

# An experimental study of the sorption of Nd and Eu on illite in KCl solutions at 25°C

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Owing to the simplicity afforded by simple oxides and oxyhydroxides, the determination of their acid-base surface and sorption properties have received considerably more attention relative to complex silicate minerals. But a thorough understanding of geochemical processes at the solution-mineral interface in soils and sedimentary environments also requires quantitative treatment of the surface chemistry of clay minerals. The objectives of this experimental investigation were to determine the acid-base surface chemistry of  $K^+$ -saturated Marblehead illite, and measure the sorption of Nd and Eu thereon at 25°C.

## Materials and methods

Marblehead illite (MH) was the solid used for all the titration and sorption experiments. All samples used

TABLE 1. Sorption of Nd and Eu on MH as a function of REE concentration ( $C_{REE}$ ) in 0.1 M KCl solution ( $pH = 4.35 \pm 0.15$ )

$C_{REE}$ (ppm)	% Nd sorbed ( $\pm 0.5$ )	% Eu sorbed ( $\pm 0.5$ )
19.8	14.6	
17.2		16.6
14.8	16.5	
12.6		15.6
9.7	17.0	
8.3		17.2
5.8	17.1	
5.1		19.3
2.8	18.0	
2.6		21.0
0.94	21.7	
0.89		26.1

in this study were pretreated as described by Aja (1989). The structural formula of the  $K^+$ -saturated sample is  $(K_{0.79}Na_{0.02})(Al_{1.43}Fe_{0.11}^{3+}Mg_{0.37}Ti_{0.08})(Si_{3.55}Al_{0.45})O_{10}(OH)_2$ . Its surface area was determined to be  $60.69 \text{ m}^2/\text{g}$  by BET-method. All other chemicals used were of reagent grade quality.

Potentiometric titration of MH were performed in aqueous KCl solutions (0.01, 0.1 and 1.0 M) using back-titration techniques (Fu *et al.*, 1991); the titrants were 0.07 M KOH and 0.07 M HCl. The suspensions were prepared by adding 0.16 g of MH to 100 ml of solution. Initially pH values of the samples were adjusted to 2.7 with 0.08 M HCl, then titrated to pH 10 with 0.07 M KOH. Titrant was added manually in a continuously stirred suspension (or solution). Equilibrium at solid-aqueous interface was presumed

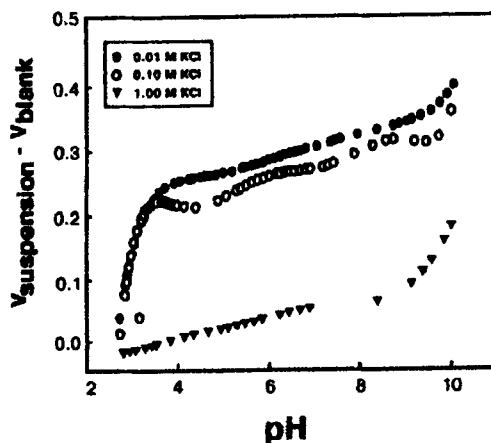


FIG. 1. Titration curves of MH in KCl solution of varying ionic strength.  $V_{\text{suspension}} - V_{\text{blank}}$  is the difference between volume of 0.07 M KOH added in 100 ml of MH suspension (1.6 g/l) and blank solution respectively to reach the measured pH values.

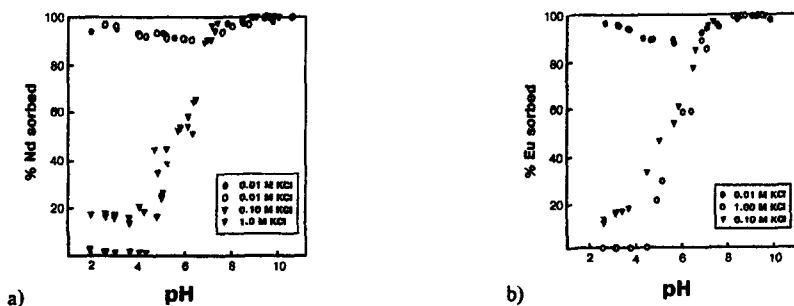


FIG. 2. Dependence of Nd (a) and Eu (b) sorbed on MH as a function of pH in suspension (6.7 g/l) at different ionic strengths. The initial concentration of REE in solution was 10 ppm.

when the pH changed by less than 0.01–0.02 unit per minute. Generally 1 to 5 minutes elapsed between successive additions of titrant which stabilizes pH readings.

The sorption experiments were conducted in 50 ml Oakridge centrifuge tubes. 15 ml of the starting solution and 0.1 g of the MH were introduced into the bottle, and the starting values of the pH measured. If needed, pH was adjusted by adding either 0.1 M HCl or 0.1 M KOH. The tightly sealed tubes were then shaken for 45 minutes and centrifuged for 15 minutes at 5200 rpm. The pH of the solution/suspension was measured and the reacted aqueous solution was extracted and filtered using a 20 ml syringe-filter assembly having a 0.22  $\mu\text{m}$  membrane. Analytical determination of REE concentration in the filtrate was conducted using a Perkin-Elmer OPTIMA 3000XL ICP-AES, in which the torch is viewed axially. An internal Gd standard was added to all samples. At least three emission lines were monitored and these were in agreement. The overall precision of the method is on the order of 5% and the limit of quantitation was 10–20  $\mu\text{g/l}$ . The pH and concentration dependencies of Nd and Eu sorption have been studied using this technique.

## Results and discussion

The results of titration experiments (Fig. 1) demonstrate sufficient differences between curves obtained at high and low ionic strength. The calculations on the basis of acid-base balance (Stumm and Morgan, 1981) have shown that proton surface charge density ( $\sigma_{\text{H}}$ ) is ionic strength-dependent; in 1.0 M KCl solutions,  $\sigma_{\text{H}}$  varies from 1500 to 1700  $\text{mC/m}^2$  whereas in 0.1 and 0.01 M KCl solutions it varies from 1800 to 2200  $\text{mC/m}^2$ . Furthermore, an isoelectric point is not defined by the  $\sigma_{\text{H}}$  vs pH curve.

The sorption of Nd and Eu exhibit similar concentration dependence at constant pH (Table 1). At high initial  $C_{\text{REE}}$  (10–20 ppm), the sorption of both elements is quite close (15–17%). With a decrease in  $C_{\text{REE}}$  ( $>5$  ppm), the sorption increases up to 22 and 26 % for Nd and Eu respectively.

The pH and ionic strength dependencies (Fig. 1) of Nd and Eu sorption in concentrated aqueous solutions (1 M KCl) approaches a sigmoid function. Under acidic conditions (pH < 4.3), REE sorption does not generally exceed 1.5% whereas at pH > 7.0, sorption is more than 90% complete. Sorption is complete (100%) at a pH  $\approx$  9.0. A similar trend also obtains for experiments conducted in 0.1 M KCl solutions. But by contrast to sorption in 1.0 M KCl solutions, up to 20% REE is sorbed at pH < 4.3. With a further decrease in ionic strength (0.01 M), the sorption curve changes dramatically; that is, REE sorption varies from about 92% (pH - 2-5), to slightly less than 90% (pH  $\approx$  5–7) and to  $\geq 92\%$  (pH > 7).

The results of MH titration as well as sorption experiments differ essentially from available data for oxide and simple silicate phases (e.g kaolinite). The theoretical explanation and thermodynamic evaluation of these results should be performed accounting that experimental range of  $\text{K}^+/\text{H}^+$  ratio in solution exceeds essentially the values corresponding stability field of MH (Aja, 1989).

## References

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