqueous solutions. A better assessment of cosolvent effects on exchange reactions requires that cosolvents effects on clay interlayer spacings be quantified, especially as a function of interlayer cation. There is also a need to expand the database of metal-ligand formation constants, particularly in cosolvents.

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