Complexes of Hard Metal Ions with Amine-*N*-polycarboxylates as Fluoride Receptors

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The equilibria were systematically studied in the reaction of hard metal complexes (M^{m+}: Al^{3+}, Zr^{4+}, Hf^{4+}, Th^{4+}; H_nL: amine-*N*-polycarboxylic acid) with fluoride. Mixed-ligand complexes were found in most systems; each metal ion shows a critical ligand having a necessary and sufficient number of donor atoms to lose the metal ion affinity for fluoride. The ML complexes of ligands containing a fewer number of donor atoms than the critical ligands have high affinities for fluoride. Among them, the zirconium(IV) complex of *N*-methyliminodiacetic acid is an excellent fluoride receptor; fluoride is quantitatively fixed on the complex at $-\log [H^+] < 4.5$ and is reversibly expelled at $-\log [H^+] > 9$ within a short time.

Specific receptors are essential for the separation and detection of chemical species in solutions. Based on a variety of concepts, novel receptors are being evolved. Recognition of anions in aqueous solutions is preceded by partial or complete dehydration, which occasionally defines the selectivity (Hofmeister sequence). It is thus challenging to be rid of this sequence and acquire specificity for hydrophilic anions, such as fluoride, phosphate and sulfate. An extra energy gain through some interaction with receptors may modify the selectivity.[1—4]

Two types of receptors have been developed for fluoride. One is based on hydrogen-bonds with protonated amines, the positions of which have been carefully considered; X-ray crystallographic studies demonstrated the presence of four to six hydrogen bonds in solid.[5—7] The maximum stability constant in solutions, so far reported, amounts to 10^5 for sapphyrin, which has been utilized for the selective transport and fluorometric determination of fluoride.[8,9] The other approach is based on an interaction with some Lewis acids, including B, Si, and Sn;[10—12] the interaction of these receptors with naked fluoride ions in organic solvents was studied. Although the latter type of receptors are of fundamental interest, they are not practically applicable.

We have studied the selection of masking reagents for several metal ions in the determination of fluoride, and have pointed out the importance of mixed-ligand complexes consisting of a central metal, a masking reagent and fluoride; their stabilities virtually govern the masking abilities.[13] The extremely high affinities found for certain combinations have suggested their possible use for fluoride receptors.[14,15] In this paper, we have described a systematic study concerning the formation of mixed-ligand complexes in aqueous solutions. The four metal ions adopted (M: Al^{3+}, Zr^{4+}, Hf^{4+}, Th^{4+}) have different ionic sizes. Seven amine-*N*-polycarboxylic acids [H_nL: HEDTA = H_3hedta, *N*′-(2-hydroxyethyl)ethylenediamine-*N*, *N*, *N*′-triacetic acid; EDTA = H_4edta, ethylenediamine-*N*, *N*, *N*′, *N*′-tetraacetic acid; CDTA = H_4cdta, *trans*-1,2-cyclohexanediamine-*N*, *N*, *N*′, *N*′-tetraacetic acid; DTPA = H_5dtpa, diethylenetriamine-*N*, *N*, *N*′, *N*″, *N*″-pentaacetic acid; TTHA = H_6ttha, triethylenetetraamine-*N*, *N*, *N*′, *N*″, *N*‴, *N*‴-hexaacetic acid; NTA = H_3nta, nitrilotriacetic acid; MIDA = H_2mida, *N*-methyliminodiacetic acid] respectively have different numbers of donor atoms. Several complexes show stability constants larger than 10^5, and their affinities are tunable by $-\log [H^+]$-change.

Experimental

Materials. Potassium fluoride was dried for 24 h at 110 °C. Fluoride solutions were stored in polyethylene containers. Zirconium(IV) and thorium(IV) solutions were prepared by dissolving $ZrO(NO_3)_2$ and $Th(NO_3)_4$ in 4 $mol\,dm^{-3}$ nitric acid solution. A hafnium(IV) stock solution was prepared by heating a $HfCl_4$ solution in concentrated $HClO_4$ and subsequently diluting it with nitric acid. An aluminum stock solution was prepared by dissolving the nitrate in 10^{-2} $mol\,dm^{-3}$ nitric acid.

Potentiometry. The $-\log [F^-]$ and $-\log [H^+]$ values were determined respectively with a fluoride ion-selective electrode (F-ISE; Denki Kagaku Keiki, DKK-7200) and a fluoride-resistant glass electrode (Ohkura Electric Co., GP-1200), each in conjunction with an Ag/AgCl reference electrode having a porous teflon junction (DKK-4400). These electrodes were calibrated with 1.00×10^{-3} $mol\,dm^{-3}$ fluoride and 1.00×10^{-3} $mol\,dm^{-3}$ nitric acid solutions of ionic strength 0.1 $mol\,dm^{-3}$ KNO_3 at 25 °C. In neutral and alkaline media, nitrogen gas was bubbled through the solutions.

Preliminary studies demonstrated that metal complexes except those of Al(III), reacted with fluoride so fast that the process could not be followed by monitoring with a F-ISE; the reactions of Al(III) complexes were rather slow as the aqua ion.[16] For an equilibrium study on Al–L–F systems, a series of solutions containing Al^{3+}, a ligand and fluoride at various $-\log [H^+]$ values was prepared and subjected to potentiometry after standing overnight. For those of Zr–L–F and Hf–L–F systems, the solutions of parent metal complexes were titrated with a potassium fluoride solution. The average number of fluorides bound to the metal ion, $\bar{n}_F$, was calculated from the $-\log [H^+]$ and $-\log [F^-]$ values and used for equilibrium analyses.

$$\bar{n}_F = (C_F - [F^-] - [HF] - 2[HF_2^-])/C_M. \qquad (1)$$

In order to compare the reactivity in a more straightforward fashion, the relative residual (R), which gives the ratio of fluoride not bound to complexes to the total fluoride, was also used.

$$R = ([F^-] + [HF])/C_F. \qquad (2)$$

Results and Discussion

Parent Complexes. Information on the solution equilibria relevant to parent complexes is necessary for studying ternary systems. Such data are available for Al–DTPA, Al–TTHA,[17,18] Zr–HEDTA, Zr–EDTA, Zr–CDTA, Zr–DTPA,[19] Hf–HEDTA, and Hf–EDTA.[20] All the metal–L complexes including the others mentioned above have stabilities sufficiently high to be quantitatively formed, even at an equimolar ratio in acidic media.

At lower $-\log [H^+]$, protonated complexes MHL as well as ML may be formed (charges of complexes are omitted).

$$ML + H^+ \rightleftharpoons MHL. \qquad (3)$$

The protonation constants of complexes ($K_{MHL}{}^{H}$) were potentiometrically determined for Al–DTPA ($10^{5.18}$) and Al–TTHA ($10^{5.86}$). These values are larger than that of acetate ion, and suggest some contribution of the protonation on imino-nitrogen atoms; carboxylate-oxygen atoms are mainly protonated. The formation of MHL was also expected in Zr–TTHA and Hf–TTHA systems.

At higher $-\log [H^+]$, on the other hand, mixed-ligand complexes with hydroxide may be formed,

$$ML + OH^- \rightleftharpoons ML(OH). \qquad (4)$$

The hydrolysis may be complicated by concomitant polymerization and precipitation reactions. Especially, Zr(IV) and Hf(IV) complexes with ligands having a fewer number of donor atoms than five, like NTA or MIDA, form precipitates even in acidic media ($-\log [H^+] > 1.5$ for Zr–MIDA and >4 for Zr–NTA), which interfere with any rigorous equilibrium study. In Zr–HEDTA and Hf–HEDTA, the formation of $M(H_{-1}L)$ or $M_2(H_{-1}L)_2$ was suggested,[19,20] where $H_{-1}L$ denotes the species formed by deprotonation from a 2-hydroxyethyl group as well as three carboxyl groups. Since concentrated acids in Zr(IV) and Hf(IV) stock solutions interfered with direct potentiometric determination, the protonation constants of the Zr–TTHA and Hf–TTHA systems and the deprotonation constants of the Zr–HEDTA and Hf–HEDTA systems were determined in the course of equilibrium analysis of ternary systems as described below.

Formation of Mixed-Ligand Complexes. Some results of equilibrium studies on the ternary systems are shown as $\bar{n}_F$ vs. $-\log [F^-]$ diagrams in Fig. 1. An abrupt increase in $\bar{n}_F$ was observed with a decrease in $-\log [F^-]$ for Zr–DTPA and Hf–DTPA (closed symbols in Fig. 1a). Such an increase was ascribed to the formation of simple fluoro complexes accompanied by the dissociation of chelating reagents,

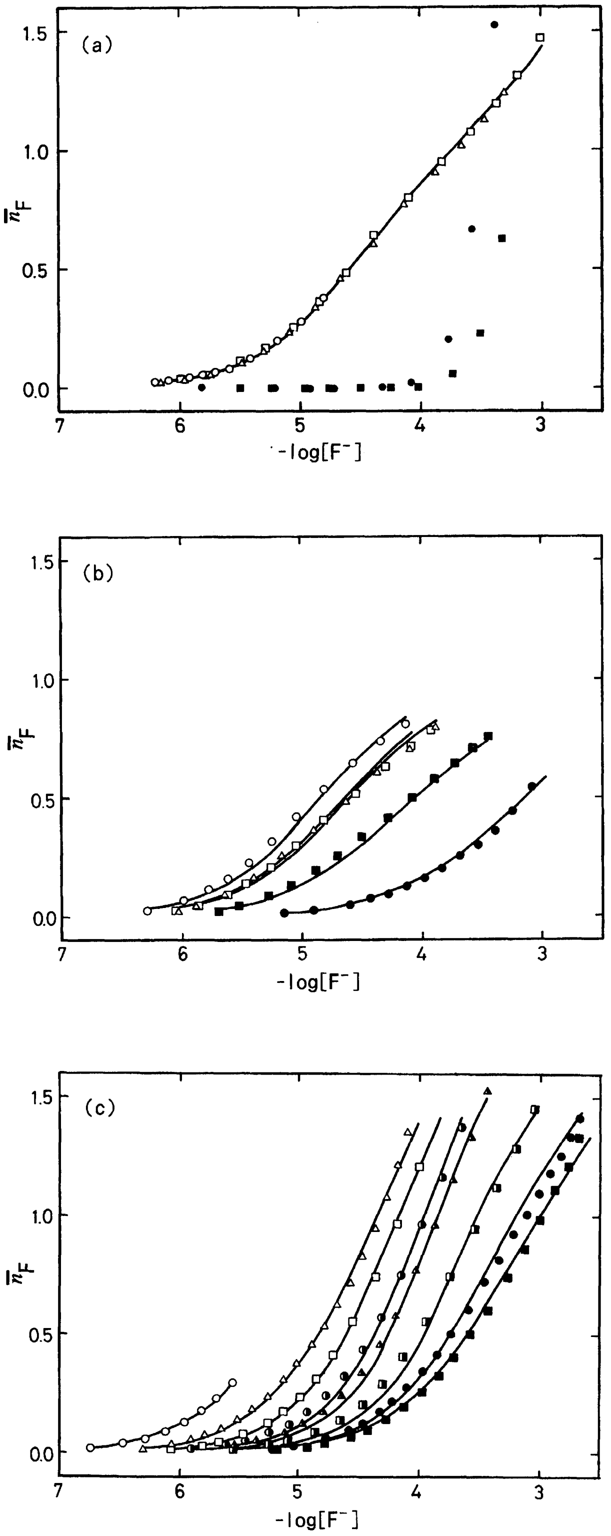

Fig. 1. Plot of $\bar{n}_F$ vs. $-\log [F^-]$ at 25 °C and 0.1 mol dm^{-3} KNO$_3$. $C_M = 10^{-3}$ mol dm^{-3}. (a) Hf–EDTA ($-\log [H^+]$: ○, 2.2; △, 3.1; □, 4.0; $C_L = 10^{-3}$ mol dm^{-3}) and Hf–DTPA ($-\log [H^+] = 2.1$; C_L/mol dm^{-3}: ●, 10^{-3}; ■, 10^{-2}); (b) Zr–TTHA ($-\log [H^+]$: ○, 2.7; □, 3.2; △, 3.3; ■, 3.9; ●, 5.0; $C_L = 10^{-3}$ mol dm^{-3}); (c) Zr–HEDTA ($-\log [H^+]$: ○, 1.0; △, 1.8; □, 2.2; ◑, 2.6; ▲, 2.8; ◨, 3.4; ●, 4.0; ■, 5.0; $C_L = 10^{-3}$ mol dm^{-3}).

$$\mathrm{ML}+n\mathrm{F}^- \rightleftharpoons \mathrm{MF}_n + \mathrm{L}', \qquad (5)$$

where L′ denotes all the ligand species not bound to the metal ion, with a difference in protonation degree taken into account. No mixed-ligand complexes were detected. The shift of a break to a smaller $-\log[\mathrm{F}^-]$ region at a higher concentration of DTPA (10^{-2} compared with 10^{-3} mol dm^{-3}) supported this assignment.

In the other systems, the increase in $\bar{n}_\mathrm{F}$ was more gradual and independent of the ligand concentration, indicating the formation of mixed-ligand complexes,

$$\mathrm{CF}_{j-1} + \mathrm{F}^- \rightleftharpoons \mathrm{CF}_j \quad (\mathrm{C}: \mathrm{MHL},\ \mathrm{ML},\ \mathrm{MH}_{-1}\mathrm{L};\ j = 1,2). \qquad (6)$$

The $\bar{n}_\mathrm{F}$ vs. $-\log[\mathrm{F}^-]$ diagram depended on $-\log[\mathrm{H}^+]$ for Zr–TTHA (Fig. 1b), Zr–HEDTA (Fig. 1c), Hf–TTHA, Hf–HEDTA, Al–DTPA, and Al–TTHA, but not for Zr–EDTA, Zr–CDTA, Hf–EDTA, and Hf–CDTA (Fig. 1a). The limiting $\bar{n}_\mathrm{F}$ value was equal to 1 for Zr–TTHA (Fig. 1b), Hf–TTHA, Al–DTPA, and Al–TTHA and 2 for Zr–HEDTA (Fig. 1c), Zr–EDTA, Zr–CDTA, Hf–HEDTA, Hf–EDTA, and Hf–CDTA (Fig. 1a). The stability constants of the mixed-ligand complexes were determined by considering the protonation equilibria of the parent complexes given above. In this calculation, the protonation constants of the metal complexes were fixed as determined for Al–DTPA and Al–TTHA, while being concomitantly refined for Zr–TTHA, Zr–HEDTA, Hf–TTHA, and Hf–HEDTA. Here, $\mathrm{MH}_{-1}\mathrm{L}$ was tentatively adopted as a species which formed at higher $-\log[\mathrm{H}^+]$ values and had extremely low affinities to fluoride in Zr–HEDTA and Hf–HEDTA. The assumption did not affect the evaluation of the reactivities of ML.

The constants obtained are summarized in Table 1. The calculated curves using the constants obtained were in good agreement with the experimental points. At lower $-\log[\mathrm{H}^+]$ and $-\log[\mathrm{F}^-]$ values, however, a deviation from the calculated curves was occasionally observed, which was ascribed to a contribution of the substitution reactions given by Eq. 5. These experimental points were omitted in a refinement of the constants, and are not included in the Figures.

Affinities of ML-Type Complexes for Fluoride. The four metal ions examined in this paper have high affinities to fluoride. Although extensive hydrolysis, especially of Zr(IV) and Hf(IV), interferes with a quantitative evaluation, the stability constant for the coordination of the first fluoride, $K_{\mathrm{MF}}{}^{\mathrm{F}}$ was estimated to be $10^{6.4}$ for Al^{3+}, $10^{9.0}$ for Zr^{4+}, $10^{8.6}$ for Hf^{4+}, and $10^{7.7}$ for Th^{4+}.[21] All the stability constants of the mixed-ligand complexes are lower than the corresponding values.

The value of $K_{\mathrm{MLF}}{}^{\mathrm{F}}$ decreases with an increase in number of donor atoms of a ligand for any metal ions; HEDTA (5 or

Table 1. Stability Constants of Mixed-Ligand Complexes with Fluoride at 25 °C and 0.1 mol dm^{-3} $\mathrm{KNO_3}$

System	C	Protonation	Stability constant		Ref.
	(charge)	constant	$\log K_{\mathrm{CF}}{}^{\mathrm{F}}$	$\log K_{\mathrm{CF_2}}{}^{\mathrm{F}}$	
Al–HEDTA	ML(0)		5.53	—[c)]	14
Al–EDTA	ML(−)		4.95	—	14
Al–CDTA	ML(−)		3.14	—	14
Al–DTPA	MHL(−)	5.18[a)]	5.3	—	This work
	ML(2−)		2.9	—	
Al–TTHA	MHL(2−)	5.94[a)]	—	—	This work
	ML(3−)		—	—	
Zr–HEDTA	ML(+)		5.37	4.11	This work
	$\mathrm{MH}_{-1}\mathrm{L}$(0)	1.18[b)]	3.50	2.4	
Zr–EDTA	ML(0)		4.62	2.8	This work
Zr–CDTA	ML(0)		4.61	3.0	This work
Zr–DTPA	ML(−)		—	—	This work
Zr–TTHA	MHL(−)	2.77[a)]	5.48	—	This work
	ML(2−)		2.9	—	
Hf–HEDTA	ML(+)		5.37	3.82	This work
	$\mathrm{MH}_{-1}\mathrm{L}$(0)	1.55[b)]	2.9	1.9	
Hf–EDTA	ML(0)		4.56	2.9	This work
Hf–CDTA	ML(0)		4.50	3.1	This work
Hf–DTPA	ML(−)		—	—	This work
Hf–TTHA	MHL(−)	3.86[a)]	5.58	—	This work
	ML(2−)		2.8	—	
Th–HEDTA	ML(+)		5.74	4.29	14
Th–EDTA	ML(0)		4.72	3.82	14
Th–CDTA	ML(0)		4.18	3.47	14
Th–DTPA	ML(−)		3.52	—	14
Th–TTHA	ML(2−)		—	—	14

a) $K=[\mathrm{MHL}]/[\mathrm{ML}][\mathrm{H}^+]$. b) $K=[\mathrm{ML}]/[\mathrm{MH}_{-1}\mathrm{L}][\mathrm{H}^+]$; $\mathrm{H}_{-1}\mathrm{L}$: species formed by deprotonation from alcoholic OH group. c) not found.

6) > EDTA, CDTA (6) > DTPA (8) > TTHA (10). A critical ligand, whose $K_{\mathrm{MLF}}{}^{\mathrm{F}}$ abruptly decreases across the series, is found for each metal ion: CDTA for Al(III), DTPA for Zr(IV) and Hf(IV), and TTHA for Th(IV). The ligand has just a necessary and sufficient number of donor atoms to encircle each metal ion. In these complexes, all the sites on a metal ion are occupied by the donor atoms of the ligand, and one of the acetate groups must be detached to give a space for accommodating fluoride; the stabilities of mixed-ligand complexes are low. An exceptional feature of Al–EDTA has been described elsewhere.[14)]

The complexes with ligands having a fewer number of donor atoms than that of the critical ligands possess coordinated water molecules, which are replaced by fluorides. Some complexes show stability constants greater than 10^5, which guarantees a quantitative (99%) reaction of 10^{-4} mol dm^{-3} fluoride with 10^{-3} mol dm^{-3} metal complex as a receptor (R): $[\mathrm{RF}]/[\mathrm{F}^-]=K_{\mathrm{RF}}[\mathrm{R}]>10^2$. Such metal complexes are effective fluoride receptors.

Affinities of Protonated and Hydrolyzed Complexes for Fluoride. The protonated complexes MHL in Al–DTPA, Zr–TTHA and Hf–TTHA show higher affinities for fluoride than ML, while that in Al–TTHA has a negligibly small affinity. In a free ligand of DTPA, the middle nitrogen atoms are protonated more readily than the terminal nitrogen atoms as studied by ^{1}H NMR.[22)] In protonated metal complexes of DTPA and TTHA, the proton in MHL is expected to be located rather at one end so as to reduce the electrostatic repulsion. When one of the terminal nitrogen atoms is protonated, two carboxylate groups attached to the nitrogen atom cannot coordinate to metal ions, and the remaining part of DTPA and TTHA can be pentadentate and heptadentate ligands, respectively. The species HL of TTHA completely envelopes Al^{3+} ions to eliminate the reactivity to fluoride. When HL of TTHA coordinates to Zr^{4+} or Hf^{4+} or when HL of DTPA coordinates to Al^{3+}, one water molecule remains on the metal ion and is replaced by fluoride.

Iyer and others have found a nearly linear relationship between the ^{27}Al chemical shift and the denticity of the ligand, and proposed the following structures:[18)] pentadentate chelation for MHL and mid-way between penta and hexadentate chelation for ML in Al–DTPA, and pentadentate chelation for both MHL and ML in Al–TTHA. The structure estimated from ^{27}Al NMR agrees with our estimation for Al–DTPA, but not for Al–TTHA.

The affinity of $\mathrm{MH_{-1}L}$ for fluoride is extremely lower than that of ML for Zr–EDTA, Zr–CDTA, Hf–EDTA, and Hf–CDTA in spite of the same electric charge. The lower affinity is ascribed to the coordination of a strongly electronegative alkoxide group or to an increase in coordination number by bridging as found for the V(III)–HEDTA system.[23)]

$-\log\,[\mathrm{H}^+]$-Dependent Affinities. Since a series of protolytic species of metal complexes have lower reactivities to fluoride, fluoride once bound to metal complexes may be expelled by simply increasing the $-\log\,[\mathrm{H}^+]$ value,

$$\mathrm{MHLF + OH^- \rightleftharpoons ML + F^-}, \tag{7}$$

$$\mathrm{MLF + OH^- \rightleftharpoons M(H_{-1}L)\ or\ ML(OH) + F^-}. \tag{8}$$

To confirm this, the effect of $-\log\,[\mathrm{H}^+]$ on the reaction of 10^{-4} mol dm^{-3} fluoride with 10^{-3} mol dm^{-3} metal complexes was studied over a wider $-\log\,[\mathrm{H}^+]$ range than equilibrium studies. The relative residual fluoride (R) was determined irrespective of the formation of precipitates; this is not a homogeneous reaction. Some results obtained for Zr(IV) complexes are shown in Fig. 2. As expected, R gradually increased with an increase in $-\log\,[\mathrm{H}^+]$ between 3 and 9. At $-\log\,[\mathrm{H}^+]>9$, fluoride was completely dissociated from any metal complexes; R values higher than 100% found at $-\log\,[\mathrm{H}^+]>9$ are ascribed to the response of F-ISE to hydroxide ion. The dissociation reaction of fluoride from the mixed-ligand complexes initiated by a pH increase took more than one hour for Al(III) complexes, but was completed within several seconds for Zr(IV) complexes.

Since the formation of HF in strongly acidic media interferes with the reaction of fluoride with metal complexes, R increases at $-\log\,[\mathrm{H}^+]<3$ for Zr–TTHA, Zr–HEDTA, and Zr–EDTA. In Zr–MIDA and Zr–NTA systems, on the other hand, no increase was found because the parent complexes are hydrolyzed even in such a low $-\log\,[\mathrm{H}^+]$ range.[19)] With a decrease in $-\log\,[\mathrm{H}^+]$, the following equilibrium becomes equally favorable as the formation of HF,

$$\mathrm{ML(OH)}_j + \mathrm{H}^+ + \mathrm{F}^- \rightleftharpoons \mathrm{ML(OH)}_{j-1}\mathrm{F}. \tag{9}$$

As a result, the lowest R values found in acidic media were 0.4% for Zr–MIDA, 0.8% for Zr–NTA, 3.1% for Zr–EDTA, 3.4% for Zr–TTHA, and 16% for Zr–HEDTA. Since the Zr(IV) complex of MIDA has the widest $-\log\,[\mathrm{H}^+]$ range and the lowest R value (apparent stability constant of $10^{5.4}$), and the reaction is both rapid and reversible, it is the best fluoride receptor. Such reactivities are maintained even in the complexes of Zr(IV) with a chelating polymer having IDA groups.[24)] Other properties, such as selectivity against

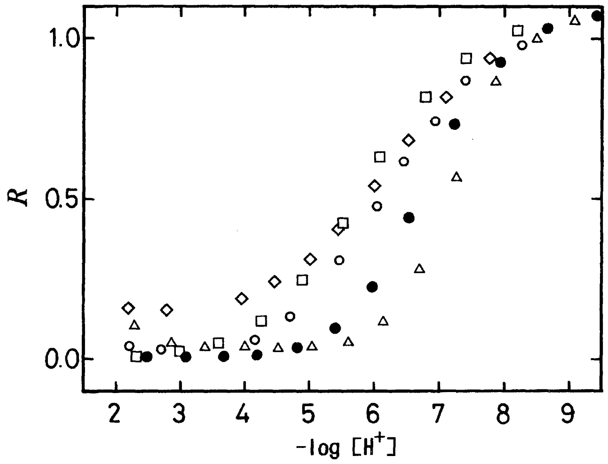

Fig. 2. Effect of $-\log\,[\mathrm{H}^+]$ on the reaction of Zr(IV) complexes with F$^-$. Ligand: ○, TTHA; △, EDTA; ◇, HEDTA; □, NTA; ●, MIDA. $C_{\mathrm{F}}=10^{-4}$ mol dm^{-3}; $C_{\mathrm{Zr}}=C_{\mathrm{L}}=3\times10^{-3}$ mol dm^{-3}. 25 °C, 0.1 mol dm^{-3} KNO$_3$.

other anions, are under investigation using these polymer complexes.

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