Electrometric Study on Thorium-Arsenite System as a Function of the pH

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(Received February 22, 1961)

The reaction between thorium nitrate and sodium(meta)arsenite solutions at different pH values has been studied by E.M.F. measurements reactants, using bright platinum as indicator involving potentiometric titrations between the electrode. The electrometric experiments give definite evidence of the formation of three arsenite compounds having the molecular formulae, $ThO_2\cdot 2As_2O_3$; $ThO_2\cdot As_2O_3$ and $3ThO_2\cdot 2As_2O_3$ at pH 9.85, 11.25 and 12.28 respectively. The proportion of ThO_2 increases with the concentration of alkali used in the preparation of alkali arsenites and the formation of thorium arsenites is thus a function of the hydrogen ion concentration. The potentiometric titration curves are regular in form; a pronounced maxima in dE/dV occurs at the end point, with either of the reagents used as the titrant and the results are accurate and reproducible. The effect of alcohol and electrolytes on the end point has been studied. The behavior of the indicator electrode and the mechanism of the electrode reaction have been discussed.

The precipitation of sodium arsenite solutions with heavy metal salts causes the formation of complex arsenites whose composition is mainly governed by the pH. The investigations of these compoundis made difficult by the adsoption of arsenic oxide by the metallic hydroxide; the conversion of ortho arsenite to pyro and meta arsenite takes place with great ease and these dissolve in excess of alkali or acid1). consequently analytical methods have failed to give a correct view of their composition. A survey of literature reveals that there are very few references to rare-metals arsenites and the earlier workers2-4) mainly confined themselves to the analytical investigations of the precipitates formed by mixing metal salts and alkali arsenites under different conditions. Besides, it appears that the formation of arsenites has not been studied at different hydrogen ion concentration of the medium which plays an important role in their precipitation. Moreover, there is hardly any reference in literature to the study of this system by electrometric techniques which have provided more conclusive evidences on the composition of such metal complexes (Saxena et al.)5) and hence the present investigation has been initiated.

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1) Fritz Ephraim, "Text book of Inorganic Chemistry" (translated by P. C. L.Thorne and E. R. Robarts), Gurney and Jackson, London (1949), p. 745.

2) A. Stavenhagen. *J. prakt. Chem.*, **2**, 51 (1895).

3) C. Reichard, *Ber.*, **27**, 1024 (1894); **31**, 2166 (1898).

4) H. Wilke, *Kolloid. Z.*, **34**, 83 (1924).

5) R.S. Saxena et al., *J. Inorg. Nucl. Chem.*, **12**, 38 (1959); *Naturwiss*, **46**, 575 (1959); *Z. anorg. u. allgem. Chem.*, **303**, 12 (1960); **297**, 146 (1958); *Z. physik. Chem.*, [*N.F.*], **19**, 94 (1959); *Anal. Chim. Acta*, **20**, 494 (1959); *Z. Naturforsch.*, **130**, 557 (1958).

TABLE I. SUMMARY OF RESULTS OF POTENTIOMETRIC TITRATIONS

Molarity of solution		Equivalence point (ml.)				Formula supported
$NaAsO_2$	$Th(NO_3)_4$	Calc.	Obs. from dE/dV in presence of			
			Alcohol		KNO_3 2 g.	
			0%	20%		
Direct titrations						
$NaAsO_2$ soln. at pH 9.85 added to 20 ml. of $Th(NO_3)_4$ soln. pH 5.6 (Fig. 1)						
M/5	M/120	3.33	3.38	3.35	3.36	$Th(AsO_2)_4$
M/10	M/200	4.0	4.08	4.08	4.05	or
M/15	M/400	3.0	3.04	3.02	3.03	$ThO_2\cdot 2As_2O_3$
$Na_4As_2O_5(2NaAsO_2+2NaOH)$ soln. at pH 11.25 added to 20 ml. of $Th(NO_3)_4$ (Fig. 2)						
M/10	M/45	4.44	4.48	4.46	4.46	$ThAs_2O_5$
M/20	M/120	3.33	3.37	3.35	3.34	or
M/40	M/300	2.66	2.70	2.67	2.68	$ThO_2\cdot As_2O_3$
$Na_3AsO_3(2NaAsO_2+4NaOH)$ soln. at pH 12.28 added to 20 ml. of $Th(NO_3)_4$ soln. (Fig. 3)						
M/10	M/100	2.66	2.68	2.66	2.68	$Th_3(AsO_3)_4$
M/20	M/180	2.96	3.0	2.98	2.98	or
M/50	M/300	4.44	4.52	4.47	4.48	$3ThO_2\cdot 2As_2O_3$
Reverse titrations						
$Th(NO_3)_4$ soln. at pH 4.6 added to 20 ml. of $NaAsO_2$ soln. at pH 9.85 (Fig. 4)						
M/40	M/20	2.50	2.47	2.50	2.48	$Th(AsO_2)_4$
M/75	M/40	2.66	2.62	2.65	2.64	or
M/100	M/60	3.0	2.96	2.99	2.98	$ThO\cdot 2As_2O_3$
$Th(NO_3)_4$ soln. added to 20 ml. of $Na_4As_2O_5(2NaAsO_2+2NaOH)$ soln. at pH 11.25 (Fig. 5)						
M/80	M/10	2.50	2.46	2.48	2.48	$ThAs_2O_5$
M/100	M/20	4.0	3.95	3.98	3.96	or
M/200	M/30	3.0	2.97	2.98	3.0	$ThO_2\cdot As_2O_3$
$Th(NO_3)_4$ soln. added to 20 ml. of $Na_3AsO_3(4NaOH+2NaAsO_2)$ soln. pH 12.28 (Fig. 6)						
M/60	M/14	3.50	3.44	3.48	3.46	$Th_3(AsO_3)_4$
M/100	M/20	3.0	2.98	3.0	2.98	or
M/400	M/60	2.25	2.21	2.24	2.22	$3ThO_2\cdot 2As_2O_3$

Experimental

Merck's guarateed extra-pure reagents thorium nitrate and $NaAsO_2$ were used. Thorium was estimated as thorium oxalate and its subsequent ignition to thorium oxide[6]. The strength of sodium arsenite solutions was checked by titrating against standardized iodine solution. The pH of $NaAsO_2$ solutions was measured using a glass electrode of the range (1∼13 pH) with the help of buffer solution. Calculated amounts of sodium hydroxide were added to sodium arsenite solutions in definite molecular proportions to vary the pH.

Using differnt concentrations of thorium nitrate and alkali arsenite solution at pH levels 9.85, 11.25 and 12.28, potentiometric titrations were carried out both by the direct and the inverse methods, i. e. when the alkalized arsenite solutions from the micro-burette were add to thorium salt in the electrode vessel and vice versa. A bright platinum foil was dipped in the solution to be titrated and used as an indicator electrode in conjunction with saturated calomel electrode through potassium nitrate salt-bridge. The titration cell was kept in an electrically maintained thermostat. The E. M. F. was measured on a Cambridge (null deflection type) pH-meter. The titer solution was continuously stirred by a magnetic stirrer. Curves were plotted between the E(obs.) and the volume of the titrant added in ml. and from the sharp break in potential indicated by the titration curves, the equivalence point was obtained. This was further checked by calculating the maximum value of dE/dV in each case. The titrations were also performed in presence of varying concentrations of ethanol and electrolytes as potassium nitrate. Twenty milliliters of the reagent was taken in the cell each time (see Table I).

Discussion

The pH of stock solution of sodium arsenite was measured by glass electrode and found to be 9.85. The variations of the latter were obtained by the progressive additions of calculated

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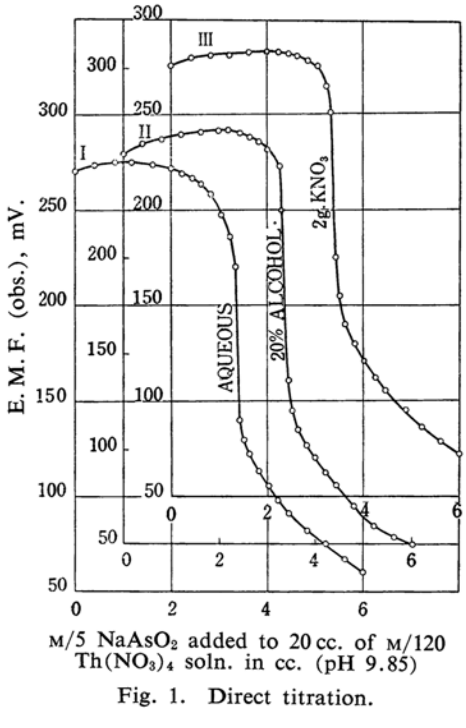
6) A. I. Vogel, "Quantitative Inorganic Analysis", p. 472.

quantities of sodium hydroxide solution to sodium arsenite. When sodium hydroxide is mixed with sodium arsenite in the molecular ratio 1 : 1 and 2 : 1, the corresponding compounds formed are $Na_4As_2O_5$ (sodium pyroarsenite) and Na_3AsO_3 (sodium orthoarsenite) and the pH of their solutions were found to be 11.25 and 12.28 respectively.

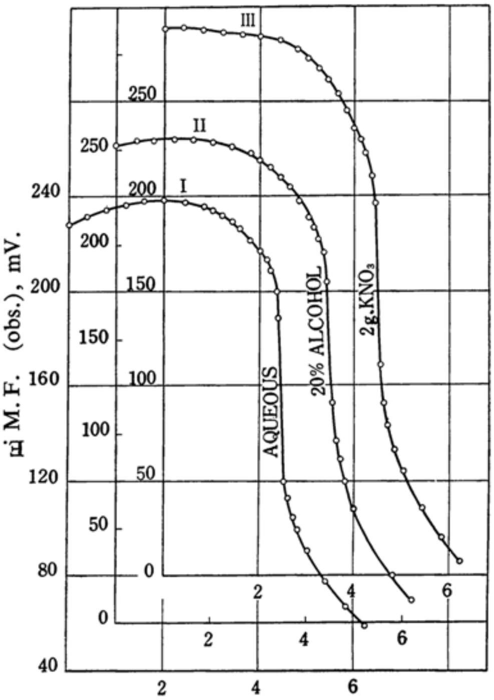
It is clear from Figs. 1 and 4 and from the summary of observations in Table I that when sodium arsenite solution at pH 9.85 is added to thorium nitrate solution and vice versa and the potential between a platinum indicator electrode and the calomel half-cell, measured and plotted against the volume of the titrant added in ml., a sharp deflection in curve occurs at a point where the molecular ratio of sodium arsenite and thorium nitrate is 4 : 1, corresponding to the formation of thick gelatinous precipitate of thorium metaarsenite $Th(AsO_2)_4$ or $ThO_2 \cdot 2As_2O_3$. At pH 11.25, the potentiometric titrations between $Th(NO_3)_4$ and $Na_4As_2O_5$ suggest the formation of thorium orthoarsenite having the molecular formula $ThAs_2O_5$ or $ThO_2 \cdot As_2O_3$ (Figs. 2 and 5). The titrations of thorium salt and Na_3AsO_3 ($2NaOH + NaAsO_2$) pH 12.28 show a sharp break in potential at the point of equivalence and the compound formed corresponds very closely to the normal compound $Th_3(AsO_3)_4$ or $3ThO_2 \cdot 2As_2O_3$ (vide Figs. 3 and 6).

In these titrations, the behavior of indicator electrode with bright platinum as electrodic metal in contact with thorium ions and



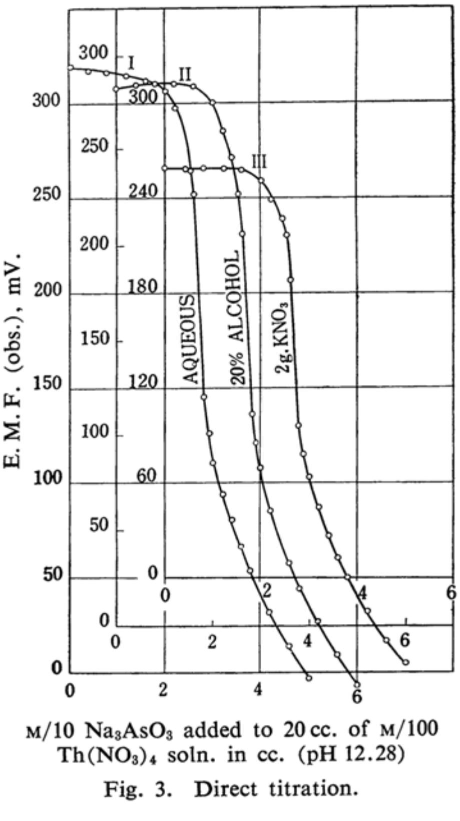
M/5 $NaAsO_2$ added to 20 cc. of M/120 $Th(NO_3)_4$ soln. in cc. (pH 9.85)

Fig. 1. Direct titration.



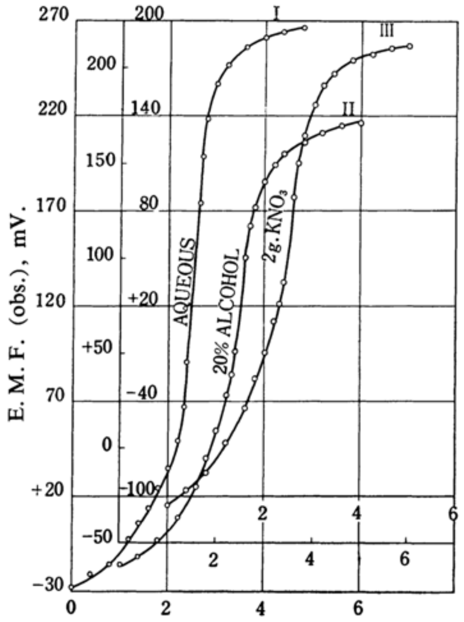
M/10 $Na_4As_2O_5$ added to 20 cc. of M/45 $Th(NO_3)_4$ soln. in cc. (pH 11.25)

Fig. 2. Direct titration.



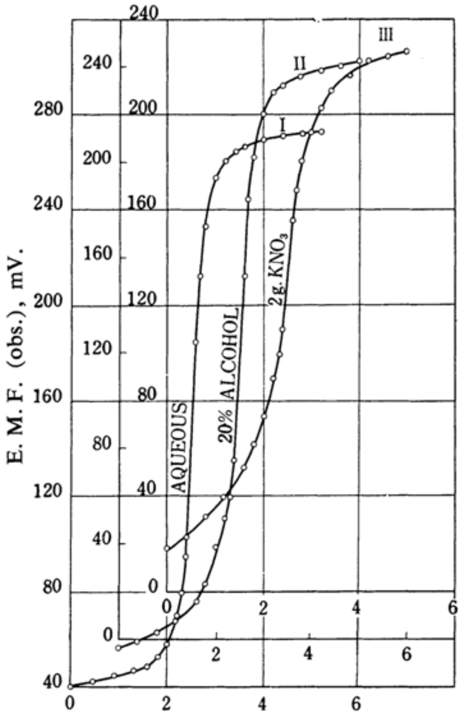
M/10 Na_3AsO_3 added to 20 cc. of M/100 $Th(NO_3)_4$ soln. in cc. (pH 12.28)

Fig. 3. Direct titration.



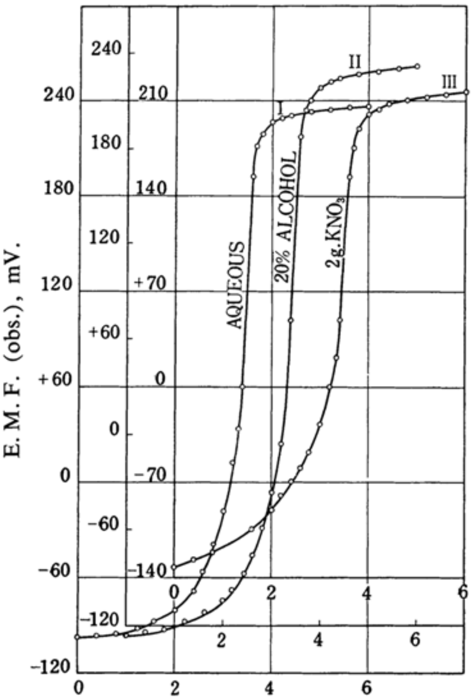
$M/20$ $Th(NO_3)_4$ added to 20 cc. of $M/40$ $NaAsO_2$ soln. in cc. (pH 9.85)

Fig. 4. Reverse titration.



$M/10$ $Th(NO_3)_4$ added to 20 cc. of $M/80$ $Na_4As_2O_5$ soln. in cc. (pH 11.25)

Fig. 5. Reverse titration.



$M/14$ $Th(NO_3)_4$ added to 20 cc. of $M/60$ Na_3AsO_3 soln. in cc. (pH 12.28)

Fig. 6. Reverse titration.

slightly soluble thorium oxide, could be interpreted as that of metal-metal oxide electrode (in this case Th-ThO_2), whose potential depends to a great extent upon the concentration of thorium ions which is grovered by its hydrogen ion concentration. The mechanism of the electrode reaction may be visualized as follows:

$$Th + 4AsO_2^- = ThO_2 \cdot 2As_2O_3 + 4e$$

$$ThO_2 + 4H + 4e \rightleftarrows Th^{4+} + 2H_2O$$

from which

$$\frac{[Th^{4+}]}{[ThO_2][H^+]^4} = K$$

and as $[ThO_2]$ (being slightly soluble) is a constant,

$$[Th^{4+}] = K'[H^+]^4$$

The potential of the electrode can therefore be represented by the Nernst equation

$$E = E_0 + 0.059/2 \log [Th^{4+}]$$

In the direct titrations, the electrode dipped in acidic thorium nitrate solution (pH 5.6), is positive. When alkalized arsenite solutions at different pH values are added from the microburette to thorium nitrate solutions, the concentration of thorium ions gradually decreases owing to their removal from solution by precipitation as thorium arsenites and consequently the E. M. F. slightly decreases after each addition of the reagent. At the point of equivalence when all the thorium ions are removed, a sharp downward jump in potential is observed which is indicated by the steep portion of the titration curves (Figs. 1—3). In the case of inverse titrations, an equilibrium is established after the additon of a few drops of thorium nitrate solution to the titration cell containing arsenite solutions. The E. M. F. shows a gradual rise from the beginning of the reaction, till in the vicinity of the end point when the last traces of arsenite have been removed by precipitation, the first excess of thorium ions added causes a sudden leap in potential indicating the end point, after which the E. M. F. assumes more or less a constant value (Figs. 4—6).

It is noted that after each addition of the reagent, the E. M. F. readily becomes steady. A thorough stirring in the neighborhood of the end point has a favorable effect. Each titration takes about half an hour for completion. The addition of alcohol in varying concentrations improves the end point as the presence of alcohol reduces the adsorption of AsO_2^- ions and also the solubility of thorium arsenite precipitates and hence a closer approach to the theoretical values is envisaged in the experimental results in aqueous-alcoholic solutions (see Table I). The presence of electrolytes such as potassium nitrate has also a favorable effect on the end point as it curtails the time for titration by coagulating the arsenite sol formed in the reaction mixture and thus increasing the sensitiveness of the titration.

Potentiometric titration curves are symmetrical on both sides of the point of equivalence; a pronounced maxima in dE/dV is obtained at the end point and the results are accurate and reproducible. The reaction between alkali arsenites and thorium salts can be successfully studied potentiometrically. There is, however, no appreciable affect of alcohol or electrolytes on the nature of the curves or the magnitude of the break in potential.

It is observed that on mixing thorium nitrate and alkalized arsenite solutions different arsenites of thorium are formed, the composition of which depends on the conditions of precipitation, particularly the concentration of sodium hydroxide in sodium arsenite. Further, the arsenite precipitates dissolve in excess of alkali and also in acids and hence the precipitation of one or the other compound is a function of the hydrogen ion concentration of the medium. The disagreement between the views of previous workers on the molecular composition of thiorum arsenite compounds as reported earlier in literature (loc. cit.) seems to be due to the fact that the experiments were not performed at definite pH values of arsenite solutions.

The reactions between thorium nitrate and thorium arsenite at different pH levels can be represented as follows:

$$\begin{aligned}&\mathrm{4NaAsO_2(2Na_2O+2As_2O_3)+Th(NO_3)_4}\\&\quad\mathrm{=Th(AsO_2)_4\,[ThO_2\cdot 2As_2O_3]+4NaNO_3}\\&\qquad\qquad\qquad\qquad\qquad\mathrm{pH\ 9.85}\end{aligned}$$

$$\begin{aligned}&\mathrm{2Na_4As_2O_5(4Na_2O+2As_2O_3)+2Th(NO_3)_4}\\&\quad\mathrm{=2ThAs_2O_5\,[ThO_2\cdot 2As_2O_3]+NaNO_3}\\&\qquad\qquad\qquad\qquad\qquad\mathrm{pH\ 11.25}\end{aligned}$$

$$\begin{aligned}&\mathrm{4Na_3AsO_3(6Na_2O+2As_2O_3+3Th(NO_3)_4}\\&\quad\mathrm{=Th_3(AsO_3)_4\,[3ThO_2\cdot 2As_2O_3]+12NaNO_3}\\&\qquad\qquad\qquad\qquad\qquad\mathrm{pH\ 12.28}\end{aligned}$$

The composition of thorium arsenites can thus be represented by the general formula $x\mathrm{ThO_2\cdot As_2O_3}$ and the amount of thorium oxide is proportional to the quantity of sodium oxide in sodium arsenite and its proportion increases with the concentration of alkali used in the preparation of arsenite solutions or, in other words, with the pH of the medium.

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