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SORPTION OF EUROPIUM(III) AND IRON(III) IN IONIC AND COLLOIDAL STATES ON SILICA GEL

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SUMMARY

The sorption of europium(III) and iron(III) in colloidal and ionic states on silica gel has been studied as a function of the pH of aqueous solutions by batch equilibrations. The behaviour of Eu^{3+} , colloidal Eu(III) , Fe^{3+} and colloidal Fe(III) on the silica gel column has also been investigated. Conditions for the sorption of europium and iron from aqueous solutions are given.

INTRODUCTION

Many papers have dealt with the use of metal oxides as sorbents for the isolation of radionuclides in ionic and colloidal states from aqueous solutions^{1–6}. In previous work the sorption of trivalent iron³ and europium⁵ in colloidal states on manganese dioxide, and the sorption of colloidal trivalent iron on alumina⁴ and iron(III) oxide⁶ from aqueous solutions was studied as a function of pH. The results obtained show that sorption is predominantly determined by the sign of the surface charge of the colloidal particles and the sorbent. As the sign of the surface charge of hydrated oxides depends on the pH of the solutions, the sorption of colloidal particles also depends on pH.

The object of this work was to obtain information on the sorption of Fe(III) and Eu(III) in ionic and colloidal states on silica gel and to define conditions for the sorption of europium and iron from aqueous solutions.

EXPERIMENTAL

Silica gel “for column chromatography” (0.2–0.5 mm) (Merck, Darmstadt, F.R.G.) was used. The silica gel was separated from powder by several decantations with water, treated with 1:1 hydrochloric acid, washed with distilled water and dried for 10 h at 110°C.

Solutions of colloidal Eu(III) were obtained by peptization of Eu(III) hydroxide (labelled with ^{152}Eu) as described in ref. 7. Large colloidal particles of Eu(III) hydroxide were isolated from the sol by centrifugation at 3400 g. The final Eu(III) colloidal solution was clear in transmitted and turbid in reflected light.

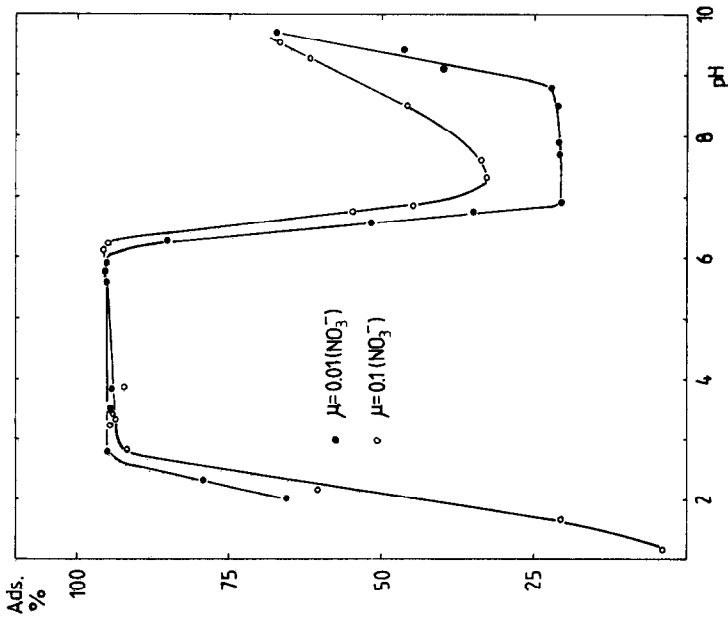
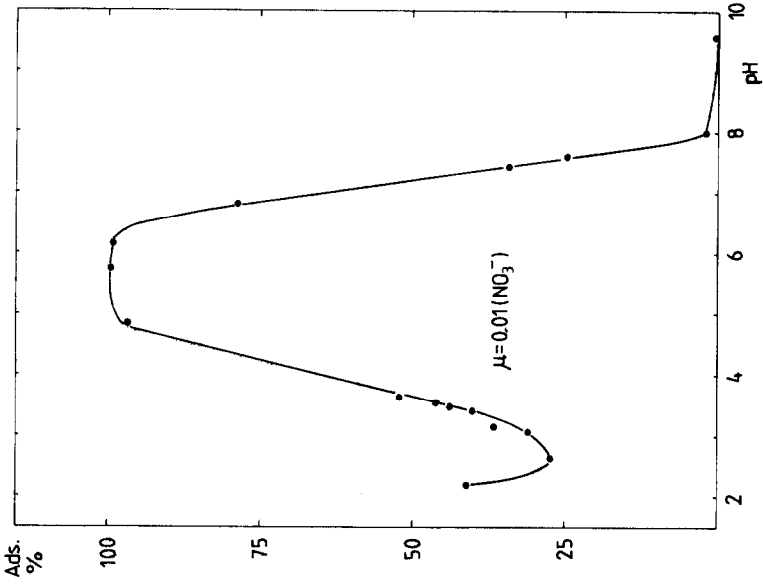


Fig. 1. Dependence of the sorption of colloidal Fe(III) ($\text{Fe}, 2 \cdot 10^{-4} M$) on pH.

Fig. 2. Dependence of the sorption of Fe^{3+} ($10^{-6} M$) on pH.

Solutions of colloidal Fe(III) labelled with ^{59}Fe (Zentralinstitut für Kernforschung, Dresden, G.D.R.) were prepared as described previously³.

The chemicals used were of analytical-reagent grade.

Sorption of europium and iron species was carried out by batch equilibration experiments. Amounts of 0.1 g of the sorbent, 2 cm³ of NaNO₃ or HNO₃ solution of appropriate concentration and pH and 0.02–0.05 cm³ of europium (or iron) solution in the ionic or colloidal state were measured into 6 cm³ glass test-tubes with stoppers. The mixture was then shaken in a thermostat for 24 h at $25 \pm 0.2^\circ\text{C}$, centrifuged at 1400 g for 3 min and samples of 0.05–1 cm³ were taken for measurement.

The column experiments have been described in a previous paper³.

To avoid sorption on glass, all the laboratory glassware used was rinsed with dichlorodimethylsilane (BDH, Poole, U.K.), as described previously³.

A Beckman pH meter, with Beckman glass and saturated calomel electrodes, was used for pH determinations.

The activity of the ^{152}Eu or ^{59}Fe was measured on a Nuclear Chicago Geiger-Müller counter with a thin window (*ca.* 2 mg cm⁻²). The activity of the experimental solutions varied from about 10^4 to 10^5 counts min⁻¹ cm⁻³.

RESULTS AND DISCUSSION

The dependence of the sorption of colloidal Fe(III) on silica gel as a function of pH is given in Fig. 1. The sorption of colloidal Fe(III), at a solution ionic strength $\mu = 0.01(\text{NO}_3^-)$, increases in the pH range 2.6–5.2. The sorption maximum lies in the pH range 5.2–6.2. In the pH range 2.6–6.5 the colloid is positively charged and the silica gel charge is negative. At pH values higher than 6.5 the sorption decreases because of electrostatic repulsion between the colloidal particles and the sorbent surface, both of which are negatively charged.

The isoelectric point of the colloidal Fe(III) is at pH 6.5^{4,6}. As reported⁸, the isoelectric point of silica gel varies from 2 to 3, depending on sample preparation. The surface charge density of the silica gel is small up to pH 7⁸.

The sorption behaviour of Fe³⁺ on silica gel is very complex, because the properties of both the silica gel and the Fe³⁺ species present in the solutions depend on pH. In solutions of pH < 1.5, Fe³⁺ exists as a hydrated cation and a hydroxo complex, Fe(OH)²⁺, is formed in the pH range 1.5–3. In solutions of pH > 3 polynuclear complexes of iron are formed⁹. Fig. 2 shows the dependence of Fe³⁺ sorption on pH. At solution ionic strength $\mu = 0.01(\text{NO}_3^-)$ the sorption of Fe³⁺ increases with increasing pH in the range 2.0–2.8. The sorption maximum is in the pH range 2.8–6.3. If the pH of the solution is increased to 7 the sorption of Fe³⁺ decreases. The sorption of trace amounts of Fe³⁺ on silica gel at pH < 3 can be explained by an ion-exchange process, and at pH from 3 to 6.3 by hydrolytic adsorption of iron polynuclear complexes at the sorbent-solution interface. The sorption behaviour of both Fe³⁺ (Fig. 2) and colloidal Fe(III) (Fig. 1) is similar in the pH range 6.3–7.0. The sorption of Fe³⁺ increases with increasing pH of the solution from 7.0 to 9.5. In this pH range the colloidal particles (or polynuclear complexes) of iron(III) are augmented and partially precipitated by centrifugation.

From the dependence of the distribution coefficients (K_d) of Fe³⁺ (10^{-6} M)

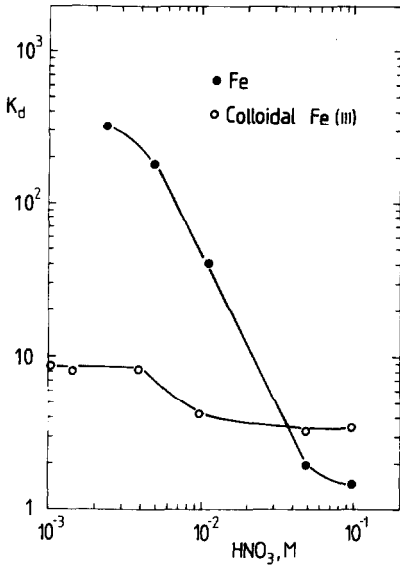


Fig. 3. Dependence of the distribution coefficients, K_d , of $Fe^{3+}(10^{-6} M)$ and colloidal Fe(III) ($Fe, 2 \cdot 10^{-4} M$) on nitric acid concentration.

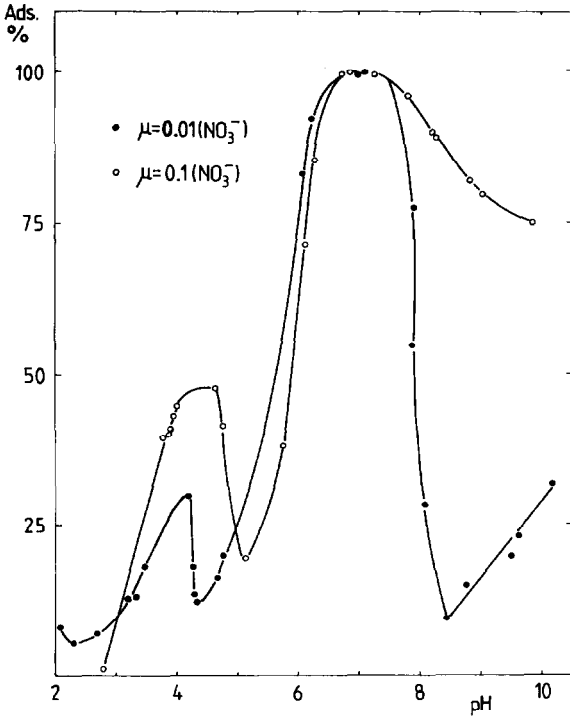


Fig. 4. Dependence of the sorption of colloidal Eu(III) ($Eu, 2 \cdot 10^{-4} M$) on pH.

on nitric acid concentration (Fig. 3), it can be concluded that the sorption of Fe^{3+} depends strongly on the acidity of the aqueous solution, as would be expected for a real ion-exchange process. The sorption of colloidal Fe(III) on the silica gel decreases slowly on increasing the nitric acid concentration from 10^{-3} to 10^{-1} M.

The results obtained in the column runs (column, $9 \text{ cm} \times 0.21 \text{ cm}^2$; elution flow-rate, $1 \text{ cm}^3 \text{ cm}^{-2} \text{ min}^{-1}$) are in agreement with those obtained by batch equilibration. Colloidal Fe(III) and Fe^{3+} are adsorbed on a silica gel column at low acidity (0.002 M nitric acid). The adsorbed colloidal Fe(III) is difficult to desorb from the silica gel column with 1.0 M nitric acid. The colloidal Fe(III) and Fe^{3+} are adsorbed on the silica gel column from solution containing 0.01 M sodium nitrate at pH 5.1–6.2.

The average molecular mass of colloidal Fe(III), as reported earlier³, is $3.3 \cdot 10^6$. From the centrifugation behaviour of colloidal solutions of both Fe(III) and Eu(III), under given experimental conditions, it can be assumed only that the average molecular mass of colloidal Eu(III) is $> 3.3 \cdot 10^6$.

The isoelectric point of colloidal Eu(III) is at pH 7–7.5⁵. The isoelectric point of silica gel varies from 2 to 3⁸. Fig. 4 shows the dependence of colloidal Eu(III) sorption on pH. There are two sorption maxima. The first maximum lies in the pH range 4–4.2 and 4.2–4.6 at solution ionic strengths $\mu = 0.01(\text{NO}_3^-)$ and $0.1(\text{NO}_3^-)$, respectively. The second sorption maximum is in the pH range 6.7–7.3. In this pH

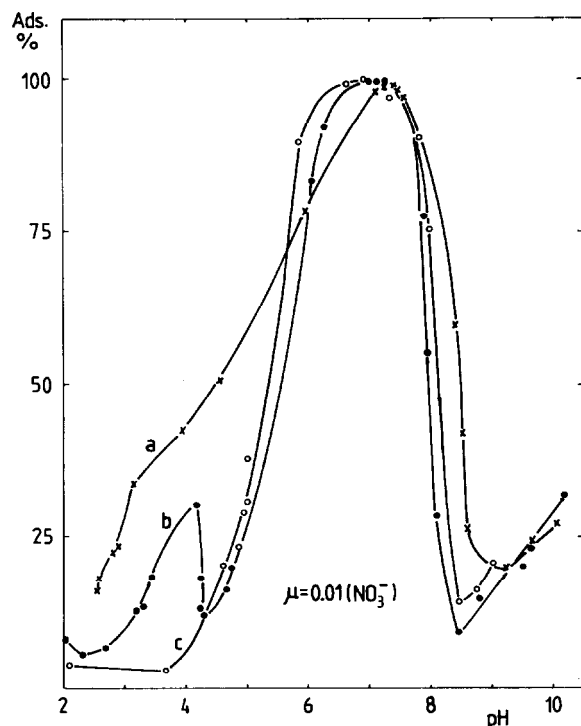


Fig. 5. Dependence of the sorption of colloidal Eu(III) ($\text{Eu}, 2 \cdot 10^{-4} \text{ M}$) on pH. Sorbents: (a) silica gel (Merck); (b) silica gel (Merck) washed with 1:1 hydrochloric acid; and (c) silica gel prepared as described in ref. 10.

range the colloid is weakly positively charged and the silica gel charge is negative. If the pH of the solution, at a solution ionic strength $\mu = 0.01(\text{NO}_3^-)$, is increased from 7.3 to 8.5, the sorption of colloidal Eu(III) decreases.

In this pH range, the surface of the Eu(III) colloidal particles and silica gel are negatively charged. The sorption of colloidal Eu(III) increases with increasing pH of the solution from 8.5 to 10. In this pH range, part of the colloidal particles of Eu(III) are augmented probably by coagulation and precipitated by centrifugation. The sorption of colloidal Eu(III) in the pH range 7.3–10 is higher at a solution ionic strength $\mu = 0.1(\text{NO}_3^-)$ than at $\mu = 0.01(\text{NO}_3^-)$. The increase in sorption on increasing the inert electrolyte concentration can be explained by the electrolyte coagulation effect².

The unusual form of the curve (Fig. 4) at pH 3–5 is difficult to explain satisfactorily. For this reason, the sorption of colloidal Eu(III) was investigated on the same silica gel that had not been treated with 1:1 hydrochloric acid and on the silica gel prepared by the method described by Gordon *et al.*¹⁰. The results in Fig. 5 show that the sorption of colloidal Eu(III) on given silica gel samples depends on the nature and pre-treatment of the SiO_2 .

The dependence of the sorption of Eu^{3+} on pH is shown in Fig. 6. The sorption of Eu^{3+} increases with increasing pH in the range 2.0–6.5. The sorption maximum is in the pH range 6.5–7.4, where the sorption behaviour of both Eu^{3+} (Fig. 6) and colloidal Eu(III) (Fig. 4) is similar. If the pH of the solution is increased to 10.5 the sorption of Eu^{3+} decreases.

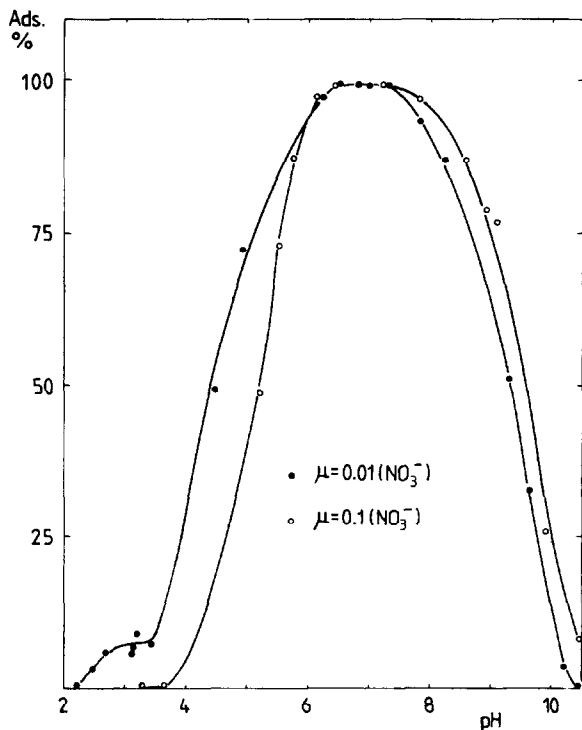


Fig. 6. Dependence of the sorption of Eu^{3+} ($5 \cdot 10^{-7} M$) on pH.

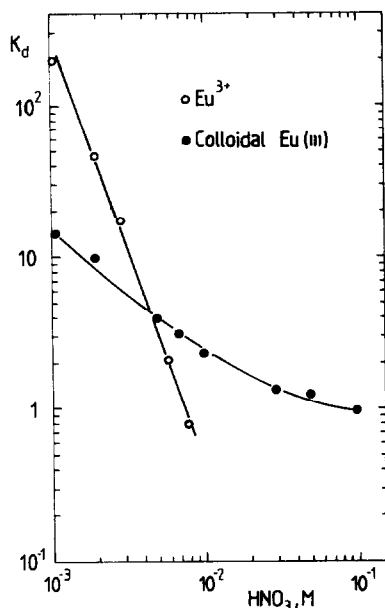


Fig. 7. Dependence of the distribution coefficients, K_d , of Eu^{3+} ($5 \cdot 10^{-7} M$) and colloidal Eu(III) ($2 \cdot 10^{-4} M$) on nitric acid concentration.

The sorption behaviour of Eu^{3+} at $\text{pH} < 5$ can be explained by an ion-exchange process, at $\text{pH} 5-7$ by interaction of hydroxo complexes of Eu^{3+} with a negatively charged silica gel surface and at $\text{pH} > 7$ by electrostatic repulsion between the negatively charged sorbent surface and colloidal particles (or polynuclear complexes) of Eu(III) . At $\text{pH} > 7$, the formation of a pseudocolloid by adsorption of hydrolysed europium on foreign colloidal material is not excluded^{11,12}.

From the dependence of the distribution coefficients (K_d) of Eu^{3+} ($10^{-7} M$) on nitric acid concentration (Fig. 7) it can be concluded that the sorption of Eu^{3+} strongly depends on the acidity of the aqueous solutions, as would be expected for a real ion-exchange process. The sorption of colloidal Eu(III) also depends on the acidity of the aqueous solution (Fig. 7).

The results obtained in the column runs (column, $9 \text{ cm} \times 0.21 \text{ cm}^2$; elution flow-rate, $1 \text{ cm}^3 \text{ cm}^{-2} \text{ min}^{-1}$) are in agreement with those obtained by batch equilibration. Colloidal Eu(III) and Eu^{3+} are adsorbed on a silica gel column at low acidity ($0.001 M$ nitric acid). It is easy to desorb both the colloidal and the ionic Eu using $0.5-1.0 M$ nitric acid. Eu^{3+} and colloidal Eu(III) are adsorbed on the silica gel column from a solution containing $0.01 M$ nitric acid at $\text{pH} 6.5-7.3$.

ACKNOWLEDGEMENT

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REFERENCES

- 1 V. Vesely and V. Pekarek, *Talanta*, 19 (1972) 219.
- 2 F. Kepák, *J. Radioanal. Chem.*, 20 (1974) 159.
- 3 N. Cvjetićanin and D. Cvjetićanin, *J. Chromatogr.*, 140 (1977) 77.
- 4 N. Cvjetićanin, D. Cvjetićanin, D. Golobočanin and M. Pravica, *J. Radioanal. Chem.*, 54 (1979) 149.
- 5 N. Cvjetićanin, D. Cvjetićanin and M. Pravica, *J. Chromatogr.*, 241 (1982) 183.
- 6 N. Cvjetićanin and D. Cvjetićanin, *J. Radioanal. Chem.*, 81 (1983) 49.
- 7 C. J. Hardy, S. R. Buxton and M. M. Lloyd, *Report ORNL-4000*, Oak Ridge National Laboratory, Oak Ridge, TN, 1967.
- 8 J. Eisenlauer and E. Killman, *J. Colloid Interface Sci.*, 74 (1980) 108.
- 9 Yu. P. Davydov, V. M. Jefremenkov, M. A. Gratchok and Yu. J. Bondar, *J. Radioanal. Chem.*, 30 (1976) 173.
- 10 A. H. Gordon, A. J. P. Martin and R. L. M. Synge, *Biochem. J.*, 37 (1943) 79.
- 11 Yu. P. Davydov, *Radiokhimiya*, 9 (1967) 89.
- 12 F. Ichikawa and T. Sato, *Radiochim. Acta*, 12 (1969) 89.