Physico-chemical Studies on the Composition of Complex Arsenates of Metals. I. Thermometric and Conductometric Studies on the Composition of Cupric Arsenate

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The formation and composition of cupric arsenate complexes has been studied by thermometric and conductometric measurements involving theremometric and conductometric titrations between copper sulfate and sodium arsenate at several concentrations of the reactants both by direct and reverse methods. In the direct thermometric titrations, the curves suggest the formation of $CuNaAsO_4$ as a greenish blue precipitate and in the inverse titrations, the formation of $CuNaAsO_4$ is supported. The intersection of the precipitation line and the titrant line in the curves, both for direct and reverse methods, indicated the equivalence point corresponding to the formation of the complex, $CuNaAsO_4$, where the ratio of $Cu : AsO_4$ is 1 : 1.

Reference in literature about the study of the composition of copper arsenate complexes by applying physico-chemical methods is scarcely available. Hirsch[1] reported a complex salt of copper and sodium arsenates with different values for the ratios $Na_2O : CuO : As_2O_5 : H_2O$. Thus the ratios 2 : 24 : 9 : 23 or sodium copper hydro-nona-arsenate, Na_2HAsO_4-$4Cu_3(AsO_4)_2 \cdot 11H_2O$, is obtained by mixing a solution of 4 molecules of cupric nitrate with 7 molecules of sodium hydro-arsenate and washing the precipitate during ten days. The ratios 1 : 12 : 5 : 12 or sodium copper dihydro-penta-arsenate, NaH_2AsO_4-$2Cu_3(AsO_4)_2 \cdot 5H_2O$, were obtained by mixing a dilute solution of 2 molecules of sodium hydro-arsenate, with 4 molecules of cupric sulfate, and washing the precipitate for many days. Salkowsky[2] also made this salt. If in preparing the first of the salts, the precipitate be washed for a shorter time, the product has the ratios 2 : 18 : 7 : 20 or sodium copper bishydro-decatetra-arsenate, $2Na_2HAsO_4 \cdot 6Cu_3 \cdot (AsO_4)_2 \cdot 19H_2O$; and this salt is made by treating a solution of copper nitrate with an excess of sodium hydroarsenate. The ratios 4 : 36 : 15 : 16 or sodium copper hydrobisdihydrodecapenta-arsenate, $Na_2HAsO_4 \cdot 2NaH_2AsO_4 \cdot 6 \cdot Cu_3(AsO_4)_2 \cdot 16H_2O$ was obtained by mixing solutions of 3 molecules of cupric sulfate and 3 molecules of sodium hydroarsenate, and washing the precipitate for three days; if the precipitate is washed until the runnings are free from sulfuric acid a higher hydrate is produced, viz., $331/2H_2O$. There is nothing here to show that these products do not represent arbitrary stages in a process of hydrolysis. Lefevre[3] obtained sodium copper arsenate, green crystalline mass, $CuNaAsO_4$ by dissolving 7~8% of cupric oxide in sodium metaarsenite melted at a low temperature. He obtained sodium copper tetraorthoarsenate, $2Na_3AsO_4 \cdot Cu_3(AsO_4)_2$, by saturating a fused mixture of sodium metaarsenite and chloride of copper oxide.

In view of the difficulties associated with analytical work and in the absence of any decisive views on the composition of cupric arsenate complexes, it was considered worthwhile to undertake the study of these complexes by physico-chemical methods. The results of thermometric and conductometric titrations have been incorporated and discussed in this paper.

Experimental

A. R. B. D. H. $CuSO_4 \cdot 5H_2O$ was used for the preparation of solution and the solution was standardized against sodium thiosulfate solution of known strength. Merck's sample of Na_3AsO_4 was used and the solution was standardized iodometrically against sodium thiosulfate of known strength.

The thermometric titration arrangement was made according to the proccedings laid down by Haldar[4]. Using different concentrations of two salts in solution, the direct and inverse thermometric and conductometric titrations i. e., when copper sulfate or Na_3AsO_4 solution from a micro-burette was added to solution taken in thermos flask or cell, were carried out. Titrations were also carried out upto total concentration of 20% by volume. Curves were plotted between total rise in temperature or corrected conductance and the volume of the titrant added in ml.

1) A. Hirsch, "Ein Beitrag zur Kenntnis der Arsenate des Kupfers", Halle a. s. (1890).
2) H. Salkowsky, *J. pract. Chem.*, **1**, 104, 166 (1868).
3) C. Lefevre. "Sur les Arsenates Cristallises", Paris (1891); *Ann. Chim. Phys.*, **6**, 27. 22 (1892).
4) B. C. Haldar, *J. Indian Chem. Soc.*, **23**, 147 (1946).

TABLE I. SUMMARY OF OBSERVATIONS OF CONDUCTOMETRIC TITRATIONS

Fig. No.	Curve No.	Conc. $CuSO_4$	Conc. Na_3AsO_4	Med. % Alc.	Points showing breaks Calcd.	Obs.	Formula support
Direct titrations :							
1	1	M/10	M/2	Aq.	2.0	2.0	$CuNaAsO_4$
1	2	M/10	M/2	10	1.8	1.8	$CuNaAsO_4$
1	3	M/10	M/2	20	1.6	1.6	$CuNaAsO_4$
1	4	M/30	M/10	Aq.	3.3	3.25	$CuNaAsO_4$
1	5	M/30	M/10	10	3.0	3.0	$CuNaAsO_4$
1	6	M/30	M/10	20	2.66	2.6	$CuNaAsO_4$
Reverse titrations :							
2	1	M/2	M/2	Aq.	2.0	2.1	$CuNaAsO_4$
2	2	M/2	M/2	10	1.8	1.7	$CuNaAsO_4$
2	3	M/2	M/2	20	1.6	1.6	$CuNaAsO_4$
2	4	M/2	M/8 20 cc.	Aq.	2.5	2.5	$CuNaAsO_4$
2	5	M/2	9 cc.	10	2.25	2.3	$CuNaAsO_4$
2	6	M/2	8 cc.	20	2.0	2.0	$CuNaAsO_4$
SUMMARY OF OBSERVATIONS OF THERMOMETRIC TITRATIONS							
Direct titrations							
3	1	M/5	M/88 20 cc.	Aq.	1.13	1.0	$CuNaAsO_4$
3	2	M/5	18 cc.	10	1.02	1.1	$CuNaAsO_4$
3	3	M/5	16 cc.	20	0.99	1.0	$CuNaAsO_4$
3	4	M/11	M/40	Aq.	5.5	5.5	$CuNaAsO_4$
3	5	M/11	M/40	10	4.95	5.0	$CuNaAsO_4$
3	6	M/11	M/40	20	4.4	4.4	$CuNaAsO_4$
Inverse titrations							
4	1	M/40	M/11 20 cc.	Aq.	5.5	5.5	$CuNaAsO_4$
4	2	M/40	18 cc.	10	4.95	4.7	$CuNaAsO_4$
4	3	M/40	16 cc.	20	4.4	4.3	$CuNaAsO_4$
4	4	M/88 20 cc.	M/5	Aq.	1.13	1.2	$CuNaAsO_4$
4	5	18 cc.	M/5	10	1.02	1.00	$CuNaAsO_4$
4	6	16 cc.	M/5	20	0.99	1.00	$CuNaAsO_4$

The experimental observations of thermometric and conductometric titrations have been given in Table I.

Discussion

The formation of the probable compounds obtained by the interaction of $CuSO_4$ and sodium arsenate can be represented by the following equations:

$$CuSO_4 + Na_3AsO_4 = CuNaAsO_4 + Na_2SO_4 \quad (1)$$

$$2\,CuSO_4 + 3Na_3AsO_4 = Cu_2Na_5(AsO_4)_3 + 2Na_2SO_4 \quad (2)$$

$$3\,CuSO_4 + 2Na_3AsO_4 = Cu_3(AsO_4)_2 + 3Na_2SO_4 \quad (3)$$

$$CuSO_4 + 2Na_3AsO_4 = CuNa_4(AsO_4)_2 + Na_2SO_4 \quad (4)$$

Taking into consideration the strength of solutions of Na_3AsO_4 (pH=8.2) and $CuSO_4$ (pH=4.15), 10 ml. of $CuSO_4$ for the formation of the compounds, $CuNaAsO_4$, $Cu_2Na_5(AsO_4)_3$, $Cu_3(AsO_4)_2$ and $CuNa_4(AsO_4)_2$ will be 2.0, 1.33, 3.0 and 1.0 respectively of Na_3AsO_4 solution. For the inverse titrations and other dilution of reagents, theoretical titer values for the formation of these compounds can be calculated accordingly.

The conductometric titrations curves (Figs. 1 and 2) both in direct and inverse titrations, yield only one point of equivalence at a molecular ratio of reactants $CuSO_4 : Na_3AsO_4$ as 1 : 1, whereas it is much different from the ratios 1 : 2, 2/3 : 1 and 3/2 : 1 as mentioned above (vid. Eqs. 2 to 4) for the formation of probable compounds.

It is observed in direct and inverse titrations that when Na_3AsO_4 solution is added to $CuSO_4$ solution and vice versa, a bluish white precipitate was formed, on adding excess of

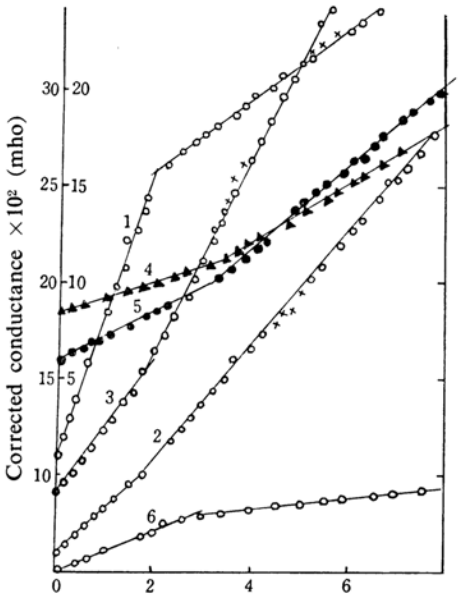

Fig. 1.

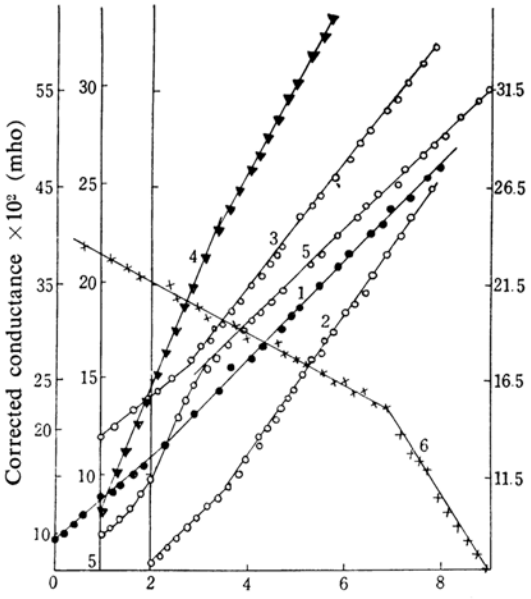

Fig. 2.

either reagent the precipitate in bulk was formed.

The diagrammatic representation of thermometric titrations in Figs. 3—4 reveals that the curves in direct and inverse titrations yield only one point of equivalence corresponding to the formation of the complex, $CuNaAsO_4$, where the ratio of reactants $CuSO_4$: Na_3AsO_4 is 1 : 1. It is evident from the summary of

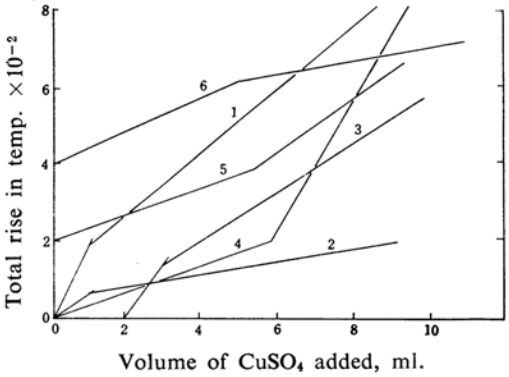

Fig. 3. Direct titrations.

Curves 1, 2, 3; M/5 $CuSO_4$ and M/88 Na_3AsO_4
Curves 4, 5, 6; M/11 $CuSO_4$ and M/40 Na_3AsO_4

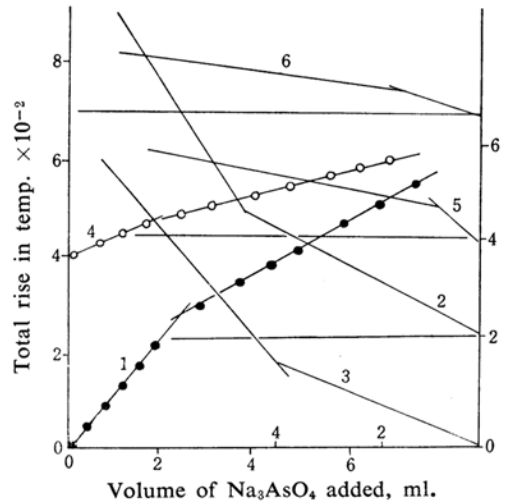

Fig. 4. Reverse titrations.

Curves 1,2,3; M/40 $CuSO_4$ and M/11 Na_3AsO_4
Curves 4,5,6; M/5 Na_3AsO_4 and M/88 $CuSO_4$

observations of thermometric and conductometric titrations that there is close agreement between the values theoretically calculated and observed. In order to show the discrepancy, which is probably due to slight effect of hydrolysis and adsorption, between theoretically calculated on the basis of strength of solutions used and observed values in aqueous and aqueous alcoholic media, the summary of observations have been given above for comparison. There is coordination in the results obtained by conductometry and Dutoit's thermovolumetry.

Lefevre's[3] observations have been supported by my thermovolumetric and conductometric studies. Views and results reported by Hirsch, and Salkowsky (loc. cit.) have not been supported by my studies.

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