284. *Studies of Ionisation in Non-aqueous Solvents. Part II. The Formation of Certain Ammines.*

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A series of reactions has been carried out in methyl and ethyl alcohols between ammonia and various salt solutions. Unlike the reaction which occurs in water, ammines are formed directly between the salts and the ammonia in these solvents.

ALTHOUGH the reactions between ammonium hydroxide and aqueous solutions of metallic salts have often been studied, the only noteworthy investigations of the analogous reactions in non-aqueous solutions are due to Naumann and his collaborators (*Ber.*, 1899, **32**, 999; 1904, **37**, 3600, 4609, 4328; 1909, **42**, 3790; 1910, **43**, 314; 1914, **47**, 250, 1371) and to Curtis and Burns (*J. Amer. Chem. Soc.*, 1917, **39**, 33). The former workers studied the behaviour of gaseous ammonia towards conveniently soluble salts in acetone, methyl and ethyl acetates, aceto- and benzo-nitriles, and pyridine, and the latter performed a series of reactions in *iso*amyl alcohol. In both cases compounds were prepared and analysed, but no use seems to have been made of physicochemical methods for the elucidation of their structures.

In the present communication a series of reactions has been studied in ethyl and methyl alcohols with the aid of conductivity titrations. This method has the advantage of being rapid and also avoids errors inherent in the isolation and drying of precipitates which may decompose on standing.

The results show that the formation of ammines, contrary to the behaviour in water, proceeds directly. This is due to the fact that little combination occurs between the ammonia and the solvent. The reactions observed, therefore, resemble those occurring between the solid salts and ammonia, and not those between ammonium hydroxide and the aqueous salt solution.

EXPERIMENTAL.

The solvents were purified and dried, and the anhydrous salts prepared, as described in Part I (J., 1938, 1027). Stock solutions of ammonia were prepared by leading the gas from a cylinder through a tall tower containing freshly burnt lime and into the alcohols. The usual precautions (*loc. cit.*) against ingress of atmospheric moisture were taken. The specific conductivities of the ammonia solutions were as follows:

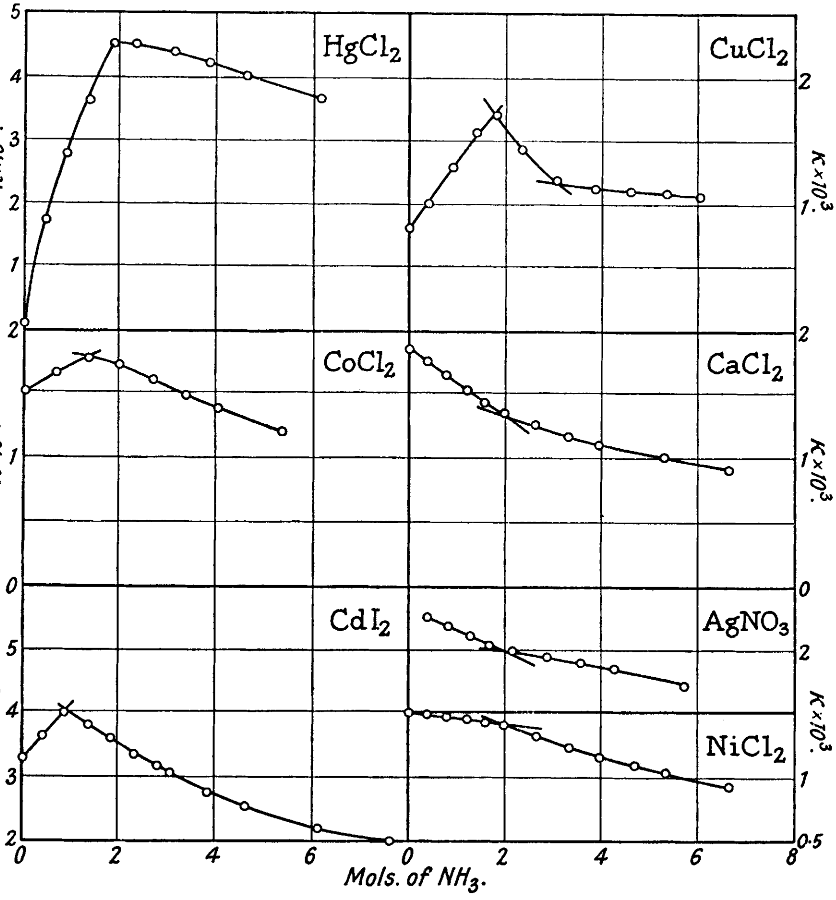
Ethyl alcohol.

Concn.	$10^6\kappa$.	Concn.	$10^6\kappa$.	Concn.	$10^6\kappa$.
0·99N/10	11·0	0·99N/20	7·85	0·99N/40	6·35
		Methyl alcohol.			
0·99N/10	43·5	0·99N/20	33·8		

In each case the conductivity is small and supports the view that little combination is possible between ammonia and solvent. As expected, ionisation is greater in methyl than in ethyl alcohol. The significance of this is that solvolysis is more likely to occur with solutions in the former than in the latter solvent, and this is found to be the case with the precipitates analysed.

Conductivities were determined at 25° in the same apparatus as before, and are shown in Figs. 1 and 2, which depict respectively conductivity titrations in methyl and in ethyl alcohol.

FIG. 1.



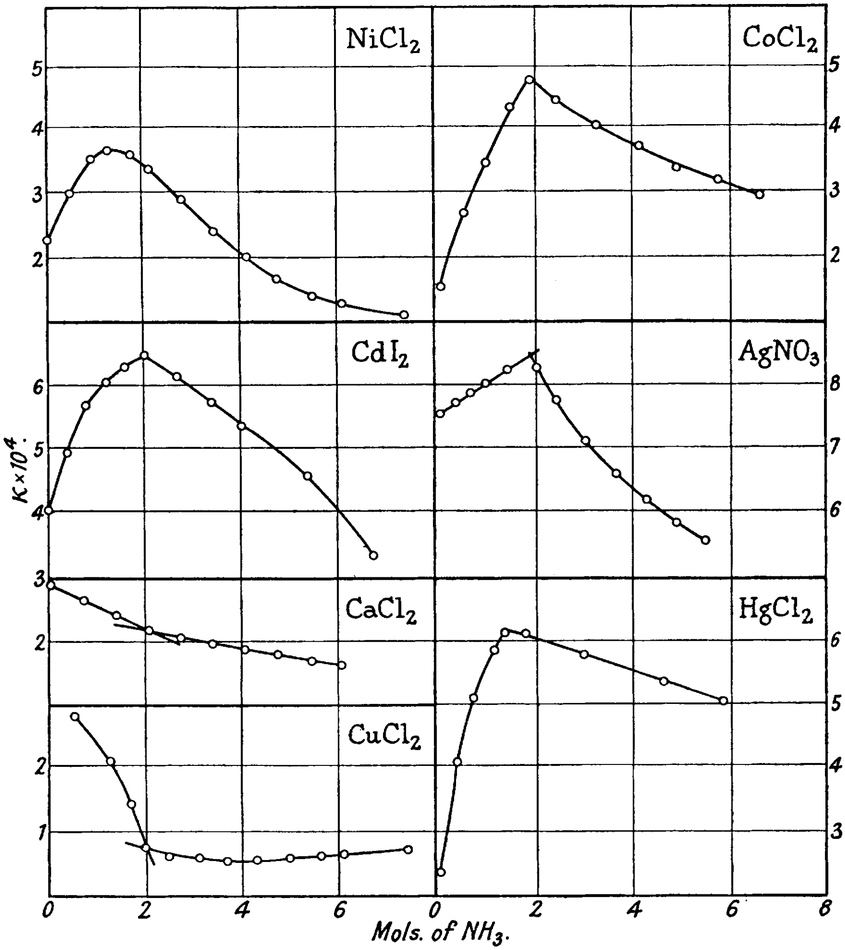
Mols. of NH_3 *plotted against specific conductivity* (κ) *in methyl-alcoholic solution.*

Precipitates for analysis were dried in a desiccator over calcium chloride at atmospheric pressure. In certain cases, where decomposition appeared to be rapid, the precipitate was washed with the corresponding alcohol, and then immediately dissolved in a suitable acid. In such cases, only the ratios of the components were determined. The ammonia was estimated by distillation into standard acid, and the halogen and metal contents found gravimetrically by standard methods.

Reaction between Ammonia and Silver Nitrate.—Mono-, di-, and tri-ammines of silver have been reported by various authors, but the diammino-compound is considered to be the only one stable in solution (Draper, *Pharm. J.*, 1886, **17**, 487; Bodländer and Fittig, *Z. physikal. Chem.*, 1902, **39**, 597; Euler, *Ber.*, 1903, **36**, 1854; Whitney and Melcher, *J. Amer. Chem. Soc.*, 1903, **25**, 70; Britton, J., 1925, **127**, 2957). Castoro (*Gazzetta*, 1907, **37**, i, 310) prepared crystals of $Ag(NH_3)_2NO_3$ by adding alcohol to a concentrated ammoniacal solution of silver nitrate, and Hantzsch (*Z. anorg. Chem.*, 1899, **19**, 104) prepared a precipitate of the same composition from benzonitrile solution by leading in ammonia. Britton and Wilson (J., 1933, 1050) have shown that aqueous solutions of silver nitrate, to which excess of ammonium hydroxide has been added, contain the salt $Ag(NH_3)_2NO_3$, and that the corresponding base $Ag(NH_3)_2OH$ is appreciably stronger than ammonium hydroxide.

When ammonia is added to silver nitrate in each of the alcoholic solutions (Figs. 1 and 2) the conductivity curves are discontinuous after the addition of 2 mols. The conductivity values of the ammonia in these alcoholic solutions (see below) suggest that little appreciable combination of the type $NH_3 + ROH = NH_4{\cdot}OR$, with ionisation to NH_4^+ and OR^-, takes place, and this view is supported by a comparison with the analogous reactions with solutions of sodium ethoxide and methoxide of similar concentrations in the same dry alcoholic solutions.

FIG. 2.



Mols. of NH_3 *plotted against specific conductivity* (κ) *in ethyl-alcoholic solution.*

In both cases a brownish-black substance is precipitated, presumably according to the equation $RONa + AgNO_3 = NaNO_3 + AgOR$ (R = Me or Et). With ammoniacal solutions, however, no precipitation whatsoever occurs. With methyl alcohol the solution darkens somewhat, but the effect is not noticeable in ethyl alcohol. In view of the higher conductivity of the ammonia solution in methyl alcohol this is to be expected, as rather more combination between this solvent and ammonia occurs. Evaporation of the solution of silver nitrate in ethyl alcohol, to which excess of ammonia had been added, deposited long needle-shaped crystals of diamminosilver nitrate (Found: NH_3, 16·63. Calc.: NH_3, 16·67%) which darkened on exposure to light. In these alcohols, therefore, at the concentrations employed the compound formed is the same as that which is stable in water, but in this case reaction proceeds by direct addition, whereas in water a hydrated oxide is first formed.

Reaction between Ammonia and Cupric Chloride.—In aqueous solution there is considerable evidence in favour of the formation of a complex ion $Cu(NH_3)_4^{++}$ when excess of ammonium hydroxide is added to copper chloride solution, the copper hydroxide formed initially redissolving (Konowaloff, *J. Russ. Phys. Chem. Soc.*, 1899, **31**, 910; Gaus, *Z. anorg. Chem.*, 1900, **25**, 236; Locke and Forsall, *Amer. Chem. J.*, 1904, **31**, 268; Dawson and McCrae, J., 1900, **77**, 1239; 1909, **95**, 380; Bonsdorff, *Ber.*, 1903, **36**, 2322; *Z. anorg. Chem.*, 1904, **41**, 132; Reychler, *Bull. Soc. chim. Belg.*, 1914, **28**, 227; Job, *Compt. rend.*, 1927, **184**, 204), though under some conditions the ion $Cu(NH_3)_2^{++}$ is formed.

In dilute solution in ethyl alcohol, addition of ammonia leads to complete precipitation of copper from cupric chloride as a bluish-green precipitate of the diammino-chloride (Found: Cu, 38·0; NH_3, 20·0; Cl, 43·0. Calc.: Cu, 37·7; NH_3, 20·2; Cl, 42·1%). The precipitation is accompanied by a fall in conductivity until 2 equivs. of ammonia have been added; thereafter there is little change. Excess of ammonia does not dissolve the compound. The same compound has been obtained from solutions in water, acetone, or *iso*amyl alcohol, but in methyl and ethyl acetates, the hexammino-compound is formed (Naumann, *loc. cit.*).

Immediate solution of the compound took place on adding water to the absolute alcohol, giving the familiar deep blue solution, which Kohlschütter (*Ber.*, 1904, **37**, 1156) has shown to contain the $Cu(NH_3)_4^{++}$ ion.

The significance of the increased combination of ammonia with methyl alcohol is shown in the reaction which occurs in the solvent with copper chloride. At first a light blue compound of indefinite composition is precipitated (Found, in wet precipitate: $Cu : Cl : NH_3 = 2{\cdot}50 : 1{\cdot}76 : 1{\cdot}00$), and then there is a fall of conductivity as the compound dissolves in excess of the ammonia until, after 3 mols. of ammonia have been added, a deep blue solution is formed and there is little further change in conductivity. On standing, this solution deposits a few deep blue crystals, but further evaporation of the solution in air leads to the deposition of the above light blue powder, so the deep blue substance is only stable in the presence of excess ammonia. The conductivity titration gives its composition as $Cu(NH_3)_3Cl_2$.

Reaction between Ammonia and Mercuric Chloride.—When aqueous ammonia is added to an aqueous solution of mercuric chloride, "infusible white precipitate," $HgCl{\cdot}NH_2$, is formed. On the other hand, when gaseous ammonia is passed over the solid salt, or when the latter is added to a boiling solution of ammonium chloride and ammonia, "fusible white precipitate," $HgCl_2,2NH_3$, is formed.

Addition of ammonia dissolved in methyl or ethyl alcohol to alcoholic solutions of mercuric chloride caused a rapid rise in conductivity. With ethyl alcohol this continued until about 1·5 mols. had been added, the values then falling again. A white precipitate settled out immediately ammonia was added, but after the addition of rather more than 1 mol. precipitation ceased. The dried precipitate was of indefinite composition (Found: Hg, 63·11; NH_3, 7·71; Cl, 22·68; $Hg : Cl : NH_3 = 1 : 2 : 1{\cdot}44$).

With methyl alcohol the precipitate was also white and of indefinite composition (Found, in wet precipitate: $Hg : Cl : NH_3 = 1{\cdot}00 : 2{\cdot}10 : 1{\cdot}75$). Curtis and Burns (*loc. cit.*) showed that the precipitate obtained in *iso*amyl alcohol was also indefinite. On the other hand, Naumann and his collaborators (*loc. cit.*) reported the preparation of $HgCl_2,2NH_3$ in methyl and ethyl acetates, acetone, and pyridine, and Weyl (*Pogg. Ann.*, 1867, **131**, 547) obtained it by dissolving mercuric chloride in liquid ammonia; in benzonitrile, however, Naumann (*loc. cit.*) prepared the compound $HgCl_2,4NH_3$. Apparently, in hydroxylic solvents the straightforward addition of ammonia to mercuric chloride leads to formation of indefinite compounds.

Reaction between Ammonia and Cobalt Chloride.—It is well known that addition of excess of ammonia to an aqueous solution of cobalt chloride leads to the formation of very stable hexammino-chloride. In ethyl-alcoholic solution, the reaction causes formation of a dirty whitish precipitate, and this is accompanied by a rise in conductivity until 2 mols. of ammonia have been added, after which it falls. Precipitation of $CoCl_2,2NH_3$, as indicated by the disappearance of colour from the solution, was complete. On standing, the precipitate turned brown and finally, on drying in air, brownish-violet. Apparently it loses some ammonia on standing (Found: Co, 32·30; NH_3, 16·35; Cl, 38·50; $Co : NH_3 : Cl = 1 : 1{\cdot}81 : 2{\cdot}01$).

A somewhat similar reaction takes place in methyl alcohol, the yellowish-brown precipitate, which goes green on exposure to air, being of indefinite composition (Found, in wet precipitate: $Co : NH_3 : Cl_2 = 3{\cdot}64 : 1{\cdot}70 : 1{\cdot}0$). Precipitation of cobalt was complete when rather less than 2 mols. of ammonia had been added. Sodium methoxide under similar conditions gives a dirty green gelatinous precipitate.

Curtis and Burns (*loc. cit.*) obtained $CoCl_2,3NH_3$ by precipitation from *iso*amyl alcohol, and

Naumann (*loc. cit.*) obtained $CoCl_2,6NH_3$ from methyl acetate. No data are recorded for other solvents.

Reaction between Ammonia and Cadmium Iodide.—Ammoniacal aqueous solutions of cadmium contain complex ions of the type $Cd(NH_3)_4^{++}$ in aqueous solutions, the hydroxide initially formed dissolving in excess of the reagent (see, *e.g.*, Dawson and McCrae, *loc. cit.*). In ethyl-alcoholic solution, however, a very small precipitation occurs on addition of ammonia to dilute solutions of cadmium iodide. The conductivity rises sharply to a maximum which corresponds to the addition of 2 mols. of ammonia, suggesting formation of $Cd(NH_3)_2I_2$, and thereafter falls. A small white crystalline precipitate (insufficient for analysis) appears on standing. In view of the proved trustworthiness of the method in cases where analysis has been possible, it is justifiable to assume that the compound is the diammine. This has been obtained by various workers in aqueous solution, and also from acetone and ethyl acetate by Naumann (*loc. cit.*).

In methyl alcohol the conductivity falls after the addition of approximately 1 mol. of ammonia. The precipitate, which is insufficient for analysis, is probably of indefinite composition. Under similar conditions sodium methoxide gives a large, bulky, white, gelatinous precipitate. Formation of methoxide thus does not occur when ammonia is used.

Reaction between Ammonia and Calcium Chloride.—The addition of excess of aqueous ammonia to calcium chloride solution leads to precipitation of the hydroxide. Heavy white precipitates are also obtained in alcoholic solutions on adding sodium ethoxide and methoxide to calcium chloride. No precipitation whatever occurs with ammonia under similar conditions. The fall in conductivity, at first rapid, becomes slower after the addition of 2 mols. of ammonia, indicating the formation of $CaCl_2,2NH_3$ in solution. Various ammines have been prepared from ammonia and the dry solid.

Reaction between Nickel Chloride and Ammonia.—It has been shown that in aqueous solution addition of ammonia to nickel chloride leads to formation of the hydroxide, which dissolves in excess of ammonia to form a complex ion $Ni(NH_3)_4^{++}$ (see, *e.g.*, Dawson and McCrae, *loc. cit.*). Heavy white gelatinous precipitates are obtainable with excess of reagent when sodium methoxide and ethoxide solutions in the dry alcohols are added to the corresponding alcoholic solutions of nickel chloride.

Very little precipitation occurs when methyl- and ethyl-alcoholic solutions of ammonia are added to yellow solutions of anhydrous nickel chloride in the corresponding alcohols. No analyses were possible, but the conductivity curves indicate the formation of the monoammine in ethyl alcohol and the diammine in methyl alcohol.

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