PHYSICO-CHEMICAL STUDIES ON THE COMPOSITION OF COPPER ARSENATE

Thermometric Studies on the composition of Cupric Arsenate

by

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The formation and composition of cupric arsenate complexes has been studied by the thermometric measurements involving thermometric titrations between $CuSO_4 5H_2O$ and disodium hydrogen-arsenate at several concentrations of the reactants both by direct and reverse methods. In the direct method thermometric titration curves suggest the formation of $CuHAsO_4$ greenish blue ppt. whereas in the reverse titrations the formation of $CuHAsO_4$ is supported.

Reference in literature about the study of the composition of cupric arsenate complexes by applying physico-chemical methods is scarcely available. W. Hampe[1] reported the formation of cuprous-pyro-arsenate $Cu_4As_2O_7$ by fusing a mixture of equal parts of cupric oxide and As_2O_3, in an atmosphere of carbon dioxide, which on white heat gives off As_2O_3 forming red cupricdi-arsenate $Cu_8As_2O_9$ or $4Cu_2OAs_2O_5$. C. Reichard[2] prepared cuprous pyro-arsenate $Cu_4As_2O_7$ by treating $NaAsO_3$ with excess of $CuSO_4$.

W. Skey[3] could not prepare copper arsenate by treating $NaAsO_3$ with Cupric salt solution.

R. Chenevix[5] J. J. Berzelius[4], J. L. Proust[6], E. Mitscherlich[7] and A. Hiesch[10] obtained a pale blue precipitate by treating cupric salt with sodium-hydro-arsenate, which could not be analysed so their emperical composition are unknown. A. C. Bacquerrel[8] obtained the green crystals on a copper strip in the suspension of silver arsenate in water. The composition of the green crystal is thought to be cupric erthe-arsenate $Cu_3 (AsO_4)_2$.

Apart from the above study in literature more variable and complex formulæ have been given e.g., $CuHAsO_4 H_2O$ (Celeriane), $CuHAsO_4 2 NH_3$ H. (Schiff)[9], $Cu_3 (AsO_4)_2$—$CuHAsO_4 5\ ^{1}/_{2}\ H_2O$([10]), in elevenite mineral $4CuOAs_2O_9 H_2O$ or $Cu_4AsO_9 H_2O$ copper hydroxy-erthe-arsenate, $Cu_3AsO_4)_2C_1 (HO)_2$ (C.F. Remmelsberg[12]) $HOCu (AsO_4)Cu$(P. Groth[12]).

Grass green mineral evanite named by W. Haidenger and analysed by E. Turner[13] R. B. Pierce[14], W. H. Hillebrand and H. S. Washington[15] gave the composition $5Cu\ OAs_2O_5\ 2H_2O$ *i.e.*, Copper-tetra-hydroxy-erthearsenate.

H. Guerin and C. Duc. Mange[16] studied the conditions of formation and properties of the two salts $5CuOAs_2O_5$—$5H_2O$ and $3CuO(NH_4)_2\ OAs_2O_5\ 5H_2O$ and showed that these two arsenates belong to a series different from copper arsenates already known. The tricupric arsenate prepared by the direct action of arsenic acid on cupric hydroxide can not be obtained by decom-

position of amoniated tri-cupric salt or double decomposition between tri-calcium arsenate and $CuCl_2$.

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 worth while to undertake the study of these complexes by physico-chemical methods.

With the results of conductometric, potentiometric, amperometric etc. in progress, the results of thermometric titrations are incorporated and discussed in this paper.

Experimental

A. R. $CuSO_4\,5H_2O$ (B. D. H.) was used for the preparation of solution and the strength of solution was checked by standardising it against sodium thio-sulphate of known strength. Merck's sample of $Na_2HAsO_4 12H_2O$ was used and the solution was standardised iodometrically against sodium thio-sulphate of known strength.

The thermometric titration arrangement was made according to the proceedings laid down by Haldar[17]. Using different concentrations of two salts in solution, the direct and reverse methods *i.e.*, (when $CuSO_4 5H_2O$ was added from micro-burette to sodium arsenate solution in thermos-flask and vice versa) titrations were followed. Titrations were also carried out upto total concentration of 20% by volume. The total rise in temperature was plotted against the titre in c.c. Blank correction was applied by performing blank experiments, doing parallel experiments by adding water to $CuSO_4$ or Na_2HAsO_4 and the readings obtained were subtracted from the corresponding readings obtained in the titrations between the solutions of $CuSO_4$ and Na_2HAsO_4. The total rise in temperature after giving due allowance for the blank correction was then plotted against the titre in c.c.

Summary of Observations of Thermometric Titrations

Conc. f $CuSO_4$	Na_2HAsO_4 conc.	Medium Curve	Points showing breaks		Formula	Fig.
			Calculated	Observed		
Direct Titrations—						
M/5·0	M/88·0	Aq.	1	1·13	1·0 $CuHAsO_4$	1
,,	20·c.c. 18	Alc10%	2	1·02	1·1 ,,	1
2	16	20%	3	0·99	1·0 ,,	1
M/11·0	M/40·0 20 cc	Aq.	4	5·5	5·5 ,,	1
,,	18 cc	Alc. 10%	5	4·95	5·0 ,,	1
,,	16	20%	6	4·4	4·4 ,,	1
Reverse Titrations—						
M/40·0 20 cc	M/11·0	Aq.	1	5·5	5·5 ,,	2
18	,,	Alc 10%	2	4·95	4·7 ,,	2
16	,,	20%	3	4·4	4·3 ,,	2
M/88·0 20 cc	M/5·0	Aq.	4	1·13	1·2 ,,	2
18	,,	Alc. 10%	5	1·02	1·00 ,,	2
16	,,	20%		0·99	1·00 ,,	2

Discussion

It will be observed from the table showing summary of observations of thermometric titrations that in direct and reverse titration curves, Figs. 1 & 2 formation of $CuHAsO_4$ where the ratio of Cu: As is 1 : 1 is supported.

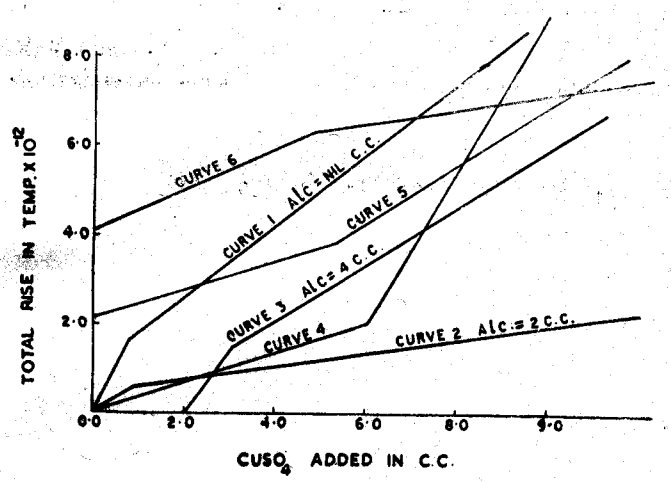

FIG. 1

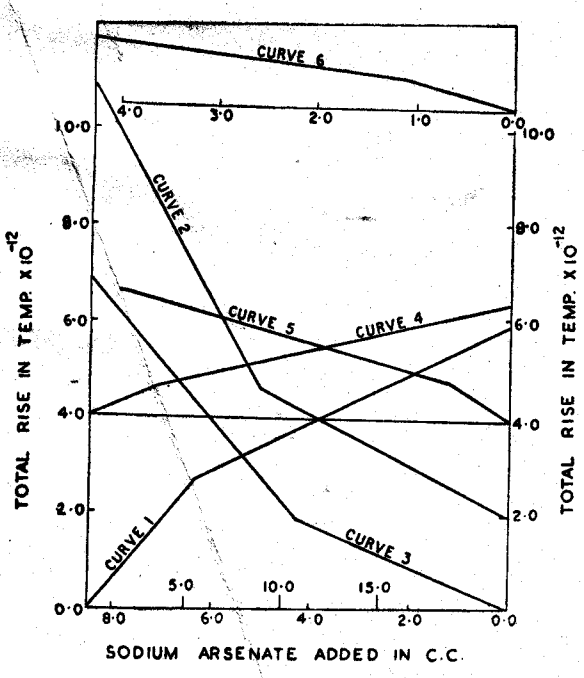

FIG. 2

With a view to show the discrepancy between the observed and calculated titre values a summary of observations in aqueous and alcoholic medium is given for comparison.

Conductometric and potentiometric studies on these complexes is in progress and will be communicated shortly.

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Reference

1 W. Hampe, *Zeit Berg. Hutt. Sal.* **22**, 102, 1874.