

Structural Features of Organic Reagents Suitable for Spectrophotometric or Fluorometric Determination of Fluoride Based on Mixed-Ligand Complex Formation

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Complexes of tetravalent metal ions with chromogenic chelating reagents having only one methyliminodiacetate group ortho to OH group were examined for spectrophotometric or fluorometric determination of fluoride. Zirconium(IV) and hafnium(IV) were superior to thorium(IV) as a central metal ion. Three triphenylmethane dyes showed comparable sensitivities. Although two azo dyes had lower blank values and higher sensitivities than triphenylmethane dyes, further modification involving enhancement of solubilities is required for practical use. Zirconium(IV) complex of a new fluorescent reagent derived from sulfonefluorescein showed an increase in fluorescence intensity on the reaction with fluoride. The mechanism of this change in spectroscopic properties is discussed.

Keywords Fluoride ion, spectrophotometry, fluorometry, chelating reagent, mixed-ligand complex

A new spectrophotometric method for fluoride ion using the zirconium(IV) complex of Semi-Xylenol Orange (SXO) was recently developed from a systematic examination of various chromogenic chelating reagents.¹ An equilibrium study on this ternary system with a fluoride ion-selective electrode (F-ISE) demonstrated formation of a mixed-ligand complex. A partly hydrolyzed Zr(IV)-SXO complex with only methyliminodiacetate (mida) group bound to the metal center reacts with fluoride to cause the deprotonation and coordination of a phenol group, giving rise to color intensification. On the other hand, the Zr(IV) complex of Xylenol Orange (XO) having two mida groups showed a low affinity to fluoride and caused little absorbance change. This suggests the importance of only one mida group ortho to an OH group within a molecule for such reactions.

In this work, several compounds [Semi-Methylthymol Blue (SMTB), Semi-Methylxylenol Blue (SMXB), Semi-Bromocresol Orange (SBCO), Methylnaphthol Orange (MNO), Naphthol Violet (NV); Fig. 1] belonging to this category of organic reagents have been examined for the validity of the hypothesis and improvement in sensitivities of spectrophotometric determination of fluoride. The effect of central metal ions other than Zr(IV) has also been studied.

For fluorometric determination of fluoride, more than ten reaction systems have been proposed. They cause a decrease in fluorescence intensity by substitution reactions, except for zirconium(IV)-4-methylumbelliferone-8-methyleneiminodiacetic acid (Zr-Calcein Blue, CB) complex, which shows an increase due to mixed-ligand complex formation.² Other fluorophores with the same

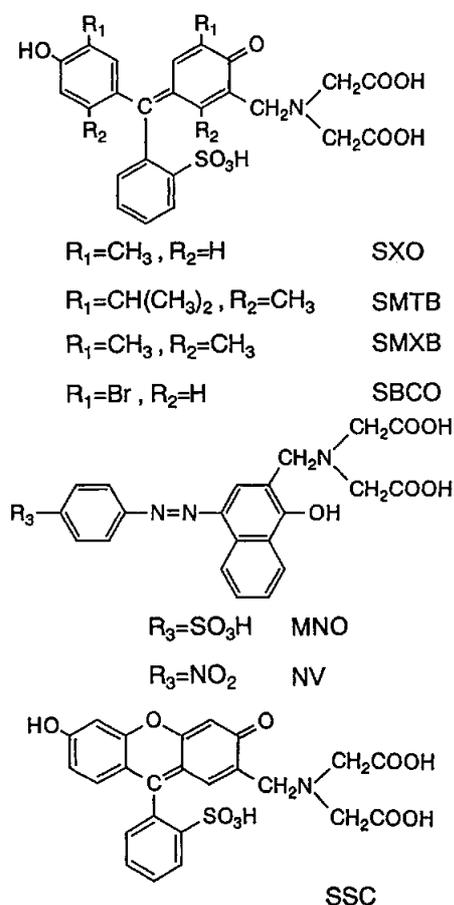


Fig. 1 Chelating reagents used in this study.

set of coordinating groups as CB and SXO might also be used. For the purpose of verifying this point, a new reagent, here named Semi-Sulfocalcein (SSC; Fig. 1), has been synthesized by Mannich condensation using sulfonefluorescein (SF), and its Zr(IV) complex has been examined as a fluorometric reagent for fluoride. Finally, the reactions of Zr(IV)-SSC and Zr(IV)-CB with fluoride have been studied and compared with that of Zr(IV)-3,5-dimethyl-2-hydroxyphenylmethyliminodiacetic acid (X), which is one of the simplest compounds of this group.

Experimental

Chromogenic reagents such as SXO, SMTB, SMXB, MNO and NV were prepared as described previously.³⁻⁷ Two new reagents, SBCO and SSC, were similarly synthesized from Bromophenol Red and sulfonefluorescein, respectively. These compounds except NV were chromatographically purified at least twice with cellulose powder as a stationary phase and BuOH/CH₃COOH as a mobile phase, to separate from the starting material and corresponding bis(mida)-type compounds. In the synthesis of SSC, several by-products, which might differ in number and position of mida groups, were found; a major species was fractionated. Reversed-phase HPLC using an ODS-column as a stationary phase and an CH₃CN/H₂O solution of tetrabutylammonium bromide as a mobile phase indicated the presence of only one component in this fraction. The structure has not been identified completely but was reasonably assigned as given in Fig. 1, from the chemical similarity to the other compounds. Since NV was decomposed on evaporating the eluted fraction, it was purified by repeated precipitation with an acid.

Purity of the reagents was also checked by following the spectral change on the dissociation of a phenolic hydroxy group. Discrete isosbestic points were observed for all the reagents except MNO. Protonation constants obtained from the absorbance change agreed well with those in literature for SXO, SMTB and SMXB (Table 1).^{5,8,9} The pK_a's of SBCO and NV were determined for the first time. For NV, 20% dioxane was used and readings of a pH meter, which was calibrated with aqueous buffers, were used without any correction. In the case of MNO, a complicated spectral change was observed, which may be ascribed to the surface-active nature of this reagent. The concentrations of these reagent solutions were determined by using the reaction with Cu(II); this also gave clear isosbestic points.

Zirconium(IV) and hafnium(IV) stock solutions were prepared as described elsewhere.^{10,11} All the solutions for both stocking and measuring were carefully prepared so as not to cause irreversible hydrolysis. Spectroscopic and potentiometric measurements were performed as described previously.¹

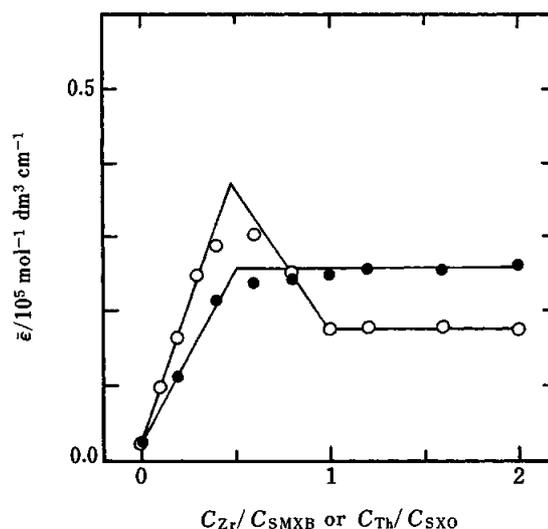


Fig. 2 Molar ratio plots for the reaction between Zr(IV) and SMXB and that between Th(IV) and SXO. $C_{SMXB}=C_{SXO}=10^{-5}$ mol dm⁻³. Reaction system, wavelength/nm, pH: (○) Zr(IV)-SMXB, 575, 2.25; (●) Th(IV)-SXO, 530, 4.0.

Results

General behavior of spectrophotometric systems

Using Zr-SMXB as a typical example, we describe the general behavior of reaction systems for spectrophotometric determination of fluoride. When varying amounts of Zr(IV) ($C_{Zr}=0-2 \times 10^{-5}$ mol dm⁻³) were reacted with a fixed concentration of SMXB ($C_{SMXB}=1 \times 10^{-5}$ mol dm⁻³) at pH 2.25, the absorbance at 575 nm reached the maximum at $C_{Zr}/C_{SMXB}=0.5$ (Fig. 2). At this ratio where two SMXB ligands may coordinate to one Zr(IV) center, both mida and phenolate groups are utilized to form fully colored complexes. At $C_{Zr}/C_L=1.0$, on the other hand, the absorbance is much lower than the maximum. Since a 1:1 complex, ML is coordination-unsaturated, a portion depending on pH hydrolyzes to form less colored complexes. This is more clearly shown by the pH dependence of absorption spectra of 1:1 mixtures (Fig. 3a). A strong absorption around 565 nm found at pH 0.35 diminishes with the increase in pH up to 4. When fluoride was added to this mixture at pH 2.25, the absorbance recovered linearly with its concentration up to 10^{-5} mol dm⁻³ (Fig. 3b); in a higher region, it reached a maximum and then decreased due to the substitution reaction of SMXB with fluoride. The best conditions were found out for each system by measuring the absorbance of a 1:1 mixture ($C_{ML}=10^{-5}$ mol dm⁻³) in the presence ($C_F=0.5 \times 10^{-5}$ mol dm⁻³) and absence of fluoride at varying pH values (Fig. 4).

Comparison of spectrophotometric systems

Performances of three metal ions were compared using SXO as a chromogenic reagent (Figs. 4a-c, Table I). Hafnium(IV) showed similar behavior to zirconium(IV)

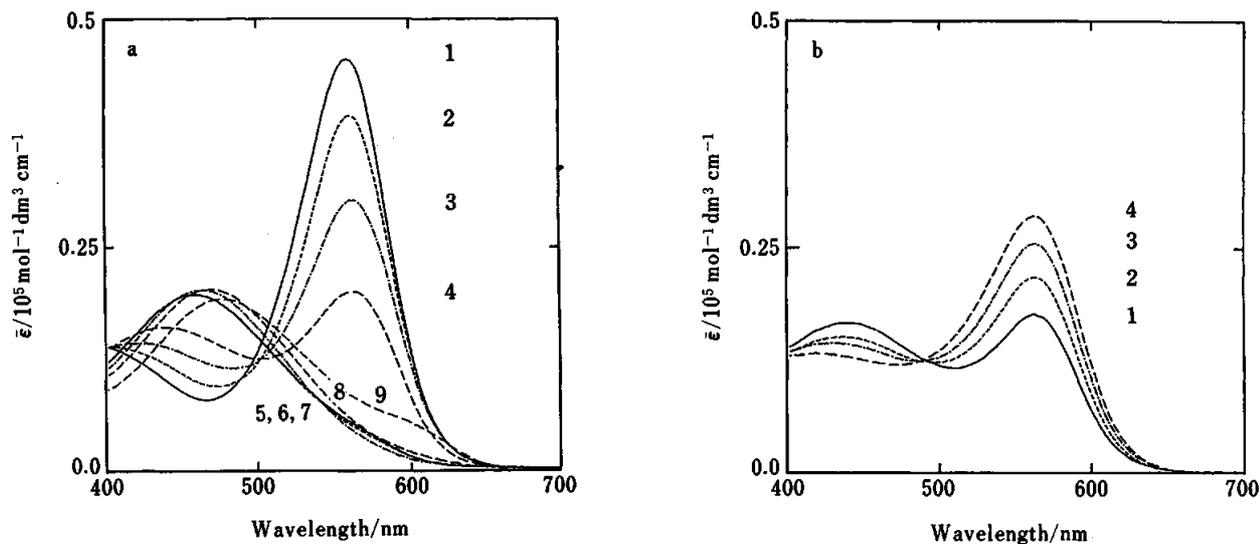


Fig. 3 Effects of pH (a) and F^- (b) on the absorption spectra in Zr-SMXB system. $C_{Zr}=C_{SMXB}=10^{-5}$ mol dm^{-3} . (a) pH: (1) 0.35, (2) 1.29, (3) 1.84, (4) 2.33, (5) 4.41, (6) 4.48, (7) 5.97, (8) 7.51, (9) 9.08. (b) pH=2.25; $C_{F^-}/mol\ dm^{-3}$: (1) 0, (2) 5×10^{-6} , (3) 10^{-5} , (4) 5×10^{-5} .

Table 1 Reagent systems for spectrophotometry of F^-

Ligand	pK_a^a	Metal	pH	λ_{max}/nm	Sandell ^b / $\mu g\ cm^{-2}$	Range ^c / $mol\ dm^{-3}$
SXO	7.4 ^d	Zr	2.0	530	0.0019	$0-1\times 10^{-5}$
		Hf	2.2	532	0.0023	$0-1\times 10^{-5}$
		Th	4.0	530	0.0056	$0-1\times 10^{-5}$
SMTB	7.6 ^e	Zr	2.0	565	0.0044	$0-1\times 10^{-5}$
SMXB	7.7 ^f	Zr	2.2	565	0.0024	$0-1\times 10^{-5}$
SBCO	5.5	Zr	2.0	475	0.0095	$0-5\times 10^{-5}$
MNO	— ^g	Zr	1.7	585	0.0011	$0-5\times 10^{-6}$
NV	7.5 ^h	Zr	1.0	632	0.0006	$0-5\times 10^{-6}$

a. Phenolic hydroxy group. b. Sandell sensitivity. c. Linear calibration range. d. Ref. 8. e. Ref. 9. f. Ref. 5. g. Complicated equilibria. h. 20% dioxane solution.

whereas thorium(IV) was quite different from these two metal ions in this respect. First, the maximum coloration attained at $C_{Th}/C_{SXO}=0.5$ in the binary system was kept at a higher ratio (Fig. 2). This agrees with the successive formation of ThL and ThL_2 complexes with molar absorptivities of 1 : 2 and implies that the ThL -type complex has less tendency to hydrolyze. Second, a decrease in absorbance rather than an increase was observed by the addition of fluoride at pH around 2 (Fig. 4c). Only a slight increase was observed at higher pH of 4.5. Thorium is not suited for this purpose.

Performances of chromogenic chelating reagents were compared using Zr(IV) as a central metal ion (Table 1). Among triphenylmethane dyes (Figs. 4a, d - f), SBCO showed quite different behavior in both binary and ternary systems, probably because of the difference in pK_a value. The others, SMTB and SMXB, showed sensitivities substantially equal to or slightly less than that of SXO. Slow decomposition of the reagent was observed for Zr-SMTB. Azo compounds, on the other hand, had lower blank values and higher sensitivities at

slightly lower pH values than triphenylmethane dyes (Figs. 4g, h, Table 1). Unfortunately, however, these reagents have some drawbacks, such as low solubility and low stability of binary systems. Addition of cationic, neutral or anionic surfactants never improved these drawbacks. Further structural modification is necessary for practical use.

Fluorometric systems

Absorption spectra of SSC were dependent on pH between 1 - 8. Recently, the crystal structure and acid-base equilibria of sulfonefluorescein, which corresponds to the fluorescent core of SSC, have been elucidated.^{12,13} The neutral form of SF has two phenol groups with partial quinonoid structure contribution in solid. The pK_a values for these phenol groups are 3.10 and 6.25, respectively. The spectral change of SSC with pH was consistent with these results on SF.

Zirconium(IV) complexes of SSC were stable over a wide pH range. The absorption maximum gradually shifted from 450 to 500 nm by the increase in pH. No

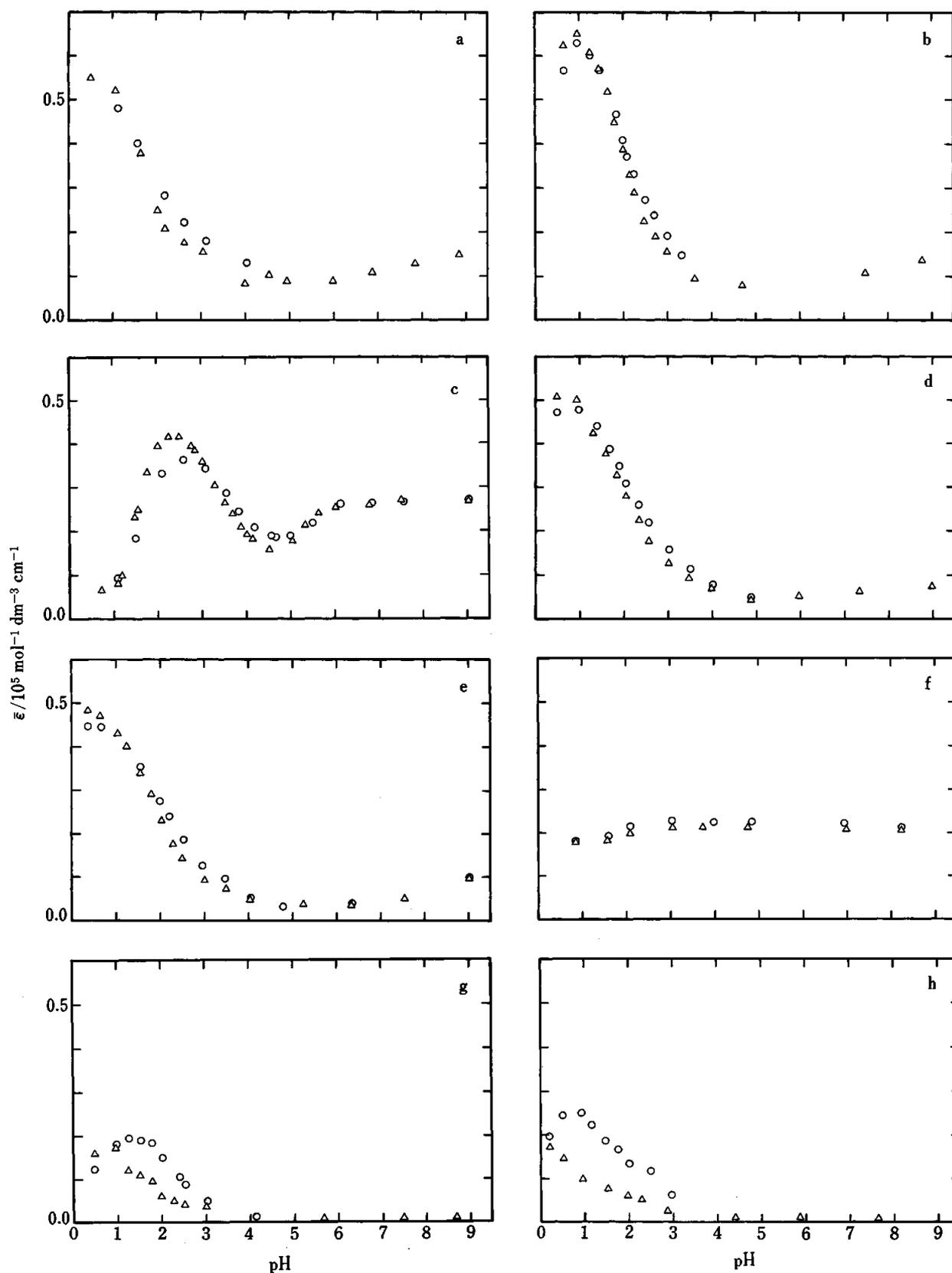


Fig. 4 Plot of apparent molar absorptivity vs. pH in the presence and absence of fluoride. $C_M=C_L=10^{-5} \text{ mol dm}^{-3}$. $C_F/\text{mol dm}^{-3}$: (Δ) 0, (\circ) 5×10^{-5} . Reagent system, wavelength/nm: (a) Zr-SXO, 530; (b) Hf-SXO, 532; (c) Th-SXO, 530; (d) Zr-SMTB, 565; (e) Zr-SMXB, 565; (f) Zr-SBCO, 475; (g) Zr-MNO, 585; (h) Zr-NV, 632.

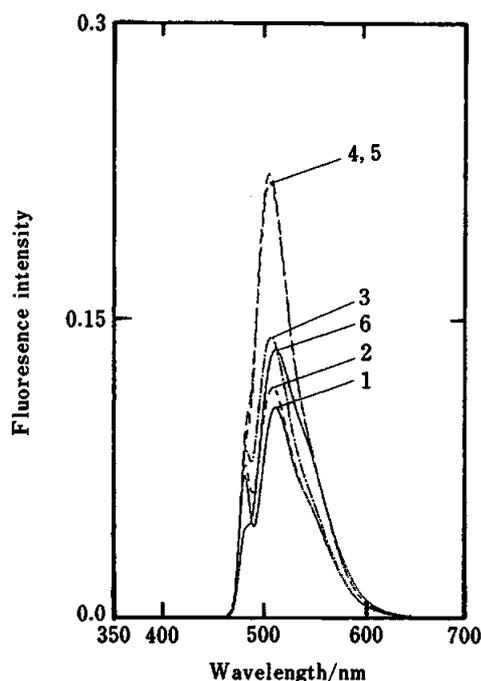


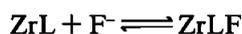
Fig. 5 Effect of F^- on fluorescence spectra in Zr-SSC system. $\lambda_{ex}=475$ nm. pH=3. $C_{Zr}=C_L=10^{-6}$ mol dm^{-3} . C_F /mol dm^{-3} : (1) 0, (2) 5×10^{-7} , (3) 10^{-6} , (4) 5×10^{-6} , (5) 10^{-5} , (6) 10^{-3} .

spectral change was observed by the addition of fluoride at any pH. In fluorescence spectra, on the contrary, an appreciable change was observed (Fig. 5). When a 1 : 1 mixture of Zr(IV) and SSC at 10^{-6} mol dm^{-3} was excited at 475 nm, fluorescence centered at 510 nm was observed. At higher pH, the intensity of emission spectra decreased. With addition of an equivalent amount of fluoride, the intensity of emission decreased at pH 1. At pH 2 and 3, the fluorescence increased up to $C_F=5 \times 10^{-6}$ mol dm^{-3} and decreased at higher than 10^{-5} mol dm^{-3} (Fig. 5). At pH > 4 or in the presence of 2-fold SSC, no change in fluorescence intensity was observed. This is the second example of a fluorescence increase by the addition of fluoride, but the sensitivity was almost half that of the Zr-CB (pH 2.5, $C_{Zr}/C_L=1.0$) system.²

Mechanism of fluorescence enhancement

The Zr-SSC (1 : 1) and Zr-CB (1 : 1) complexes were titrated potentiometrically with potassium fluoride at various $-\log[H^+]$ (1.6–2.5) and C_C (10^{-4} – 3×10^{-4} mol dm^{-3}) values. The results are shown as \bar{n}_F versus $-\log[F^-]$ in Fig. 6. The gradual increase in \bar{n}_F with a decrease in $-\log[F^-]$ indicates the formation of mixed-ligand complexes with F^- in these systems.

The \bar{n}_F versus $-\log[F^-]$ plot depends both upon $-\log[H^+]$ and C_{Zr} , indicating the change in protonation and polymerization degrees on this reaction. The conventional data treatment resulted in identifying the following reactions (charges of complexes are omitted).



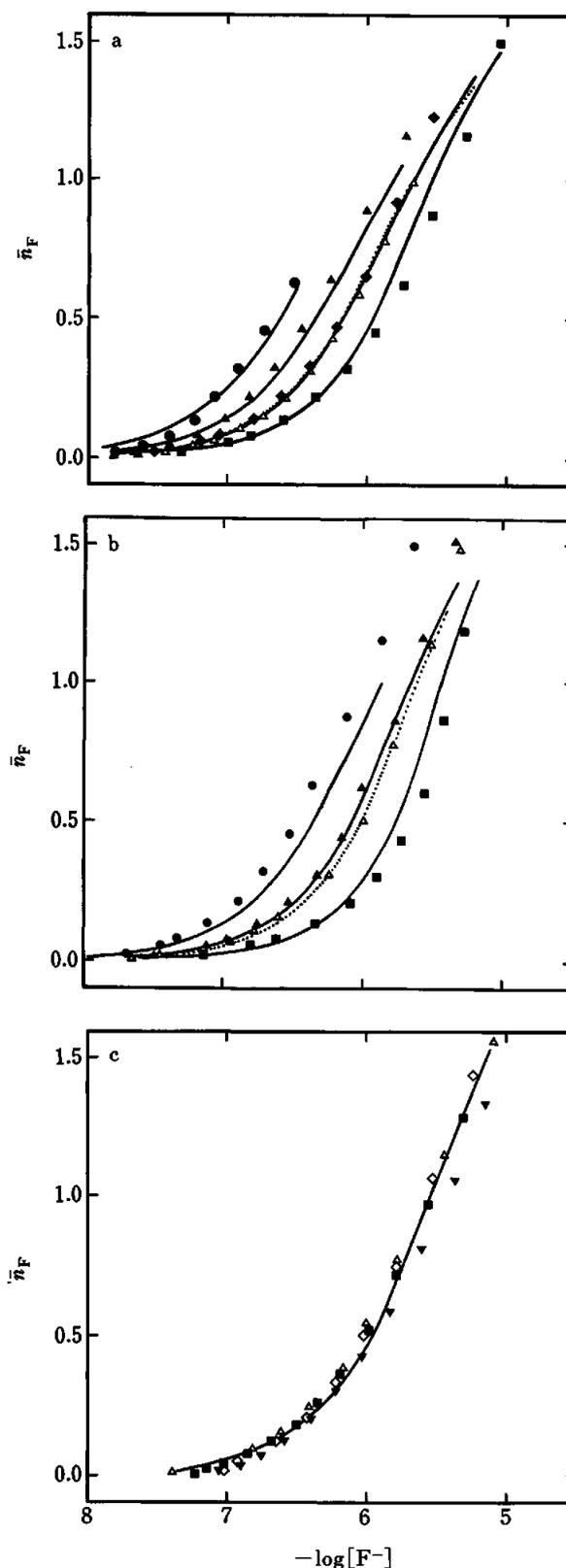
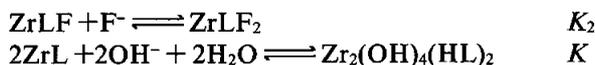
$$K_1$$


Fig. 6. Plot of \bar{n}_F vs. $-\log[F^-]$ for Zr-SSC- F^- (a), Zr-CB- F^- (b) and Zr-X- F^- (c) systems. (a) $-\log[H^+]$: (●) 1.7, (▲, △) 2.0, (◆) 2.2, (■) 2.5; C_{ML} /mol dm^{-3} : (●, ▲, ◆, ■) 10^{-4} , (△) 3×10^{-4} . (b) $-\log[H^+]$: (●) 1.8, (▲) 2.0, (△) 2.1, (■) 2.5; C_{ML} /mol dm^{-3} : (●, ▲, ■) 10^{-4} , (△) 3×10^{-4} . (c) $-\log[H^+]=2.0$; C_{ML} /mol dm^{-3} : (▼) 10^{-4} , (◇) 3×10^{-4} , (△) 10^{-3} , (■) 2×10^{-3} . Solid and dotted lines were calculated using the constants obtained.

Table 2 Equilibrium constants for Zr-L-F⁻ systems

L	log K ₁	log K ₂	log K
SSC	7.2±0.1	5.2±0.1	29.8±0.1
CB	7.1±0.2	5.1±0.2	29.2±0.2
SXO	7.5±0.1	5.3±0.1	29.3±0.1



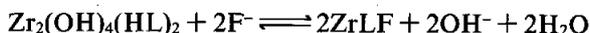
The constants obtained are summarized in Table 2, which also includes those for Zr-SXO. In the last paper on Zr-SXO¹, only K₁ and K were calculated with the data of $\bar{n}_F < 0.6$. In this work, all the data were included to give K₂ as well as K₁ and K. The constants obtained resemble each other and the same reaction as in the case of Zr-SXO is operative to the fluorescence enhancement.

The zirconium(IV) complex of X, which is the simplest compound having one mida group ortho to OH group, was also subjected to the same measurement (Fig. 6c). The \bar{n}_F versus $-\log[\text{F}^-]$ diagram depends on $-\log[\text{H}^+]$ but not on C_{Zr} over a wider range (10⁻⁴ – 2×10⁻³ mol dm⁻³). Thus the polymerization degree does not change on the reaction of Zr-X with fluoride.

Discussion

Ternary systems consisting of one metal ion and two ligands which have been used for various analytical purposes may be classified into three groups. The first takes advantage of the catalytic effect on the complexation reaction¹⁴, the second the exchange reaction giving negative signals¹⁵, and the third the mixed-ligand complex formation giving positive signals.¹⁶⁻¹⁸ The third method generally suffers from less blank signals and has better reproducibility, but only a few have been known for monodentate anions. When residual water molecules on the metal complex of a chromogenic reagent are replaced by such anions to form a mixed-ligand complex, its effect on the electronic structure of the reagent via a central metal ion is not large enough to cause a drastic change in spectral characteristics. Only the reagents like porphyrins having a narrow absorption band might be used for spectrophotometric determination of anions.¹⁹ Slight shifts of broad bands found in common complexes like Cu(II)-PAN cannot be used for such purposes.²⁰

The reaction with fluoride in this study is essentially different from these simple reactions. Central metal ions of parent complexes react with hydroxide ions with concomitant detachment and protonation of a coordinated phenolate group in acidic media.



On the reaction with fluoride, a phenolic OH group is deprotonated and coordinated to form mixed-ligand complexes having spectral characteristics similar to the parent complex. Dimerization of hydrolyzed species may also contribute to the change. In a survey of the literature, only one example was found, which might be based on a similar reaction mechanism, *i.e.* spectrophotometry of halides and pseudohalides with Hg(II)-methylthymolblue complex.²¹⁻²³

We acknowledge a Grant-in-Aid for Scientific Research (No. 02640444 and 05640680) from the Ministry of Education, Science, and Culture, and we thank the Nippon Sheet Glass Foundation for Materials.

References

1. A. Yuchi, N. Hokari, H. Wada and G. Nakagawa, *Analyst* [London], **118**, 219 (1993).
2. T. L. Har and T. S. West, *Anal. Chem.*, **43**, 136 (1971).
3. D. C. Olson and D. W. Margerum, *Anal. Chem.*, **34**, 1299 (1962).
4. T. Yoshino, H. Imada, T. Kuwano and K. Iwasa, *Talanta*, **16**, 151 (1969).
5. J. Ueda, *Nippon Kagaku Kaishi*, **1977**, 350.
6. B. Budesinsky, *Z. Anal. Chem.*, **195**, 324 (1963).
7. B. Budesinsky, *Collect. Czech. Chem. Commun.*, **22**, 1579 (1957).
8. M. Murakami, T. Yoshino and S. Harasawa, *Talanta*, **14**, 1293 (1967).
9. T. Yoshino, S. Murakami and M. Kagawa, *Talanta*, **21**, 199 (1974).
10. A. Yuchi, J. Baba, H. Wada and G. Nakagawa, *Analyst* [London], **116**, 45 (1991).
11. A. Yuchi, T. Niwa and H. Wada, *Analyst* [London], **120**, 167 (1995).
12. H. Kanazawa, K. Senga, Z. Tamura and Y. Iitaka, *Anal. Sci.*, **10**, 521 (1994).
13. Z. Tamura, T. Morioka, M. Maeda and A. Tsuji, *Bunseki Kagaku*, **43**, 339 (1994).
14. S. Yamada, A. Murata and M. Tanaka, *Mikrochim. Acta* [Wien], **1988**, 291.
15. J. F. Verchere and A. M. Dona, *Analyst*, **20**, 437 (1992).
16. A. K. Babko, *Talanta*, **15**, 721 (1968).
17. A. T. Pilipenko and M. M. Tananaiko, *Talanta*, **21**, 501 (1974).
18. P. R. Haddad, *Talanta*, **24**, 1 (1977).
19. P. F. Pasternack and G. R. Parr, *Inorg. Chem.*, **15**, 3087 (1976).
20. A. Galik, *Anal. Chim. Acta*, **57**, 39 (1971).
21. T. Nomura, *Nippon Kagaku Zasshi*, **88**, 961 (1967).
22. T. Nomura, *Bull. Chem. Soc. Jpn.*, **41**, 1619 (1968).
23. T. Nomura and S. Komatsu, *Nippon Kagaku Zasshi*, **90**, 168 (1969).

(Received November 4, 1994)

(Accepted January 9, 1995)