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Studies of Scandium in Various Solutions. II. The Extraction of Scandium(III) with Tributyl Phosphate from Perchlorate-Chloride and Perchlorate-Nitrate Media

By Tatsuya SEKINE, Takeshi HAMADA and Mitsuo SAKAIRI

Department of Chemistry, Tokyo College of Science, Kagurazaka, Shinjuku-ku, Tokyo

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The distribution of scandium(III) between organic tributyl phosphate solutions and aqueous perchlorate, nitrate, chloride solutions or mixed solutions of perchlorate-nitrate, perchlorate-chloride has been determined.

The distribution of scandium between 50% tributyl phosphate - chloroform and 4 M H(Cl, ClO_4) or 4 M H(NO_3, ClO_4) in some chloride or nitrate concentration region was higher than any of that distribution between the organic phase and 4 M perchloric acid, 4 M hydrochloric acid or 4 M nitric acid. It seems that the enhancement of the distribution ratios can be attributed to the extraction of mixed ligand complexes, but no simple relationship has been established between the distribution ratios and the proportion of the complex species in the aqueous phase as calculated from the previous data.

The extraction of scandium(III) in hydrochloric or nitric acid solutions with tributyl phosphate (TBP) was studied by Peppard, Mason and Maier.1) They reported that the extraction of the metal ion increases very sharply with the increase in the acid concentration.

The complex formation of scandium(III) with chloride ions or nitrate ions in 4 M perchloric acid media was studied by Sekine and Hasegawa2) by an ion-exchange method, and the stability constants for the complex species, $ScCl^{2+}$, $ScCl_2{}^+$, $ScCl_3$, $ScNO_3{}^{2+}$ and $Sc(NO_3)_2{}^+$, were determined.

For the present work, the authors determined the distribution of scandium(III) between organic solutions containing TBP and aqueous solutions of 4 M H(Cl, ClO_4) or 4 M H(NO_3, ClO_4) in order to study the variation in the metal distribution with the formation of scandium complexes in the aqueous phase.

Experimental

Tracers and Reagents.—^{46}Sc, ^{140}La, $^{152+154}Eu$, ^{177}Lu and ^{241}Am were used as the radioactive tracers. All the reagents used were of analytical grade. The preparation and the purification of the tracers and the reagents were carried out in ways which have been described previously.2-5)

Procedures.—All the procedures were carried out in a thermostatted room at 25±0.5°C. The concentration of the sodium perchlorate solutions was determined by weighing the residue left after a certain amount of the solution had been evaporated in an air-bath at 120°C. The concentration of the acids was determined by titrations using potassium hydrogen carbonate as the standard. The organic phases were pre-equilibrated with the corresponding aqueous phase just before the experiments. In the experiments with sodium perchlorate, the aqueous phase was buffered with a small amount of acetate at pH 4 to 5. The organic and aqueous phases were agitated in glass tubes with a stopper by a mechanical shaker and then centrifuged. Two-milliliter aliquots were pipetted from both phases, and the γ-radioactivity was determined. The distribution ratios of the metal ions were calculated as:

$$D=\frac{\gamma\text{-count-rate per ml. of org. phase}}{\gamma\text{-count-rate per ml. of aq. phase}}$$

Results and Discussion

The results are given in Figs. 1 to 4. The organic phase was 10% TBP (by volume) in hexane for the experiments in Fig. 1, and 50% TBP (by volume) in chloroform for the other experiments.

The results in the figures may be summarized as follows:

i) Scandium(III) is extracted from perchlorate media into the organic phase better than trivalent lanthanides or americium. The results for the other four ions showed nearly the same tendency as had been reported previously.6,7) (Fig. 1)

ii) The distribution of scandium(III) from 4 M (H, Na)ClO_4 is independent of the change in

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1) D. F. Peppard, G. W. Mason and J. L. Maier, *J. Inorg. Nucl. Chem.*, **3**, 215 (1956).

2) T. Sekine and Y. Hasegawa, This Bulletin, **39**, 240 (1966).

3) T. Sekine, *J. Inorg. Nucl. Chem.*, **26**, 1463 (1964); *Acta. Chem. Scand.* **19**, 1435 (1965).

4) T. Sekine, This Bulletin, **38**, 1972 (1965).

5) T. Sekine and M. Ono, ibid., **38**, 2087 (1965).

6) S. Siekierski, *Polish Academy of Science, Institute of Nuclear Research*, 130/v (1960); *J. Inorg. Nucl. Chem.*, **12**, 129 (1959).

7) H. Yoshida, ibid., **26**, 619 (1964).

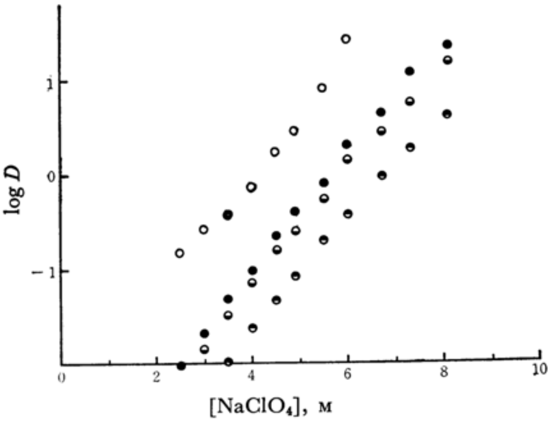

Fig. 1. Variation of the distribution ratios of Sc(III) (○), La(III) (●), Lu(III) (◒) and Am(III) (◓) between 10% TBP in hexane and sodium perchlorate solutions at various concentrations (pH 4—5). The results of Eu(III) are nearly the same as La(III).

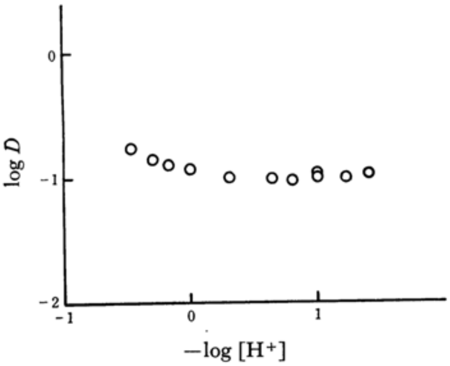

Fig. 2. Variation of the distribution ratio of Sc(III) between 50% TBP in chloroform and 4 M (H, Na)ClO$_4$ with the hydrogen ion concentration.

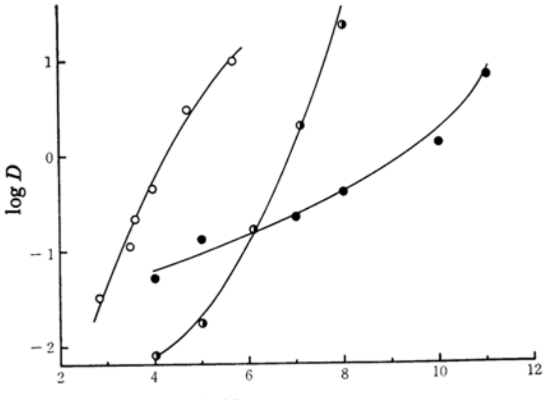

Fig. 3. Variation of the distribution ratio of Sc(III) between 50% TBP in chloroform and perchloric acid (○), hydrochloric acid (◑) or nitric acid (●) with the acid concentration.

the hydrogen ion concentration. However, it is slightly increased when the hydrogen ion concentration is above 1 M. (Fig. 2)

iii) The distribution of scandium from the perchloric acid solutions into the organic phase is much higher than that from hydrochloric or nitric acid solutions. Below 6 M, the distribution of scandium(III) from nitric acid is higher than that from hydrochloric acid, but the distribution ratios show an inverse order above 6 M. (Fig. 3)

iv) The distribution of scandium(III) from 4 M perchloric acid is enhanced by a replacement of the acid with 4 M hydrochloric or nitric acid. The enhancement is made larger by replacements with nitric acid than by those with hydrochloric acid. When the nitric acid content in the aqueous phase is about 0.6 M, the distribution ratio is four times that from pure perchloric acid, but the distribution ratio becomes lower than that from pure perchloric acid when more than half of the

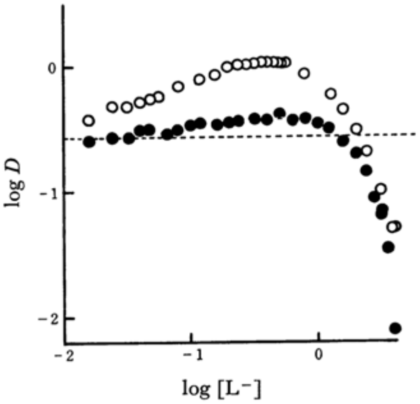

Fig. 4-a. Variation of the distribution ratio of Sc(III) between 50% TBP in chloroform and 4 M H(Cl, ClO$_4$) (●) or 4 M H(NO$_3$, ClO$_4$) (○) as functions of the chloride or nitrate concentration.

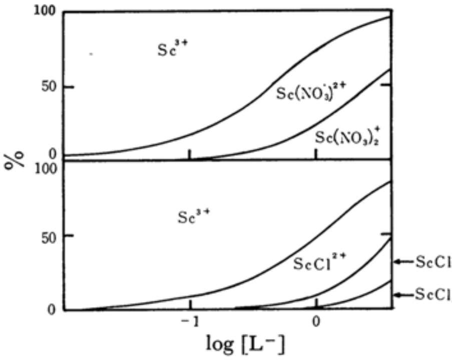

Fig. 4-b. Percentage ratios of Sc(III) nitrate or chloride complex species in 4 M perchloric acid as a function of the ligand concentration calculated from the stability constants given in Ref. 2.

acid is replaced with nitric or hydrochloric acid. (Fig. 4-a)

When L denotes nitrate or chloride ions, the scandium species in the organic phase distributed from the mixed acid media may generally be described as;

$$Sc(ClO_4)_aL_bH_{a+b-3}(TBP)_c$$

From the results in Fig. 4-a, one may conclude that the distribution of the mixed complex species is higher than that of the species containing only one kind of anion.

However, it seems difficult to establish any simple relationship between the variation in the distribution ratios and the compositions of the complex species in the corresponding aqueous phase, which are given in Fig. 4-b.

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