PHYSICO-CHEMICAL STUDIES ON THE COMPOSITION OF COMPLEX ARSENITES OF METALS—PART IV

CONDUCTOMETRIC AND POTENTIOMETRIC STUDIES ON THE COMPOSITION OF CADMIUM ARSENITE

by

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ABSTRACT

The formation and precipitation of cadmium arsenite has been studied by conductometric and potentiometric titrations between cadmium nitrate and sodium arsenite (meta) at different concentrations with either of the substances used as the reagent in titration. In the case of direct titrations (cadmium nitrate added to sodium arsenite in the conductivity cell), one distinct break in the curves is observed corresponding to the formation of the Cd $(AsO_2)_2$ where the molecular ratio is 2 : 1. The direct and reverse potentiometric titrations curves give one maxima in dE/dV at point corresponding to the formation of the complex Cd $(AsO_2)_2$ where the molecular ratio of reactants Cd: AsO_2 is 1:2. The composition has been arrived at by comparing the calculated values with observed values by conductometric and potentiometric titrations. The composition of cadmium arsenite arrived at both by conductometry and potentiometry is best represented as Cd $(AsO_2)_2$.

Introduction

In continuation of our studies on the composition of complex metallic thiosulphate of cadmium (J.I.C.S. 1959, 36, 103, 108), arsenite complexes of cadmium (J.I.C.S. 1959, 36, 286) and arsenite complexes of bismuth (Proc. of Ind. Sci. Cong. abst. III, 1959, p. 73) and further studies on the composition of thiosulphates of bismuth, arsenite complexes of copper and cadmium and arsenite complexes of cadmium and copper, by the authors, attempts have been made in this paper to substantiate the conclusions arrived at on the composition of complex arsenite of cadmium, by previously applied methods *i.e.*, thermometric titrations. The results of potentiometry and conductometry have been incorporated and discussed in this paper.

Experimental

Conductomeiric titrations

A.R. (B.D.H.) reagents were used for the preparation of solutions. Air free conductivity water was used for the preparation of standard solutions and further dilutions. Solutions were standardised by the method described earlier (loc-cit.). The conductivities were measured by Kohlrausch Universal Bridge (W.G. Pye Ltd.). The alternating current was supplied by a low frequency oscillator (1000 C/s) and the point of balance was indicated by minima of sound in the head phone. The titration cell was immersed in an electrically maintained thermostat. The conductance obtained after each

dilution was corrected for the dilution effect by multiplying the observed conductance by V/X, where V refers to the total volume of the solution and X is the volume in ml. of the reactant already taken in the cell[2] (Davies Conductivities of solutions, page 238). Curves were plotted between the corrected conductance thus obtained and the volume of the titrant the breaks in the curves correspond to the formation of different compounds. Using different concentrations of the reactants, the titrations were carried out both by direct and inverse methods *i.e.*, when cadmium nitrate from a micro-burette was added to sodium arsenite solution in the conductivity cell and *vice versa*. Titrations were also carried out in varying concentrations of alcohol upto total concentration of 20% by volume.

Potentiometric titrations

Using different concentrations of reactants potentiometric and conductcmetric titrations were performed both by direct and reverse methods. A platinised platinum foil was immersed in the solution of the titre and used as an indicator electrode in conjunction with a saturated calomal electrode. The E.M.F. was measured by employing a cambridge pH meter. The temperature of the electrode cell was kept constant by keeping it in an electrically maintained thermostat. The titre solution was stirred after each addition with the help of an electric stirrer. Near the end point, in order to have the clear idea of the formation of the complexes, 0.1 or 0·2 c.c. was added at a time. The titrations were also carried out in increasing amounts of alcohol, upto total-concentration of 30% by volume. The curves were also plotted between E (observed) taken as the ordinate and the volume of the titrant added in ml. as abscissa.

Summary of observations of conductometric titrations

Fig. No.	Curve No.	Conc. of $Cd(NO_3)_2$	Conc. of $NaAsO_2$	Points showing breaks Formula			
				Med. %Alc.	Calc.	Obsd.	Supported
DIRECT TITRATIONS							
1	1	M/5	M/20, 10 c.c.	0	1·25	1·3	$Cd(AsO_2)_2$
1	2	,,	M/20, 9 c.c.	10	1·125	1·1	,,
1	3	,,	M/20, 8 c.c.	20	1·00	1·0	,,
1	4	,,	M/40, 20 c.c.	0	1·25	1·25	,,
1	5	,,	M/40, 18 c.c.	10	1·125	1·2	,,
1	6	,,	M/40, 16 c.c.	20	1·00	1·0	,,
REVERSE TITRATIONS							
2	1	M/20, 10 c.c.	M/5	0	5·0	5·0	,,
2	2	M/20, 9 c.c.	,,	10	4·5	4·5	,,
2	3	M/20, 8 c.c.	,,	20	4·0	4·0	,,
	4	M/80, 20 c.c.	M/5	0	2·5	2·5	,,
	5	M/80, 18 c.c.	,,	10	2·25	2·2	,,
2	6	M/80, 16 c.c.	,,	20	2·0	1·95	,,

Summary of observations of Potentiometric titrations—contd.

Fig. No.	Curve No.	Conc. of Cd $(NO_3)_2$	Conc. of $NaAsO_2$	Points showing breaks Formula			
				Med. % Alc.	Calc.	Obsd.	Supported
DIRECT TITRATIONS							
1	1	M/5	M/20, 20 c.c.	0	2·5	2·5	$Cd(AsO_2)_2$
1	2	,,	M/20, 18 c.c.	10	2·25	2·3	,,
1	3	,,	M/20, 16 c.c.	20	2·0	2·0	,,
1	4	,,	M/20, 14 c.c.	30	1·7	1·7	,,
1	5	,,	M/25, 20 c.c.	0	2·0	2·1	,,
1	6	,,	M/25, 18 c.c.	10	1·8	1·8	,,
1	7	,,	M/25, 16 c.c.	20	1·6	1·5	,,
1	8	,,	M/25, 14 c.c.	30	1·4	1·4	,,
REVERSE TITRATIONS							
2	1	M/30, 10 c.c.	M/5	0	3·33	3·3	,,
2	2	M/30, 9 c.c.	,,	10	3·0	3·1	,,
2	3	M/30, 8 c.c.	,,	20	2·66	2·7	,,
2	4	M/30, 7 c.c.	,,	30	2·33	2·3	,,
2	5	M/20, 10 c.c.	,,	0	5·0	5·0	,,
2	6	M/20, 9 c.c.	,,	10	4·5	4·5	,,
2	7	M/20, 8 c.c.	,,	20	4·0	4·0	,,
2	8	M/20, 7 c.c.	,,	30	3·5	3·4	,,

Discussions

It is observed that in all the titrations on mixing the reagents cadmium nitrate (pH=4·6) and sodium arsenite (pH=9·3), a white precipitate is obtained in the beginning and then no further remarkable change of colour is observed.

The direct conductometric titration curves yield a break corresponding to the formation of the compound Cd $(AsO_2)_2$ or $CdoAs_2O_3$ where the molecular ratio of the reactants cadmium nitrate and sodium arsenite (meta) is 1 : 2 . On reversing the process of addition of reagents the curves obtained show one break corresponding to the point of equivalence in the ratio of Cd : AsO_2 as 1 : 2 , indicating the formation of the compound $CdOAs_2O_3$.

The potentiometric titration curves in direct titrations give one maxima in dE/dC corresponding to the formation of the above mentioned compound. The inverse titrations i.e., when sodium arsenite meta is added to cadmium nitrate solution taken in the electrode vessel, curves show a sharp change in potential at the point of equivalence and formation of the compound $CdOAs_2O_3$ or Cd $(AsO_2)_2$ where the ratio of reactants $NaAsO_2$: Cd is 2 : 1. The results of conductometric and potentiometric titrations are accurate and reproducible.

Our conductometric and potentiometric titrations support our results of the thermometric studies on these complexes[3] (J.I.C.S. 1959, 36, 286), but

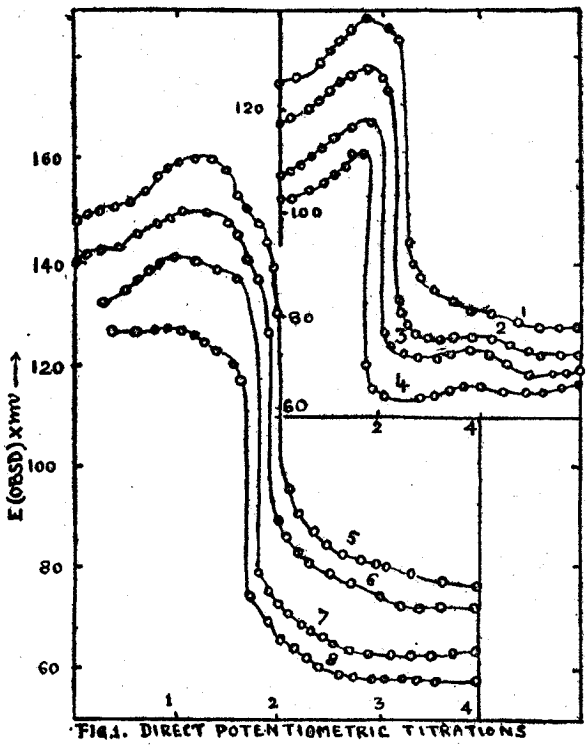

FIG. 1. DIRECT POTENTIOMETRIC TITRATIONS

in the light of our above studies formation of the compound $CdAs_2O_5$ reported by Reichard[4] (Z. anal. Chem. 1898, 37, 749) is untenable.

It is also interesting to note that the formation of the compounds of the type $CdNa(AsO_2)_3$ and $CdNa_2(AsO_2)_4$ and the additive compounds like $CdNO_3(AsO_2)$ and $CdNO_3(AsO_2)_3$ is completely ruled out on the basis of our results.

Thus the reaction between cadmium nitrate ($pH = 4{\cdot}6$) and sodium arsenite ($pH = 9{\cdot}3$) at pH can not take place according to the following scheme of reactions :

$$Cd(NO_3)_2 + 3\ NaAsO_2 = CdNa(AsO_2)_3 + 2\ NaNO_3$$
$$\text{,,} + \text{,,} = CdNO_3(AsO_2) + \text{,,}$$
$$\text{,,} + 4\ \text{,,} = CdNa_2(AsO_2)_4 + 2\ \text{,,}$$
$$2\ \text{,,} + 3\ \text{,,} = Cd_2Na_3(AsO_2)_3 + 3\ \text{,,}$$

The probable equation of this reaction is as follows :—

$$Cd(NO_3)_2 + NaAsO_2 = Cd(AsO_2)_2 + 2\ NaNO_3$$

Further work is in progress to study this reaction by the method of continuous variation of Job and the results will be communicated in future.

The results of the present studies can be applied for the estimation of cadmium in solution.