

## Conductometric and Potentiometric Study of the Interaction between Sodium Succinate and Thorium Chloride

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With 2 Figures

### Abstract

The interaction between sodium succinate and thorium chloride solutions in presence of glucose solutions of suitable concentrations has been investigated adopting conductometric and potentiometric titration methods. The experimental data shows the formation of the normal disuccinate,  $\text{Th}(\text{C}_4\text{H}_4\text{O}_4)_2$ , near about the point of equivalence, where the ratio of metal : succinate is nearly 1 : 2. In the absence of glucose solutions a highly unstable colloidal solution is obtained. Addition of peptiser viz., glucose, increases the stability and the rapid precipitation of the dispersed phase is controlled in a manner as to give stable and transparent gels. The conductometric and potentiometric titration curves are explained.

### Introduction

Thorium succinate is described as a white gelatinous precipitate obtained by the interaction of succinic acid with hot, neutral thorium solutions<sup>1</sup>). In a recent publication<sup>2</sup>), we have described the preparation of thorium succinate gels obtained by the interaction of sodium succinate and thorium chloride solutions of suitable concentrations in presence of stabilising glucose solutions. In this paper is presented a quantitative assessment of the nature of the insoluble substance separating out in the gelling region as a result of metathesis of the interacting solutions.

### Experimental

#### Materials

Thorium chloride employed was of Analar grade. The thorium content was estimated by the usual method<sup>3</sup>). Fresh stock solutions of MERCK's extra pure sodium succinate were prepared. Glucose used was of B. D. H. (A. R.) quality.

<sup>1</sup>) T. V. S. SURYANARAYNA and B. S. V. RAGHAVA RAO, *J. Indian, Chem., Soc.*, **28**, 511 (1951).

<sup>2</sup>) Y. D. UPADHYA and S. P. MUSHRAN, *Naturwissenschaften*, **45**, 514 (1958).

<sup>3</sup>) A. I. VOGEL, *Text Book of quantitative inorganic analysis* (1953) 471.

### Conductometric measurements

The conductometric apparatus was a L & N drum type bridge, length 1000 cm, an audioscillator with a tuning fork giving a constant frequency of 1000 c/sec, a tunable headphone and an immersion cell of the type G. M. 4221.

### Potentiometric measurements

pH measurements were carried out using a L & N pH meter with a glass electrode. The instrument was properly standardised by the determination of its asymmetric potential using a standard potassium hydrogen phthalate buffer.

The conductometric and potentiometric titrations were carried out at a both temperature of  $28 \pm 0.1^\circ\text{C}$ .

### Gelling region

Gelation was studied by the method described by BOSE and MUSHRAN<sup>4)</sup> employing drops of 35%  $\text{BaSO}_4$  suspension as 'gel indicator'. For the determination of the gelling region a record for mixtures of the interacting solutions for which the gelling time was within 5 hours was maintained.

### Method

Different quantities of sodium succinate were taken in a series of test tubes. In another set of test tubes were taken fixed quantities of suitable thorium chloride and glucose solutions. The total volume was kept constant in all the cases. The tubes were kept in a circulation bath at  $28 \pm 0.1^\circ\text{C}$ . The reactions were mixed by adding the solution back and forth for four times. Each mixture was left undisturbed in the circulation bath for an hour after which the conductivity and pH of each was measured.

In tables I and II are presented the results for two different concentrations of the interacting solutions.

The results presented in the above tables are represented graphically in Figs. 1 and 2.

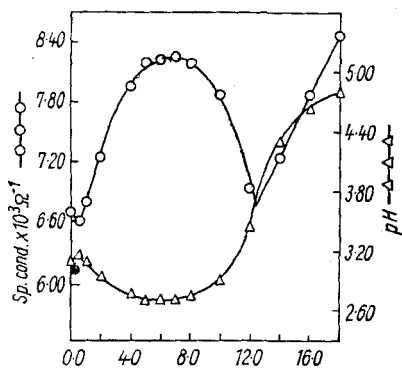


Fig. 1

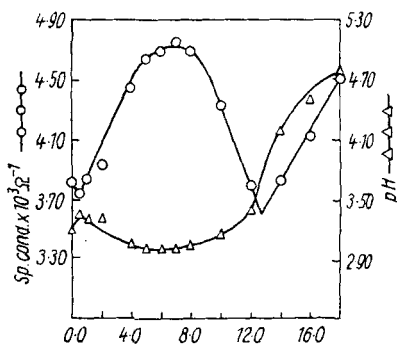


Fig. 2

<sup>4)</sup> S. K. BOSE and S. P. MUSHRAN, Proc. Natl. Acad. Sci. (India), 27 A, 21 (1958).

Table I

Specific conductivity and pH depending upon the varying amounts of sodium succinate

M/4.78 Thorium chloride = 2.00 mls.

7,5 % Glucose solution = 1.5 mls.

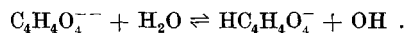
Total volume = 28.50 mls.

0.06 M sodium succinate (ml)	pH	Sp. Cond. · 10 <sup>3</sup> Ω <sup>-1</sup>	Remarks
0.00	3.10	6.701	No gel
0.20	3.10	6.700	No gel
0.50	3.15	6.680	No gel
0.80	3.12	6.774	No gel
1.00	3.10	6.797	No gel
2.00	2.95	7.246	No gel
4.00	2.75	7.952	No gel
5.00	2.70	8.185	Transparent gel
6.00	2.70	8.217	Transparent gel
7.00	2.70	8.247	Transparent gel
8.00	2.75	8.190	Precipitate
10.00	2.90	7.857	Preprecipitate
12.00	3.45	6.931	Precipitate
14.00	4.30	7.246	Precipitate
16.00	4.62	7.858	Precipitate
18.00	4.80	8.457	Precipitate

### Discussion

An inspection of the Figs. 1 and 2 on the measurement of the conductivity shows that the stepwise addition of increasing quantities of sodium succinate to a fixed quantity of thorium chloride brings about a fall in the electrical conductance in the early stages, followed by a progressive increase to a maximum and then a fall to a minimum and finally a gradual increase until excess of sodium succinate has been added. The changes in the pH values indicate a slight increase followed by a decrease and then a subsequent increase with a clear inflexion point in the curve.

A solution of sodium succinate is slightly alkaline due to the hydrolysis of the salt according to the equation:



A solution of thorium chloride is, however, acidic due to the hydrolysis of the salt as:

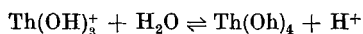
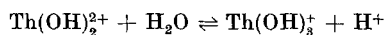
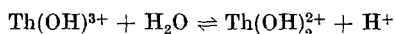
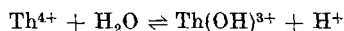


Table II

Specific conductivity and pH depending upon the varying amounts of sodium succinate

M/9.56 Thorium chloride = 2.00 mls.

3.75% Glucose solution = 1.50 mls.

Total volume = 28.50 mls.

0.03 M Sodium succinate (ml)	pH	Sp. cond. · 10 <sup>3</sup> Ω <sup>-1</sup>	Remarks
0.00	3.20	3.821	No gel
0.20	3.30	3.782	No gel
0.50	3.35	3.736	No gel
0.80	3.34	3.780	No gel
1.00	3.33	3.836	No gel
2.00	3.32	3.932	No gel
4.00	3.05	4.454	No gel
5.00	3.00	4.636	Transparent gel
6.00	3.00	4.692	Transparent gel
7.00	3.00	4.751	Transparent gel
8.00	3.05	4.692	Precipitate
10.00	3.15	4.330	Precipitate
12.00	3.39	4.330	Precipitate
14.00	4.20	3.821	Precipitate
16.00	4.50	4.125	Precipitate
18.00	4.81	4.506	Precipitate

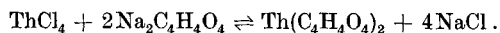
The titration of thorium chloride against a weak base sodium succinate would, therefore, bring about a gradual increase of pH because of the removal of hydrogen ions due to the formation of water according to:



This scheme of reaction suggests a fall in electrical conductance because of the removal of the hydrogen ions. A perusal of Figs. 1 and 2, however, shows that though in the initial stages this scheme is followed, there are definite departures as more quantities of sodium succinate are added. The pH gradually diminishes indicating the increase of hydrogen ion concentration which definitely would bring about an increase in the conductivity. The maximum hydrogen ion concentration recorded corresponds to the pH = 2.70. It appears that as the sodium succinate was added, and sodium chloride thereby formed, a considerable quantity of succinate ions, instead of combining with metal, were set free to form hydro-succinate ions and some free acid. The increase in hydrogen ion concentration with the subsequent increase in conductivity is, therefore, mainly ascribed to the hydrogen ions from the first stage dissociation of succinic acid, the hydrosuccinate

having reacted with the hydroxide of the metal formed as a result of the hydrolysis of the metal chloride.

As more and more of sodium succinate is added, the hydrogen ion concentration decreases bringing about a decrease in the conductance values because of the removal of highly conducting hydrogen ions by the hydroxyl ions, which are now available in larger amounts, due to the presence of large quantities of sodium succinate. At this stage the normal thorium succinate i. e. thorium di-succinate starts being precipitated until when the ratio of thorium : succinate attains a value of 1:2, when complete precipitation of thorium succinate takes place. Here a break in the conductivity curve is observed, after which the conductivity rises due to the presence of excess of sodium succinate. In short, therefore, the formation of hydro-succinate is more probable in highly acidic media and it appears that in early stages of the addition of the sodium-succinate, the proportion of the acid succinate formed is more and decreases with increasing amount of the sodium succinate added. It is also clear that thorium disuccinate is chiefly produced in larger and larger amounts as the equivalent point is attained. The inflexion point in the pH curve also occurs at a point where the ratio of metal : succinate is nearly 1:2 suggesting the formation of a di-succinate where the following reaction is complete :



It is interesting to note that increase in conductance in the first few stages may also be partly due to the replacement of  $\text{Th}^{4+}$  by the more conducting  $\text{Na}^+$ . This, however, would suggest a continuous increase in the value of the conductance, there is, however, a decrease after a maximum value of the conductance has been attained. Undoubtedly, therefore, in the later stages when the hydrogen ions decrease considerably the decrease in the conductance is more significant and more than counter-balances the increase due to the replacement. A decrease in the conductance is also expected because of the appearance of the thorium di-succinate as the equivalent point is reached, as it is capable of adsorbing the hydrogen ions in large amounts.

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