

Semi-Xylenol Orange Complex of Zirconium(IV) as a Photometric Reagent System for Fluoride Based on Mixed Ligand Complex Formation

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An equimolar mixture of zirconium(IV) and Semi-Xylenol Orange (SXO) reacts rapidly with fluoride ion at pH 2 to cause an increase in absorbance at about 530 nm. The calibration graph was linear up to 1×10^{-5} mol dm⁻³. In a flow injection system, a detection limit (signal-to-noise ratio = 3) of 2.5×10^{-7} mol dm⁻³ was obtained with a sample throughput of 60 h⁻¹. Potentiometric studies of this reaction system with a fluoride ion-selective electrode demonstrated that an increase in absorbance can be ascribed to the coordination of the phenolic oxygen of SXO on the reaction of a partly hydrolysed Zr–SXO complex with fluoride ion to give the mixed ligand complex.

Keywords: Fluoride determination; spectrophotometry; zirconium(IV); Semi-Xylenol Orange; mixed ligand complex

Although methods for the determination of F⁻ have largely shifted from spectrophotometry to potentiometry using an ion-selective electrode,¹ the former is adopted on occasion for reasons of precision and reproducibility. Numerous spectrophotometric methods for F⁻ have been reported and can be classified into three groups: (i) substitution of coloured complexes with F⁻, e.g., Zr^{IV}–Solochrome Cyanine R;² (ii) catalytic action of F⁻ on the complexation of polymeric hydrolysed species, e.g., Zr^{IV}–Xylenol Orange (XO);³ (iii) mixed ligand complex formation, e.g., La^{III}–Alizarin Complexone (La–ALC).⁴ The methods in group (i) use a decrease in absorbance and thus suffer from large blank absorbances. The methods in group (ii) have high sensitivity, but lack reproducibility because of the difficulty in controlling the degree of hydrolysis of the metal ions. In these respects, the methods in group (iii) are superior, but there are only a few reaction systems that are known^{4–6} and these are not always satisfactory; the most widely used reagent, La–ALC,⁴ has the drawback of slow reaction rates in aqueous solutions.

In this work, the reactions between F⁻ and the Zr^{IV} complexes of several organic reagents (L) have been studied, and a reaction that uses the known chromogenic reagent, Semi-Xylenol Orange (SXO), has been developed. The reaction of Zr–SXO with F⁻ is much faster than, and has comparable sensitivity to, that of La–ALC. Although the reagent blank is high, as with La–ALC, F⁻ was successfully determined using a simple flow injection (FI) system.

To obtain a guide for further development of organic reagents suited to spectrophotometric determination of F⁻, the reaction system was studied potentiometrically using a fluoride ion-selective electrode, as has been carried out for La–ALC.⁷ Formation of mixed ligand complexes is confirmed, and the colour development mechanism presented.

Experimental

Reagents

Potassium fluoride was dried in a platinum crucible for 24 h at 110 °C. Fluoride solutions were stored in polyethylene containers. The SXO and XO were prepared and purified as described previously.⁸ A Zr^{IV} stock solution was prepared by dissolving ZrO(NO₃)₂ in 1.5 mol dm⁻³ HNO₃, which prevents the formation of polymeric hydrolysed species.^{9–11} The concentration of Zr^{IV} was determined by titration with ethylenediaminetetraacetic acid (EDTA) in 1 mol dm⁻³ HNO₃ at 90 °C using XO as indicator. All other reagents used were of analytical-reagent grade.

Preparation of Solutions

Extra care was taken not to cause irreversible hydrolysis and polymerization when handling the Zr^{IV} solutions. The SXO solution was slowly poured into an acidic Zr^{IV} solution with vigorous stirring, and the pH carefully adjusted with ammonia solution. If necessary, buffer and/or F⁻ was added and the solution diluted with distilled water. The Zr–SXO (1:1) solution thus obtained was stable for at least 1 week.

Measurement

All measurements were performed at 25.0 °C. As a measure of H⁺ concentration, an activity scale (pH) was used in the spectrophotometric studies, whereas a concentration scale ($-\log[H^+]$) was used in the potentiometric studies. The equipment used for potentiometry was the same as that described previously.¹² Several solutions containing metal complexes (0.1 mol dm⁻³ KNO₃) were titrated with a potassium fluoride solution at various $-\log[H^+]$ values. The average number of F⁻ ions bound to a metal ion, \bar{n}_F , was calculated using $-\log[H^+]$ and $-\log[F^-]$.¹²

Flow Injection

The reagent solution (Zr–SXO, 1×10^{-5} mol dm⁻³; and ClCH₂COOH–ClCH₂COO⁻, 0.1 mol dm⁻³; pH 2) and redistilled water were each delivered at 1.0 cm³ min⁻¹ with a double-plunger reciprocal pump. The sample was injected into the water stream using a rotary valve with a 100 mm³ loop. Sample and reagent solutions were mixed in a coil (20 cm × 0.5 mm i.d.), which was wound around a narrow cylinder in a figure-of-eight fashion.¹³ The absorbance at 530 nm was monitored using a spectrophotometer equipped with a flow cell (10 mm light path and 8 mm³ volume) and a chart recorder. A back-pressure coil (100 cm × 0.25 mm i.d.) was attached to the outlet of the flow cell.

Results and Discussion

Chromogenic Chelating Reagents

Initially, a systematic study of the reactions between F⁻ and the Zr complexes was made using five chromogenic chelating reagents; absorption spectra were recorded for an equimolar mixture of Zr^{IV} and the organic reagent (1×10^{-5} mol dm⁻³) both in the presence (0.5×10^{-5} mol dm⁻³) and absence of F⁻ over the pH range 0–9. The organic reagents examined were

SXO, XO, Alizarin Red S (ARS), 5-amino-3-(3-chloro-2-hydroxy-5-nitrophenylazo)-4-hydroxynaphthalene-2,7-disulfonic acid (Gallion) and 2-(4-sulfophenylazo)-1,8-dihydroxy-3,6-naphthalenedisulfonic acid (SPADNS). Appreciable differences in absorbance were observed with SXO at a pH of about 2. Further studies were carried out with both SXO and XO, which showed markedly different behaviour despite having similar structures.

Binary Systems

Absorption spectra were recorded for a series of solutions containing $1 \times 10^{-5} \text{ mol dm}^{-3}$ SXO or XO and various concentrations of Zr^{IV} (c_{Zr}) at pH 2. In Zr-XO, the absorbance at 550 nm increased linearly with c_{Zr} up to $c_{\text{Zr}} = c_{\text{L}}$, because the molar absorptivities of 1:2 complexes are almost twice those of 1:1 complexes as is often the case (here, 1:1 complexes denote all the complexes having this metal-to-ligand ratio irrespective of degree of polymerization, protonation or hydrolysis). In Zr-SXO, on the other hand, an absorbance maximum was found at $c_{\text{Zr}} = c_{\text{L}}/2$. This suggests unusual structures for 1:1 complexes (*vide infra*).

The reactions of Zr^{IV} with SXO and XO have only been examined in strongly acidic media to avoid any possible hydrolysis of Zr^{IV} .^{8,14,15} The effect of pH on the complexation in binary systems was studied (Fig. 1). For Zr-SXO (1:1) (hereafter, such numerals in parentheses denote the metal-to-ligand concentration ratio), the solution was strongly coloured at pH 0.5. With an increase in pH up to 4, the absorbance around 530 nm decreased, whereas that around 460 nm increased. An isosbestic point was observed at 488 nm up to pH 2.5, but at higher pH the spectral change was complicated. The absorption spectrum at $\text{pH} > 4$ ($\lambda_{\text{max}} = 460\text{--}470 \text{ nm}$) is different from that of a free ligand ($\lambda_{\text{max}} = 440 \text{ nm}$). The loss of colour from a solution at high pH was reversed upon a decrease in pH, therefore, SXO is neither dissociated from Zr^{IV} nor decomposed. These findings are explained by the formation of a hydrolysed 1:1 complex (*vide infra*).

The absorbance of Zr-SXO (1:2) was larger than that of Zr-SXO (1:1) at any pH. The difference in absorbance is

ascribed to the formation of 1:2 complexes in acidic media, and to the presence of a free ligand at pH 5–9. The hydrolysed 1:1 complexes are preferentially formed at pH 5–9 even in the presence of excess reagent.

For Zr-XO, on the other hand, the absorbance increased steeply between pH 1 and 2, and more gradual decoloration was found than with Zr-SXO at higher pH.

Ternary Systems

The spectral change in Zr-SXO (1:1) upon the addition of F^- at pH 2 is shown in Fig. 2. The absorbance at 530 nm increased in proportion to the F^- concentration, up to $1 \times 10^{-5} \text{ mol dm}^{-3}$, reached a maximum of around 0.4 at between 2×10^{-5} and $3 \times 10^{-5} \text{ mol dm}^{-3}$ (not shown) and decreased at much higher concentrations ($1 \times 10^{-2} \text{ mol dm}^{-3}$).

The effect of pH on the absorbance change is shown in Fig. 3. An increase in absorbance upon the addition of F^- was found at pH 1.5–2.5. In contrast, the absorbance decreased at pH 1, and no changes were observed at a $\text{pH} > 3$. With Zr-SXO (1:2), the change of absorbance was small and was not linear against F^- concentration, at any pH. The Zr-XO system showed no appreciable changes in absorbance under any conditions.

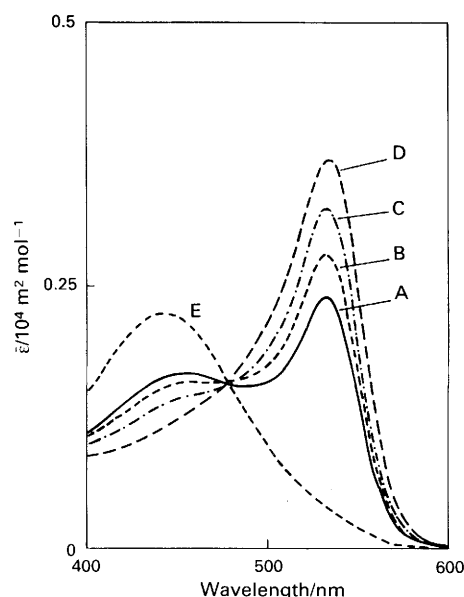


Fig. 2 Absorption spectra of Zr-SXO at various F^- concentrations. c_{Zr} and c_{SXO} , $1 \times 10^{-5} \text{ mol dm}^{-3}$; pH, 2. A, 0; B, 5×10^{-6} ; C, 1×10^{-5} ; D, 5×10^{-5} ; and E, $1 \times 10^{-2} \text{ mol dm}^{-3}$.

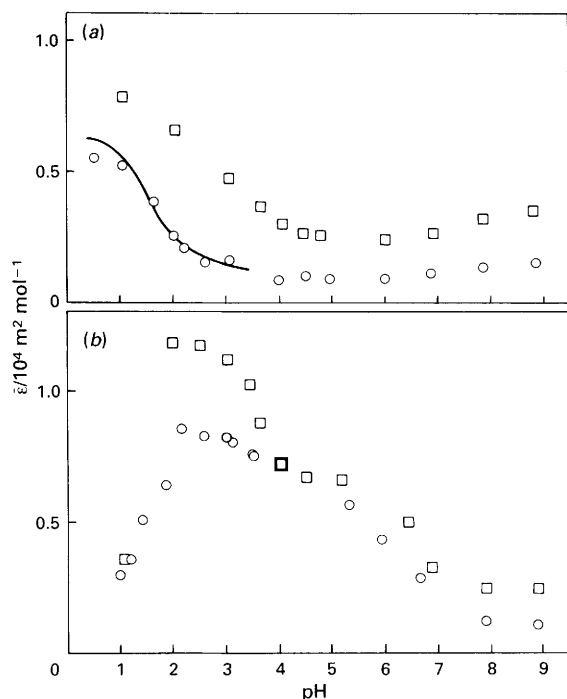


Fig. 1 Plot of apparent molar absorptivity versus pH for (a) Zr-SXO and (b) Zr-XO. c_{Zr} , $1 \times 10^{-5} \text{ mol dm}^{-3}$; c_{L} : \circ , 1×10^{-5} ; and \square , $2 \times 10^{-5} \text{ mol dm}^{-3}$. Wavelength: (a) 530; and (b) 560 nm. The solid curve was calculated by using the constants obtained

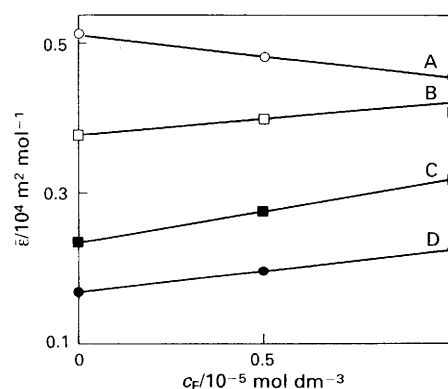


Fig. 3 Effect of pH on absorbance change by addition of F^- to Zr-SXO. c_{Zr} and c_{SXO} , $1.0 \times 10^{-5} \text{ mol dm}^{-3}$. Wavelength, 530 nm. pH: A, 1; B, 1.5; C, 2; and D, 2.5.

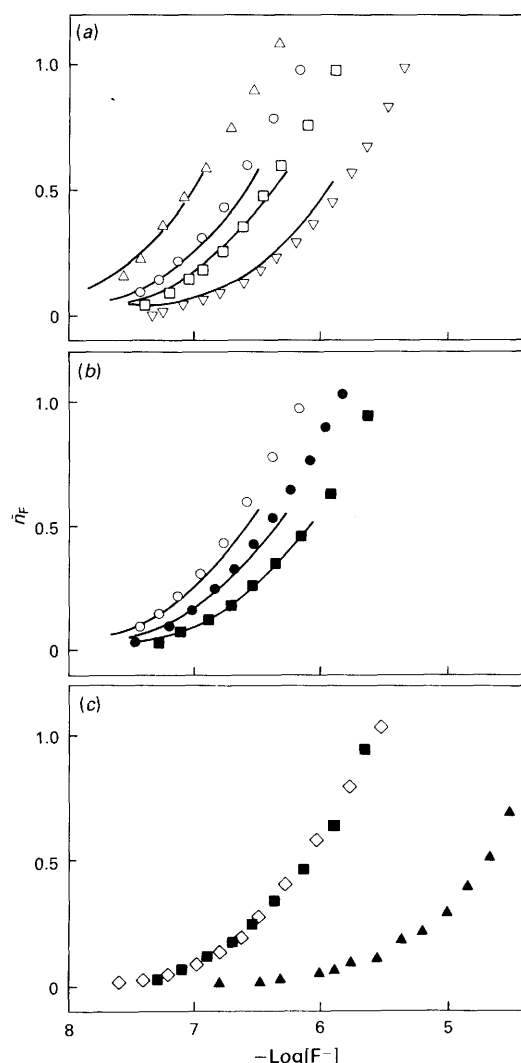


Fig. 4 Plot of $\bar{\eta}_F$ versus $-\log[F^-]$ at 25 °C and 0.1 mol dm⁻³ KNO₃. (a) Reagent system, Zr-SXO, c_{Zr} , 1×10^{-4} mol dm⁻³, $-\log[H^+]$: Δ , 1.5; \circ , 2.0; \square , 2.2 and ∇ , 2.7. (b) Reagent system, Zr-SXO, $-\log[H^+]$, 2.0, c_{Zr} : \circ , 1×10^{-4} ; \bullet , 3×10^{-4} ; and \blacksquare , 1×10^{-3} mol dm⁻³. (c) Reagent system: \blacksquare , Zr-SXO; \blacktriangle , Zr-XO; and \diamond , Zr-CB, $-\log[H^+]$, 2.0, c_{Zr} , 1×10^{-3} mol dm⁻³. The solid curves were calculated by using the constants obtained

Evidence for Mixed Ligand Complexes and the Colour Change Mechanism

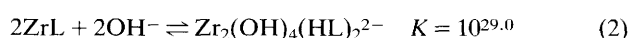
The Zr-SXO (1:1) and Zr-XO (1:1) systems were titrated potentiometrically with potassium fluoride at various $-\log[H^+]$ (1.5–2.7) and c_{Zr} (1×10^{-4} – 1×10^{-3} mol dm⁻³) values. The 4-methylumbelliferone-8-methyleneiminodiacetic acid (Calcein Blue; CB) complex of Zr^{IV}, Zr-CB, which is known as an excellent fluorescent reagent for F⁻,¹⁶ was also subjected to examination. The results are shown as $\bar{\eta}_F$ versus $-\log[F^-]$ in Fig. 4. The increase in $\bar{\eta}_F$ with a decrease in $-\log[F^-]$ demonstrated the formation of mixed ligand complexes with F⁻ in these systems.^{17,18}

The $\bar{\eta}_F$ versus $-\log[F^-]$ plot for Zr-SXO (1:1) depends both on $-\log[H^+]$ and c_{Zr} [Fig. 4(a) and (b)]. This indicates a change in the degree of hydrolysis and polymerization on the formation of the mixed ligand complex. Various combinations of species were assumed and stability constants for each set were refined to give a minimum error square sum about $\bar{\eta}_F$. In this calculation, data for $\bar{\eta}_F > 0.6$ were omitted to avoid the complexity caused by the formation of higher ratio complexes

Table 1 Effects of foreign anions on the absorbance of Zr-SXO-F⁻ (the absorbance of Zr-SXO-F⁻ was 0.285 for $c_F = 4 \times 10^{-6}$ mol dm⁻³ in the absence of foreign ions)

Foreign ion	Concentration/mol dm ⁻³			
	10 ⁻⁵	10 ⁻⁴	10 ⁻³	10 ⁻²
Cl ⁻	0.287	0.291	0.291	0.291
NO ₃ ⁻	0.285	0.288	0.288	0.291
CO ₃ ²⁻	0.290	0.293	0.290	0.290
SO ₄ ²⁻	0.285	0.295	0.322	—
SO ₃ ²⁻	0.288	0.297	0.325	—
PO ₄ ³⁻	0.287	0.300	—	—

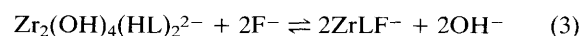
and the dissociation of ligands. The following equilibria were identified:



The calculated curves using the constants obtained are in good agreement with the experimental points, as shown in Fig. 4. Moreover, an absorbance decrease in the binary system (Fig. 1) can also be reproduced using eqn. (2), except for strongly acidic media in which the SXO is partly dissociated from Zr^{IV}.

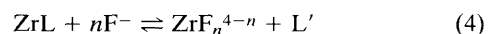
The equilibrium constant for eqn. (1) is extremely large because of the coordination-unsaturation of ZrL. This reaction is ascribed to the replacement of a water molecule with F⁻.^{17,18} As the spectrum of ZrLF is similar to that of ZrL, no appreciable changes are observed in the absorption spectrum at pH 1.5, where ZrL is the predominant species (Fig. 3).

The ZrL complex also has a high affinity for OH⁻ and hydrolyses to form a dimer with an increase in pH, as shown by eqn. (2). On this occasion, a phenolate group of SXO is detached from Zr^{IV} and is protonated to give HL, which coordinates with Zr^{IV} only by using a methyleneiminodiacetate group and is itself not deeply coloured. The formation of hydrolysed complexes has been well characterized in the complexation of Zr^{IV} with aminopolycarboxylates.¹⁹ At a pH around 2, the partly hydrolysed complex is predominant and its reaction with F⁻ is expressed by:



In contrast to eqn. (1), this reaction causes a colour change.

At a high pH, the equilibrium given by eqn. (3) shifts to the left, and the reactivity with F⁻ is much decreased. At a low pH, on the other hand, the reactions of method group (i) also contribute to the decrease in absorbance (Fig. 3):



Thus, the reaction with F⁻ is highly pH-dependent. In Zr-SXO (1:2), 1:2 complexes are also formed to reduce the affinity for F⁻.

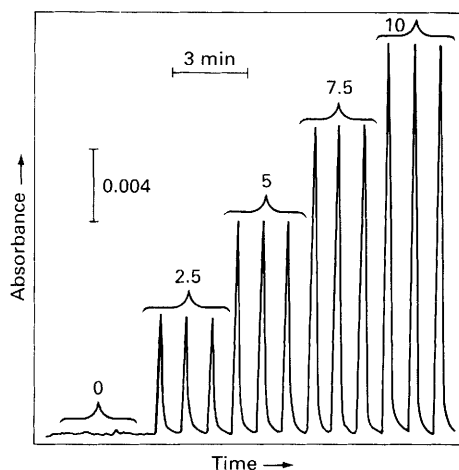
The Zr-CB complex has almost the same reactivity to F⁻ as Zr-SXO, at pH 2 and $c_{Zr} = 1 \times 10^{-3}$ mol dm⁻³. This reagent has virtually the same functional groups as SXO, to coordinate to Zr^{IV}. The change in fluorescence of Zr-CB owing to F⁻ is ascribed to the same reaction as for Zr-SXO. Chelating reagents with a methyleneiminodiacetate group *ortho* to a phenolic hydroxy group are generally suitable for this purpose.

In contrast to Zr-SXO and Zr-CB, Zr-XO has a lower reactivity to OH⁻ (Fig. 1) and F⁻ [Fig. 4(c)]. This suggests an essentially different species such as M₂L₂, which has been proposed for the bismuth complex.²⁰ Xylenol Orange is a potential octadentate ligand but cannot coordinate to a single metal ion using all these donor atoms. In M₂L₂, coordination saturation can be expected for octa-coordinate Zr by double-bridging.²⁰

Table 2 Spectrophotometric determination of F⁻ by FI

Reaction system	Method group	Detection limit/ mol dm ⁻³	Sampling rate/h ⁻¹	Remarks	Ref.
Zr-SXO	(iii)	2.5×10^{-7}	60		This work
Zr-SPADNS	(i)	1.1×10^{-6}	50		21
U-Arsenazo III	(i)	2.6×10^{-6}	30		22
Zr-ARS	(i)	—	100		23
Zr-MTB*	(ii)	5.3×10^{-7}	40		24
La-ALC	(iii)	1.6×10^{-6}	24	60 °C, water-acetone	25
La-ALC	(iii)	2.6×10^{-6}	60	Stopped-flow, surfactant	26

* MTB = Methylthymol Blue.

**Fig. 5** Calibration output for Zr-SXO-F⁻. c_{Zr} and c_{SXO} , 1×10^{-5} mol dm⁻³ (values shown are for $c_{\text{F}}/10^{-6}$ mol dm⁻³)

Batchwise Determination

Four acid-base pairs having pK_a values of around 2 were examined as pH buffers. Even 1×10^{-5} mol dm⁻³ solutions of H₂PO₄⁻-HPO₄²⁻ and H₃P₂O₇⁻-H₂P₂O₇²⁻ reacted with Zr-SXO to cause a change in absorption spectra. A 1×10^{-2} mol dm⁻³ HSO₄⁻-SO₄²⁻ solution decreased both the sensitivity and linearity of the calibration graphs. On the other hand, 0.1 mol dm⁻³ ClCH₂COOH-ClCH₂COO⁻ did not show any effect except a slight increase in the blank absorbance, and thus was employed.

When the concentration (1×10^{-5} mol dm⁻³) of Zr-SXO (1:1) is doubled, the sensitivity is increased by 50%. Cationic and anionic surfactants and water-miscible organic solvents have occasionally shown sensitivity enhancements in the spectrophotometric determination of F⁻, but no effects were found in this system. Under the optimum conditions, Zr-SXO (1:1) at pH 2, the calibration graph was linear up to 1×10^{-5} mol dm⁻³ F⁻ and the Sandell sensitivity was 1.9×10^{-3} µg cm⁻². The reaction is fast and can be used for the spectrophotometric determination of F⁻.

The effects of foreign ions on the absorbance of Zr-SXO-F⁻ are shown in Table 1. Chloride, nitrate and carbonate are tolerated up to 1×10^{-2} mol dm⁻³. Metal ions, especially aluminium, must be separated before the determination is carried out.

Application to FI

Parameters affecting the FI signal were varied (pH, 1.6-2.3; sample volume, 25-180 mm³; mixing coil length, 0-20 cm, flow rate, 0.5-1.5 cm³ min⁻¹) and were optimized as described in the Experimental section. A typical calibration output is shown in Fig. 5. When the Zr-SXO (1:1) concentration was

increased from 1×10^{-5} to 3×10^{-5} mol dm⁻³, the sensitivity was increased 2-fold, but a higher blank absorbance increased the detection limit. Compared with other FI methods for F⁻ (Table 2), the Zr-SXO method is simple (no heating, short coil) and has a lower detection limit.

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