

4.2 Sorption on mineral surfaces

4.2.1 Electrokinetics of dioctahedral smectites and europium interaction at low pH

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Introduction

The charging of clay minerals is complex since it involves interactions of solutes with various crystal planes that have different properties. Amphoteric sites at the edges induce pH-dependent charges and basal surfaces involve a negative permanent charge resulting from the isomorphous substitutions within the tetrahedral and octahedral sheets [1]. In the present study, the electrophoretic mobility has been investigated as a function of pH on four Na-saturated dioctahedral smectites < 0.2 μm separated from blended bentonites and their related reduced-charge materials (RCM) previously characterized [2]. The blended bentonites selected were Calcigel® (Bavaria, Germany), Volclay® (Wyoming, USA), the Cabo de Gata bentonite (Almería, Spain) and the bentonite P provided by Süd-Chemie AG (Germany) thereafter called BC, BV, BS and BP respectively. In addition, interaction with dissolved europium at low pH has been studied in comparison with other trivalent or divalent and monovalent cations. Clay concentrations were 1 g/l in all cases.

Mobilities in the absence and presence of Europium at low pH

As expected, the electrophoretic mobility of the dioctahedral smectites were negative and almost constant over the pH range of 2 to 10 (Figure 1 shows the results for the BV samples). However, the smectite

from Wyoming (USA) (BV) characterized by the lowest layer charge of 0.26 eq/f.u and the largest mean layer diameter of 277 nm showed the highest mobility.

The RCM materials characterized by collapsed interlayers and consequently a higher contribution from the edge surfaces showed a slightly lower mobility and a decrease of mobility at $\text{pH} < 2$ for the BV sample as observed by others [3].

The ion-exchange that is responsible for the uptake of metal cations at low pH can be conveniently tested by adding solutions of the metal ion of interest. The low pH conditions (in the following the pH is set to about pH 2) have the advantages that (i) stock solutions of the metal ions can be easily prepared at the low pH (no or limited hydrolysis, no interference from any potential complexing anion), (ii) the metal ion concentration can be increased to nearly any concentration of interest, and (iii) the pH is strongly buffered and does not change significantly. However, contact times of clay at low pH have to be limited to prevent side reactions due to dissolution. In some cases, a clay sample was left at low pH for extended times (i.e. longer than the duration of the experiments the results of which are shown), but in none of these investigation changes of the mobility were observed. Thus, dissolution of the clay and subsequent re-adsorption of e.g. dissolved aluminum is not interfering in the reported results.

Addition of europium leads to mobilities that are close to zero for Europium concentrations above 5 mM (Figure 2). There is as would be expected scatter in the mobilities. Some of the data points have been repeated using a separate cell, the same sample aliquot, a new sample aliquot and combinations thereof. The largest errors quantified from these data are about 0.5 $\mu\text{m/s}/(\text{V/cm})$.

Overall, no significant difference between the clays (including the other three samples investigated for which the experimental data is not shown) with respect to europium interaction at this low pH occurs. With respect to the results in Figure 1, it can also be stated that there is no difference between the dioctahedral smectites and the reduced-charge samples. Finally, there is no significant over-charging of the clays, considering the experimental uncertainties, i.e.

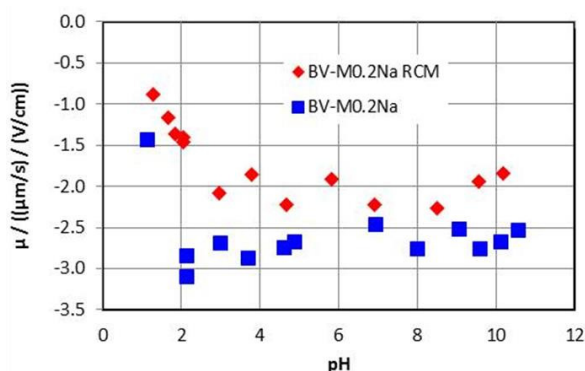


Fig. 1: Electrophoretic mobility of samples BV-MO.2Na RCM and BV-MO.2Na as a function of pH in 2 mM monovalent salt.

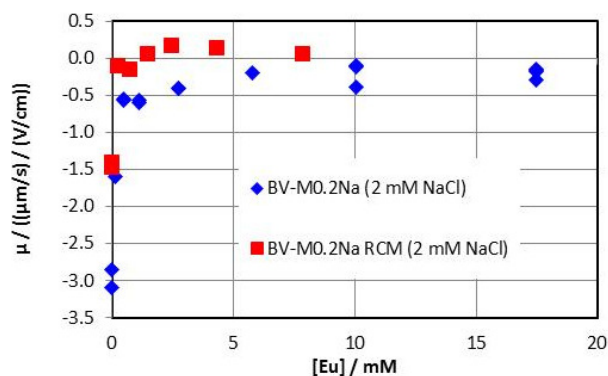


Fig. 2: Electrophoretic mobility of samples BV-M0.2Na RCM and BV-M0.2Na as a function of Europium concentration at pH about 2 in 2 mM monovalent salt.

the data suggest that the negative charge of the clays is just neutralized.

With some of the clays a separate set of experiments has been carried out to study whether the nature of the trivalent ion has an influence on the behavior. Figures 3 A and B show that with trivalent cations that are more strongly hydrolyzing than europium the same behavior is retrieved. Changing the charge of the ion, however, results in clear differences. Thus, in the presence of sodium, the BS-M0.2Na clay remains negatively charged up to at least 200 mM (Figure 3 C). In the case of BC-M0.2Na RCM, addition of Barium also results in a negative surface in the concentration range studied (Figure 3 D). Relating the curves for the differently charged ions, the sequence is obvious: The higher the charge, the closer to zero the electrokinetic mobility becomes.

Conclusions

The electrokinetic data show that the studied clay samples cannot be significantly overcharged, i.e. within the concentration ranges studied, even the trivalent cations do not cause significant positive mobilities. The interaction with the trivalent cations appears to be non-specific and all the trivalent cations cause neutralization of the electrokinetic surface charge. From comparison with cations of lower charge, it becomes clear that they are not able to cause complete neutralization of the electrokinetic charge.

References

- [1] Leroy, P., Tournassat, C., Bernard, O., Devau, N., Azaroual, M., 2015. The electrophoretic mobility of montmorillonite. Zeta potential and surface conductivity effects. *J. Colloid Interface Sci.* 451, 21-39.
- [2] Thomas, F., Michot, L.J., Vantelon, D., Montargès, E., Prélot, B., Cruchaudet, M., Delon, J.F., 1999. Layer charge and electrophoretic mobility of smectites. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 159, 351-358.
- [3] Delavernhe, L., Steudel, A., Darbha, G.K., Schäfer, T., Schuhmann, R., Wöll, C., Geckeis, H., Emmerich, K., 2015. Influence of mineralogical

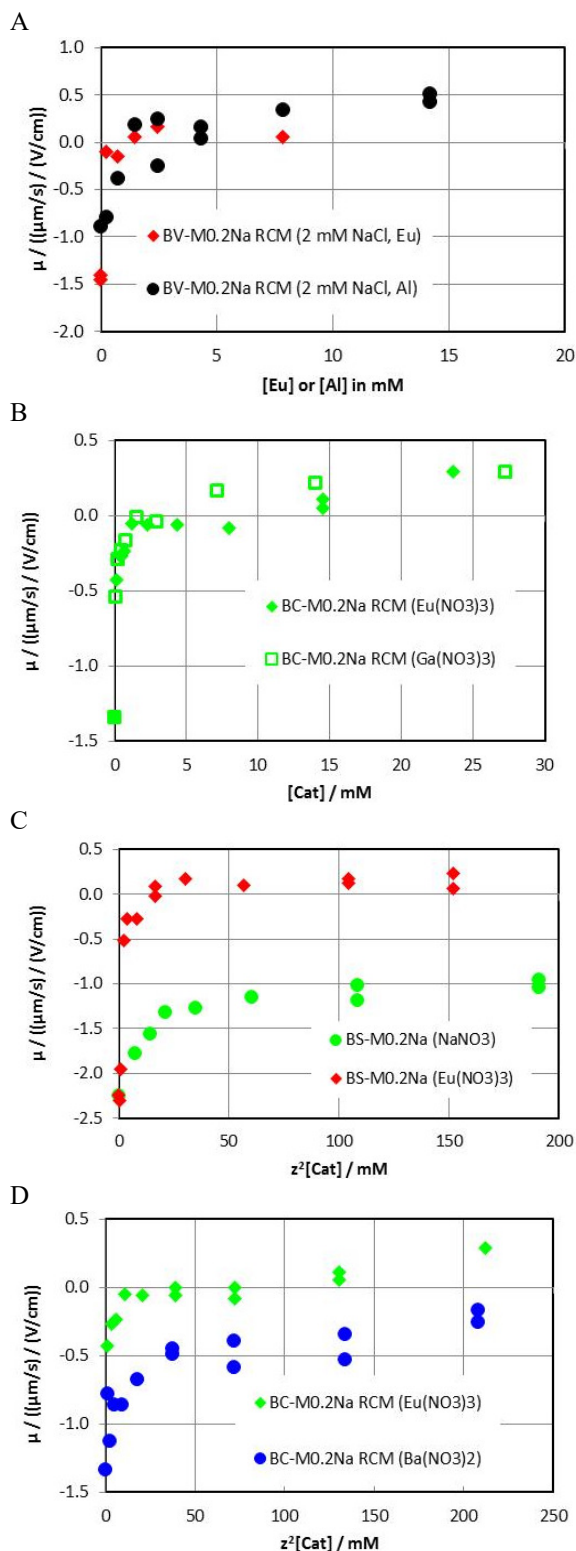


Fig. 3: Electrophoretic mobility of selected samples at pH about 2 starting from 2 mM monovalent salt as a function of concentration (A, B) or "effective" concentration (C, D). A and B: Effect of nature of trivalent cation. C and D: Effect of ion charge.

and morphological properties on the cation exchange behavior of dioctahedral smectites. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 481, 591-599.