much lower than with Alamine 336 in the [HNO_3] range 0·5–4·5 M, but at higher acidities the difference is not appreciable.

Except for slight deviations in the case of $D_{U(IV)}$ values at low ($\leqslant$3·75 per cent) concentrations of Alamine oxide, and which can be attributed to extraction of uranium by the DBC diluent, the slopes [1·95 for Pu(IV) and 0·9 for U(VI)] for the plots in Fig. 2 are consistent with the extraction of the species $Pu(NO_3)_6{}^{-2}$ and $UO_2(NO_3)_3{}^{-1}$, as in the case of extraction by amines.

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Composition and stability of metal-chromotrope 2B chelates of scandium and yttrium

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p-NITROBENZENE-AZO chromotropic acid (trivial name Chromotrope 2B (CTB); Colour Index 16575

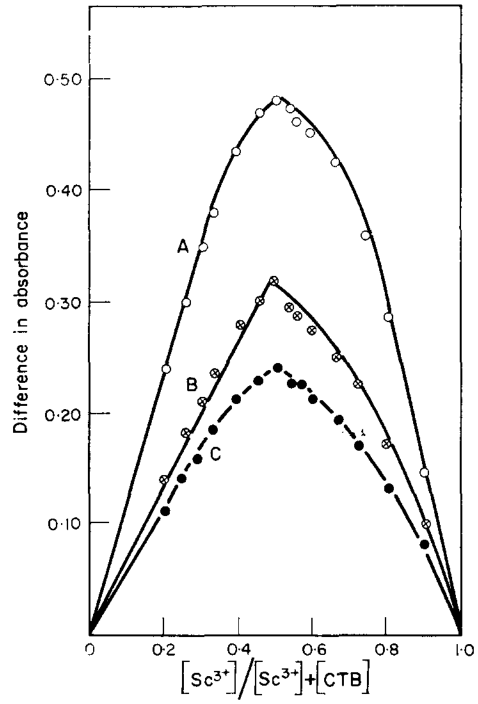

FIG. 1.—Determination of the composition in Sc—CTB system by the method of continuous variations with equimolecular solutions, at 580 mμ; pH 4·5
Curve A: $c = 2{\cdot}00 \times 10^{-4}$M
Curve B: $c = 1{\cdot}33 \times 10^{-4}$M
Curve C: $c = 1{\cdot}00 \times 10^{-4}$M

has been reported to form a complex with thallium (III).(1) Complex formation with thorium,(2) lanthanum(3) and the lanthanons(4) has already been studied in these laboratories.

The present communication describes spectrophotometric studies on the chelate formation between scandium (III) and yttrium (III) with CTB.

EXPERIMENTAL

Solutions of scandium and yttrium chlorides (Johnson, Matthey & Co.) were prepared and standardized. Aqueous solutions of CTB (BDH reagent) were prepared by direct weighing. Absorbance measurements were carried out at 25°C using a Unicam SP 500 spectrophotometer as described earlier.(5) The composition of the chelates were obtained by (i) the method of continuous variations, (ii) the mole ratio method and (iii) the slope ratio method.

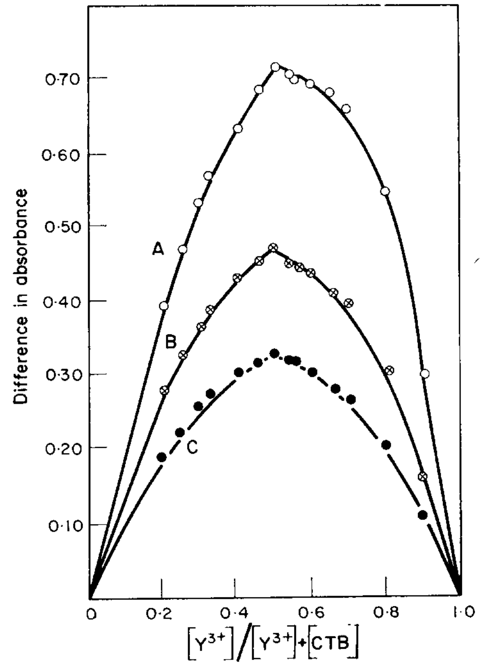

FIG. 2.—Determination of the composition in Y-CTB system by the method of continuous variations with equimolecular solutions at 590 mμ; pH 6·0
Curve A: $c = 3{\cdot}33 \times 10^{-4}$M
Curve B: $c = 2{\cdot}00 \times 10^{-4}$M
Curve C: $c = 1{\cdot}33 \times 10^{-4}$M

RESULTS AND DISCUSSION

The λ_{max} of aqueous solutions of CTB is 515 mμ both at pH 4·5 and 6·0. The scandium chelate at pH 4·5 and yttrium chelate at pH 6·0 show the λ_{max} at 530 mμ with varying proportions of metal to CTB. The chelates have the same λ_{max} between pH 3·0 and 7·5 in the case of Sc-CTB and 3·5–9·5 in Y-CTB chelate, showing the pH range of stability of the chelates.

The colour formation is instantaneous and the absorbance values remain constant even up to 72 hr. No significant change occurs when the order of the addition of the reactants is altered.

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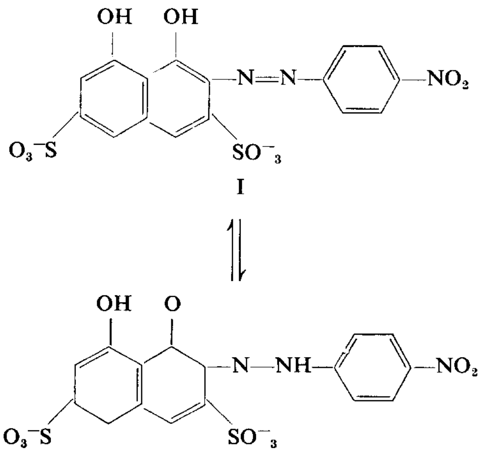
The scandium-CTB (pH 4·5) and yttrium-CTB (pH 6·0) complexes both form 1:1 complexes (Figs. 1 and 2).

The value of log K (K = apparent stability constant) as obtained by two different methods from absorbance data are tabulated below. The values of the change in free energy of formation* (ΔG°) have also been calculated.

TABLE 1.—APPARENT STABILITY CONSTANTS (log K) OF THE CHELATES

Chelate	Method	pH	log K	ΔG° at 25°C (kcals,)
Sc(III) – CTB	Mole ratio(6)	4·5	4·9 ± 0·1	−6·8 ± 0·2
	DEY *et al.*(7)	4·5	4·9 ± 0·1	−6·8 ± 0·2
Y(III) – CTB	Mole ratio	6·0	4·7 ± 0·2	−6·5 ± 0·3
	DEY *et al.*	6·0	4·6 ± 0·1	−6·4 ± 0·2

Suggestions on the structure of the chelate. SOMMER and HNILIČKOVÁ,(8) from a detailed study of the substituted chromotropic acids deduced the following structures for CTB in different media.



I

II

Weakly acidic, neutral and weakly alkaline media (pH 1–13).

If the chelation occurs between the two hydroxyl oxygens, by the replacement of hydrogen ions in I, an anionic complex will be formed. On the other hand if chelation occurs between the two oxygens in II, the chelates will be neutral, since only one hydrogen will be replaced. Again, if one of the nitrogens and one oxygen are involved in the chelation, the complex will still be neutral. It has been observed in the present study that the chelates are anionic in nature as indicated by the electrophoresis experiments and also by complete adsorption of both the chelates by ion exchange resin Amberlite IR-45 (OH), thus suggesting chelation by the replacement of two phenolic oxygens, in I.

Acknowledgement—The authors are thankful to the Council of Scientific and Industrial Research,

* $\Delta G^\circ = -RT \ln K$

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Effects of metal ions on intermolecular and intramolecular catalysis of mutarotation

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LI AND JEAN[1] have shown that imidazole catalyses the mutarotation of glucose and that in the pH region 4·8–6·8, over an imidazole (free base) concentration of 0–0·08 M, the following equation holds at 25°:

$$k = 0{\cdot}0104 + 1{\cdot}14\,(\text{Im}) \qquad (1)$$

The rate constant, k, of mutarotation, was determined by use of the equation

$$k = \frac{1}{t}\log_{10}\frac{(R_0 - R_\infty)}{(R_t - R_\infty)} \qquad (2)$$

where t is time in minutes, and R_0, R_∞, and R_t are the initial angle of rotation, the final equilibrium angle, and the angle at time t, respectively. For the mutarotation of glucose in aqueous media and at 25°, LI *et al.*[2] obtained the equation $k = 0{\cdot}0102 + 0{\cdot}283\,(\text{H}^+)$, while KUHN and JACOB's equation[3] is $k = 0{\cdot}0104 + 0{\cdot}334\,(\text{H}^+)$, and HUDSON's equation[4] is $k = 0{\cdot}0096 + 0{\cdot}258\,(\text{H}^+)$, so that in the pH region 4·8–6·8 investigated by LI and JEAN, the catalytic effect of hydrogen ion is entirely negligible. Any catalysis by the imidazolium ion was also shown to be undetected, so that the value 1·14 in Equation (1) may be considered the catalytic coefficient of the free base imidazole, in liters per mole minute. In the presence of 0·02 M nickel nitrate and cadmium nitrate, LI and JEAN found a decrease in the rate of the intermolecular imidazole catalysis and ascribed the effect to complexation of imidazole by the metal ion so that the value of (Im) in Equation (1) is decreased. The metal ions themselves at a concentration of 0·02 M do not affect the rate of mutarotation.

As part of a research program on mixed ligand studies,[5] it was considered of interest to determine the effect of metal-glycylglycine complex on imidazole catalysis of mutarotation of glucose and to determine the formation constants of ternary M(II)-glycylglycine-imidazole complexes. The results are presented in this note.

Glucosamine hydrochloride is glucose with the hydroxyl group on carbon 2 replaced by $—\text{NH}_3^+$. When an alkali is added to an aqueous solution of glucosamine hydrochloride, glucosamine is produced. If the free base amino group acts as an intramolecular catalyst for the mutarotation, then the presence of metal ion which binds the amino group should inhibit the rate of mutarotation. The effects of metal ions and of metal-glycylglycine complexes on the intramolecular catalysis of mutarotation are included in this note.

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