

FACTORS INFLUENCING RETENTION OF LANTHANIDE IONS BY MONTMORILLONITE

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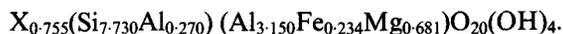
ABSTRACT: A method for the preparation of Ln-montmorillonite (Ln = La, Ce, Sm, Gd, Er and Y) that ensures saturation of the CEC is described and the most favourable equilibrium conditions are discussed. The H^+ - Ln^{3+} exchange rate in acid montmorillonite and the effect of concentration and pH on the retention of Ln^{3+} ions by the clay are also investigated. The presence of montmorillonite modifies the pH value at which precipitation of hydroxides begins, a process that actually occurs at $pH \sim 5$.

The lanthanide elements have only rarely been studied as exchange cations on montmorillonites. Published papers have described the thermodynamics of the Y-Cs, Ce-Cs ionic exchange (Fryssinger & Thomas, 1960), the retention-adsorption of traces of La^{3+} and the thermodynamic selectivity of adsorption of La^{3+} , Dy^{3+} , Ho^{3+} and Yb^{3+} ions on clays (Aagaard, 1974).

The present paper describes a preparative method for Ln-montmorillonite that ensures complete saturation of the CEC by Ln^{3+} ions (Ln = La, Ce, Sm, Gd, Er and Y). The most favourable equilibrium conditions, as well as the factors that affect the retention of the Ln^{3+} ions by montmorillonite, are described.

MATERIALS AND METHODS

The montmorillonite used came from the La Serrata Bed, Almeria. Its structural formula is (Martin Vivaldi & Linares Gonzalez, 1968):



In its natural state the principal exchange cation is Mg^{2+} , the clay having a total CEC of 97.6 mEq/100 g (based on the weight of sample heated at 900°C).

The original montmorillonite was treated for several hours with hydrogen peroxide at 80°C and dried over a steam bath. It was then re-suspended and saturated with Na using a 1 N solution of NaCl. The Na-sample was centrifuged at 1600 rpm for 10 min. and material remaining in suspension ($\leq 1 \mu m$ e.s.d.) extracted. This was washed twice in 2 N NaCl-0.1 N HCl solution, a further two times with 2 N NaCl solution and, finally, with deionized water to peptization. This Na-montmorillonite was used as starting material for preparation of the H-montmorillonite and subsequent products.

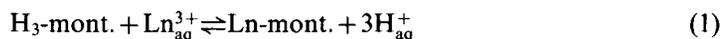
The acid montmorillonite was prepared with Dowex 50-WX-8 resin (Aldrich & Buchanan, 1958). The resulting H-montmorillonite was used immediately, being added dropwise to solutions of lanthanide salts in nitrate form.

The Ln^{3+} ions were determined complexometrically (Schwarzenbach, 1959; Woyski & Harris, 1963; Busev *et al.*, 1970), using EDTA and Solochrome Black as indicator for La, Ce and Sm, and Xilenol Orange for Gd, Er and Y.

EXPERIMENTAL RESULTS AND DISCUSSION

H^+ - Ln^{3+} ionic exchange

The apparent rate of the H^+ - Ln^{3+} ionic exchange ($\text{Ln} = \text{La}$, Ce, Sm, and Er) was studied in acid montmorillonite at 20°C with simultaneous measurements of the conductivity and the pH as a function of time. The exchange reaction is:



As reaction (1) advances, the number of H_{aq}^+ ions increases and consequently the pH falls and the specific conductivity rises. The experimental procedure was as follows. 100 ml of 1.5–2% suspension of H-montmorillonite and a 0.2 M solution of Ln^{3+} containing 1 symmetry (1 symmetry addition, S, is equivalent to 97.6 mEq/100 g of montmorillonite) were mixed. The conductivity and the pH were both measured at 1 min intervals after shaking. Figs 1 & 2 show the results obtained for the different ions. The ionic exchange process takes place almost instantaneously in all cases, from which it could be inferred that the affinity of the montmorillonite for the Ln^{3+} ions is much greater than its protonic affinity (Fig. 4 appears to confirm this assumption).

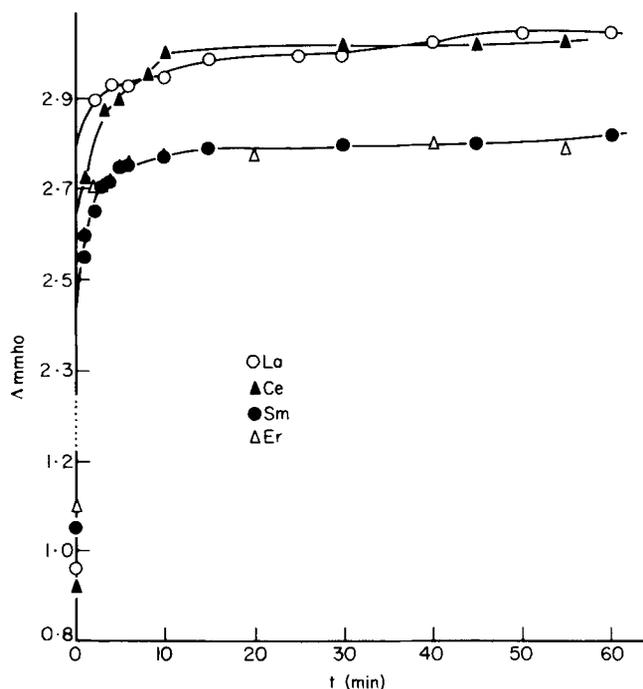


FIG. 1. Variation of conductivity as a function of time for the reaction:
 $\text{H}_3\text{-mont} + \text{Ln}_{\text{aq}}^{3+} \rightleftharpoons \text{Ln-mont} + 3\text{H}_{\text{aq}}^+$

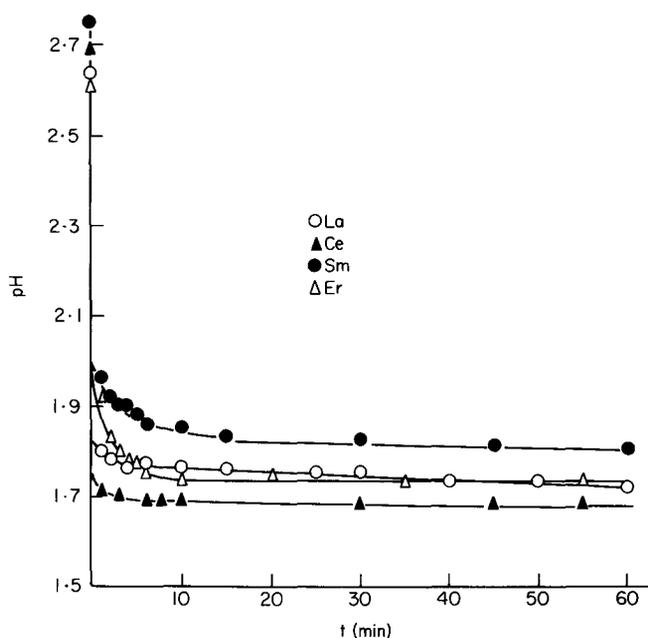


FIG. 2. Variation of pH as a function of time for the reaction:

$$\text{H}_3\text{-mont} + \text{Ln}_{\text{aq}}^{3+} \rightleftharpoons \text{Ln-mont} + 3 \text{H}_{\text{aq}}^+$$

In experiments with the different ions, it was observed that shaking the suspension of 1% H-montmorillonite and the solution of Ln^{3+} salt for 5 min lead to the same retention of Ln^{3+} as shaking for 3 h. As both the pH and the conductivity remained constant after shaking solutions of Ln^{3+} with H-montmorillonite suspension (Figs 1 & 2), it was thought that a 'titration' of the latter was possible using solutions of lanthanide salt. Experiments were thus carried out (Fig. 3) in which the variation of the equilibrium pH resulting from dropwise addition of 0.1 M solution of $\text{La}_{\text{aq}}^{3+}$ to a 1% suspension of H-montmorillonite was measured. It was found that the pH eventually stabilized, i.e. equation (1) reached equilibrium when only 80% of the exchange capacity of the montmorillonite was saturated. Addition of a slight excess of La^{3+} once the pH curve became asymptotic (Fig. 3) did not modify the pH or augment the retention of La^{3+} by the montmorillonite. It thus appeared as if the exchange process ceased once 80% of the exchange capacity was saturated.

Effects of concentration

Fig. 4 illustrates the general features of Ln^{3+} retention in relation to concentration of nitrate salts added to H-montmorillonite. The other ions showed similar behaviour. From this it may be deduced that the affinity of montmorillonite for Ln^{3+} ions is much greater than its protonic affinity. With 1 S input the following equilibrium was obtained: 0.2 S in solution and 0.8 S in montmorillonite. 0.8 S in montmorillonite represents an 80% CEC saturation by La^{3+} ion. Fig. 4 shows that 18 S are necessary to reach CEC saturation. This relationship is different from that described in the literature (e.g. Bingham *et al.*, 1964). The existence of a step zone at higher symmetry additions is due to exchangeable Al^{3+}

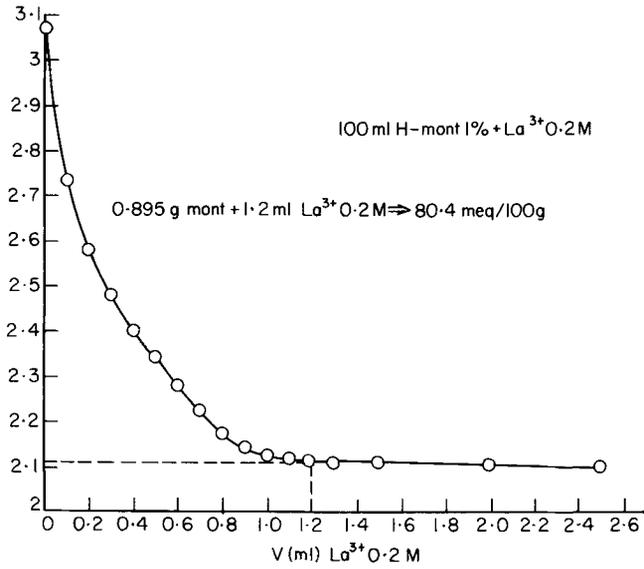


FIG. 3. Variation in pH following the addition of successive amounts of 0.2 M La^{3+} .

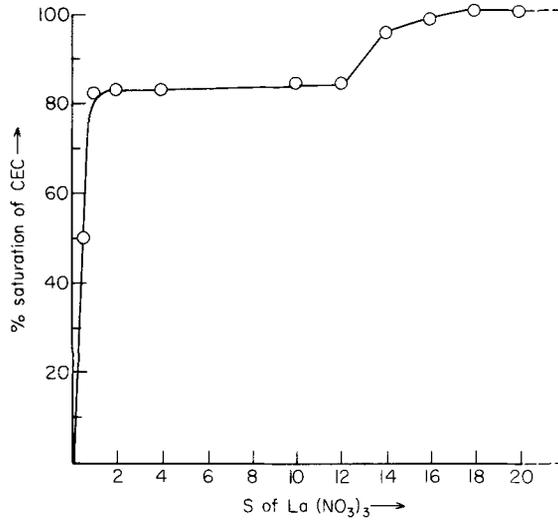
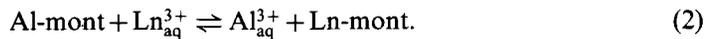


FIG. 4. Percentage saturation of the CEC as a function of added symmetries of La^{3+} .

which occurs in all acid montmorillonites from the partial destruction of the silicate framework.

The presence of Al^{3+} implies the existence of a new equilibrium that is produced simultaneously to the one expressed in equation (1):



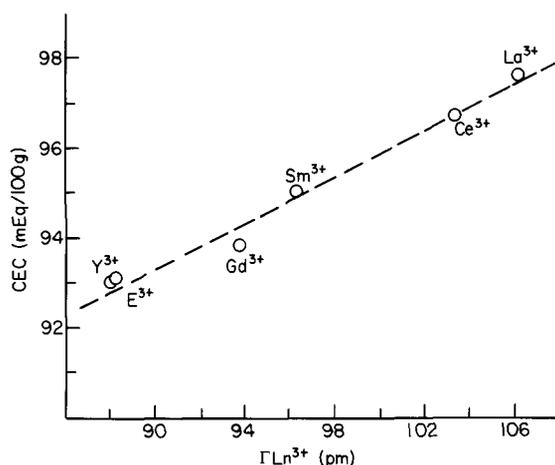


FIG. 5. Retention of Ln^{3+} as a function of Ln^{3+} crystalline ionic radii.

This reaction is less displaced towards the right than reaction (1) due to the competition between ions of the same charge.

As equation (1) progresses, a strongly acid medium which favours the production of Al^{3+} is produced. If this acid medium is removed, CEC saturation is achieved with 7–10 S. The exact procedure used is as follows. Lanthanide salt equivalent to 2 S was added to a 1% suspension of H-montmorillonite. This was shaken for 20 min, centrifuged at 8000 rpm, and the supernatant acid removed. The sediment was re-suspended in a solution of Ln^{3+} containing 5–8 S and with a pH of 5. After washing to eliminate excess nitrate, a homoionic montmorillonite with 100% of the CEC saturated with exchangeable Ln^{3+} was produced.

Retention of the various Ln^{3+} ions by H-montmorillonite was studied by adding equivalent amounts of the different salts to suspensions of the H-clay. On adding 2 and 20 S of each salt to a 1% suspension of H-montmorillonite it was found that, for both symmetry additions, the amount of Ln^{3+} retained was directly proportional to the crystallographic radius of the ion (Fig. 5). From this it may be inferred that the ions of smaller hydrated radius are retained to a larger degree or, alternatively, the retention process is directly related to the ionic potential of the hydrated species.

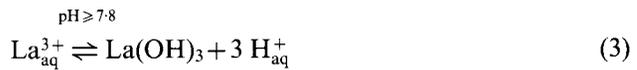
Effects of pH

The relationship between Ln^{3+} retention and the pH of the solution at equilibrium with the clay was studied. For this purpose neutral or slightly acid solutions of lanthanide salts (pH = 6–7.5) were used. Once the salt-free homoionic montmorillonite was obtained, the Ln^{3+} was extracted with acidified 2 M KCl solution (pH = 2.5) to dissolve hydroxides possibly formed with the medium used in preparation of the samples. Results are listed in Table 1. As may be seen from this Table, as the pH increases Ln^{3+} ions are retained in excess of the exchange capacity. This behaviour has been observed previously by several authors (Bingham *et al.*, 1964; Maes *et al.*, 1975) for divalent ions. Maes *et al.* (1975) found a linear relationship between the pH of the equilibrium solution and the CEC. Bingham *et al.* (1964) concluded that increase in retention was due to hydroxide precipi-

TABLE 1. Effect of pH on La³⁺ retention by H-montmorillonite (20 S added in all cases).

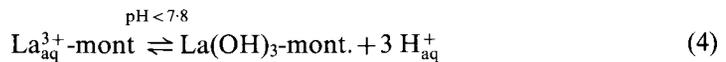
Equilibrium pH H-mont + La _{aq} ³⁺	La ³⁺ retention (mEq/100 g)	% of C.E.C.
7.5	142.0	146
6.7	125.7	129
2.6	97.5	100

tation. To date, no conclusive explanation has been found in the literature for the precipitation of hydroxides at pH values lower than the initial ones of the precipitation in aqueous solution in the absence of clay. If hydroxide precipitation occurs, hydrolysis of the hydrated Ln³⁺ ion must take place, i.e.



In the present experiments the existence of hydrolysis was proved by the drop in pH when a solution of La(NO₃)₃ (pH = 6.3) was added to 1% Na-montmorillonite suspension (pH = 7.6). The pH fell to 4.8, and remained at this value for 12 h at constant temperature.

The presence of montmorillonite modifies the pH value at which the reaction shown in equation (3) occurs. Precipitation commences at a lower pH (~5), i.e.



This is supported by an intuitive model that considers the structure of the montmorillonite as the determining cause. In this model the Ln_{aq}³⁺ cation is placed between the layers at points where there is excess negative charge, which subjects the water molecules directly coordinated to Ln³⁺ to a very intense electric field, especially those located between the layer and the cation. Under these conditions some water molecules dissociate, yielding OH⁻ and H⁺. Hydroxides precipitate and H_{aq}⁺ ions appear in the exchange positions; these in turn are displaced by the Ln_{aq}³⁺ ions in excess. The process stops when the medium becomes more acid.

CONCLUSIONS

The most important factors influencing H⁺-Ln³⁺ ionic exchange and saturation of the CEC of montmorillonite in aqueous medium have been established.

1. *Exchange rate.* This depends principally on the species to be exchanged. The reaction is instantaneous in the H-Ln exchange but seems to be slower for Al-Ln exchange. Temperature is not an important factor since experiments at 10, 20 and 40°C gave identical results as far as the exchange rate and retention of ions was concerned.

2. *Concentration.* This is an important factor due to the presence of exchangeable Al³⁺ on exchange sites of H-montmorillonite. Concentrations equivalent to 20 S (20 times the amount of exchange cations) must be used to displace other cations at the exchange sites of the clay and replace them by Ln³⁺.

TABLE 2. Ln³⁺ ions retained by montmorillonite in homoionic samples expressed in mEq/100 g clay.

Ion	Ln ³⁺ retained		Ionic crystallographic radius (picometers)
	total	Ln ³⁺ exch.	
La ³⁺	98.0	97.5	106.1
Ce ³⁺	97.6	96.7	103.4
Sm ³⁺	97.0	95.0	96.4
Gd ³⁺	94.3	93.8	93.8
Er ³⁺	93.1	93.0	88.1
Y ³⁺	93.0	93.0	88.0

3. *Acidity of the medium.* This is the most important factor. At low pH values (~ 2), aluminization occurs and this increases if the acid medium persists. At pH values > 5 , even though aluminization is stopped, lanthanide hydroxide precipitates, causing abnormally high retention of Ln³⁺ by the clay (Table 1). By careful control of the exchange pH in the 4–5 zone aluminization is halted and the concentration needed for the exchange solution is lowered. Under these conditions addition of 5 S is enough for saturation of the exchange capacity.

4. *Nature of the exchange ion.* Its influence is determined by the precipitation pH of its hydroxide and the size of the ion. As the crystallographic radius diminishes the ions are more acid and precipitate at lower pH values. The fact (Table 2) that retention of Ln³⁺ ions is of the same order when the same number of symmetries of lanthanide salt are used at the same exchange pH (4.8) indicates that the possible presence of LnOH²⁺ and Ln(OH)₂⁺ species must be rejected, since their formation is favoured for the more acid ions (Baes & Mesmer 1976). Likewise, retention of Ln³⁺ diminishes slightly (to 4.5% less than the CEC) as the ionic radii diminish, while if the above hydroxyl species existed the opposite would occur. The fact that the maximum retention of Er³⁺ and Y³⁺ ions is ~ 93 mEq/100 g (Table 2) when 20 S are used seems to indicate the presence in the montmorillonite of sites of little accessibility for hydrated ions of large size.

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RÉSUMÉ: On décrit une méthode de préparation de montmorillonite-Ln (Ln = La, Ce, Sm, Gd, Er et Y) qui permet de saturer la CEC; on discute les conditions d'équilibre les plus favorables. On a aussi étudié les vitesses d'échange $H^+ - Ln^{3+}$ dans le cas de la montmorillonite acide, l'effet de la concentration et du pH sur la fixation des ions Ln^{3+} dans l'argile. Le présence de la montmorillonite modifie la valeur du pH de début de précipitation des hydroxides, processus qui a lieu effectivement vers pH 5.

KURZREFERAT: Es wird eine Methode für die Präparation von Ln-Montmorillonite (Ln = La, Ce, Sm, Gd, Er und Y) beschrieben, die die Sättigung des CEC garantiert und die günstigsten Gleichgewichtsbedingungen werden diskutiert. Die $H^+ - Ln^{3+}$ Austauschrate in saurem Montmorillonit und der Einfluß der Konzentration und des pH-Wertes auf die Einbehaltung von Ln^{3+} -Ionen durch den Ton wurden ebenfalls untersucht.

Durch die Gegenwart von Montmorillonit wird der pH-Wert, bei dem die Ausfällung von Hydroxiden beginnt, verändert. Eigentlich sollte dieser Prozeß bei pH ~ 5 stattfinden.

RESUMEN: Se propone un método de preparación de Ln-Mont (Ln = La, Ce, Sm, Gd, Er e Y) que asegura la saturación de la capacidad de cambio de la arcilla, investigando las condiciones de equilibrio favorables a ello. Así mismo se estudia la velocidad de cambio $H^+ - Ln^{3+}$ en montmorillonita ácida y el efecto de la concentración y del pH sobre la retención de los iones Ln^{3+} por montmorillonita. La presencia de montmorillonita modifica el valor del pH al cual tiene lugar el inicio de la precipitación de hidróxidos, verificandose ésta a pH ~ 5.