

Sodium-Copper Exchange on Wyoming Montmorillonite in Chloride, Perchlorate, Nitrate, and Sulfate Solutions

Z. Z. Zhang* and D. L. Sparks

ABSTRACT

The effect of anions on the Na-Cu exchange reactions on montmorillonites is not well understood and discrepancies exist in the literature. This study was conducted to examine the role of anions on the Na-Cu exchange reaction on Wyoming montmorillonite. The copper exchange capacity (CuEC) and Na-Cu exchange reactions on Wyoming montmorillonite were studied in Cl^- , ClO_4^- , NO_3^- , and SO_4^{2-} solution media at a constant total metal charge concentration of $0.0200 \text{ mol. L}^{-1}$. We found that the values of CuEC were similar in Cl^- , ClO_4^- , NO_3^- , and SO_4^{2-} electrolyte media, and the quantity of Cu extracted by $\text{Na}_2\text{-EDTA}$ solution was only 1.0 to 1.2% of the CuEC and was not affected by anions. The apparent adsorbed metal charge, Q , and Vanselow selectivity coefficients, K_v , were determined across a wide range of exchanger phase composition, with Cu^{2+} occupying 30 to 95% of the charge sites. We found that the values of Q increased with Cu saturation in each of the anionic media, and the increase was not affected by anions. The increase in Q was attributed to decrease in negative adsorption of anions. We observed that K_v was independent of exchanger composition in each of the four anionic media. The values of K_v in the SO_4^{2-} medium were lower than those in other anionic media because of the complexation reaction between Cu^{2+} and SO_4^{2-} . The data showed that Cu^{2+} ions were not specifically adsorbed under our experimental conditions and that the exchanger phase behaved as an ideal mixture. It was concluded that no detectable monovalent complexes such as CuCl^+ and CuNO_3^+ were adsorbed on Wyoming montmorillonite in the Na-Cu exchange reaction.

BOWER AND TRUOG (1941) found that a number of cations that form weak bases, such as Cu^{2+} and Zn^{2+} , were adsorbed in excess of cations that form strong bases. Sieling (1941) also observed that Cu^{2+} was adsorbed in exchange reactions in excess of Ca^{2+} and similar ions. DeMumbrum and Jackson (1956) reported that the CEC of Otay montmorillonite measured with 0.25 M Cu(OAc)_2 between pH 4.0 and 5.0 was $\sim 10\%$ greater than that measured with Ca or K. Maes et al. (1976) studied exchange reactions of Na and transition metals on Camp Berceau montmorillonite. The Na-Cu exchange reaction was conducted with mixed NaCl/CuCl_2 solutions in a 0.01 M Cl^- background. They found that (i) when Cu^{2+} ions occupied $<60\%$ of the charge sites, the apparent adsorbed metal charge ($Q = q_{\text{Na}} + q_{\text{Cu}}$) remained constant and equal to NaEC; (ii) when Cu^{2+} ions occupied $>60\%$ of the charge sites, Q increased with increasing Cu in the exchanger phase; and (iii) when the clay was saturated with Cu, Q was $\approx 10\%$ larger than the value of NaEC. Sposito et al. (1981) studied Na-Cu exchange on Wyoming montmorillonite with mixed $\text{NaClO}_4/\text{Cu(ClO}_4)_2$ solutions in a 0.01 M

ClO_4^- background. They found that neither Q nor K_v , the Vanselow selectivity coefficient, increased with increasing Cu saturation. Because the previous study on Na-Cu exchange on montmorillonite (Maes et al., 1976) was conducted in a Cl^- medium and because ClO_4^- does not appear to form a monovalent complex with Cu^{2+} ions, Sposito et al. (1981) hypothesized that the monovalent complex, CuCl^+ , was responsible for the increase in Q observed in the study of Maes et al. (1976). This arises because all of the adsorbed Cu(II) species were formally treated as Cu^{2+} , while CuCl^+ was in fact a monovalent complex.

Sposito et al. (1983a,b) extended the hypothesis of the adsorption of the monovalent complex, CuCl^+ , to other divalent cations, such as Ca^{2+} and Mg^{2+} in their studies of Na-Ca, Na-Mg, and Ca-Mg exchange on Wyoming montmorillonite conducted in 0.05 M Cl^- and ClO_4^- media. They found that Q remained constant in a ClO_4^- medium while it increased with adsorption of divalent cations in a Cl^- medium. They interpreted these results as evidence for the adsorption of CaCl^+ and MgCl^+ in the exchange experiments conducted in a Cl^- medium. Therefore, the Na-Ca and Na-Mg exchange reactions were binary reactions in a ClO_4^- medium and ternary reactions in a Cl^- medium (Sposito et al., 1983a,b). Suarez and Zahow (1989) studied Ca-Mg exchange on Wyoming montmorillonite in $0.0125 \text{ M SO}_4^{2-}$ medium and 0.025 , 0.05 , and 0.1 M Cl^- media. They found that values of Q were the same in SO_4^{2-} and Cl^- media and that Q did not increase with increasing Cl^- concentration despite the increase in proportions of Ca^{2+} and Mg^{2+} complexed as CaCl^+ and MgCl^+ . Since the adsorption of CaCl^+ and MgCl^+ complexes should result in larger values of Q in the Cl^- medium than those in SO_4^{2-} medium, as Ca^{2+} and Mg^{2+} do not form positively charged complexes with SO_4^{2-} , Suarez and Zahow (1989) concluded that no detectable CaCl^+ and MgCl^+ complexes were adsorbed on Wyoming montmorillonite.

Due to the discrepancies in the literature on the effect of anions on metal exchange reactions, this study was initiated to further examine the role of anions on Na-Cu exchange on Wyoming montmorillonite. The CEC of the Wyoming montmorillonite was measured using CaCl_2 as well as the Cu salts of Cl^- , ClO_4^- , NO_3^- , and SO_4^{2-} . The Na-Cu exchange reactions were studied in 0.02 M Cl^- , ClO_4^- , NO_3^- solutions, and 0.01 M SO_4^{2-} solutions. The main objective of this study was to ascertain if CuCl^+ and CuNO_3^+ monovalent complexes were adsorbed on Wyoming montmorillonite during the Na-

Z. Z. Zhang, National Exposure Res. Lab., U.S. EPA, 960 College Station Rd., Athens, GA 30605-2700; and D. L. Sparks, Delaware Agric. Exp. Stn., Dep. of Plant and Soil Sciences, College of Agricultural Sciences, Univ. of Delaware, Newark, DE 19717-1303. Published as Miscellaneous Paper no. 1601 of the Delaware Agric. Exp. Stn. Received 18 May 1995. *Corresponding author (zhang.zhenzhong@epamail.epa.gov).

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Abbreviations: CuEC, copper exchange capacity; EDTA, ethylenediaminetetraacetic acid; CEC, cation-exchange capacity; NaEC, exchange capacity measured with sodium; ICP, inductively coupled plasma; TMC, total metal charge; CaEC, exchange capacity measured with calcium; ANOVA, analysis of variance.

Cu exchange reaction and to examine if Cu^{2+} ions were specifically adsorbed on montmorillonite during the Na-Cu exchange reaction.

MATERIALS AND METHODS

Sodium-Montmorillonite

Wyoming montmorillonite, SWy-1, was obtained from the Source Clays Repository of the Clay Minerals Society at the University of Missouri. The $<2\text{-}\mu\text{m}$ fraction of the clay sample was separated by centrifugation, Na-saturated, and freeze-dried using the procedures of Zhang et al. (1990). In this procedure, CO_3^{2-} impurity in the clay sample was removed by adding 0.05 M HCl solution to clay samples during Na saturation. The amount of the HCl solution added was determined from titration of the clay sample from the original pH 9.0 to pH 7.0.

Cation-Exchange Capacity

The CEC of the Wyoming montmorillonite was determined using a modified procedure of Roth et al. (1969). A 0.2500 g Na-montmorillonite sample was weighed into Corex (Corning Inc., Corning, NY) glass centrifuge tubes and 10 mL of double deionized water were added to pre-wet the clay samples. Then 10 mL of 0.5 M solutions of CaCl_2 , CuCl_2 , $\text{Cu}(\text{ClO}_4)_2$, $\text{Cu}(\text{NO}_3)_2$, and CuSO_4 were added to the centrifuge tubes containing the pre-wetted clay samples to yield an initial concentration of 0.25 M. Three replicate clay samples were reacted with each solution. The centrifuge tubes were shaken at a low speed on a reciprocal shaker for 16 h and centrifuged at $10\,000 \times g$ for 30 to 40 min, and the supernatant solution was discarded. Then 20 mL of 0.25 M solutions of CaCl_2 , CuCl_2 , $\text{Cu}(\text{ClO}_4)_2$, $\text{Cu}(\text{NO}_3)_2$, and CuSO_4 were added to respective centrifuge tubes, shaken for 8 h, and centrifuged, and the supernatant solution was discarded. Next, the clay samples were washed four times with respective 0.0100 M solutions of CaCl_2 , CuCl_2 , $\text{Cu}(\text{ClO}_4)_2$, $\text{Cu}(\text{NO}_3)_2$, and CuSO_4 by centrifugation and decantation. The centrifuge tubes were shaken for 4 to 16 h for each washing. Preliminary experiments showed that Ca and Cu concentrations of the supernatant solutions in the fourth washing were not different from 0.0100 M. The pH values of the supernatant solutions from the final wash were measured and the centrifuge tubes were weighed to determine the mass of carryover solution in each clay sample. Finally, the clay samples were extracted four times with 20 mL of 0.10 M MgSO_4 solution. The centrifuge tubes were shaken for 4 to 16 h at a low speed in each extraction. The supernatant solutions from each sample were collected after centrifugation and made up to 200 mL for analysis of Ca or Cu using ICP spectrophotometry. The concentrations of Ca and Cu in the solution were measured three times and the means were used in the calculations. The values of CEC for Ca and Cu were determined as following:

$$\text{CEC} = 2(n_M - C_M M_w) \quad [1]$$

where n_M is the total moles of Ca^{2+} or Cu^{2+} per kilogram of clay extracted by MgSO_4 solution, C_M is the molar concentrations of Ca^{2+} or Cu^{2+} ions in the equilibrium supernatant solution and M_w is the mass of carryover solution per kilogram of clay before extracting with MgSO_4 solution. To further examine if Cu^{2+} and its monovalent complexes are specifically adsorbed at nonexchangeable sites on clay edges, the clay samples were extracted twice with 20 mL of 0.05 M $\text{Na}_2\text{-EDTA}$ after the MgSO_4 solution extraction. The centrifuge tubes were shaken

and centrifuged as before. The supernatant solutions from each sample were collected and analyzed for Cu using ICP.

Sodium-Copper Exchange Experiments

Mixed solutions of $\text{NaCl}/\text{CuCl}_2$, $\text{NaClO}_4/\text{Cu}(\text{ClO}_4)_2$, $\text{NaNO}_3/\text{Cu}(\text{NO}_3)_2$, and $\text{Na}_2\text{SO}_4/\text{CuSO}_4$ at a constant TMC concentration of $0.0200 \text{ mol}_e \text{ L}^{-1}$ were prepared by mixing 0.0200 M solutions of NaCl, NaClO_4 , and NaNO_3 with respective 0.0100 M solutions of CuCl_2 , $\text{Cu}(\text{ClO}_4)_2$, and $\text{Cu}(\text{NO}_3)_2$ and 0.0100 M Na_2SO_4 with 0.0100 M CuSO_4 at different volume combinations ranging from 9:1 to 1:9. A 0.2400 to 0.2600 g Na-montmorillonite sample was weighed into each of the Corex glass centrifuge tubes and then 15 mL of the mixed solutions were added to these tubes. Three replicate clay samples were reacted with each mixed solution. The centrifuge tubes were placed on a reciprocal shaker for 16 h, centrifuged at $10\,000 \times g$ for 30 to 40 min, and the supernatant solutions were discarded. This process was repeated once, and the supernatant solutions were collected for determining pH and diluted accordingly for analysis of Na and Cu using atomic absorption spectrophotometry. The solution concentrations of Na and Cu from each clay sample were measured three times, and the means were used to determine the equilibrium concentrations of Na^+ and Cu^{2+} ions in the supernatant solution of the Na-Cu exchange reaction. These concentrations of Na and Cu were also used in the correction term for calculation of the adsorbed metal charges of Na^+ and Cu^{2+} ions. Next, the centrifuge tubes were weighed to determine the mass of carryover solution in each clay sample, and the clay samples were extracted four times with 15 mL of 0.10 M MgSO_4 solution by shaking, centrifuging, and decanting. The supernatant solutions from each clay sample were collected, made to a 200- or 250-mL volume and analyzed for Na and Cu. The adsorbed metal charges of Na^+ and Cu^{2+} ions on the exchanger phase were determined as follows:

$$q_{\text{Na}} = n_{\text{Na}} - C_{\text{Na}} M_w \quad [2]$$

$$q_{\text{Cu}} = 2(n_{\text{Cu}} - C_{\text{Cu}} M_w) \quad [3]$$

where the symbols n , C , and M have been defined in Eq. [1].

RESULTS AND DISCUSSION

Calcium and Copper Exchange Capacities

The experimental data for CEC measurement with Ca^{2+} and Cu^{2+} ions are presented in Table 1. The pH values of the supernatant solutions of the fourth washing with 0.0100 M CaCl_2 and respective Cu electrolytes are also reported. The mean value of CaEC from the three replicate measurements is $0.839 \pm 0.007 \text{ mol}_e \text{ kg}^{-1}$ (0.007 is the standard deviation). This value is in excellent agreement with the experimental data of $0.835 \pm 0.021 \text{ mol}_e \text{ kg}^{-1}$ reported by Suarez and Zahow (1989). The data in Table 1 show that values of CuEC measured with different Cu electrolytes are not significantly different from each other. Thus, these data showed that the CuEC of montmorillonite was independent of anions present in the electrolyte media, and monovalent complexes such as CuCl^+ and CuNO_3^+ did not appear to be adsorbed on the clay in the exchange reaction when the concentration of Cl^- and NO_3^- was 0.02 M. According to the tabulated data of Smith and Martell (1976), the stability constants for the CuCl^+ and CuNO_3^+ complexes are 2.5 ($\log K = 0.40$) and 3.2 ($\log K = 0.50$), respec-

Table 1. Experimental cation-exchange capacity (CEC) data for Wyoming montmorillonite measured with CaCl₂ and Cu salts of Cl⁻, ClO₄⁻, NO₃⁻, and SO₄²⁻.

Electrolyte	pH [†]	CaEC or CuEC [‡]			Mean	Cu-EDTA [§]
		1	2	3		
		mol _c kg ⁻¹				
CaCl ₂	5.80 ± 0.03	0.832	0.839	0.845	0.839 ± 0.007	
CuCl ₂	4.31 ± 0.05	0.871	0.888	0.883	0.881 ± 0.009	0.0103 ± 0.0009
Cu(ClO ₄) ₂	4.54 ± 0.03	0.856	0.851	0.871	0.859 ± 0.010	0.0093 ± 0.0001
Cu(NO ₃) ₂	4.41 ± 0.04	0.850	0.864	0.856	0.857 ± 0.007	0.0085 ± 0.0001
CuSO ₄	4.53 ± 0.02	0.872	0.875	0.878	0.875 ± 0.003	0.0090 ± 0.0008

[†] The pH values of the supernatant solutions in the fourth washing with 0.0100 M solutions of calcium chloride and copper salts were measured and the mean of the three replicates for each electrolyte is reported.

[‡] CaEC = exchange capacity measured with calcium; CuEC = exchange capacity measured with copper.

[§] The clay samples were extracted twice with 0.05 M Na₂-ethylenediaminetetraacetic acid (EDTA) after MgSO₄ extraction. The mean of the three replicates for each Cu electrolyte is reported.

tively. For a 0.01 M CuCl₂ or Cu(NO₃)₂ solution, activity coefficients of Cl⁻ or NO₃⁻ and the monovalent complex CuCl⁺ or CuNO₃⁺ are approximately the same, and the activity coefficient of Cu²⁺ is 0.522 based on the Davies equation (Sposito, 1981). It can be shown based on the above data that [CuCl⁺]/[Cu²⁺] = 0.026 and [CuNO₃⁺]/[Cu²⁺] = 0.033. Thus, only ~3% of Cu²⁺ is complexed as CuCl⁺ or CuNO₃⁺ in the equilibrium supernatant solutions under our experimental conditions. Therefore, it is conceivable that the anions should not affect the measured CuEC, unless there is a strong preference for the adsorption of monovalent CuCl⁺ and CuNO₃⁺ complexes.

The mean value of CuEC for the 12 measurements presented in Table 1 is 0.868 ± 0.013 mol_c kg⁻¹. This value is ~4% larger than that of the CaEC. The underlying causes of this increase remain unclear, although the hydrolysis reaction of Cu²⁺ has been considered as a plausible cause. The pH values of the supernatant solutions in the fourth wash with 0.0200 mol_c L⁻¹ Cu solutions ranged from 4.31 to 4.54. We did not adjust the pH to higher values because of the following two considerations. First, the extent of the hydrolysis reaction of Cu²⁺ increases with increasing pH, and secondly, adding a strong base would yield partially Cu-saturated clay samples. Although it can also be argued that protons would compete with Cu at the low pH levels, as stated earlier, we are more concerned with possible adsorption of monovalent CuOH⁺ ions at higher pH values. The hydrolysis reaction of Cu²⁺ is given as (Smith and Martell, 1976),

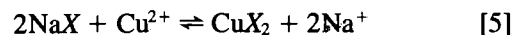


with log *K* = -7.70. Thus, the hydrolysis reaction does not occur significantly in a solution at pH levels of 4.31 to 4.54. However, the extent of Cu²⁺ hydrolysis on clay surfaces is not necessarily the same as in solution, since the presence of a surface may shift the equilibrium to the left or right depending on which Cu species is preferentially adsorbed. Therefore, one cannot completely rule out the possibility that the observed increase in CuEC over CaEC is due to the adsorption of monovalent CuOH⁺ ions. Significant hydrolysis reactions can affect CuEC at higher pH values. DeMumbrum and Jackson (1956) observed a large increase in CuEC above pH 6 and attributed this increase to hydrolysis of Cu²⁺ and resultant precipitation of Cu(OH)₂.

Stumm and Bilinski (1973) indicated that the edge surfaces of montmorillonite may favor the adsorption of a monovalent ion pair or complex over the divalent metal cation. Sposito et al. (1981) suggested that the above mechanism may apply to the adsorption of CuCl⁺ on the edge surfaces of montmorillonite. Our experimental data showed that the quantity of Cu extracted by Na₂-EDTA solution was only 1.0 to 1.2% of the CuEC and was not affected by anions (Table 1). Thus, it can be concluded that the predominate adsorption reaction occurred at the cation exchanger sites on the clay surfaces and that specific adsorption of Cu²⁺ and its monovalent complexes such as CuCl⁺ and CuNO₃⁺ at nonexchangeable sites on the clay edges was relatively insignificant under our experimental conditions. At a much lower Cu concentration, however, specific adsorption at nonexchangeable sites on clay edges may play an important role.

Sodium-Copper Exchange

The Na-Cu exchange reaction in our study can be written as



where X represents one mole of charge on the clay exchanger. The experimental data for the Na-Cu exchange reaction are presented in Table 2. Each entry in Table 2 is the mean of three replicate experiments. The first column gives the pH, and the second and third columns, C_{Na} and C_{Cu}, respectively, are equilibrium concentrations of Na⁺ and Cu²⁺ ions in the supernatant solutions before extracting with 0.10 M MgSO₄. The TMC concentration of the supernatant solutions is given by

$$\text{TMC} = C_{\text{Na}} + 2C_{\text{Cu}} \quad [6]$$

In our exchange experiments, the mixed solutions were prepared at a constant TMC of 0.0200 mol_c L⁻¹. The mean values of TMC of the supernatant solutions, based on the data presented in Table 2, were 0.0199 mol_c L⁻¹ for Cl⁻, 0.0194 mol_c L⁻¹ for ClO₄⁻, 0.0200 mol_c L⁻¹ for NO₃⁻, and 0.0200 mol_c L⁻¹ for SO₄²⁻ media, respectively. Thus, the equilibrium TMC concentrations in the supernatant solutions are essentially the same as the initial solution concentrations, indicating that the monovalent

Table 2. Experimental data (mean of triplicate experiments) for Na-Cu exchange at 298 K on Wyoming montmorillonite in Cl^- , ClO_4^- , NO_3^- , and SO_4^{2-} solution media at a constant total metal charge concentration of $0.0200 \text{ mol}_e \text{ L}^{-1}$.

pH	C_{Na}		C_{Cu}		Q	K_v
	mol L ⁻¹		mol _e kg ⁻¹			
			<u>Cl⁻</u>			
6.32 ± 0.03	2.00E-02	1.19E-04	0.544 ± 0.010	0.272 ± 0.008	0.816 ± 0.004	1.399 ± 0.093
6.11 ± 0.05	1.91E-02	5.65E-04	0.314 ± 0.006	0.497 ± 0.013	0.812 ± 0.008	1.209 ± 0.011
5.98 ± 0.02	1.86E-02	6.46E-04	0.295 ± 0.004	0.530 ± 0.014	0.825 ± 0.018	1.208 ± 0.071
5.80 ± 0.04	1.72E-02	1.48E-03	0.180 ± 0.003	0.626 ± 0.007	0.806 ± 0.009	1.621 ± 0.024
5.68 ± 0.03	1.53E-02	2.36E-03	0.131 ± 0.001	0.684 ± 0.002	0.815 ± 0.003	1.259 ± 0.036
5.54 ± 0.08	1.30E-02	3.26E-03	0.095 ± 0.001	0.724 ± 0.004	0.819 ± 0.002	1.288 ± 0.041
5.34 ± 0.06	1.02E-02	4.74E-03	0.063 ± 0.001	0.786 ± 0.005	0.849 ± 0.005	1.356 ± 0.047
5.32 ± 0.04	7.57E-03	5.97E-03	0.044 ± 0.002	0.806 ± 0.002	0.850 ± 0.004	1.198 ± 0.047
5.17 ± 0.03	5.05E-03	7.23E-03	0.027 ± 0.001	0.824 ± 0.003	0.852 ± 0.003	1.161 ± 0.073
			<u>ClO₄⁻</u>			
6.30 ± 0.04	1.97E-02	1.22E-04	0.531 ± 0.008	0.277 ± 0.006	0.808 ± 0.004	1.378 ± 0.079
6.12 ± 0.06	1.86E-02	5.83E-04	0.305 ± 0.007	0.513 ± 0.010	0.818 ± 0.006	1.220 ± 0.029
5.99 ± 0.05	1.83E-02	7.79E-04	0.271 ± 0.014	0.545 ± 0.011	0.816 ± 0.025	1.153 ± 0.150
5.78 ± 0.02	1.67E-02	1.43E-03	0.174 ± 0.005	0.638 ± 0.003	0.812 ± 0.004	1.347 ± 0.062
5.64 ± 0.06	1.46E-02	2.31E-03	0.120 ± 0.003	0.701 ± 0.002	0.821 ± 0.003	1.407 ± 0.082
5.54 ± 0.02	1.24E-02	3.39E-03	0.089 ± 0.001	0.732 ± 0.002	0.821 ± 0.002	1.280 ± 0.026
5.47 ± 0.05	9.75E-03	4.70E-03	0.067 ± 0.003	0.800 ± 0.009	0.867 ± 0.012	1.151 ± 0.135
5.40 ± 0.03	7.39E-03	5.88E-03	0.042 ± 0.002	0.815 ± 0.003	0.857 ± 0.004	1.302 ± 0.113
5.35 ± 0.05	4.84E-03	7.18E-03	0.025 ± 0.001	0.827 ± 0.006	0.852 ± 0.004	1.266 ± 0.081
			<u>NO₃⁻</u>			
6.26 ± 0.04	2.03E-02	1.22E-04	0.521 ± 0.009	0.272 ± 0.006	0.792 ± 0.014	1.467 ± 0.043
6.20 ± 0.02	1.91E-02	6.01E-04	0.312 ± 0.016	0.510 ± 0.011	0.822 ± 0.025	1.198 ± 0.096
6.00 ± 0.02	1.88E-02	8.25E-04	0.248 ± 0.021	0.557 ± 0.018	0.805 ± 0.004	1.372 ± 0.133
5.75 ± 0.03	1.72E-02	1.49E-03	0.172 ± 0.002	0.632 ± 0.004	0.804 ± 0.002	1.375 ± 0.044
5.63 ± 0.05	1.50E-02	2.38E-03	0.121 ± 0.003	0.697 ± 0.004	0.818 ± 0.004	1.399 ± 0.036
5.57 ± 0.07	1.27E-02	3.42E-03	0.086 ± 0.003	0.722 ± 0.009	0.809 ± 0.011	1.370 ± 0.053
5.53 ± 0.02	1.06E-02	4.59E-03	0.061 ± 0.001	0.784 ± 0.002	0.846 ± 0.002	1.554 ± 0.045
5.46 ± 0.04	7.77E-03	5.97E-03	0.041 ± 0.001	0.808 ± 0.003	0.849 ± 0.003	1.483 ± 0.075
5.41 ± 0.03	5.03E-03	7.23E-03	0.025 ± 0.002	0.824 ± 0.001	0.849 ± 0.001	1.348 ± 0.100
			<u>SO₄²⁻</u>			
6.50 ± 0.05	2.02E-02	1.82E-04	0.533 ± 0.004	0.258 ± 0.004	0.791 ± 0.004	0.933 ± 0.030
6.30 ± 0.02	1.92E-02	6.84E-04	0.333 ± 0.005	0.466 ± 0.005	0.799 ± 0.007	0.896 ± 0.051
6.10 ± 0.08	1.83E-02	8.73E-04	0.295 ± 0.029	0.492 ± 0.015	0.787 ± 0.037	0.847 ± 0.106
5.83 ± 0.05	1.68E-02	1.66E-03	0.200 ± 0.002	0.589 ± 0.002	0.789 ± 0.004	0.867 ± 0.013
5.74 ± 0.06	1.48E-02	2.51E-03	0.147 ± 0.002	0.645 ± 0.007	0.791 ± 0.006	0.860 ± 0.034
5.60 ± 0.04	1.26E-02	3.42E-03	0.109 ± 0.002	0.688 ± 0.006	0.797 ± 0.005	0.855 ± 0.021
5.57 ± 0.03	1.08E-02	4.47E-03	0.078 ± 0.002	0.754 ± 0.003	0.832 ± 0.004	1.030 ± 0.099
5.50 ± 0.05	8.57E-03	5.51E-03	0.057 ± 0.004	0.783 ± 0.003	0.839 ± 0.007	1.026 ± 0.120
5.48 ± 0.04	6.19E-03	6.64E-03	0.039 ± 0.001	0.813 ± 0.002	0.852 ± 0.001	0.953 ± 0.022

Cu complexes are not adsorbed during the Na-Cu exchange reaction, since adsorption of monovalent Cu complexes would decrease TMC concentrations in the supernatant solutions. The fourth and fifth columns, q_{Na} and q_{Cu} , are adsorbed charges of Na^+ and Cu^{2+} ions, and the sixth column, Q , is the apparent adsorbed metal charge. The last column is the Vanselow selectivity coefficient, determined from the following equation:

$$K_v = \frac{\gamma_{\text{Na}}^2 C_{\text{Na}}^2 N_{\text{Cu}}}{\gamma_{\text{Cu}} C_{\text{Cu}} N_{\text{Na}}^2} \quad [7]$$

where N_{Na} and N_{Cu} are the mole fractions of Na^+ and Cu^{2+} on the exchanger phase, given by

$$N_{\text{Na}} = \frac{q_{\text{Na}}}{q_{\text{Na}} + 0.5q_{\text{Cu}}} \quad \text{and} \quad N_{\text{Cu}} = \frac{0.5q_{\text{Cu}}}{q_{\text{Na}} + 0.5q_{\text{Cu}}} \quad [8]$$

and γ_{Na} and γ_{Cu} are the single-ion activity coefficients for Na^+ and Cu^{2+} ions in the solution phase. The single-ion activity coefficients, γ_i , were calculated according to the Davies equation (Sposito, 1981).

The data in Table 2 show that (i) the values of Q did not appear to be different among the four anionic media, and (ii) the values of Q increased with increasing q_{Cu} to

approach the value of CuEC in each of the four anionic media. The increase in Cl^- and NO_3^- media did not appear to be different from that in ClO_4^- and SO_4^{2-} media. To examine if indeed Q was independent of the anionic media, we performed ANOVA on the data for Q reported in Table 2 using an ANOVA procedure in EXCEL (Microsoft Corporation, Redmond, WA). The results showed that the values of Q measured with the four anionic media were not significantly different from each other at the 95% confidence interval. These results are in agreement with the CEC data presented in Table 1 and the constant TMC discussed above, further validating that no detectable monovalent complexes such as CuCl^+ and CuNO_3^+ are adsorbed on Wyoming montmorillonite in the Na-Cu exchange reaction. In the Na-Cu exchange study of Sposito et al. (1981), no increase in the values of Q was found in ClO_4^- medium. A further examination of the data in Table 2 showed that (i) the values of Q increased only slightly for each of the anionic media when Cu occupied <90% of the charge sites on the clay samples and that (ii) significant increases in the values of Q occurred at higher Cu loadings. The highest Cu loading in the study of Sposito et al. (1981) was about

81% of the charge sites. Therefore, the experimental data presented in Table 2 are in fact not contrary to those of Sposito et al. (1981). We observed an increase in the values of Q for each of the four anionic media studied, simply because our study covered a wider range of exchanger phase composition, with Cu^{2+} occupying 30 to 95% of the charge sites.

A plausible explanation for the increase in the values of Q with increasing saturation of Cu and other divalent cations observed by earlier researchers (Van Bladel et al., 1972; Maes et al., 1976; Maes and Cremers, 1979; and Sposito et al., 1983a,b) is the decrease in negative adsorption of anions. The total negative charge of clay particles suspended in an electrolyte solution is neutralized by the sum of excess cation charges (apparent adsorbed metal charge, Q) and deficit of anion charges (negative adsorption of anions). For a clay mineral with constant surface charge, Q increases with decreasing negative adsorption of anions. The apparent adsorbed metal charge is not equivalent to the total charge of clay unless the negative adsorption of anions is negligible. For a 1:1 electrolyte, the deficit of an anion on a negatively charged clay surface is given by (van den Hul, 1982; Chan et al., 1984):

$$\Gamma^- S = \frac{2SC^0}{\kappa} \left[1 - \exp\left(\frac{e\psi_d}{2kT}\right) \right] \quad [9]$$

where Γ^- is the deficit of anion per unit surface area, S is the specific surface area of the clay, the product $\Gamma^- S$ is the deficit of anion per unit mass of the clay, C^0 is the molar concentration of the electrolyte in the equilibrium solution, κ is the Debye-Huckel parameter, e is the electronic charge, ψ_d is the electrostatic potential at the origin of the diffuse layer, k is the Boltzmann constant, and T is the absolute temperature. For a Na-saturated Wyoming montmorillonite in a 0.02 M NaCl solution at 298 K, $\kappa = 3.287 \times 10^6 \sqrt{C^0}$ (cm^{-1}), assuming $\psi_d = -60$ mV and $S = 8.00 \times 10^6 \text{ cm}^2 \text{ g}^{-1}$, one finds $\Gamma^- S = 0.0474 \text{ mol}_c \text{ kg}^{-1}$. This value is ~5% of the total charge and is in excellent agreement with the experimental data of Edwards et al. (1965a) and Miller and Low (1990). The deficit of Cl^- on Ca-montmorillonite was considerably lower than that on Na-montmorillonite (Edwards et al., 1965a,b). This is due to a number of factors, such as a reduction in S due to formation of quasicrystals (Quirk and Aylmore, 1971) and a decrease in the magnitude of ψ_d as inferred from the decrease in electrophoretic mobility of the clay particles with increasing saturation of Ca (Ban On et al., 1970). Amrhein and Suarez (1990) observed that the anion deficit decreased with increasing Ca saturation in their Na-Ca exchange study. It is conceivable that anion deficit also decreases with increasing saturation of Cu and other divalent cations. Thus, the observed increase in Q with increasing saturation of Cu and other divalent cations can be attributed to a decrease in the negative adsorption of anions.

The experimental K_v data are plotted against the charge fraction of Cu^{2+} on the exchanger phase, E_{Cu} , in Fig.

1, where

$$E_{\text{Cu}} = \frac{q_{\text{Cu}}}{Q} \quad [10]$$

Unlike the data entry in Table 2, which was the mean of three replicates, data from individual replicate experiments were presented in Fig 1. No trend in the values of K_v with increasing E_{Cu} can be seen, i.e., the values of K_v are not affected by the composition of the exchanger phase and remain essentially constant for each anionic medium. The mean values of K_v from the experimental data presented in Fig. 1 are 1.260 ± 0.086 in Cl^- , 1.278 ± 0.115 in ClO_4^- , 1.396 ± 0.113 in NO_3^- , and 0.919 ± 0.087 in SO_4^{2-} media, respectively. The Na-Cu exchange isotherms in the four anionic media are presented in Fig. 2. The data presented in Fig. 2 were also from individual replicate experiments. The ordinate in Fig. 2, E_{Cu} , is the charge fraction of Cu^{2+} on the clay exchanger, while the abscissa, \tilde{E}_{Cu} , is the charge fraction of Cu^{2+} ions in the supernatant solution,

$$\tilde{E}_{\text{Cu}} = \frac{2C_{\text{Cu}}}{C_{\text{Na}} + 2C_{\text{Cu}}} \quad [11]$$

The solid curves in Fig. 2 were obtained based on the equation relating E_{Cu} to \tilde{E}_{Cu} . (Sposito et al., 1981),

$$E_{\text{Cu}} = 1 - \left\{ 1 + \frac{2}{\beta \text{TMC}} \left[\frac{1}{(1 - \tilde{E}_{\text{Cu}})^2} - \frac{1}{(1 - E_{\text{Cu}})} \right] \right\}^{-1/2} \quad [12]$$

where

$$\beta = \frac{\gamma_{\text{Na}}^2}{\gamma_{\text{Cu}} K_v} \quad [13]$$

It can be seen that the experimental errors in this study were relatively small, as evidenced by the small scattering among the replicates, and that there is excellent agreement between the solid curves and the experimental data for each of the four anionic media studied, further demonstrating the constancy of K_v over the entire range of exchanger phase composition.

The lower K_v values in the SO_4^{2-} medium compared with other anionic media were due to the unaccounted decrease in C_{Cu} in Eq [7] resulting from complexation of Cu^{2+} with SO_4^{2-} . In the above calculation, C_{Cu} was assumed to be equal to the total Cu(II) concentration in the solution. The complexation reaction is as follows:



with $\log K = 2.36$ (Smith and Martell, 1976). It can be shown that, unlike complexation reactions resulting in CuCl^+ and CuNO_3^+ , the complexation reaction as shown in Eq. [14] proceeds notably with a large fraction of total Cu(II) in the CuSO_4^0 complex form. The stability constant for the CuSO_4^0 complex can be written as

$$K = \frac{[\text{CuSO}_4^0]}{[\text{Cu}^{2+}][\text{SO}_4^{2-}]} \frac{\gamma_{\text{CuSO}_4}}{\gamma_{\text{Cu}} \gamma_{\text{SO}_4}} \quad [15]$$

where γ refers to an activity coefficient and the brackets

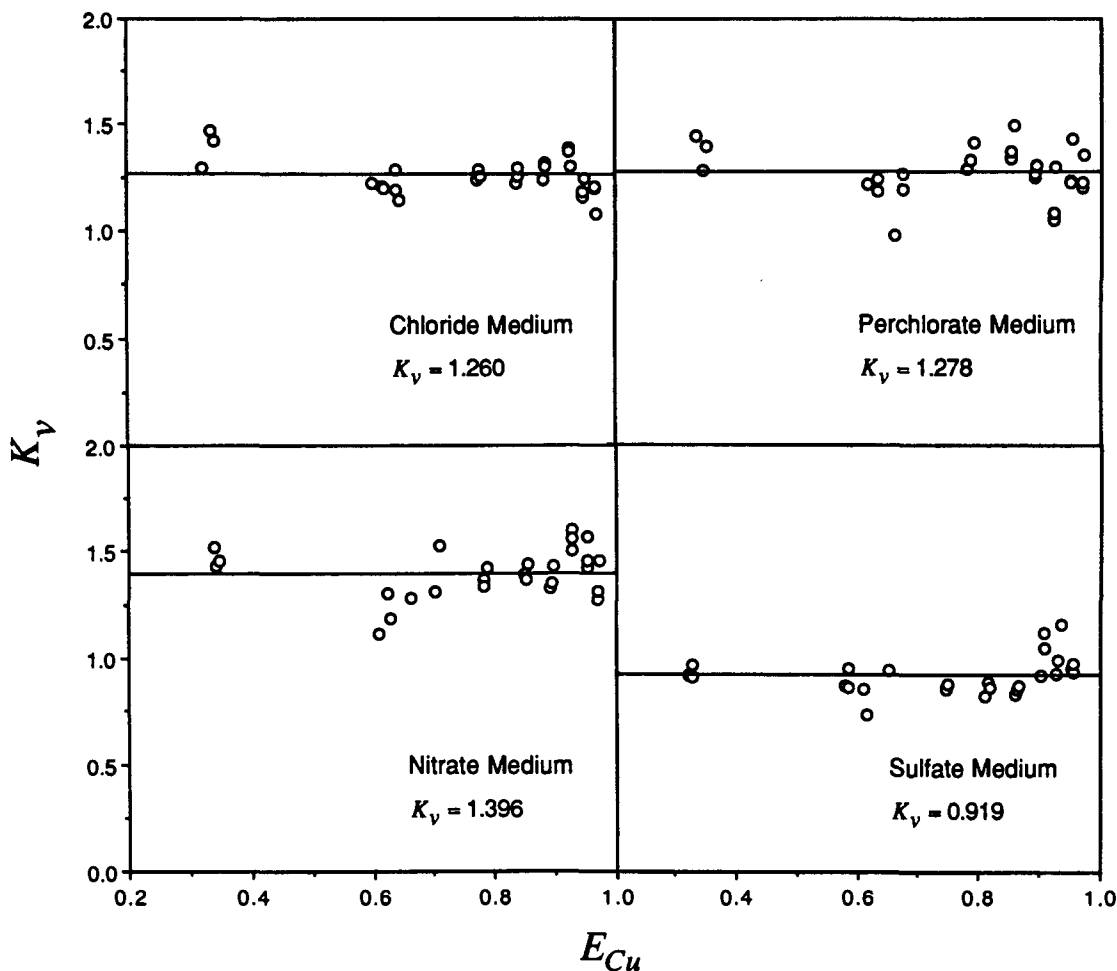


Fig. 1. Vanselow selectivity coefficients, K_v , for Na-Cu exchange on Wyoming montmorillonite at 298 K in 0.02 mol/L Cl^- , ClO_4^- , NO_3^- , and SO_4^{2-} media as related to the charge fraction of Cu^{2+} on the exchanger phase, E_{Cu} .

denote concentrations. For a 0.01 M CuSO_4 solution, $\gamma_{\text{Cu}}\gamma_{\text{SO}_4} = \gamma_{\pm}^2 = 0.1681$ (Conway, 1952), and assuming $\gamma_{\text{Cu}}\gamma_{\text{SO}_4} = 1.0$, one finds, $[\text{CuSO}_4] = 0.0023$ M and $[\text{Cu}^{2+}] = 0.0077$ M, i.e., the concentration of Cu^{2+} was only 77% of the total Cu(II) concentration. When the reported values of K_v for the SO_4^{2-} medium in Table 2 are divided by a factor of 0.77, the results are approximately the same as the values of K_v in the other anionic media. In addition, it should be noted that in the supernatant solutions of the Na-Cu exchange experiments, the equilibrium as shown in Eq. [14] should be shifted slightly to the right, because of the excess amount of SO_4^{2-} anions. Therefore, one should avoid conducting exchange experiments of divalent metals in an anionic medium in which the metals form stable complexes, because the values of K_v obtained are further affected by the accuracy in the stability constant of the complex and the mean activity coefficient of the electrolyte.

In addition to the Vanselow approach, the approach of Gaines-Thomas (Gaines and Thomas, 1953) has also been employed in the studies of cation exchange. In their mono-divalent cation-exchange studies, several researchers observed that the Gaines-Thomas selectivity coefficient, K_{GT} , increased with increasing saturation of the divalent cations for transitional metals (Maes et al., 1976;

Maes and Cremers, 1979) and earth alkali ions (Van Bladel et al., 1972). The larger values of K_{GT} at higher divalent cation saturation were interpreted as a higher affinity for the divalent cations. The above consideration was based on the fundamental assumption that K_{GT} is a measure of relative affinities of cations for a surface and the criteria for ideal behavior in an exchanger phase is a constant K_{GT} that is independent of exchanger phase composition. Sposito and Mattigod (1979) critically examined this assumption and showed it to be incorrect. They indicated that one should use K_v , instead of K_{GT} , as a measure of relative affinities of cations for a surface and that it is the constancy of K_v , not K_{GT} , that determines whether an exchanger phase is ideal. For a mono-divalent exchange reaction as shown in Eq. [5], K_{GT} and K_v are related as (Sposito and Mattigod, 1979)

$$K_{\text{GT}} = \frac{4K_v}{2 - E_M} \quad [16]$$

where E_M is the charge fraction of the divalent cation. Note from Eq. [16] that K_{GT} will not be constant when K_v is constant. For a nonpreference mono-divalent exchange reaction, $K_v = 1.0$ over the entire exchanger phase composition, whereas the values of K_{GT} increase from

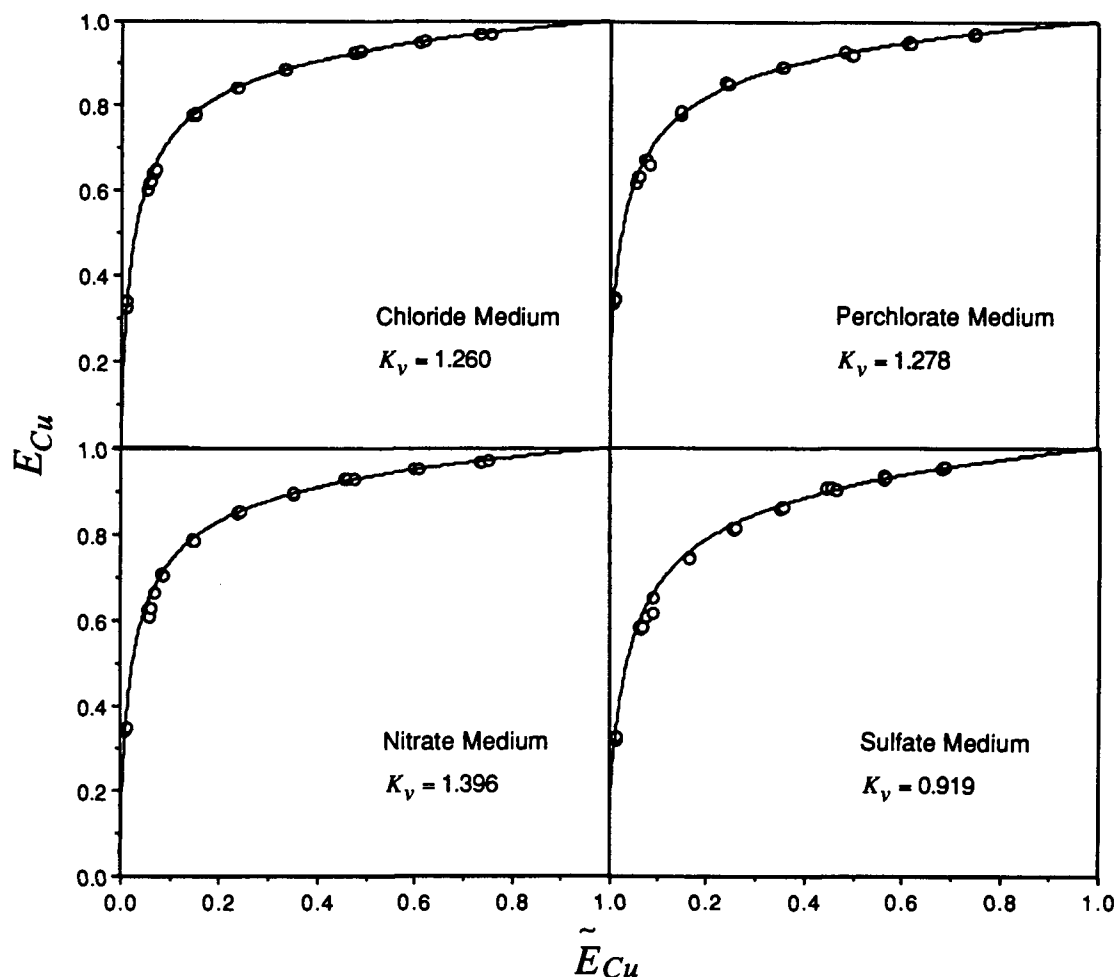


Fig. 2. The Na-Cu exchange isotherms on Wyoming montmorillonite at 298 K in 0.02 mol. L⁻¹ Cl⁻, ClO₄⁻, NO₃⁻, and SO₄²⁻ media (K_v = Vanselow selectivity coefficients; E_{Cu} = charge fraction of Cu²⁺ ions on the exchanger phase; \tilde{E}_{Cu} = charge fraction of Cu²⁺ ions in the solution phase).

2.0 ($E_M \rightarrow 0$) to 4.0 ($E_M \rightarrow 1.0$). Thus, selectivity coefficients based on the charge fraction in a heterovalent exchange reaction are subject to misinterpretation with regard to relative ion affinities for a surface (Babcack, 1981). The earlier conclusion that clay surfaces at higher divalent cation saturation had a higher affinity for divalent cations may actually be an artifact of the dependence of K_{GT} on the exchanger phase composition. Consequently, earlier conclusions regarding relative ion affinities for clay surfaces inferred from selectivity coefficients based on charge fractions, such as K_{GT} and the Gapon selectivity coefficient, should be further examined using K_v .

Sposito and Mattigod (1979) analyzed the experimental data of Maes et al. (1976) and showed that Na-trace metal exchange reactions were quite probably ideal on Camp Bertreau montmorillonite. The data presented in Fig. 1 also showed that Na-Cu exchange on Wyoming montmorillonite is ideal across the entire range of exchange phase composition in each of the four anion media studied. These results also suggest that Cu²⁺ ions are not specifically adsorbed to any appreciable extent on the surfaces of montmorillonite, since specific adsorption would result in larger K_v values at lower E_{Cu} values. Furthermore, the above results are in agreement with

the findings of Bingham et al. (1964) from studies of Cu retention on montmorillonite showing that Cu²⁺ ions on montmorillonite behave much like other divalent cations, such as Ca²⁺ and Mg²⁺ ions and with the results of Clementz et al. (1973) and McBride and Mortland (1974) from studies of electron spin resonance and infrared spectroscopy showing that Cu²⁺ ions were hydrated in the form of Cu(H₂O)₆²⁺ and tumbled rapidly when there were several layers of water molecules between the clay layers. Since the Cu²⁺ ions are hydrated, they react electrostatically with montmorillonite surfaces to form outer-sphere complexes, much like other divalent cations.

CONCLUSIONS

In summary, we found that the values of CuEC of Wyoming montmorillonite were similar in Cl⁻, ClO₄⁻, NO₃⁻, and SO₄²⁻ electrolyte media and the quantity of Na₂-EDTA solution extracted Cu was only 1.0 to 1.2% of the CuEC and was not affected by anions. We found that the values of Q increased with q_{Cu} in each of the anionic media, and the increase in the Cl⁻ and NO₃⁻ media did not appear to be different from that in the

ClO_4^- and SO_4^{2-} media. The increase in Q with increasing Cu saturation in this study and the general increase in Q with increasing saturation of other divalent cations are attributed to decreasing negative adsorption of anions. We also observed that K_d was independent of exchanger composition in each of the four anionic media, indicating Cu^{2+} ions were not specifically adsorbed to any appreciable extent on Wyoming montmorillonite and that the exchanger phase behaved as an ideal mixture. All of the above results suggest that no detectable monovalent complexes such as CuCl^+ and CuNO_3^+ were adsorbed on Wyoming montmorillonite in the Na-Cu exchange reaction.

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