PHYSICO-CHEMICAL STUDIES ON THE COMPOSITION OF COMPLEX THIOSULPHATES OF METALS—PART VI

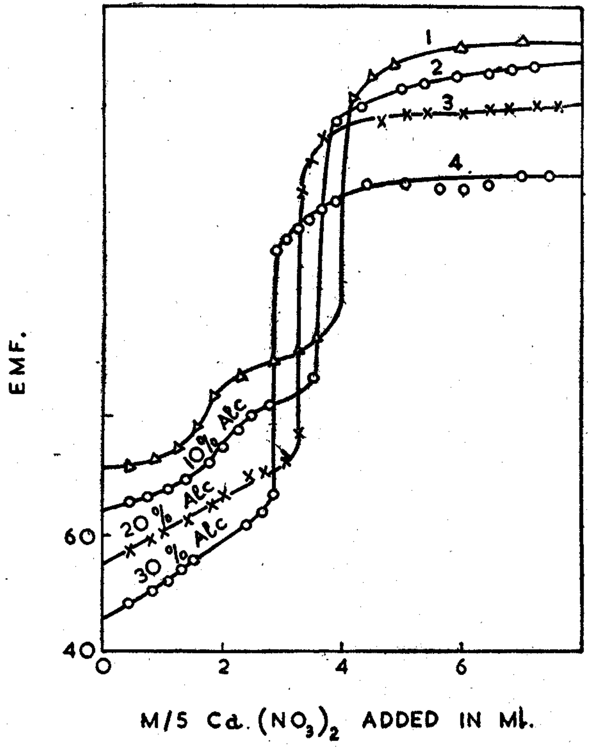
POTENTIOMETRIC STUDIES ON THE REACTION BETWEEN CADMIUM NITRATE AND SODIUM THIOSULPHATE

by

M. S. Bhadraver and J. N. Gaur

Lohia College, University of Rajasthan, Rajasthan

The formation and composition of cadmium thiosulphate complex has been studied by potentiometric titrations between cadmium nitrate and sodium thiosulphate both by direct and the inverse methods. The equivalence point obtained from the maximum value of dE/dC corresponds to the formation of a compound having the composition CdS_2O_3 when Cd $(NO_3)_2$ was added from a micro-burette to sodium thiosulphate in the electrode vessel. Only such titrations in which $Na_2S_2O_3$ was used as a titre, give satisfactory results. The curves are regular in form, a pronounced jump in the dE/dC occurs at the end point and the results are accurate and reproducible. The inverse titrations i.e., when $Na_2S_2O_3$ is added to Cd $(NO_3)_2$ do not give satisfactory results due to unsteady and unconstant values of E.M.F. The effect of ethanol



on the end point as well as on the nature of the curves have been studied. There is no indication of the formation of compounds $CdNa_2(S_2O_3)_2$, $Na_4Cd\,(S_2O_3)_3$, $Na_2\,Cd_2\,(S_2O_3)_3$ and $Cd_3Na_2\,(S_2O_3)_3$ and additive compounds of the type $Cd_3\,(NO_3S_2O_3)$ $Cd_4\,(NO_3)_2\,(S_2O_3)_3$.

Reference in literature about the elaborate study of the composition of cadmium thiosulphate complexes by applying physico-chemical methods is scarcely available. G. Vortmann and C. Padsberg[1] obtained cadmium thiosulphate $CdS_2O_32H_2O$ by triturating a mixture of stoichiometric proportion of cadmium sulphate and barium thiosulphate with a little water, and mixing the filterate with alcohol. A. Fock and K. Kluss [2] used strontium thiosulphate and used a mixture of alcohol and ether as the precipitant. The yellowish white monoclinic crystals have the (010) cleavage nearly complete. The yellowish white, monoclinic crystals slowly decomposed when kept in closed vessels, more rapidly when heated forming cadmium sulphide and sulphate and sulphur dioxide. A. Fock and K. Kluss obtained mono-clinic prisms of ammonium cadmium tetrathiosulphate $3(NH_4)_2\,S_2O_3\,CdS_2O_3H_2O$ formed in proportion 1 : 4 to 7, the trihydrate is formed in monoclinic plates. By mixing an excess of sodium thiosulphate with cadmium acetate, trihydrated trisodium cadmium tetra thiosulphate $3Na_2\,S_2O_3\,CdS_2O_3\,3H_2O$ is formed in yellow, deliquescent, triclinic crystals. G. Vortmann and C. Padsberg obtained yellow plates of the enhydrate by adding alcohol to a solution of cadmium nitrate and an excess of sodium thiosulphate and rubbing up the oil with alcohol. The crystals lose 4 molecules of water over conc. H_2SO_4. A. Fock and K. Kluss prepared hexa hydrate by adding alcohol to a solution of cadmium acetate and an excess of sodium thiosulphate. P. Jochum[7] said that at least 3 parts of a cold saturated solution of sodium thiosulphate are needed for two parts of similar solution of cadmium acetate and he obtained yellowish white needles of sodium dicadmium trithiosulphate, $Na_2S_2O_3\,2CdS_2O_3\,7H_2O$ and with a solution of these salts in molar proportions, sodium tricadmium tetra thiosulphate $Na_2S_2O_3\,3CdS_2O_3\,9H_2O$. A. Fock and K. Kluss could not prepare this. salt. H. Euler[4] found that although sodium cadmium dithiosulphate $Na_2S_2O_3\,CdS_2O_3$ has not been obtained in the solid state it is probably present in solution and the equilibrium constant K for $CdX(S_2\,O_3)_2\,X(Na_2S_2O_3) = K\,(CdNa_2S_2O_3)_4$ is $3{\cdot}5 \times 10^{-8}$ to 5.0×10^{-8}. A. Fock and K. Kluss prepared potassium cadmium octothiosulphate $5K_2S_2O_3\,3\,CdS_2O_3$ by mixing equal volumes of conc. solution of cadmium acetate and potassium thiosulphate. The salt can not be recrystallised from water without decomposition. They also made potassium cadmium tetra thiosulphate $3\,K_2S_2O_3\,CdS_2O_3\,2H_2O$, by adding alcohol to a soln. of 6 mols of potassium thiosulphate and a mol of cadmium acetate. The salt can be crystallised from water without decomposition, over H_2SO_4 in vacuum, it loses a molecule of water. By treating a mixed solution of calcium thiosulphate and cadmium acetate with alcohol a gummy mass of ca-cd-thiosulphate is formed.

In view of the difficulties associated with analytical work and in the absence of any decisive views on the composition of cadmium thiosulphate attempts have been made in this paper to study the formation and composition of cadmium thiosulphate, which has given more conclusive evidence on the composition of cadmium thiosulphate.

Experimental

Standard solutions of cadmium nitrate and sodium thiosulphate were prepared and estimated as described[5,6] in earlier communications J.I.C.S. 1959, 36, page 103.

The electrode system used was the following :—

Pt/Cd$(NO_3)_2$/KCl Aq. Calomel

The E.M.F. was measured by a Cambridge pH meter. The solutions stirred by the help of an electrically driven stirrer. The titration cell was kept immersed in an electrically maintained thermostat. Using different concentrations of reactants, potentiometric titrations were followed both by direct and reverse methods. Curves were plotted between the potential between platinum electrode and S.C.E. and the volume of the titrate. A sharp inflection in the curves occurs at the end point which is marked by a pronounced maxima in dE/dV. The titrations were also carried out in presence of varying percentage of alcohol by volume. 20 or 10ml. of the reagent was taken in beaker serving as the titration cell.

Summary of Observations of potentiometric titrations

Fig	Curve	$Na_2S_2O_3$	CdS_2O_3	ml. of CdS_2O_3 Calc. value	Reqd. for the form. of Obsd. from dE/dC in presence of alcohol			
					0 %	10%	20%	30%
DIRECT TITRATIONS								
1	1 to 4	M/20	M/5	2·5	2·5	2·25	2·0	1·8
1	5—8	M/25	M/5	4·0	4·0	3·6	3·2	2·8

Discussion

It is observed that when Cd$(NO_3)_2$ is added to a solution of $Na_2S_2O_3$ taken in the electrode vessel and the potential between platinum electrode and a saturated calomel electrode is measured and plotted against the volume of cadmium nitrate added in m. l., a sharp rise in the curve occurs at the point where the molecular ratio of reactants Cd$(NO_3)_2$ and $Na_2S_2O_3$ is 1 : 1, corresponding to the formation of CdS_2O_3. No appreciable rise in potential is observed at the point corresponding to the formation of the complexes $CdNa_2(S_2O_3)_2$, $CdNa_4$ $(S_2O_3)_3$ $Na_2Cd_2(S_2O_3)_3$ (visualised by the previous workers (loc. cit.) Alcohol has however no effect on the end point or the nature of curves.

The inverse titrations (i.e., when $Na_2S_2O_3$ solution from micro-burette is added to Cd$(NO_3)_2$ solution in the electrode cell) do not give satisfactory results. The E.M.F. varies and does not attain steady value and this inconsistency of the potential makes the inverse titrations impracticable.

It may be noted that stirring in the immediate neighbourhood of electrode is necessary during the titration, one has to wait near the end point until the potential becomes constant, this may be ascribed to the adsorbing tendency of CdS_2O_3 solution to adsorb Cd ions and hence the potential near the equivalence point is very slow in becoming constant.

It is observed that when Cd $(NO_3)_2$ is added to $Na_2S_2O_3$ solution, a white precipitate of CdS_2O_3 is obtained which shows no remarkable changes in colour.

In the light of our electrometric studies the formation of $3Na_2S_2O_3CdS_2O_3$ $3H_2O$,$Na_2S_2O_3$ $2CdS_2O_3$ $7H_2O$,$Na_2S_2O_3$ $3CdS_2O_3$ $9H_2O$ and $Na_2S_2O_3$ CdS_2O_3 as reported by earlier workers (loc. cit). by analytical methods are not supported, probably these are true double compounds rather than the true complexes.

References

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