

256. *Studies of Ionisation in Non-aqueous Solvents. Part IV. The Formation of Certain Ammines in Methyl and Ethyl Acetates and in Acetone.*

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As in the cases of the alcohols previously studied, ammine formation occurs when ammonia reacts with the salts studied in methyl and ethyl acetates, and in acetone. In some cases the ammonia content of the ammine is higher than that observed when methyl and ethyl alcohols are used as solvents.

IN Part II (J., 1939, 1337) it was shown that, although the formation of ammines proceeds in water *via* the hydroxide, which is first precipitated, yet in hydroxylic solvents, such as methyl and ethyl alcohols, direct combination between gaseous ammonia and the dissolved salt occurs. In this communication an analogous series of reactions has been studied in the non-hydroxylic solvents methyl and ethyl acetates and acetone. It was expected that in these solvents also direct combination between the gas and the salt would take place, although, since the dielectric constants of the solvents were different from those of the alcohols, differences in the compositions of the ammines formed might be found. This was supported by the analyses of the precipitates obtained and, in the case of acetone, by the conductivity titrations. In general the results are in agreement with those of Naumann and his collaborators (*Ber.*, 1899, **32**, 999; 1904, **37**, 3600, 4609, 4328; 1909, **42**, 3790; 1910, **43**, 314; 1914, **47**, 250, 1371).

EXPERIMENTAL.

As methyl and ethyl acetates contained appreciable amounts of aldehyde, this was removed as the bisulphite compound, after which the esters were shaken with dilute sodium carbonate solution and then with water. Partial dehydration was effected with fused potassium carbonate, and the drying completed over phosphoric oxide. The esters were then decanted off and fractionated. Their b. p.'s were: methyl acetate, 57—57.5°; ethyl acetate, 77°. Weaver's test (*J. Amer. Chem. Soc.*, 1922, **44**, 2824) showed these solvents to be water-free.

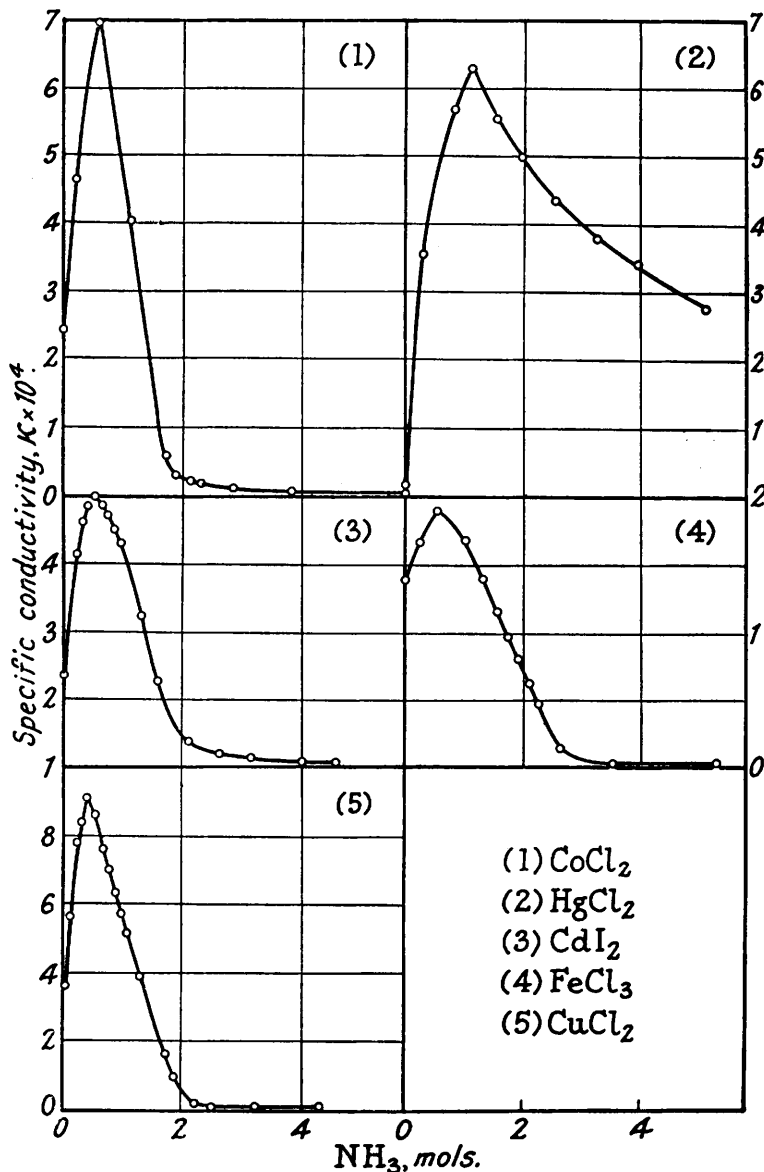
The acetone was purified by Koch's method (J., 1928, 272). Water was tested for by anhydrous copper sulphate, since Weaver's test fails in the presence of acetone, probably because cuprous acetylide dissolves in aqueous acetone. The dry acetone boiled at 56°.

It was impossible to prepare solutions of ammonia in the esters, since continual slow precipitation of amide took place. Consequently, conductivity titrations were only possible in acetone solution. Here again it was not possible to keep the ammonia solution, for the constituents interacted and the ammonia concentration fell continuously. Dilute ammonia solutions in acetone were therefore made, standardised, and used immediately. The apparatus employed for the conductivity titrations was as previously described (Part I; J., 1938, 1027) and the results are shown in the diagram. The precipitates for analysis were prepared by passing dry ammonia into the solutions made by dissolving the anhydrous salts in the solvents. In general, saturated solutions of the salts were made, for the solubilities, particularly in the esters, were not great. Since addition of ammonia to the acetates produced acetamide, which might possibly have reacted with the solutes, separate tests were made by adding a solution of acetamide in each ester to the salt solutions: only in the case of copper chloride was a slight precipitate formed. However, the precipitate with ammonia from a solution of copper chloride in methyl acetate was of definite composition, so either acetamide caused no precipitation in this reaction, or subsequent washing of the precipitate removed the substance. All precipitates were well washed in sodium-dried ether and were free from acetamide. They were then dried in air, and in most cases the slightly damp solid was then dissolved in acid and analysed to determine the ratio of the components. In this way possible decomposition on standing was avoided.

Reactions with Cobalt Chloride.—In all three solvents, cobalt chloride gave a deep blue solution, from which ammonia precipitated a dirty white substance, $\text{CoCl}_2 \cdot 4\text{NH}_3$, in the esters, and a mauve substance, $\text{CoCl}_2 \cdot 2\text{NH}_3$, in acetone. Precipitation appeared to be complete, since the filtrate was colourless (Found: in methyl acetate, $\text{Co} : \text{Cl} : \text{NH}_3 = 1 : 1.97 : 4.01$; in ethyl acetate, $\text{Co} : \text{Cl} : \text{NH}_3 = 1 : 2.02 : 4.08$; in acetone, $\text{Co} : \text{Cl} : \text{NH}_3 = 1 : 2.00 : 1.97$). The last result agrees with the titration curve, in which there was an initial rise in conductivity followed

by a fall until 2 mols. of ammonia had been added, after which there was little change. The first precipitate was probably indefinite, and changed to the diammine on addition of ammonia. Prolonged passage of ammonia into the solution in acetone changed the mauve compound into the dirty white substance $\text{CoCl}_2 \cdot 4\text{NH}_3$ (Found : $\text{Co} : \text{Cl} : \text{NH}_3 = 1 : 2.02 : 3.98$).

Naumann (*loc. cit.*) reported the preparation of $\text{CoCl}_2 \cdot 2\text{NH}_3$ in acetone, but in methyl and ethyl acetates he claimed to have prepared $\text{CoCl}_2 \cdot 6\text{NH}_3$. We could not prepare this substance



even after prolonged passage of ammonia into the cobalt chloride solution. In methyl and ethyl alcohols the compound formed is $\text{CoCl}_2 \cdot 2\text{NH}_3$, so it is possible to prepare different cobalt-ammines by varying the solvent in which the reaction is performed.

Reactions with Cadmium Iodide.—The solutions were colourless and ammonia precipitated from each a white substance which, in ethyl acetate and in acetone, was $\text{CdI}_2 \cdot 2\text{NH}_3$. The titration curve showed that the precipitate in acetone was initially of indefinite composition and then changed into the diammine, the conductivity falling rapidly with addition of ammonia

until 2 mols. had been added, after which there was little further conductivity change. In methyl acetate an indefinite substance was obtained, probably a mixture of ammines (Found : in ethyl acetate, Cd : I : NH₃ = 1 : 1.96 : 2.02; in methyl acetate, Cd : I : NH₃ = 1 : 2.86 : 5.65; in acetone, Cd : I : NH₃ = 1 : 1.98 : 1.96).

Naumann (*loc. cit.*) gives no details of the reactions in methyl acetate, but reports the preparation of CdI₂.2NH₃ in ethyl acetate and acetone.

Reactions with Mercuric Chloride.—Colourless solutions of mercuric chloride in the three solvents gave thick, white solids when gaseous ammonia was passed in. That from acetone was of indefinite composition as shown by the titration curve and also by analysis (Found : Hg : Cl : NH₃ = 1 : 2 : 1.56); in ethyl acetate, it was HgCl₂.2NH₃ (Found : Hg : Cl : NH₃ = 1 : 1.95 : 1.99), and in methyl acetate the substance was of indefinite composition (Found : Hg : Cl : NH₃ = 1 : 2 : 0.77).

Reactions with Copper Chloride.—From the green solutions of copper chloride in the three solvents, ammonia precipitated blue substances. In the esters the amount was small and analysis was impossible with the substance from ethyl acetate solution, and difficult with that from methyl acetate. This appeared to be CuCl₂.3NH₃ (Found : Cu : Cl : NH₃ = 1 : 1.95 : 2.96). Naumann, however (*loc. cit.*), claimed to have prepared CuCl₂.6NH₃ from each ester. From acetone solution the precipitate was CuCl₂.2NH₃ (Found : Cu : Cl : NH₃ = 1 : 1.96 : 2.01) : this is confirmed by the conductivity titration, for the initial indefinite substance changed on further addition of ammonia into CuCl₂.2NH₃, a rapid fall of conductivity occurring until 2 mols. of ammonia had been added; thereafter there was little change in conductivity. Naumann also prepared CuCl₂.2NH₃ from acetone.

Reactions with Ferric Chloride.—Yellowish-brown solutions were formed in all three solvents. Ammonia precipitated brown substances in each case. The precipitates were bulky and difficult to wash. From both esters and from acetone the substances were FeCl₃.3NH₃ (Found : in methyl acetate, Fe : Cl : NH₃ = 1 : 3.02 : 2.96; in ethyl acetate, Fe : Cl : NH₃ = 1 : 3.06 : 3.08; in acetone, Fe : Cl : NH₃ = 1 : 3.00 : 2.99).

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