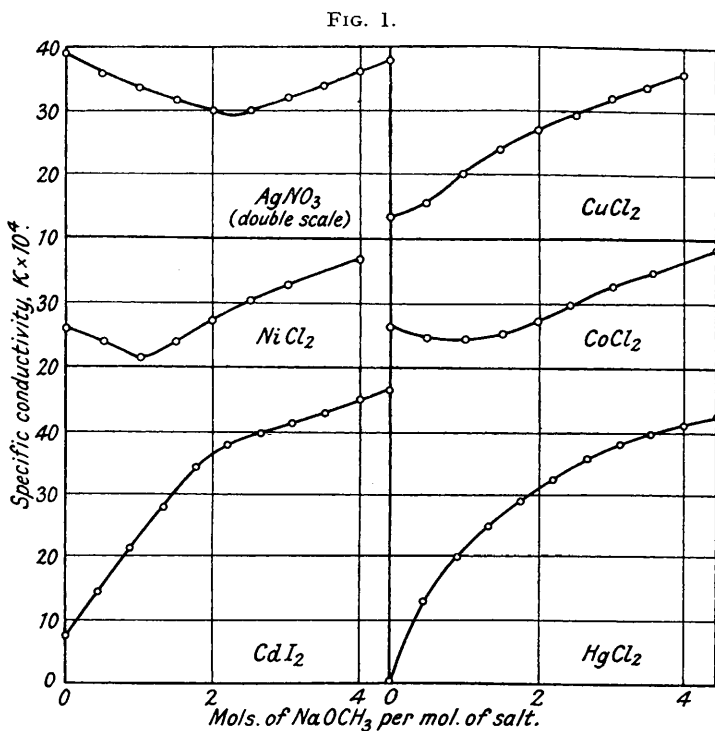


99. *Studies of Ionisation in Non-aqueous Solvents. Part V. The Formation of Certain Methoxides and Ethoxides in Methyl and in Ethyl Alcohol.*

By WILLIAM L. GERMAN and THOMAS W. BRANDON.

The reactions between solutions of sodium methoxide and of sodium ethoxide and conveniently soluble salts in methyl and ethyl alcohols have been studied with the aid of conductivity titrations. As with dilute solutions of sodium hydroxide in water, the reactions, in most cases, lead to the formation of basic compounds.

THE reactions between certain metallic salts and (i) sodium methoxide in methyl alcohol and (ii) sodium ethoxide in ethyl alcohol have been studied with the aid of conductivity titrations. Britton (J., 1925, 127, 2110) has shown that aqueous sodium hydroxide precipitates basic salts from dilute solutions of most of the



salts here discussed, and it appears that similar results are obtained when sodium hydroxide is replaced by sodium methoxide or ethoxide, and the solvent medium by methyl or ethyl alcohol. This similarity is not surprising in view of the high degree of ionisation of these salts in the two alcohols, as the following table shows.

Values of Δ/Δ_∞ at 18°.

| $c \times 10^4$. | 19.5. | 39. | 78. | 156. | Ref. |
|---|-------|------|------|------|--|
| NaOH in water | 0.98 | 0.97 | 0.96 | 0.93 | I.C.T., Vol. VI. |
| NaOCH ₃ in CH ₃ ·OH | 0.86 | 0.82 | 0.77 | 0.73 | Tijmstra, <i>Z. physikal. Chem.</i> , 1904, 49 , 350. |
| NaOC ₂ H ₅ in C ₂ H ₅ ·OH | 0.83 | 0.76 | 0.66 | 0.60 | Hengevelt, Thèse, 1911. |

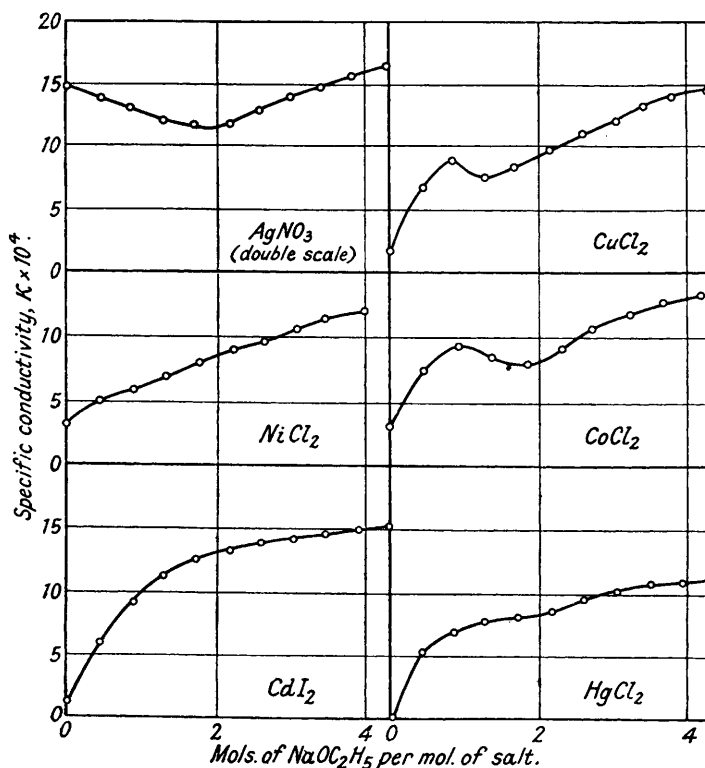
EXPERIMENTAL.

The solutions of sodium alkoxide were prepared by dropping clean, dry sodium into the alcohol, purified as described in Part I (J., 1938, 1027), moisture being excluded. They were analysed by diluting a sample with water and titrating it with standard hydrochloric acid. The stock solution was then diluted with the alcohol until approximately 0.1N.

The conductivity apparatus was the same as already described (Part I, *loc. cit.*). The compounds for analysis were prepared by mixing the appropriate solutions and allowing them to stand. The precipitates were filtered off in a dry atmosphere, well washed with the dry alcohol, and then placed in a vacuum desiccator over fused calcium chloride and evacuated at intervals until constant weight was obtained. The precipitates were then dissolved in excess of standard dilute acid and the OR radical determined by titrating the excess acid with standard sodium hydroxide solution: $XOR + HCl = XCl + HOR$ (X = univalent metallic radical; R = alkyl group). The metallic contents of the precipitates were determined by the usual methods.

The results of the conductivity titrations in methyl and in ethyl alcohol are given in Figs. 1 and 2 respectively.

FIG. 2.



Reactions with Silver Nitrate.—With both sodium methoxide in methanol and sodium ethoxide in ethanol, brownish-black precipitates were formed in which the ratio of metal to alkyl radical was 1 : 1. The conductivity curves show a decided break in each case at this point, and the reaction is thus one of complete double decomposition: $AgNO_3 + NaOR = AgOR \downarrow + NaNO_3$.

Reactions with Cadmium Iodide.—With sodium methoxide instantaneous double decomposition took place, with deposition of a white precipitate (Found: Cd, 53; OMe, 29%. Cd : OMe = 1 : 1.98) which settled readily. The conductivity curve changes direction after the addition of two molecules of methoxide and the reaction is thus one of simple double decomposition.

With sodium ethoxide in ethanol no immediate precipitation occurred, and only after the addition of rather less than 2 mols. did a white, gelatinous precipitate begin to form. The conductivity titration indicates that this substance was of indefinite composition, but on standing in contact with excess ethoxide it changed into a normal compound (Found: Cd, 53.2; OEt, 42.6%. Cd : OEt = 1 : 2.01).

Reactions with Copper Chloride.—With both alkoxides indefinite compounds were formed. With sodium methoxide precipitation was delayed until about 1 mol. of methoxide had been added, the first precipitate being light green and gelatinous. After 2 mols. had been added the precipitate was emerald-green, becoming blue and voluminous, but the conductivity curve shows that reaction was complete before this stage. The precipitate was therefore basic, and one prepared by adding excess of sodium methoxide to copper chloride solution had the composition: Cu, 51.9; OMe, 40.4%. Cu : OMe = 1 : 1.60.

With sodium ethoxide in ethanol the reaction was similar, precipitation being slow at first, and the initial light

green precipitate turned black when excess of the ethoxide had been added. This precipitate was a basic compound (Found: Cu, 39.3; OEt, 50.1%. Cu : OEt = 1 : 1.80). The conductivity curve indicates that the reaction does not afford a definite compound.

Reactions with Cobalt Chloride.—When sodium methoxide solution was added to a solution of cobalt chloride in methanol there was no immediate precipitation but the solution became turbid and further additions led to deposition of a white flocculent precipitate, which gradually changed to a dirty buff colour, leaving a colourless supernatant liquid. The conductivity curve indicates that the reaction is complete before 2 mols. of methoxide have been added, and that the precipitate is of indefinite composition. One prepared by adding excess of methoxide solution to the cobalt chloride solution had the composition: Co, 43.5; OMe, 41.1%. Co : OMe = 1 : 1.94. In ethanol, sodium ethoxide showed a similar behaviour: a white gelatinous precipitate formed slowly, which gradually darkened, and when 1 mol. of the ethoxide solution had been added the solution was practically colourless. The conductivity curve shows an inflexion after the addition of between 1 and 2 mols. of ethoxide, indicating formation of a basic substance. When excess of the ethoxide was present the precipitate had turned brown and settled readily (Found: Co, 41.9; OEt, 46.3%. Co : OEt = 1 : 1.57).

Reactions with Nickel Chloride.—Addition of sodium methoxide caused no precipitation until rather more than 2 mols. had been added, whereupon there was a slight turbidity. The conductivity curve showed a break when rather less than 1 mol. had been added, indicating basic compound formation. This is confirmed by analysis of the whitish-green precipitate formed by adding excess of methoxide to the nickel chloride solution and allowing it to stand (Found: Ni, 41.1; OMe, 33.5%. Ni : OMe = 1 : 1.54).

In the reaction with sodium ethoxide the conductivity curve gave no indication of definite compound formation; precipitation was obtained more readily than in the previous case, the precipitate being light green and flocculent. That obtained by adding excess of sodium ethoxide to the nickel chloride solution was of indefinite composition (Found: Ni, 40; OEt, 55.9%. Ni : OEt = 1 : 1.82).

Reactions with Mercuric Chloride.—Solutions of mercuric chloride gave an intense orange precipitate when solutions of sodium methoxide in methanol were added. The conductivity curve changed direction after the addition of rather less than 1 mol. and the precipitate was basic. The compound prepared by adding excess of the methoxide was insoluble in dilute acid, and only the metal was determined [Found: Hg, 85.4. Calc. for $\text{Hg}(\text{OMe})_2$: Hg, 76.5%].

In ethanol, sodium ethoxide precipitates from mercuric chloride an orange precipitate. The conductivity curve shows a discontinuity after the addition of 2 mols., indicating formation of a definite compound [Found: Hg, 68.7. $\text{Hg}(\text{OC}_2\text{H}_5)_2$ requires Hg, 69.0%].

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