

Scandium Hydroxide and Scandate Ions.

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The precipitation of scandium hydroxide by alkali, or ammonium, hydroxide solutions is followed turbidimetrically and shown to be incomplete owing to formation of scandate or hexamminoscandium ions according to the alkali hydroxide used. The composition of the scandate is indeterminate; the ammino-complex is considered to be $[\text{Sc}(\text{NH}_3)_6]^{3+}$. Polarographic studies on the scandate complex give -1.88 ± 0.01 v for the half-wave potential of the Sc^{3+} ion.

THE addition of hydroxyl ion to solutions of simple scandium salts precipitates white, gelatinous scandium hydroxide. The water solubility of this hydroxide has been stated as *ca.* 5×10^{-7} mole/l. (Moeller and Kremers, *Chem. Reviews*, 1945, **37**, 116) but precipitation is never complete within this limit.

Although Sterba-Bohm and Melitchar (*Coll. Czech. Chem. Comm.*, 1935, **7**, 131) had earlier claimed the isolation of $\text{K}[\text{Sc}(\text{OH})_5\text{H}_2\text{O}] \cdot 3\text{H}_2\text{O}$ from potassium hydroxide-scandium hydroxide solutions, and Weiser and Milligan (*J. Phys. Chem.*, 1938, **42**, 669, 673) had confirmed the "peptisation" of scandium hydroxide by alkali hydroxide, Fischer and Bock (*Z. anorg. Chem.*, 1942, **249**, 146) considered scandium hydroxide to be only soluble in concentrated alkali hydroxide solutions. Radiochemical studies (unpublished) have, however, confirmed the earlier work.

Precipitation and redissolution of scandium hydroxide are readily followed turbidimetrically (see Fig. 1). Discontinuities at low alkali : scandium ratios may indicate the

formation of basic salts at *ca.* pH 6.5. Turbidity, and thus immediate precipitation, attains its maximum at pH 8.5 with an alkali : scandium ratio of 3—4.1 : 1. Redissolution of the hydroxide commences at an alkali : scandium ratio of 5 : 1.

Ivanov-Emin and Oustromov (*J. Gen. Chem., U.S.S.R., 1944, 14, 772*) gave pH 4.8—4.9 for the precipitation incidence of scandium hydroxide and this is largely confirmed by the present work. The Russian workers claimed, however, that precipitation is complete at pH 5.45 after the addition of 1.8 equivs. of sodium hydroxide. It is now thought that the pH curves obtained by them provide additional evidence for the formation of basic compounds, as suggested by the earlier stages of the turbidimetric curves. This belief is enhanced by the Russian workers' indication that, before final coagulation, the precipitate is $\text{Sc}(\text{OH})_x\text{A}_y\text{H}_2\text{O}$ where A is the anionic species present and x varies with the valency of A.

The incompleteness even of the maximum precipitation by sodium hydroxide is shown by comparison with the turbidity attained by a slurry of scandium hydroxide equivalent in concentration to the scandium solution titrated.

Replacement of sodium hydroxide by potassium hydroxide does not materially alter the progress of precipitation and redissolution of scandium hydroxide. Precipitation by

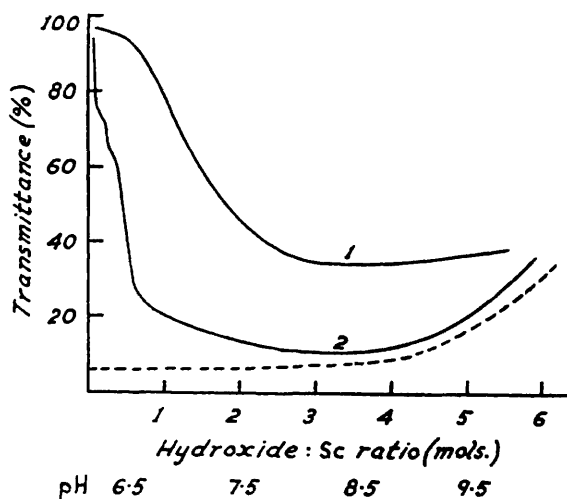


FIG. 1. *Precipitation of scandium hydroxide.* Turbidity produced by (1) aq. NH_3 , (2) NaOH , (broken line) pure $\text{Sc}(\text{OH})_3$, in the same concentrations.

aqueous ammonia is more complicated, however, and, as shown more fully below, involves the formation, not of an anionic scandate ion, but of a cationic amino-complex. Whilst results on the precipitation of scandium hydroxide by alkali hydroxide varied insignificantly throughout the experiments, conditions for redissolution of the hydroxide varied appreciably with concentrations of reactants. With increasing scandium concentrations, higher pH and $\text{OH} : \text{Sc}$ ratios were necessary for redissolution (Fig. 2). The complex ion found in alkaline solution can be decomposed by the judicious addition of acid. Scandium hydroxide is first precipitated and then redissolves as acidity increases below *ca.* pH 4.5. Comparison of turbidity curves approached from the acid and the alkaline side showed only slight hysteresis.

That the complex is anionic is indicated by its behaviour with ion-exchange resins. Cation-exchangers (Dowex-50 and Zeo-Karb 225) showed negligible adsorption of scandium from alkaline solutions, but almost complete extraction was obtained on anion-exchange resins (Amberlite IRA-400 and Deacidite FF). Attempts were made to evaluate the charge on the complex ion by determining the ion displaced from the resin (fluoride), but the results were inexplicably inconsistent (Table 1).

The successful investigation of other complex ions by polarography (Lingane, *Chem. Reviews*, 1941, 29, 1) prompted the application of this technique to the present study. Leach and Terrey (*Trans. Faraday Soc.*, 1937, 33, 480) obtained -1.8_4 v for the half-wave potential of Sc^{3+} in acid solution, but we have been unable to confirm completely their

deposition curves. Particularly was this so when potassium chloride was the supporting electrolyte. The decomposition potential of the potassium ion (-1.9 v) lies so close to the half-wave potential of scandium that separation of the Sc^{3+} and the K^+ wave was not

TABLE 1. Ion-exchange data for scandate ion.

Initial solution: 200 ml. at pH 9.7 containing 0.69 g. of Sc_2O_3 .

Resin	Sc_2O_3 (g.) in eluate	F (g.) in eluate	Ratio Sc : F	Sc_2O_3 (g.) in eluate	F (g.) in eluate	Ratio Sc : F
Amberlite IRA-400	0.010	0.775	1 : 2.7			
" "	0.015	1.085	1 : 3.8			
Dowex-50	0.65	—	—	0.012	0.515	1 : 1.8
Zeo-Karb 225	0.66	—	—	0.009	0.918	1 : 3.2
				0.019	0.766	1 : 2.7
				0.003	0.667	1 : 2.3

possible (Fig. 3a); similar results were obtained with lithium (-2.0 v) and barium (-1.8 v) chlorides as supporting electrolytes. Adequate waves were, however, obtained with tetramethylammonium ions (-2.6 v) as the support, and with this system an $E_{\frac{1}{2}}$ value of

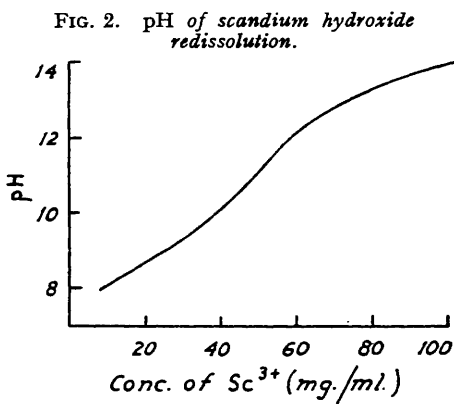
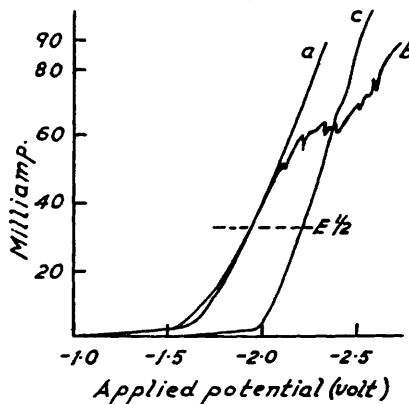


FIG. 3. Polarography of scandium ions.



-1.88 ± 0.01 v was obtained for the Sc^{3+} ion (Fig. 3b). No evidence was found for the existence of Sc^{2+} ions (cf. Noddack and Brukl, *Angew. Chem.*, 1937, 50, 362).

The half-wave potential of a simple ion is known to be displaced to more negative values on complex formation. Such behaviour was shown by scandium in alkaline solution (Fig. 3c), but the shift in potential obliterated the diffusion-current plateau between the scandium and tetramethylammonium waves, so that it was impossible to determine the precise position of the displaced scandium wave; a shift of *ca.* -0.3 v is, however, quite evident.

Because of the indeterminate position of its decomposition wave, it was not possible to identify the complex scandium ion in the manner used by Lingane (*loc. cit.*) for the bismuthite ion. The polarograph therefore merely provides confirmatory evidence of the formation of a scandate ion without, however, aiding its identification.

According to Cartledge (*J. Amer. Chem. Soc.*, 1928, 50, 2855, 2863) the basicity, amphotericity, or acidity of a hydroxide is determined by the function $\sqrt{\phi}$ where ϕ is the ionic potential of the element. For scandium $\sqrt{\phi} = 2.1$, indicating a basic hydroxide. Similarly, Sun (*J. Chinese Chem. Soc.*, 1937, 5, 148) reports that elements yielding basic hydroxides have ϕ values < 6.0 . The evidence is that scandium is anomalous in this respect in that it forms an amphoteric hydroxide. Since similar anomalies are known only where the element also forms ammino-complexes, the formation of amminoscandium compounds might be expected.

Precipitation of scandium hydroxide by aqueous ammonia was known by the earliest workers to be incomplete. Fischer and Bock (*loc. cit.*) attributed this to the presence of carbonates in the ammonia solution, but since incomplete precipitation is observed in a carbonate-free system, their contention cannot be tenable. Instead, the extent of precipitation can now be correlated with the ammonium-ion concentration. Precipitation of scandium hydroxide by ammonia is a complicated reaction and, when followed turbidimetrically (Fig. 1), is seen to require not only a slightly higher pH for its commencement, but is never so complete as with alkali hydroxide. Contrariwise, however, although the turbidimetric curve shows little indication of redissolution of precipitated scandium hydroxide even at high concentrations of ammonia, a fresh scandium hydroxide, washed free from other anions, can be partially redissolved in carbonate-free ammonia solution or by passing ammonia gas through its slurry. The ammoniacal solution, freed from excess of scandium hydroxide by filtration or centrifuging, can be freed from free ammonia (as shown by smell or litmus) by blowing carbon dioxide-free air or nitrogen through it. From such a de-ammoniated solution, scandium hydroxide is precipitated by the judicious addition of sodium hydroxide, and simultaneously ammonia is evolved. Further additions of sodium hydroxide redissolve the precipitated scandium hydroxide as previously indicated. NH_3 : Sc ratios in the ammine solution are very close to 6 : 1 (Table 2) which could correspond to a hexamminoscandium ion $[\text{Sc}(\text{NH}_3)_6]^{3+}$, the three positive charges being taken up in this instance by hydroxyl ions. The complex ammine, if such it be, does not appear to be very stable as evaporation of the solution causes decomposition with evolution of ammonia and precipitation of scandium hydroxide.

TABLE 2. *Composition of aminoscandium solutions.*

Sc ₂ O ₃ (g.) obtained	NH ₃ (g.) evolved	Ratio Sc : NH ₃	Sc ₂ O ₃ (g.) obtained	NH ₃ (g.) evolved	Ratio Sc : NH ₃
	<i>Decomposed by NaOH.</i>			<i>Decomposed by heat.</i>	
0.50	0.695	1 : 5.65	0.58	0.848	1 : 5.94
0.53	0.743	1 : 5.72	0.60	0.890	1 : 6.03
0.49	0.688	1 : 5.70	0.60	0.871	1 : 5.90

Scandium hydroxide also dissolves in solutions of ammonium chloride and nitrate, and these solutions are similarly decomposed by addition of sodium hydroxide.

Aluminium readily forms ammino-complexes (Klemm *et al.*, *Z. anorg. Chem.*, 1931, **200**, 343, 367), but those of the lanthanons are produced only under stringent conditions of temperature and pressure (Bergstrom, *J. Phys. Chem.*, 1925, **29**, 160; Huttig and Dauschau, *Monatsh.*, 1951, **82**, 742). It is to be expected that scandium and yttrium would display ammonia-co-ordinating tendencies intermediate between these two extremes. No data have been presented on the formation of aminoyttrium complexes, so this appears to be the first recorded production of "rare earth" ammino-complexes in aqueous solution.

A distinguishing feature of scandium solutions in ammonium or sodium hydroxide solutions lies in their behaviour on ion-exchange resins. Whereas scandium in ammoniacal or neutral ammine solution is readily adsorbed by a cation-exchange resin, and negligibly so on an anion-exchanger, the reverse is the case with solutions of scandium hydroxide in sodium hydroxide (see above).

EXPERIMENTAL

The scandium salts had been derived and purified as indicated in the preceding paper. Other reagents were generally of "AnalaR" grade. The tetramethylammonium salt used was the normal grade for polarographic work.

Turbidimetric titrations were made by means of a Parr photoelectric turbidimeter. pH determinations were made on a Cambridge electrometer, and polarography was conducted on a Tinsley pen-recording instrument with the supporting electrolytes at 0.1M-concentrations.

Adsorption of the scandate complex on ion-exchange resins was observed by shaking, for 48 hr., aliquot parts (200 ml.) of 0.05M-alkaline scandium solutions with Dowex-50 and Zeo-Karb

225 resins (100 g. each) in their sodium forms, and Amberlite IRA-400 and Deacidite FF resins in their fluoride forms. The scandium content of the mother-liquors was determined by adjustment of pH to 8.0, filtration and ignition of the precipitate to oxide. Control precipitation of the initial solution permitted quantitative comparison of the degree of absorption (Table 1).

Amminoscandium solutions were prepared as indicated earlier. Analyses were generally made by adding sodium hydroxide to the solution (to pH 8.2—8.8; Tropeolin OOO indicator), passing nitrogen through the solution, and boiling it to liberate the ammonia which was absorbed in standard acid in the usual way and thus determined. Scandium was determined by filtration and ignition of the precipitated hydroxide. Although precipitation of scandium hydroxide is now known to be incomplete, the ratios of Sc : NH₃ in the ammino-complex determined in this way are quite close to those determined by thermal decomposition (Table 2).

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