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

POTENTIOMETRIC STUDIES ON THE REACTION BETWEEN CADMIUM NITRATE AND SODIUM THIOSULPHATE

by

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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 $\text{CdS}_2\text{O}_3$ when $\text{Cd(NO}_3)_2$ was added from a micro-burette to sodium thiosulphate in the electrode vessel. Only such titrations in which $\text{Na}_2\text{S}_2\text{O}_3$ was used as a titrator, 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 $\text{Na}_2\text{S}_2\text{O}_3$ is added to $\text{Cd(NO}_3)_2$ 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 CdNa₂(S₂O₃)₂, Na₄Cd(S₂O₃)₃, Na₂Cd₂(S₂O₃)₅ and Cd₃Na₂(S₂O₃)₃ and additive compounds of the type Cd₃(NO₃S₂O₈)Cd₄(NO₃)₂(S₂O₃)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 obtained cadmium thiosulphate CdS₂O₆2H₂O 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 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(NH₄)₂ S₂O₃ CdS₂O₆H₂O 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 3Na₂ S₂O₃ CdS₂O₆ 3H₂O is formed in yellow, deliquescent, triclinic crystals. G. Vortmann and C. Padsberg obtained yellow plates of the enhydrates 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. H₂SO₄. A. Fock and K. Kluss prepared hexa hydrate by adding alcohol to a solution of cadmium acetate and an excess of sodium thiosulphate. P. Jochem 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, Na₃S₄O₁₁ 2CdS₂O₆ 7H₂O and with a solution of these salts in molar proportions, sodium tricadmium tetra thiosulphate Na₂S₄O₁₁ 3CdS₂O₆ 9H₂O. A. Fock and K. Kluss could not prepare this salt. H. Euler found that although sodium cadmium dithiosulphate Na₂S₂O₇ CdS₂O₆ has not been obtained in the solid state it is probably present in solution and the equilibrium constant K for CdX(S₂O₇)₂ X(Na₂S₂O₇) = K (CdNa₂S₂O₇)₄ is 3·5 × 10⁻⁸ to 5·0 × 10⁻⁸. A. Fock and K. Kluss prepared potassium cadmium octothiosulphate 5K₂S₂O₇ 3 CdS₂O₆ 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 K₂S₂O₇ CdS₂O₆ 2H₂O, by adding alcohol to a soln. of 6 mols of potassium thiosulphate and a mol of cadmium acetate. The salt can be crystalised from water without decomposition, over H₂SO₄ 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 in earlier communications J.I.C.S., 1959, 36, page 103.

The electrode system used was the following:

Pt/Cd(NO₃)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 10 ml. of the reagent was taken in beaker serving as the titration cell.

Summary of Observations of potentiometric titrations

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<tr>
<th>Fig</th>
<th>Curve</th>
<th>Na₂S₂O₃</th>
<th>CdS₂O₃</th>
<th>ml. of CdS₂O₃</th>
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<td>Calc.</td>
<td>dE/dC in presence of alcohol</td>
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Discussion

It is observed that when Cd(NO₃)₂ is added to a solution of Na₂S₂O₃ 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. 1., a sharp rise in the curve occurs at the point where the molecular ratio of reactants Cd(NO₃)₂ and Na₂S₂O₃ is 1 : 1, corresponding to the formation of CdS₂O₃. No appreciable rise in potential is observed at the point corresponding to the formation of the complexes CdNa₂(S₂O₃)₂, CdNa₄(S₂O₃)₃Na₂Cd₂(S₂O₃)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 Na₂S₂O₃ solution from micro-burette is added to Cd(NO₃)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$_2$O$_3$ 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$_2$S$_2$O$_3$ solution, a
white precipitate of CdS$_2$O$_3$ is obtained which shows no remarkable changes
in colour.

In the light of our electrometric studies the formation of 3Na$_2$S$_2$O$_3$CdS$_2$O$_3$
3H$_2$O, Na$_2$S$_2$O$_3$ 2CdS$_2$O$_3$, 7H$_2$O, Na$_2$S$_2$O$_3$ 3CdS$_2$O$_3$, 9H$_2$O and Na$_2$S$_2$O$_3$ CdS$_2$O$_3$ 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

6. Do.
7. Jochum, P., *Ueber die Einwirkung des unterschweigensauren Natrons
auf Metallsalze*, Berlin, 1885.