STUDY OF THE INTERACTIONS OF SCANDIUM AND CHROMAZUROL S WITH CETYLPYRIDINIUM, CETYLTRIMETHYLAMMONIUM OR CARBETHOXYPENTADECYLTRIMETHYLAMMONIUM BROMIDE

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The interactions of scandium and chromazurol S with cation active tensides were studied, *i.e.* with cetyltrimethylammonium, carbethoxypentadecyltrimethylammonium and cetylpyridinium bromide. The formation of a ternary negatively charged complex with component ratio 1 : 2 : 2 was confirmed. The ternary complex can be employed for very sensitive spectrophotometric determination of 0·04—0·4 μg of scandium in 1 ml of analyzed solution.

Chromazurol S was used for the spectrophotometric determination of scandium on the basis of formation both of the binary[1,2] and of the ternary complex in the presence of diantipyrilmethane[3], 1,10-phenanthroline[4] and cation active tenside zephiramine[5]. In this work we studied the ternary complex of scandium and chromazurol S or eriochromcyanine R with other cation active tensides, *i.e.* cetylpyridinium, cetyltrimethylammonium and carbethoxypentadecyltrimethylammonium bromide. We used the first tenside in the determination of U(VI) with chromazurol S (ref.[6]) or eriochromcyanine R (ref.[7]) and in the determination of fluoride by bleaching of the aluminium complex with both reagents[8]; the third tenside was used, *e.g.*, in the determination of osmium[9].

Study of the interaction of the above components confirms formation of a ternary complex with defined stoichiometry and suggests the possibility of using these reactions for the photometric determination of scandium.

EXPERIMENTAL

Instruments and Chemicals

The spectrophotometric measurements were carried out on a recording Specord UV VIS spectrophotometer (Zeiss, Jena) or SP 8—100 (Pye-Unicam, Cambridge, England) instrument. The pH measurements were carried out on a PHM-62 instrument (Radiometer, Copenhagen,

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Denmark). The GK 2401 B glass electrode was calibrated using pH 4·01 and 7·00 buffers from the same manufacturer.

The stock solution was prepared by dissolving 0·1534 g of very pure Sc_2O_3 in 20 ml of conc. HCl and diluting with water to 100 ml; the solution contained 1 mg Sc per ml. The working solution containing 10 μg per ml was prepared by diluting the stock solution. Solutions of $1 . 10^{-3}$M chromazurol S (CAS) and eriochromcyanine R (ECR) were prepared in the usual way[6,7]. Solutions of cetylpyridinium bromide (CPB), $1 . 10^{-3}$M, cetyltrimethylammonium bromide (CTMAB), $5 . 10^{-3}$M and carbethoxypentadecyltrimethylammonium bromide (CPTB, Septonex), $5 . 10^{-3}$M were prepared by dissolving the appropriate amount of the substance in redistilled water.

The effect of the ionic strength was studied with 1M-KCl, NaCl, NH_4Cl, NH_4NO_3, KNO_3 and 0·33M-K_2SO_4 and $(NH_4)_2SO_4$ solutions. The pH was adjusted using acetate buffers.

All solutions were prepared from *p.a.* chemicals in redistilled water.

RESULTS

Formation and Composition of the Ternary Complex

The ternary complex of scandium with chromazurol S or eriochromcyanine R is formed in the presence of all three cation active tensides, *i.e.* CTMAB, CPTB and CPB, as depicted in Fig. 1 for CTMAB. It follows from the absorption curves that, under the given conditions the binary complex with chromazurol S it not formed and its spectrum is almost identical with that of a mixture of the reagent and CTMAB (curves 2 and 3). For eriochromcyanine R a small shift toward formation of the binary complex of the metal with the coloured ligand (curve 2) can be observed compared with the ligand alone (curve *1*). In the simultaneous presence of all three components, *i.e.* metal, ligand and cation active tenside (CTMAB), the spectra of both indicators (curves *3* and *3'*) exhibit the usual bathochromic and hypsochromic shifts much more markedly for chromazurol S. On the basis of this fact, further attention was paid to this substance.

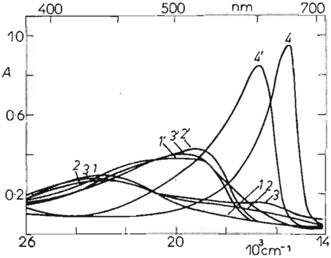

FIG. 1

The Absorption Spectra of the Ternary Complex of Scandium with Chromazurol S and Eriochromcyanine R in the Presence of Cetyltrimethylammonium Bromide

$c_{Sc} = 3·1 . 10^{-6}$M, $c_{CAS} = 3·2 . 10^{-5}$M; $c_{ECR} = 8 . 10^{-5}$M; $c_{CTMAB} = 1 . 10^{-4}$M; pH 5·63. Curves: *1* CAS, *1'* ECR, *2* Sc + CAS, *2'* Sc + ECR, *3* CAS + CTMAB, *3'* ECR + + CRMAB, *4* Sc + CAS + CTMAB, *4'* Sc + ECR + CTMAB.

Formation of the Sc–CAS–T* complex proceeds in weakly acid medium of about the same pH for all three tensides; in each case a reaction involving the same dissociated form of the dye HL^{3-} occurs. The concentration of the dye and tenside and especially their concentration ratio have a marked effect on complex formation. At a concentration of Sc of $4 \cdot 4 \, . \, 10^{-6}$M, a seven-fold excess of the dye and a 14–21-fold concentration excess of one of the tensides is most suitable. A summary of the most suitable conditions for formation of the ternary complex of Sc permitting its determination is given in Table I.

Complexes with all the tensides are formed at laboratory temperature, instantaneously for CTMAB and CPB, and are stable for more than 12 h; complexes with CPTB are relatively unstable and exhibit maximum absorbance only between 8 and 20 minutes after mixing of the components. The ternary complexes are not affected by the ionic strength of the solution in the range $I = 0 \cdot 05 - 0 \cdot 2$ in the presence of chloride or sulphate; it was found that nitrate ions decrease the absorbance and increase complex precipitation.

Further attention was directed to the composition of the Sc–CAS–T complex. Using the methods described by Babko[10], a component ratio for the ternary complex, *i.e.* metal : ligand : tenside, of 1 : 2 : 2 was found (Fig. 2). As the ratio Sc : CAS = = 1 : 2 is known[3], the amount of ligand bound was found from the number of bonds releasing protons according to Nonova and Evtimova[11], confirming the overall component ratio 1 : 2 : 2. In addition, experiments were carried out on extraction of the ternary complex into gradually less polar solvents, *i.e.* nitromethane ($\varepsilon = 38 \cdot 2$), N-butanol ($\varepsilon = 17 \cdot 4$) and benzene ($\varepsilon = 2 \cdot 28$). It was found that the extractability of the complex decreases with decreasing permittivity of the solvent, so that

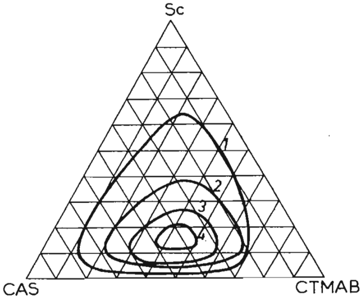

FIG. 2

Isochromes of the Ternary Complex of Scandium with Chromazurol S and Cetyltrimethylammonium Bromide

$c_{SC} + c_{CAS} + c_{CTMAB} = 1 \, . \, 10^{-5}$M; absorbance: *1* 0·30, *2* 0·50, *3* 0·70, *4* 0·90.

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* T^{x} is the cation active tenside.

extraction into benzene does not occur. Experiments with the studied tensides were carried out under optimal conditions (Table I) and pH in the interval 4·8 to 6·5, where CAS exists in the dissociated form HL^{3-} and Sc primarily in the $Sc(OH)^{2+}$ form[12]. On the basis of the component ratio found for the complexes and the fact that the complex was not extracted into benzene and is thus probably charged, as was orientatively confirmed by zonal electrophoresis, the complex can be depicted as

$$[Sc(OH)^{2+} \ldots HL^{3-} \ldots T_2^+]^{2-} .$$

Photometric Determination of Scandium

Conditions for formation of the ternary complexes of Sc (Table I) are also optimum for determination of trace amounts of this element. Thus calibration curves were constructed for all the cation-active tensides and were evaluated statistically (Table II). The values in this table indicate that the determination methods for Sc are generally very sensitive and that method *I* with CTMAB remains most favourable; the following procedure is thus recommended:

TABLE I

Optimum Conditions for the Formation of the Ternary Complex of Scandium with Chromazurol S and Cetyltrimethylammonium Bromide, Carbethoxypentadecyltrimethylammonium Bromide or Cetylpyridinium Bromide

$c_{Sc} = 4 \cdot 4 \,.\, 10^{-6}$M.

System	λ_{max}, nm	pH	$c_{CAS} \,.\, 10^5$M	$c_T \,.\, 10^5$M
Sc–CAS–CTMAB	654	5·50—7·00	3·2	10·0
Sc–CAS–KPTB	640	4·75—6·50	3·6	8·0
Sc–CAS–CPB	650	5·45—6·75	3·2	6·4

TABLE II

Determination of Scandium

The limits of the standard deviations of parameters *a* and *b* are given; *v*, %, is the coefficient of variation.

Method	System	*a*	*b*	μg Sc/ml	*v*, %	ε
I	Sc–CAS–CTMAB	—0·04 ± 0·02	3·12 ± 0·07	0·04—0·40	2·2	149 000
II	Sc–CAS–KPTB	—0·05 ± 0·01	2·67 ± 0·01	0·04—0·40	3·5	127 000
III	Sc–CAS–EPB	—0·01 ± 0·01	3·04 ± 0·02	0·04—0·40	4·2	143 000

To a solution containing 1·0 to 10·0 μg Sc are gradually added 5 ml of acetate buffer of pH 5·7, 0·8 ml of 1 . 10^{-3}M-CAS, 0·5 ml 5 . 10^{-3}M-CTMAB and the solution is diluted with distilled water to a volume of 25·0 ml. After standing for 8 minutes solution is measured photometrically at 645 nm against a blank solution.

Determination of Sc by methods *II* and *III* is similar except that the measurement is carried out at wavelengths of 640 and 650 nm.

CONCLUSION

Study of the interaction of Sc and CAS with the bromides of the above-mentioned cation-active tensides represents a new method for the spectrophotometric determination of microgram amounts of Sc. The determination of Sc and the stoichiometric composition of the coloured product were studied at concentrations of the tenside lower than the critical micelle concentration C_k (CTMAB – 0·8 . 10^{-4}M, CPTB – 7·7 . 10^{-4}M (ref.[13]) and CPB – 7·6 . 10^{-4}M); thus ternary complex formation occurs in solution. An advantage of the studied system lies in the relatively small effect of the ionic strength in salt solutions. In study of the stoichiometric composition, a component ratio in the ternary complex of Sc : CAS : T = 1 : 2 : 2 was found and the results of the extraction and zonal electrophoresis indicate that the complex is charged and has the composition $[Sc(OH)^{2+}...HL^{3-}...T_2^+]^{2-}$.

The Lambert–Beer law is valid over the concentration range 0·04–0·4 μg Sc per ml of solution. The calibration curve was constructed from 7 points, each of which was measured five times. The procedure is one of the most sensitive methods for the spectrophotometric determination of Sc using triphenylmethane dyes. The procedure is relatively rapid and is not affected by temperature or by time.

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