

Selective Adsorption of Fluoride Ion by La(III)-loaded
Chelating Resin Having Phosphonomethylamino Groups

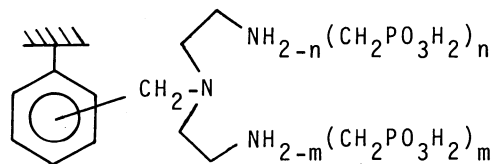
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Adsorption characteristics of La(III)-loaded chelating resin containing phosphonomethylamino groups for fluoride ion has been studied. Fluoride ion is effectively adsorbed on the column packed with La(III)-loaded resin at pH ranging 3.0- 4.0. The retained fluoride ion has been released from the column by elution with 1 mol dm^{-3} sodium hydroxide solution without any leakage of the metal ion. The column can be used repeatedly after regeneration.

In recent years appreciable amounts of hydrofluoric acid and ammonium fluoride are used in the fields of electronic and semiconductor industries as the reagents for etching or acid-washing of silicon and germanium. As a consequence, the removal of fluoride ion from the industrial effluents has become of increasing importance.

It is known that some lanthanide metal complexes (La(III), Ce(III)) of alizalin complexane can form colored complexes selectively with fluoride ion.¹⁾ The high selectivity toward fluoride ion seems to be a rather general trend for other complexes of some higher valent metal ions. For example, it has been pointed out that metal-loaded chelating resins ($M=\text{La(III)}, \text{Ce(III)}, \text{Zr(IV)}$) can adsorb fluoride ion selectively.^{2,3)} However these patents do not describe the fundamental details of the observations. In addition, these adsorbents have some drawbacks such as terrible leaking of loaded metals upon recycle use presumably owing to the lower stability of the polymer-metal linkage.

Recently we have prepared the cross-linked polystyrene resin having multidentate amine-N-phosphonate groups (PMA resin). The PMA resin forms highly stable complex with La(III) ion. The La(III)-loaded PMA resin can adsorb fluoride ion repeatedly without significant loss of the metal ion.



PMA resin ($n, m = 0, 1, 2$)

Here we report the adsorption characteristics of the La(III)-PMA resin and the application to the selective removal of fluoride ion.

The PMA resin was prepared by phosphonomethylation of dien resin⁴⁾ in which diethylenetriamine (dien) is linked to polystyrene resin uniquely through the imino nitrogen. The polymer matrix was macroreticular type styrene-10%-divinylbenzene copolymer with 60-100 mesh (Mitsubishi Chemical Co.). Nitrogen and phosphorus contents of the PMA resin are 6.0 and 11.2%, respectively; One gram of the resin contains approximately 1.4 mmol of diethylenetriamine unit and about 65% of the amino protons are phosphonomethylated.

Figure 1 shows the exchange capacity and distribution coefficients (K_d) of the PMA resin for La(III) ion as the function of pH. The distribution coefficient is defined as ; $K_d = \text{amount of metal adsorbed on one gram of the resin} / \text{amount of metal remaining in } 1 \text{ cm}^3 \text{ of the solution}$. The capacity of the resin for La(III) is approximately 1.1 mmol g^{-1} in the pH range 2.5-3.5. The log K_d vs. pH profile shows that La(III) is strongly retained on the resin at pH higher than 3.0, indicating the durability of the polymer-metal bonding.

The PMA-La(III) resin readily adsorbs fluoride ion from acidic solution by the ligand exchange with coordinated water as has been postulated in La(III) complex of

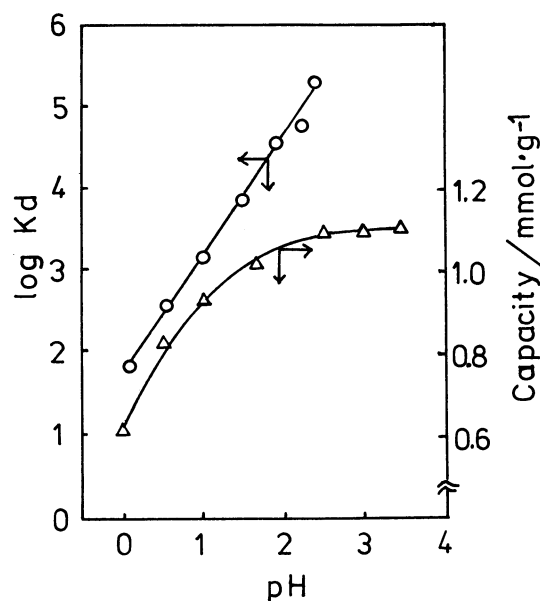


Fig.1. Exchange capacity and distribution coefficient of PMA resin for La(III).

alazine complexane.⁵⁾ The exchange capacity of the PMA-La(III) resin for fluoride ion was determined by the batchwise procedure with the fluoride ion which is excess over the La(III) content. The amount of fluoride ion was determined colorimetrically.⁶⁾ The capacity decreased with increase of pH. At pH 3.5, 4.0, 5.0, and 6.0, the capacity was 1.64, 1.34, 0.75, and 0.47 mmol per gram of resin, respectively.

Figure 2 shows the time-course profile for the adsorption of fluoride ion. The rate of adsorption appears to depend on the pH of solution i.e., the rate decreases with increase of pH. At pH 3.5, more than 95% of fluoride ion can be removed within 60 min, whereas a much longer reaction time of the order of weeks is required to attain 95% removal of fluoride ion at pH 6.0. These results can be interpreted by the deprotonation of the coordinated water associated with increase of pH, which may prevent the access of F^- ion due to the increased negative charge around the metal ion. Therefore pH of the feed solution should be adjusted to relatively low value. However, when pH is lower than 3.0, gradual leaking of metal ion inevitably takes place. Thus the optimal pH would lie in the range 3.0-4.0.

Column adsorption of fluoride ion was demonstrated by using a glass column packed with PMA-La(III) resin ($\phi 1.0 \times 10$ cm, 5 g). A buffered solution (0.1 mol dm^{-3} -phthalate) containing $50 \text{ } \mu\text{g cm}^{-3}$ of fluoride ion was continuously passed through the column at a constant rate of $1.0 \text{ cm}^3 \text{ min}^{-1}$. The feed solution must be buffered to prevent the change in pH; the adsorption of F^- accompany with the selective attraction of H^+ on the resin to neutralize the negative charge. The column breakthrough profiles are given in Figure 3. The breakthrough point varies with the pH of feed solution, which coincides with the pH dependance of the adsorption rate. The adsorbed fluoride ion can be released completely from the resin by elution with 1 mol dm^{-3} sodium hydroxide solution (200 cm^3) without any loss of La(III) ion. The column can be used in the successive operations after rinsing with a buffered solution (pH 3.5, 0.1 mol dm^{-3} -phthalate). The breakthrough curves after three adsorption and regeneration cycles are essentially the same as the initial run (Figure 3). The high durability of the present resin toward metal dissociation can be attributed to the high stability of the La(III) complex formed with the multidentate aminophosphonate group. Interference from Cl^- ,

NO_3^- and SO_4^{2-} was not significant when they were present at concentrations of about hundred times higher than that of fluoride ion.

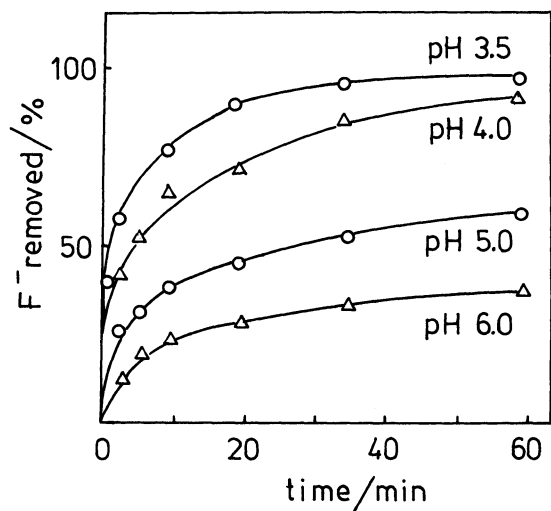


Fig. 2. Time-course profile for adsorption of F^- .

Conditions; PMA-La(III)resin=3 g
 $[\text{F}^-]_{\text{feed}} = 50 \mu\text{g cm}^{-3} (200 \text{ cm}^3)$
 $I = 1.0 \text{ mol dm}^{-3} (\text{NaClO}_4)$, 25°C

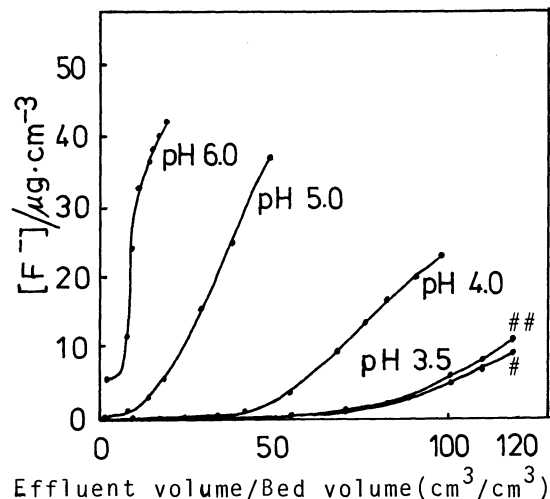


Fig. 3. Breakthrough curves of the adsorption of F^- for several pH values.

; initial run (pH 3.5)
 ##; third run (pH 3.5)

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