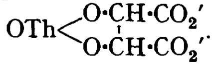
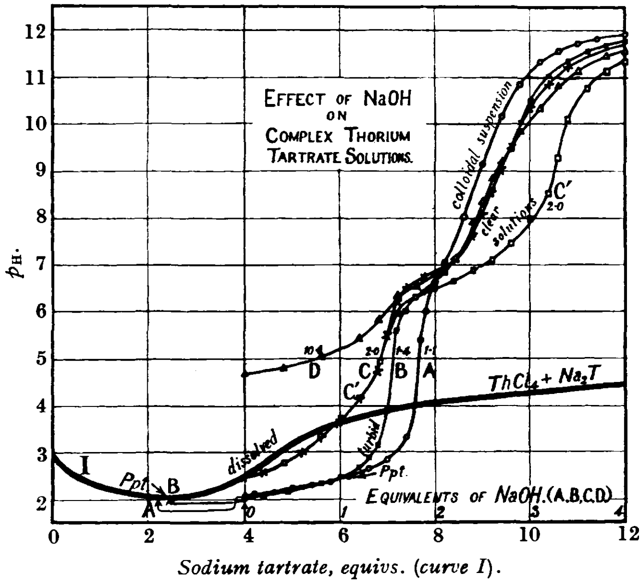
3. *Physicochemical Studies of Complex Formation involving Weak Acids. Part VI. Alkaline Solutions of Thorium Tartrate.*

By H. T. S. Britton and William E. Battrick.

Part IV (J., 1932, 196) recorded a study of the complex formation occurring in alkaline solutions of lanthanum tartrate, lanthana having been selected as an example of a moderately strong base. The work on a very weak base, thoria, is now described. Like lanthana, thoria is held in alkaline solutions as a somewhat indefinite basic tartrate, the composition of which depends on the treatment accorded to the solutions. The cause of this is still unknown, but the present work reveals that a small amount of the sodium tartrate is incorporated in the complex. These conclusions, although in harmony with preliminary work by Britton (J., 1926, 269) and subsequent work by Dumanski and Chalisew (*Kolloid-Z.*, 1929, **47**, 121) and Morton (*Trans. Faraday Soc.*, 1932, **28**, 84) on the nature of hydroxy-acid complexes, are in direct opposition to the usually accepted view that definite complex metallic tartrates are formed in which the metallic base is situated in the alcoholic groups. For instance, according to Rosenheim, Samter, and Davidsohn (*Z. anorg. Chem.*, 1903, **35**, 424), optical activity experiments reveal that the thorium exists in alkaline tartrate solutions in a complex anion  $\mathrm{OTh}{<}\begin{matrix}\mathrm{O{\cdot}CH{\cdot}CO_2'} \\ | \\ \mathrm{O{\cdot}CH{\cdot}CO_2''}\end{matrix}$.

The present work deals with a potentiometric and conductometric study of the formation of complex solutions by addition of sodium tartrate to thorium chloride, and also of the behaviour of these solutions towards sodium hydroxide.

Fig. 1.



EXPERIMENTAL.

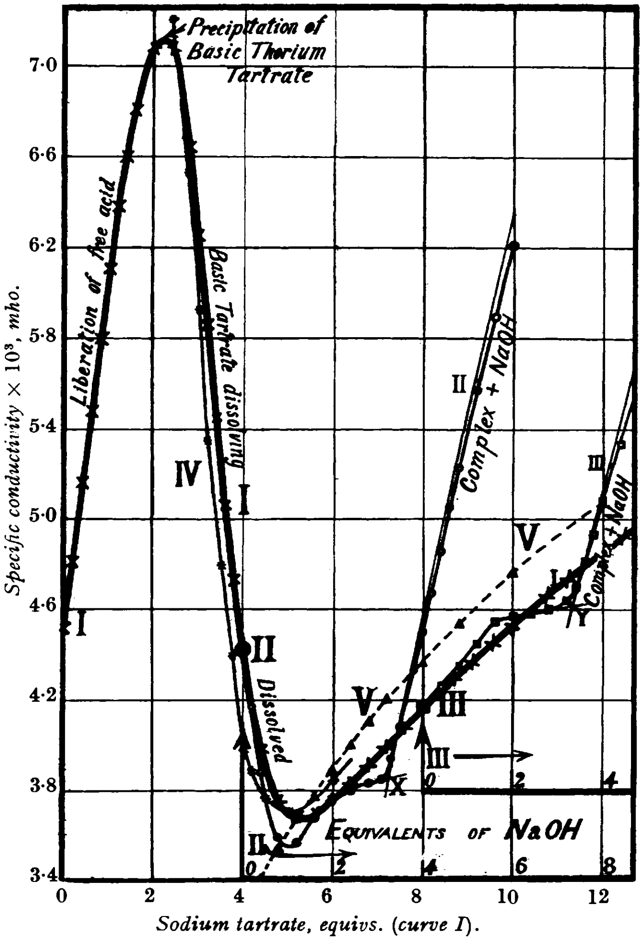
The variations in p_H at 18°, measured by means of the hydrogen and quinhydrone electrodes, and in sp. conductivity at 25°, during the progressive addition of $0{\cdot}05M$-$Na_2C_4H_4O_6$ to 100 c.c. of $0{\cdot}01M$-$ThCl_4$ are indicated by curves I in Figs. 1 and 2 respectively. During the first 2·3 equiv. the p_H fell to the low value of 2·07 and the sp. conductivity rapidly rose from $4{\cdot}53 \times 10^{-3}$ to $7{\cdot}1 \times 10^{-3}$ mho. At this point of max. acidity, pptn. of basic thorium tartrate began, but the ppt. had largely redissolved when 4 equiv. of tartrate had been added; the precise point at which complete dissolution took place depended on such factors as the rate of addition, agitation, and temp. The p_H curve corresponding to the addition of excess $Na_2C_4H_4O_6$ shows that the solution was strongly buffered in the region of p_H 4 through the presence of the acid which had been liberated during pptn. and had failed to recombine with the Th on the dissolution of the basic tartrate. The broken line V in Fig. 2 represents the sp. conductivities due to the NaCl which would have been formed if the normal thorium tartrate had been pptd., and the added $Na_2C_4H_4O_6$. The actual conductivities are somewhat lower; this may be due to diminished ionisation of the complex tartrate solution, since the sp. conductivity of any $NaHC_4H_4O_6$ present is not likely to be very different from that of a corresponding amount of $Na_2C_4H_4O_6$.

A series of hydrogen-electrode titrations with $0{\cdot}1N$-NaOH was made on $ThCl_4$ solutions to which various proportions of $Na_2C_4H_4O_6$ had been added, *viz.*, 1·1, 1·4, 2·0, and 10 mols. to 1 mol. $ThCl_4$. The respective curves are given in Fig. 1 and are marked A, B, C, and D. The solutions titrated were, respectively, 100 c.c. of $0{\cdot}01M$-$ThCl_4$ + 22·0 c.c. of $0{\cdot}05M$-$Na_2C_4H_4O_6$; 100 c.c. of $0{\cdot}01M$-$ThCl_4$ + 28 c.c. of $0{\cdot}05M$-$Na_2C_4H_4O_6$; 100 c.c. of $0{\cdot}01M$-$ThCl_4$ + 40 c.c. of $0{\cdot}05M$-$Na_2C_4H_4O_6$; and 100 c.c. of $0{\cdot}01M$-$ThCl_4$ + 40 c.c. of $0{\cdot}25M$-$Na_2C_4H_4O_6$. In the first case, the initially clear solution began to precipitate soon after 1 equiv. of NaOH had been added. Above p_H 7 the ppt. passed into a fine colloidal suspension, but at no time did the solution become entirely clear. The amount of $Na_2C_4H_4O_6$ present corresponded to the limiting amount for complex formation; smaller amounts gave rise to precipitable solutions. If the complex anion suggested by Rosenheim, Samter, and Davidsohn (*loc. cit.*) had existed in these solutions, then it would have been expected that 1 mol. of $Na_2C_4H_4O_6$ would have sufficed to produce a clear solution on the addition of alkali. In the second titration the ppt. had completely dissolved on addition of 1·5 equiv. of NaOH.

It was suspected that the low p_H of 2·07 set up when just over 1 mol. of $Na_2C_4H_4O_6$ was added to the $ThCl_4$ was caused by the liberation of HCl by hydrolysis, and that therefore the first section of curve B was that of the neutralisation of this acid. This supposition was substantiated by the following data, which are the p_H values set up during the titration and those of a quinhydrone electro-titration by 0·1*N*-NaOH of 128 c.c. of solution containing 15·4 c.c. of 0·1*N*-HCl (*i.e.*, equal to the vol. of 0·1*N*-NaOH required for neutralisation, *cf.* B) :

NaOH, equivs.	0	0·4	0·8	1·0	1·2	1·3	1·4	1·5
p_H, obs.	2·04	2·18	2·34	2·49	2·68	2·90	3·13	3·90
p_H due to HCl	2·02	2·14	2·32	2·47	2·67	2·86	3·13	3·64

FIG. 2.



Sodium tartrate, equivs. (curve I).

Hence, it appears that the reaction occurring during the addition of the first 2·46 equiv. of $Na_2C_4H_4O_6$ to the $ThCl_4$ can be represented by the equation

$$ThCl_4 + 1{\cdot}23Na_2T + 1{\cdot}54H_2O \longrightarrow 1{\cdot}54HCl + 2{\cdot}46NaCl + Th(OH)_{1\cdot54}T_{1\cdot23}.$$

If the basic tartrate, thus formed, underwent no further reaction on further addition of $Na_2C_4H_4O_6$, other than the partial pptn. that occurred, it would be expected that the ensuing reaction would be with the HCl alone. To test this view, a solution having the NaCl and HCl concns. indicated by the equation was prepared and titrated conductometrically with 0·05*M*-$Na_2C_4H_4O_6$. Curve IV in Fig. 2 shows that the initial κ was but slightly higher than that prevailing when 2·46 equiv. of $Na_2C_4H_4O_6$ had been added to the $ThCl_4$. The rapid fall in conductivity that ensued on adding $Na_2C_4H_4O_6$ to the HCl solution nearly reproduced that shown by curve I, and therefore proves that the equation is approx. true. This would point to the equation

$$ThCl_4 + 2Na_2T + 1{\cdot}54H_2O \longrightarrow 0{\cdot}77H_2T + 4NaCl + Th(OH)_{1\cdot54}T_{1\cdot23}$$

as representing the reaction with 2 mols. of $Na_2C_4H_4O_6$. It happens, however, that the p_H of the titration mixture of the reactants in the above proportion was only 2·50. Such a low p_H could not have been set up by 1·54 equiv. of tartaric acid (*i.e.*, 15·4 c.c. of 0·1*N*-$C_4H_6O_6$ in 140 c.c. of solution); and consequently it appears that there must have still existed some hydrolysed HCl in the solution; in fact, it is estimated that 0·42 equiv. of HCl must have remained as such, and therefore that an equiv. of $Na_2C_4H_4O_6$ must have escaped attack. The equation for the reaction with 2 mols. of $Na_2C_4H_4O_6$ would thus become :

$$ThCl_4 + 2Na_2T + 1{\cdot}54H_2O \longrightarrow 0{\cdot}42HCl + 0{\cdot}56H_2T + 3{\cdot}58NaCl + [Th(OH)_{1\cdot54}T_{1\cdot23} + 0{\cdot}21Na_2T]$$

As the 0·21 mol. of $Na_2C_4H_4O_6$ was not attacked by the HCl, it was considered that the $Na_2C_4H_4O_6$ had become associated with the soluble basic thorium tartrate in forming an inert complex that neither contributed to the conductivity of the solution nor exerted any buffer action on its [H$^\bullet$]. A solution was prepared containing the solutes in the concns. suggested by the foregoing equation, with the exception of the basic thorium tartrate and the little associated $Na_2C_4H_4O_6$, and the p_H values at 18° and sp. conductivities at 25° were measured when 0·05*M*-$Na_2C_4H_4O_6$ was added. In Table I the data obtained are compared with those given in the original $ThCl_4$ titrations at the comparable stages.

TABLE I.

A. Titration of 100 c.c. of 0·01*M*-$ThCl_4$ + 40 c.c. of 0·05*M*-$Na_2C_4H_4O_6$ with 0·1*N*-$Na_2C_4H_4O_6$.
B. Titration of 140 c.c. of a solution containing 4·20 c.c. of 0·1*N*-HCl, 11·2 c.c. of 0·1*M*-$C_4H_6O_6$ and 35·8 c.c. of 0·1*M*-NaCl, with 0·05*M*-$Na_2C_4H_4O_6$.

Na_2T, equiv.	0·00	0·25	0·50	1·00	1·50	2·00	3·00	4·00
$\kappa_A \times 10^3$, mhos ...	4·42	4·14	3·90	3·70	3·69	3·76	3·96	4·17
$\kappa_B \times 10^3$, mhos ...	4·48	4·10	3·85	3·65	3·62	3·70	3·90	4·11

Na_2T, equiv.	0·0	0·4	0·8	1·2	1·6	2·0	2·4	3·2	4·0	5·2	7·2	10·0
p_H (A)	2·50	2·75	3·03	3·28	3·46	3·63	3·75	3·95	4·08	4·23	4·41	4·56
p_H (B)	2·48	2·74	3·02	3·27	3·47	3·63	3·72	3·95	4·09	4·23	4·40	4·57

The excellent agreement between the two sets of data justifies the belief that some $Na_2C_4H_4O_6$ is directly involved in causing the basic tartrate to undergo dissolution.

The accuracy of the last equation is also borne out by the first part of the p_H curve, C, in Fig. 1, corresponding to the reaction of a solution, containing $1ThCl_4 + 2Na_2C_4H_4O_6$, with NaOH. This will be seen more clearly from the following p_H values, which were obtained at 18° with the quinhydrone electrode.

A. Titration of 100 c.c. of 0·01*M*-$ThCl_4$ + 40 c.c. of 0·05*M*-$Na_2C_4H_4O_6$ with 0·1*N*-NaOH.
B. Titration of 140 c.c. of a solution containing 4·2 c.c. of 0·1*N*-HCl, 11·2 c.c. of 0·1*M*-H_2T and 35·8 c.c. of 0·1*N*-NaCl with 0·1*N*-NaOH.

NaOH, equiv.	0·0	0·4	0·8	1·0	1·2	1·3	1·4	1·5
p_H (A)	2·50	2·78	3·31	3·67	4·10	4·35	4·70	5·38
p_H (B)	2·48	2·81	3·32	3·68	4·10	4·33	4·65	5·42

Fig. 1 shows that soon after p_H 6 was passed the curves A, B, C, and D underwent inflexion, indicating that the added alkali was being used in decomposing the basic tartrate, *viz.*, $Th(OH)_{1\cdot54}T_{1\cdot23}$, existing in the now perfectly clear solutions. It is possible to compute the compositions of the soluble basic tartrate from the amounts of NaOH that were added to set up any particular p_H value. Thus in Table II are recorded the calc. values of *x* in the soluble basic complex $Th(OH)_xT_{2-\frac{1}{2}x}$.

TABLE II.

Direct titrations with 0·1*N*-NaOH.

$\frac{Na_2T}{ThCl_4}$.	*x* at p_H 7.	*x* at p_H 10·5.
1·4	2·17 (*a*)	3·00 (*a*)
2·0	2·10 (*a*)	3·05 (*a*)
2·0	2·52 (*c*)	3·48 (*c*)
10·0	2·17 (*a*)	3·14 (*a*)

(*a*) Immediately after mixing. (*b*) After boiling. (*c*) After standing.

Back-titrations with 0·1*N*-HCl.

$\frac{Na_2T}{ThCl_4}$.	NaOH, equivs.	*x* at p_H 7.	*x* at p_H 10·5.
1·4	4·0	2·48 (*a*)	3·23 (*a*)
1·4	4·0	3·08 (*c*)	3·63 (*c*)
2·0	4·0	2·57 (*a*)	3·47 (*a*)
2·0	4·0	3·03 (*c*)	3·70 (*c*)
2·0	6·0	2·69 (*a*)	3·68 (*a*)
2·0	6·0	3·14 (*b*)	3·82 (*b*)
10·0	4·0	2·43 (*a*)	3·26 (*a*)

The first part of the above table shows that the basic complex underwent partial decomp. on addition of alkali, and assumed the approx. composition $Th(OH)_3T_{0\cdot5}$ at p_H 10·5 in the case of immediate titrations. Ageing of the solutions, however, produced much more basic complexes, *e.g.*, $Th(OH)_{3\cdot48}T_{0\cdot26}$. C′ in Fig. 1 was constructed from the p_H values of solutions to which various quantities of NaOH had been added and which were then placed in stoppered bottles for several weeks until repeated p_H measurements showed that no further decomp. was occurring. It also shows the pronounced tendency for the basic complex to become more basic on ageing. The effect of adding excesses of alkali, even though small, was to yield still more basic complex tartrates, as shown by the values of *x* corresponding to the HCl back-titrations.

The formation of the complexes on the progressive addition was also investigated conductometrically. The curves II and III in Fig. 2 refer respectively to the titrations with

0·1*N*-NaOH of the mixtures: (1) 100 c.c. of 0·01*M*-$ThCl_4$ and 40 c.c. of 0·05*M*-Na_2T; (2) 100 c.c. of 0·01*M*-$ThCl_4$ and 80 c.c. of 0·05*M*-Na_2T. In both curves the beginning of the passage of free NaOH into the solutions is indicated by marked breaks, at X and Y. Just before these stages are reached the addition of alkali is seen to cause but a slight increase in conductivity, suggesting that the $Na_2C_4H_4O_6$ then being formed is passing as such into solution and is therefore probably involved in the complex equilibria with the soluble basic tartrate. The slopes of curves II and III are due essentially to free NaOH, for the divergence from the thin upper (theoretical) curves is not very great. That some divergence exists indicates that even in alk. solutions a slight attack of the basic complex occurred.

As a rule in conductometric titrations, the slopes due to free NaOH do not appear until the solution attains a p_H value of 10—10·5. The quantities of alkali added in the present titrations before these slopes became apparent show that in both titrations the basic tartrate complex had acquired the composition given by $Th(OH)_{3\cdot30}T_{0\cdot35}$. When it is remembered that considerably longer time is required in carrying out these conductometric titrations in order to ensure constancy of temp. than is the case with potentiometric titrations, it will be realised that this observation is in satisfactory agreement with those recorded in the previous table. Back-conductometric titrations led to similar conclusions to those drawn from the corresponding hydrogen-electrode titrations.

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