

EXCHANGE SELECTIVITY OF LANTHANIDE IONS IN MONTMORILLONITE

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ABSTRACT: The exchange of Ca^{2+} and Na^+ by lanthanide ions ($\text{Ln}^{3+} = \text{Pr}^{3+}, \text{Gd}^{3+}, \text{Er}^{3+}$) in montmorillonite was investigated at two different ionic strengths (0.01 and 0.1 mol/kg). Preferential sorption of Ln^{3+} was observed and variable selectivity coefficients were found depending upon the lanthanide concentration in the solid, and ionic strength. The highest exchange extent of Ln^{3+} always occurred for the system $\text{Na}^+/\text{Ln}^{3+}$, but the exchange selectivities of Ln^{3+} were generally higher in the exchange system $\text{Ca}^{2+}/\text{Ln}^{3+}$. Although the relative affinity of montmorillonite for the three lanthanide ions was similar, distinctive behaviour between Pr^{3+} and the heavier lanthanides, Gd^{3+} and Er^{3+} , was noted. The study of Ln^{3+} adsorption in trace amounts showed specific adsorption of lanthanides at high concentrations of Na^+ in the external solution and that the exchange stoichiometries in the interlayer regions were 3:1 at equilibrium pH = 4.

The interaction of lanthanide ions (Ln^{3+}) with clay minerals has been the subject of considerable study for purposes as varied as application to industrial catalytic processes (Shabtai, 1980), radioactive waste storage (Komarneni & White, 1983), and determination of origin of parent rocks (Steinberg & Courtois, 1976). All these processes involve ion-exchange reactions. Different aspects dealing with the ion-exchange of lanthanide ions in clays, such as factors influencing the exchange process (Bruque *et al.*, 1980; Olivera *et al.*, 1988) and exchange selectivity of these ions (Frysjer & Thomas, 1960; McBride, 1980; Olivera *et al.*, 1987) have been considered. All these studies indicated that the ion-exchange reactions are complex.

Whereas the hydrolysis of Ln^{3+} in clays is well established (Bruque *et al.*, 1980; Miller *et al.*, 1982; Laufer *et al.*, 1984; Olivera *et al.*, 1988), the available information on the selective sorption of Ln^{3+} by clays still remains scarce. Thus, the aim of this work was to contribute new data on the ion-exchange selectivity of Ln^{3+} in montmorillonite. Three lanthanide cations (Pr^{3+} , Gd^{3+} and Er^{3+}) were compared with Na^+ and Ca^{2+} and different equations are discussed.

EXPERIMENTAL

The montmorillonite used was from Tidinit, Morocco. After removal of carbonates and organic matter, the clay was saturated with Na^+ and the $<2 \mu\text{m}$ fraction of the resulting Na-mont. was used as starting material. The structural formula determined by chemical analysis was $(\text{Si}_{7.94}\text{Al}_{0.06})(\text{Al}_{2.90}\text{Fe}^{3+}_{0.2}\text{Mg}_{0.98})\text{O}_{20}(\text{OH})_4$. The cation exchange capacity

(CEC) of a Ca-exchanged sample was found to be 125 mEq/100 g on the basis of the weight of sample heated at 900°C.

Exchange selectivity

Two series of experiments were carried out:

(a) Na-mont. and Ca-mont. suspensions (0.5% each) were brought into contact with solutions of LnCl_3 ($\text{Ln} = \text{Pr, Gd and Er}$) containing between 3×10^{-4} and 6×10^{-3} mEq Ln^{3+}/l . The exchange isotherms were obtained at ionic strength (I) of 0.01 and 0.1 adjusted by addition of NaCl or CaCl_2 solutions, respectively. The final volume of the suspension was 25 ml.

(b) Na-mont. suspensions (0.5%) were brought into contact with mixed $\text{LnCl}_3/\text{NaCl}$ solutions containing 4×10^{-5} M Ln^{3+} and 0.04–0.64 M Na^+ . The final volume was 25 ml.

In both series of experiments, the exchange process was allowed to proceed for one day at 25°C and the pH of the equilibrated solutions was adjusted to ~ 4 in order to minimize hydrolysis of the lanthanides (Olivera *et al.*, 1988).

The selectivity coefficients were determined from series (a), while the distribution coefficients were obtained from series (b).

Analysis

Lanthanide ion contents in the equilibrium solutions were determined spectrophotometrically with Arsenazo III following the analytical procedure of Goryushina *et al.* (1963). The activity coefficients of the dissolved ions were computed from the Pitzer-Brewer equation (Pitzer & Brewer, 1961).

RESULTS AND DISCUSSION

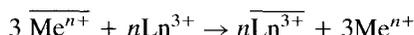
The exchange of Me^{n+} ($\text{Me} = \text{Na, Ca}$) by Ln^{3+} takes place according to the following equation:



where bars denote adsorbed ions. This reaction has a corresponding selectivity coefficient which is given by

$$K_{\text{Me}}^{\text{Ln}} = \frac{[\overline{\text{Ln}^{3+}}]^n (\text{Me}^{n+})^3}{[\overline{\text{Me}^{n+}}]^3 (\text{Ln}^{3+})^n}$$

where the concentrations of the adsorbed species are measured by the equivalent fractions in solid and those of the dissolved species are the ion activities in solution. In order to minimize the effect of hydrolysis of the lanthanide cations on the ion-exchange process, reactions were run in the following direction (Olivera *et al.*, 1987):



Figs. 1–3 show the isotherms of $\text{Na}^+/\text{Ln}^{3+}$ and $\text{Ca}^{2+}/\text{Ln}^{3+}$ exchange obtained at two difference excess concentrations of NaCl and CaCl_2 . As expected, Ca^{2+} competed more effectively for exchange sites than did Na^+ . The differences in the degree of occupation by

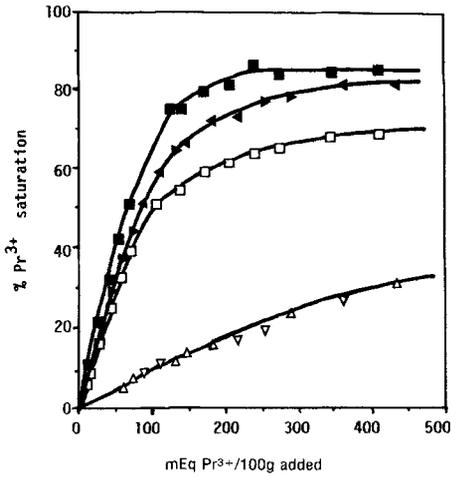


FIG. 1. Exchange isotherms for Pr^{3+} adsorption on homoionic montmorillonite at two ionic strengths (I_{NaCl} ■ 0.01 and □ 0.1; I_{CaCl_2} ▲ 0.01 and △ 0.1).

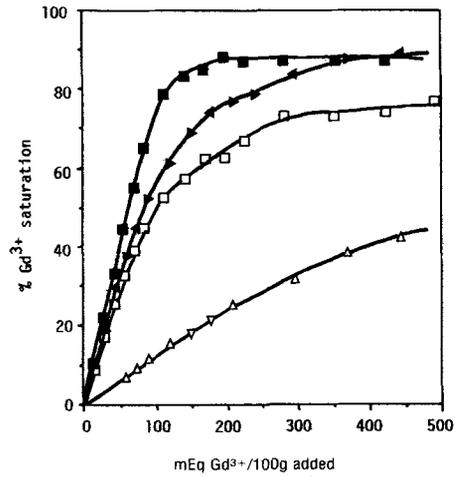


FIG. 2. Exchange isotherms for Gd^{3+} adsorption on homoionic montmorillonite at two ionic strengths (I_{NaCl} ■ 0.01 and □ 0.1; I_{CaCl_2} ▲ 0.01 and △ 0.1).

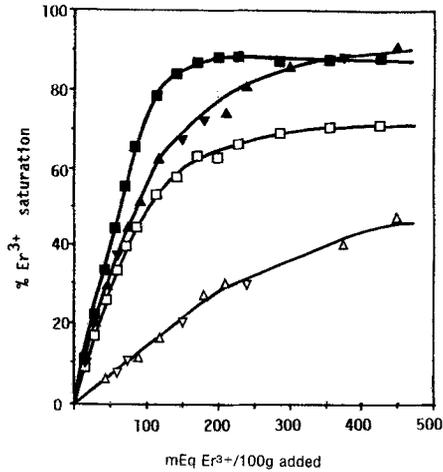


FIG. 3. Exchange isotherms for Er^{3+} adsorption on homoionic montmorillonite at two ionic strengths (I_{NaCl} ■ 0.01 and □ 0.1; I_{CaCl_2} ▲ 0.01 and △ 0.1).

the three different Ln^{3+} cations were more marked for the $\text{Ca}^{2+}/\text{Ln}^{3+}$ system than for the $\text{Na}^+/\text{Ln}^{3+}$ system and always increased in the following order: $\text{Pr} < \text{Gd} < \text{Er}$. These curves reflect a similar behaviour to that observed in vermiculite at a lower ionic strength (Olivera *et al.*, 1987).

Retention decreased with increasing ionic strength. At low exchange levels and low ionic strength range, occupation of the exchange sites increased very rapidly but the plateau of the curve was reached before complete saturation (*ca.* 80–90%). At $I = 0.1$ and under the experimental conditions employed, the degree of lanthanide occupation was only 60–70% for the $\text{Na}^+/\text{Ln}^{3+}$ exchange and 30–45% for the $\text{Ca}^{2+}/\text{Ln}^{3+}$ exchange. In any case the

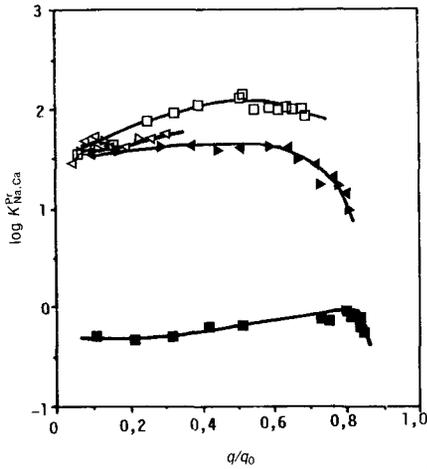


FIG. 4. Variation of the selectivity coefficient K_{Me}^{Pr} with surface composition at two ionic strengths (I_{NaCl} ■ 0.01 and □ 0.1; I_{CaCl_2} ▲ 0.01 and △ 0.1).

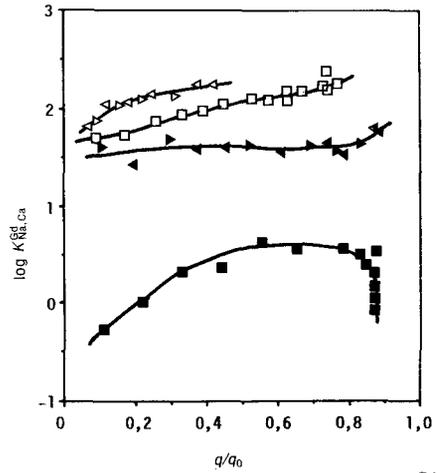


FIG. 5. Variation of the selectivity coefficient K_{Me}^{Gd} with surface composition at two ionic strengths (I_{NaCl} ■ 0.01 and □ 0.1; I_{CaCl_2} ▲ 0.01 and △ 0.1).

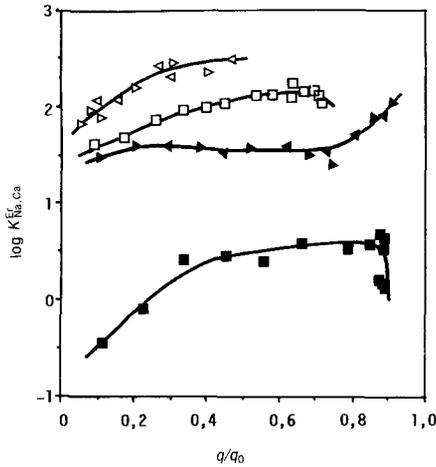


FIG. 6. Variation of the selectivity coefficient K_{Me}^{Er} with surface composition at two ionic strengths (I_{NaCl} ■ 0.01 and □ 0.1; I_{CaCl_2} ▲ 0.01 and △ 0.1).

differences between the lanthanide cation studied were less significant than those observed in vermiculite, a clay mineral with a higher charge density and stronger charge localization.

The relationships between the selectivity coefficients and the fraction of Ln^{3+} occupied sites (q/q_0) are shown in Figs. 4–6. The higher the equilibrium concentration of Na^+ (or Ca^{2+}), the larger and the less markedly dependent on the concentration were the K_{Me}^{Ln} values, consistent with previous findings for ion-exchange processes involving trivalent lanthanide cations (McBride, 1980; Olivera *et al.*, 1987). Such a dependency was more marked for the Na^+/Ln^{3+} system than for the Ca^{2+}/Ln^{3+} system, thus indicating that the mass action equation was obeyed more strictly by the latter system than by the former.

With the Na^+/Ln^{3+} system at $I = 0.01$, the preference of montmorillonite for Ln^{3+}

increased with the relative concentration of this lanthanide ion in the solid and then decreased at $q/q_0 = 0.8$. This behaviour has been observed in other exchange systems involving lanthanides in montmorillonite (Frysjer & Thomas, 1960) and vermiculite (Olivera *et al.*, 1987). Different variation of the selectivity for Ln^{3+} is found at $I = 0.1$.

The other exchange system studied, $\text{Ca}^{2+}/\text{Ln}^{3+}$, showed differences in the behaviour of Pr^{3+} and the other two heavier lanthanide cations. The $K_{\text{Me}}^{\text{Ln}}$ values of the last two remained constant or increased at high exchange levels, in clear contrast with $K_{\text{Me}}^{\text{Pr}}$, which decreased in the same conditions. These results clearly show the dependency of the selectivity coefficients on the ionic strength and the ionic interlayer composition.

McBride & Bloom (1977) developed a Langmuir-type equation as an alternative to the mass action equation that takes no account of the dissolved counterion concentration:

$$(M^{3+}) = K \left(\frac{\theta}{1 - \theta} \right)^n$$

where the activity of M^{3+} in solution is a function of the equivalent fraction of this ion in the solid, $\theta = q/q_0$.

Figs. 7–9 show the plots of $\log[\theta/(1 - \theta)]$ vs. $\log[\text{Ln}^{3+}]$ for the $\text{Na}^+/\text{Ln}^{3+}$ and $\text{Ca}^{2+}/\text{Ln}^{3+}$ exchange systems. As can be seen, the experimental data conform to the McBride-Bloom (1977) equation. The values of the constants in the McBride-Bloom equation are listed in Table 1. They depend on the particular counterion and ionic strength used, but there are no large differences between the three lanthanide ions in each exchange system. However, there are significant differences between the $\text{Na}^+/\text{Ln}^{3+}$ and $\text{Ca}^{2+}/\text{Ln}^{3+}$ systems.

For a given amount of adsorbed Ln^{3+} , the larger n is, and the higher is the Ln^{3+} concentration remaining in solution. Therefore, the n values obtained suggest that Ca-mont. has a greater affinity for the lanthanide ions than does Na-mont. at the two ionic strengths assayed.

The results obtained for the $\text{Ca}^{2+}/\text{Ln}^{3+}$ system conform to the McBride-Bloom equation quite well throughout the range of ionic composition of the exchanger studied at the two ionic strengths used, with $n \approx 1$. This function, with $n = 1$, is also descriptive of the adsorption of Ln^{3+} and Al^{3+} by Ca-mont. in 0.01 M CaCl_2 (McBride, 1980), thereby indicating that the lanthanide cations are adsorbed with a similar affinity over the ionic strength range 0.01–0.1. However, the initial and final points in the plots of the $\text{Na}^+/\text{Ln}^{3+}$ system usually deviate from a straight line, which is consistent with the fact that the selectivity constants are smaller at both low and high Ln^{3+} adsorption levels. Such behaviour was also observed in the exchange of lanthanide ions in Mg-vermiculite (Olivera *et al.*, 1987).

The layers of Na-mont. are known to be completely dispersed in water; also, a diffuse ionic bilayer surrounding the colloid particles can remain stable at low ionic strengths. However, for a lanthanide-montmorillonite with a composition (q/q_0) of only 0.50, the distance between individual layers is much shorter ($d_{002} = 14.5 \text{ \AA}$). This value should be close to that expected in an aqueous suspension as small amounts of adsorbed Ln^{3+} would favour the immediate tactoid formation of the dispersed clay layers (Banin, 1968). Above this occupation level, the basal spacing (d_{002}) does not change significantly and is $\sim 15 \text{ \AA}$ at the highest level of lanthanide occupation in montmorillonite, with no significant differences between the three Ln^{3+} ions in this respect. Therefore, the interlayer spacing in montmorillonite undergoes a major change in the $\text{Na}^+/\text{Ln}^{3+}$ exchange process. On the other hand, the variation of the said interlayer spacing of montmorillonite as a result of the

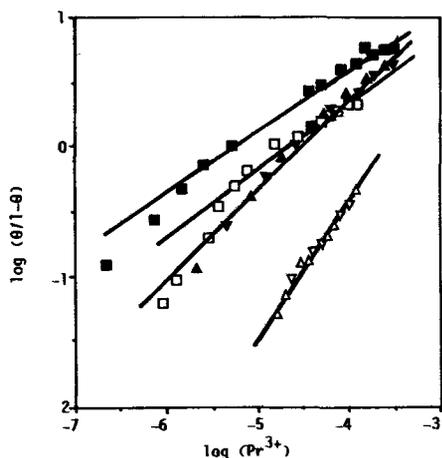


FIG. 7. Relationship between the Pr^{3+} adsorption function $(\theta/1-\theta)$ and the solution of Pr^{3+} at two ionic strengths (I_{NaCl} ■ 0.01 and □ 0.1; I_{CaCl_2} ▲ 0.01 and △ 0.1).

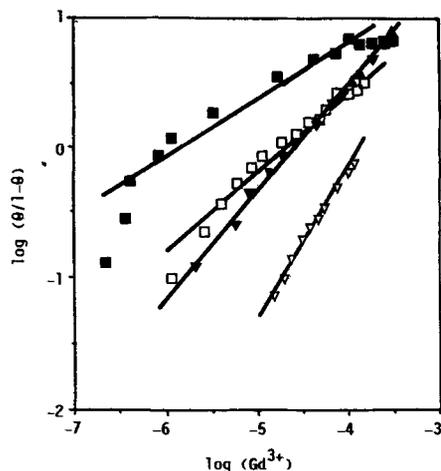


FIG. 8. Relationship between the Gd^{3+} adsorption function $(\theta/1-\theta)$ and the solution of Pr^{3+} at two ionic strengths (I_{NaCl} ■ 0.01 and □ 0.1; I_{CaCl_2} ▲ 0.01 and △ 0.1).

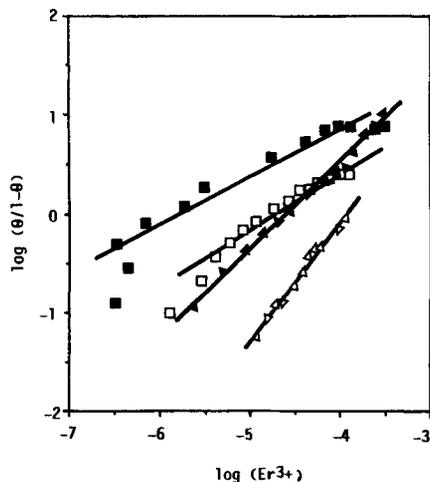


FIG. 9. Relationship between the Er^{3+} adsorption function $(\theta/1-\theta)$ and the solution of Er^{3+} at two ionic strengths (I_{NaCl} ■ 0.01 and □ 0.1; I_{CaCl_2} ▲ 0.01 and △ 0.1).

$\text{Ca}^{2+}/\text{Ln}^{3+}$ exchange is only 0.6 Å throughout the range of ionic composition of the interlayer (d_{002} is 14.5 Å for Ca-mont. and 15.1 Å for Ca-Ln-mont.).

These results suggest that the interlayer regions of tactoids prefer trivalent to univalent and divalent ions over a wide range of ionic composition, consistent with other previously reported results and theoretical calculations (McBride, 1980; Shainberg & Kemper, 1966). Increasing ionic strengths favour the formation of tactoids at smaller θ values, which in turn increases the selectivity of Na-mont. at $I = 0.1$. However, at high exchange levels, the affinity of a montmorillonite with a high charge density for lanthanide cations should be

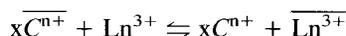
TABLE 1. Values of Langmuir constants for Ln³⁺ adsorption in Na- and Ca-montmorillonites.

| | Ionic strength <i>I</i> | Pr ³⁺ | | Gd ³⁺ | | Er ³⁺ | |
|------------------------------------|----------------------------|------------------|---------------------------|------------------|---------------------------|------------------|---------------------------|
| | | <i>n</i> | <i>K</i> .10 ⁵ | <i>n</i> | <i>K</i> .10 ⁵ | <i>n</i> | <i>K</i> .10 ⁵ |
| Na ⁺ /Ln ³⁺ | 0.01 | 1.9 | 0.7 | 2.1 | 0.2 | 2.0 | 0.2 |
| | 0.10 | 1.3 | 2.4 | 1.5 | 2.0 | 1.5 | 2.1 |
| Ca ²⁺ /Ln ³⁺ | 0.01 | 1.4 | 2.9 | 1.2 | 2.6 | 1.2 | 2.6 |
| | 0.10 | 1.0 | 26.4 | 0.9 | 15.0 | 0.8 | 12.0 |

lower as a result of the difficulty for a trivalent ion surrounded by a large hydration sphere to effectively neutralize the negative charge of the layer. This may account for the sharp decrease in the selectivity coefficients observed at $q/q_0 \approx 0.8$ in the Na⁺/Ln³⁺ system, even though the entropy changes related to the arrangement of water and interlayer ions may also play a major role in the selective sorption of Ln³⁺ by clays (McBride, 1979, 1980; Marshall, 1964).

DISTRIBUTION COEFFICIENTS

The adsorption of trace amounts of Ln³⁺ from mixed solutions containing an excess of NaCl was studied in order to determine the ion-exchange stoichiometry and the adsorption limits of Ln³⁺.



the equilibrium constant of which is:

$$K = \frac{[\overline{Ln^{3+}}](C^{n+})^x}{[Ln^{3+}](\overline{C^{n+}})^x}$$

where *K* is the apparent equilibrium constant and the concentrations of the adsorbed and dissolved species are given in mol/g and mol/l, respectively.

The distribution coefficient of Ln³⁺ is given by

$$D = \frac{[\overline{Ln^{3+}}]}{[Ln^{3+}]}$$

Therefore, *D* is directly proportional to the amount of Ln³⁺ extracted from the solution on addition of the exchange ion. Under the working conditions used where trace amounts of Ln³⁺ replace trace amounts of interlayer ions, the concentration of Cⁿ⁺ in montmorillonite can be considered to be constant and equal to the exchange capacity of the mineral, *q*₀, so

$$\log D = \log(q_0^x K) - x \log [C^{n+}]$$

where log *D* is directly proportional to log [Cⁿ⁺].

Fig. 10 shows the variation of *D* as a function of [Na⁺] in the external solution, for the three Ln³⁺ ions studied. Two distinct regions are apparent in these curves. At low Na⁺ concentration, log *D* decreases linearly with the concentration of the external solution. A second region of the curve is apparent at Na⁺ concentration >0.2 M. In this region the adsorption of Ln³⁺ is constant and specific for each lanthanide ion, increasing with the ionic

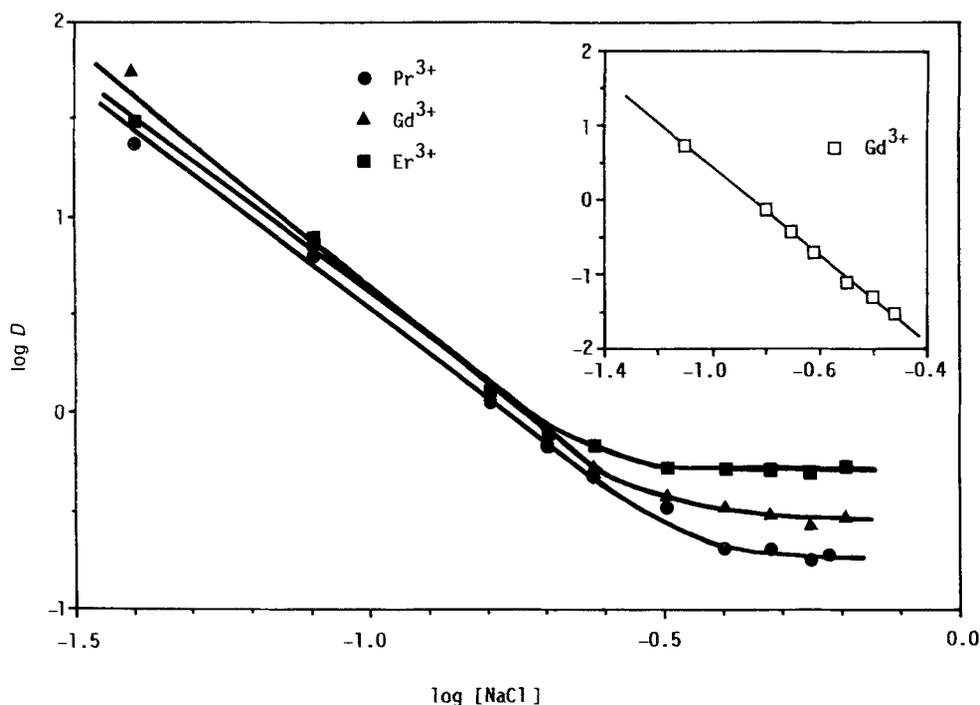


Fig. 10. Variation of the distribution coefficient, D of Pr^{3+} , Gd^{3+} , and Er^{3+} in montmorillonite as a function of the NaCl concentration in the external solution. In the inset, corrected values of $\log D$ for Gd^{3+} are plotted.

potential through the lanthanide series: $\text{Pr} < \text{Gd} < \text{Er}$. In these conditions, the concentration of Na^+ is high enough to impede the interlayer adsorption of Ln^{3+} , and thus the most energetic negative charge site would be responsible for this specific adsorption of Ln^{3+} at high levels of Na^+ in solution. Specific adsorption of metal transition cations has already been described for other exchange systems in montmorillonite (Tiller & Hodgson, 1962).

When the corrected values of D (obtained by subtracting the asymptotic values of the curves from the experimental ones) are plotted against the concentration of Na^+ in solution, the slopes found were: -2.92 , -2.96 , -2.94 for Pr^{3+} , Gd^{3+} and Er^{3+} , respectively, indicating that the exchange stoichiometry was 3Na^+ for Ln^{3+} in the interlayer region; therefore, under the experimental conditions employed the hydrolysis of Ln^{3+} did not occur. A stoichiometry close to the theoretical value was found by Bonnot-Courtois & Jaffrezic-Renault (1982) for $\text{Na}^+/\text{Ln}^{3+}$ exchange in a montmorillonite with particle size $< 35 \mu\text{m}$.

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