CHEMISTRY LETTERS, pp. 1191-1194, 1994.

# Rapid Adsorption and Desorption of Fluoride on Zirconium(IV) Complex with Hydrophilic Chelating Polymer

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Zirconium(IV) was fixed on a hydrophilic polymer having iminodiacetate groups, developed for affinity chromatography, in a stoichiometric amount. Fluoride ion was rapidly adsorbed on this polymer–complex in acidic media, and the adsorbed fluoride was quantitatively desorbed in basic media. The complex can be repeatedly used after regeneration with an acid.

Preconcentration is indispensable for the determination of fluoride less than $10^{-6}$ mol $dm^{-3}$ (20 ppb). Various techniques so far reported, including steam distillation, micro–diffusion and solvent extraction, are tedious.1) Adsorption using a vacant coordination site of metal complexes fixed on polymers is promising in this respect. Several earlier attempts based on such idea demonstrated excellent thermodynamic properties,2–5) but still consumed rather long time for equilibration as a pretreatment of the determination of fluoride. In this paper, we examined a polymer–complex of zirconium(IV) with packing materials developed for affinity chromatography,6) and achieved an extremely rapid adsorption and desorption of fluoride.

Zirconium(IV) (100 $\mu$mol) was reacted with a hydrophilic chelating polymer (**1**; TSKgel AF–chelate TOYOPEARL 650M) containing 33 $\mu$mol iminodiacetate groups at various acidities. Equilibrium was attained within few days. The adsorption occurred at $[H^+] < 3$ mol $dm^{-3}$ and reached a maximum of 33 $\mu$mol at $[H^+] < 0.3$ mol $dm^{-3}$. The same complex(**1**–Zr) was obtained irrespective of metal sources such as $ZrO(NO_3)_2$ and $ZrOCl_2$. In the loading of $ZrOCl_2$, chloride was not included in the polymer. Another chelating resin of polystyrene–divinylbenzene copolymer type (**2**; Amberlite IRC–718) also adsorbed Zr(IV) under the similar conditions, but the adsorption was extremely slow. The maximum adsorption (1.0 mmol $g^{-1}$) did not exceed half the amount of iminodiacetate groups(2.0 mmol $g^{-1}$).

The pH-titration curves of **1**-Zr and **1** are shown in Fig. 1. The first deprotonation reactions can be expressed as $pK_a = -\log[H^+] + n \log\{(1-\alpha)/\alpha\}$ [$n$=2.5 and $pK_a$=6.3 for **1**-Zr; $n$=2.5 and $pK_a$=3.5 for **1**],[7] where $\alpha$ is the degree of neutralization and $K_a$ is the dissociation constant. The large values for an empirical parameter $n$ indicate strong interaction between adjacent sites on both a metal-free polymer and a polymer-complex. No leakage of Zr(IV) was found within this $-\log[H^+]$ range.

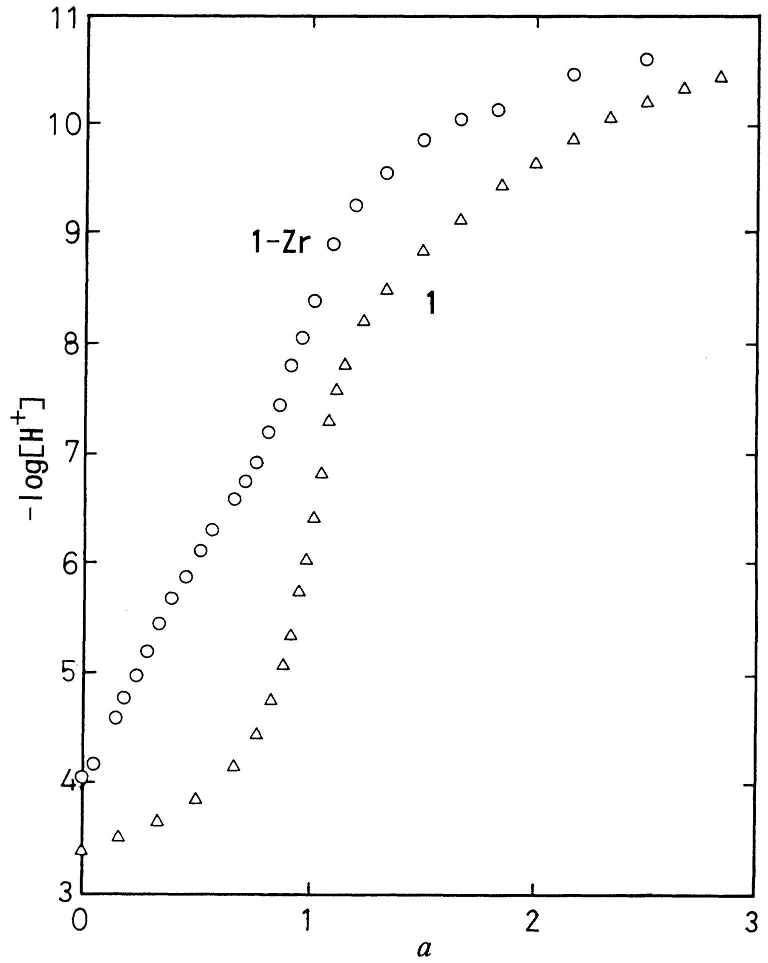

Fig. 1. Plot of $-\log[H^+]$ *vs* titration fraction($a$) for **1**-Zr and **1**. 25°C, 0.1 mol $dm^{-3}$ $KNO_3$.

The adsorption of fluoride(4 $\mu$mol) on **1** or **1**-Zr (33 $\mu$mol Zr) was studied at various $-\log[H^+]$ values(Fig. 2). No affinities were found with polymer **1** only whereas 99% fluoride was adsorbed at $-\log[H^+]$=2.5 and completely desorbed at $-\log[H^+]$=9 on **1**-Zr. Almost the same thermodynamic performance was observed for **2**-Zr. The results for the potentiometric titration of **1**-Zr with fluoride solutions were expressed as $\log K' = -\log[F^-] + n \log\{(1-\beta)/\beta\}$ for $\beta < 0.3$ ($\beta$: the fraction of a polymer-complex free from fluoride). The apparent stability constant for formation of the mixed ligand complexes with fluoride $K'$ was around $10^5$. More than 95% fluoride was adsorbed if the F:Zr molar ratio was kept lower than 0.2. With increase in the ratio, the recovery of fluoride decreased, and finally zirconium(IV) started to leak as fluoro complexes at a ratio higher than 2.

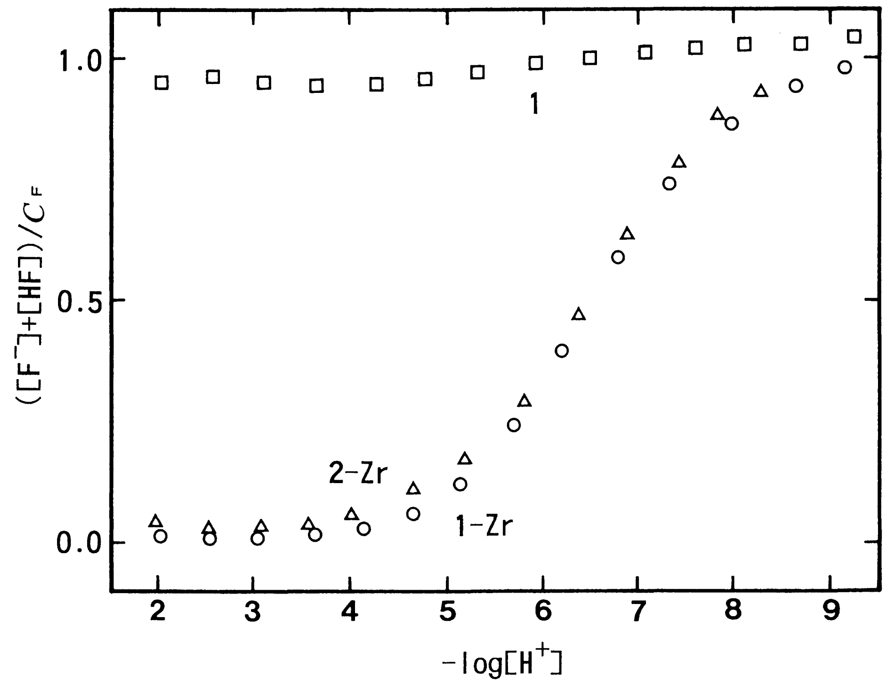

Fig. 2. Plot of ([F$^-$]+[HF])/$C_F$ vs -log[H$^+$] for **1**-Zr, **2**-Zr and **1**. 25°C, 0.1 mol dm$^{-3}$ KNO$_3$. $C_F$ = 4 $\mu$mol, $C_{Zr}$= 33 $\mu$mol, Volume= 40 cm$^3$.

In summary, relevant reactions are expressed as follows:

$$\text{-RZr(OH)}_2 + \text{KF} \rightleftharpoons \text{-RZr(OH)}_2\text{F}\cdot\text{K} \quad (1)$$

$$\text{-RZr(OH)}_2\text{F}\cdot\text{K} + \text{OH}^- \rightleftharpoons \text{-RZr(OH)}_3\cdot\text{K} + \text{F}^- \quad (2)$$

$$\text{-RZr(OH)}_3\cdot\text{K} + \text{H}^+ \rightleftharpoons \text{-RZr(OH)}_2 + \text{K}^+ \quad (3)$$

where –R denotes an iminodiacetate group on the polymer. The starting complex in acidic media reacts with fluoride to form anionic mixed ligand complexes with fluoride and hydroxide,[8)] which may be electrically neutralized with a counter ion(eq 1). The hydroxide ion can expel the adsorbed fluoride through the formation of mixed ligand complexes only with hydroxide(eq 2), which are reversibly converted to the starting complex by any acids(eq 3).

The time course for the adsorption of fluoride to polymer–complexes at –log[H$^+$]= 3.5 and that for the desorption at –log[H$^+$]=9.4 are shown in Fig. 3. Both reactions were completed within at most few minutes for **1**–Zr, but took several hours for **2**–Zr. Analytical applications of **1**–Zr are now in progress.

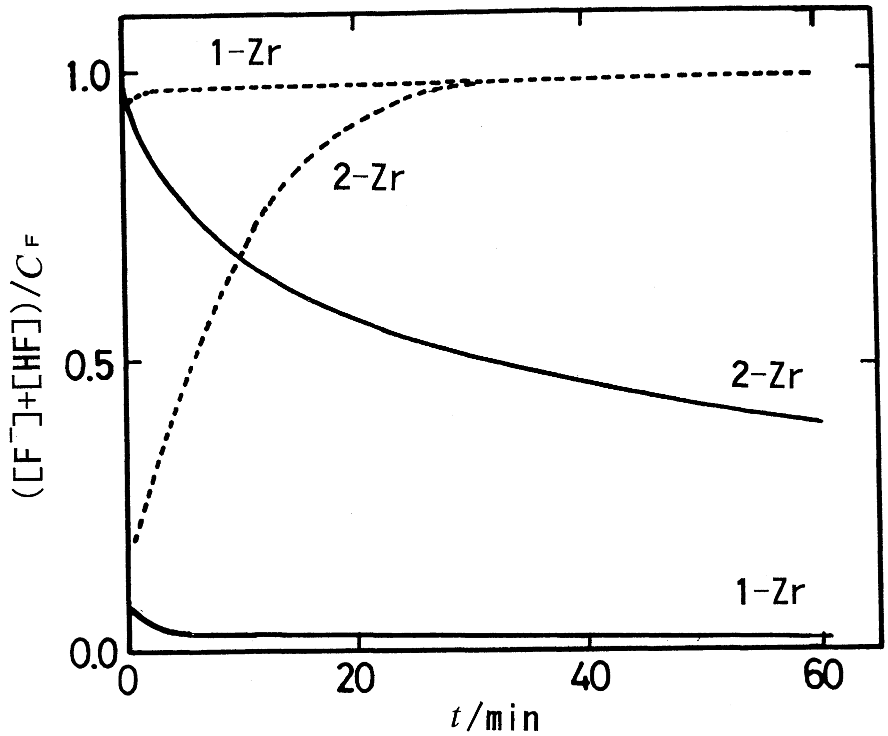

Fig. 3. Time course for adsorption(———, $-\log[H^+]=3.5$) and desorption(- - - -, $-\log[H^+]=9.4$) of fluoride on **1**-Zr and **2**-Zr. $C_F=1\times10^{-4}$ mol dm$^{-3}$, $C_{Zr}=33$ $\mu$mol.

This investigation was supported by a Grant-in-Aid for Scientific Research No. 05640680 from the Ministry of Education, Science and Culture.

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(Received April 11, 1994)