CONDUCTOMETRIC STUDIES ON HALIDE COMPLEXES IN FORMIC ACID MEDIUM

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Complex equilibria have so far been studied mainly in aqueous medium, and reports on the formation of complexes in non-aqueous media are rather rare. Due to the lack of experimental data no general theoretical treatment can be given of complex formation in non-aqueous media.

Although the variation of the complex stabilities with the solvent used has been studied by IRVING and ROSOTTI [1], they failed in finding rules of general validity. This makes observations concerning complex formation in non-aqueous systems useful.

Owing to the relatively low stability of halide complexes, rather concentrated solutions have to be used to get them formed. This makes the maintenance of constant ionic strength and calculation of activity coefficients rather difficult. Data known at present — termed stability quotients instead of stability constants — are mostly of informatory nature.

The investigation of the reactions of a number of cations in formic acid medium has been described earlier [2]. Although formic acid as a solvent is similar to water, remarkable differences have been found in the behaviour of cations in it as compared to that in water. In general, the solubility of inorganic compounds is reduced, the degree of association increased in the presence of formic acid. The stability of metal halide complexes was found to be rather high, so that cadmium and zinc sulphide, which quantitatively precipitated form chloride-free formic acid, did not precipitate in the presence of chloride ions.

The aim of the present work has been to investigate the halide complexes of some metal ions. As the first step, attempt was made to prove the presence of complexes and to find out their stoichiometry by conductometric titration. Stability constants can only be determined after that. Since group Ia cations form precipitates with halide ions which do not dissolve in excess halide, not these but group Ib and group III cations, Cd(II), (Cu(II), Fe(II), Co(II) and Zn(II) ions were studied.

The behaviour of the halide complexes of these ions in alcohol (3), acetone (4) and acetic acid (5) has already been studied, but no similar experiments have so far been made in formic acid.

In the first series of measurements the conductivity was measured as follows: the solution of a halide ion in formic acid was added in small portions to the solution of a metal ion in formic acid and the conductivities measured after each addition. In the second series of measurements the solution of the metal ion in formic acid was added to the solution of the halide ion in small portions, and the conductivities measured as in the first series.

Equipment and reagents used

A Radelkisz OK—102 type conductometer and OK—902 type bell electrode were used to conductivity measurements. Titrations were carried out in a double-walled thermostated glass vessel. A VEB—U—8 type ultrathermostat was used to ensure constant temperature, 25°C during measurements. Solutions were mixed with a magnetic stirrer. A tube packed with silica gel was used to exclude atmospheric humidity.

Reagents used: 0.1 M cadmium(II) perchlorate, 0.3 M copper(II) perchlorate, 0.5 M iron(II) perchlorate, 0.5 M zinc(II) perchlorate and 0.65 M cobalt(II) perchlorate solutions in formic acid. Metal perchlorates were prepared of Merck analytical grade metal oxides by evaporation with a.g. perchloric acid followed by drying in vacuum drying pistol over phosphorus pentoxide. Analytical grade sodium chloride, sodium bromide and ammonium iodide were dried similarly to metal perchlorates. Halides were applied as 0.5 M solutions in formic acid.

Experimental

a) Reaction of copper(II) ions with chloride and bromide ions

On adding chloride ions to the solution of copper(II) perchlorate in formic acid the solution turns green, then, in the presence of greater amount of chloride a rusty precipitate is formed.

In the course of titration a 0.36 M solution of copper(II) chloride in formic acid was added in small portions to 0.2 M sodium chloride. In Fig. 1 conductivity is plotted against the $Cl^- : Cu^{2+}$ ratio. There is a minimum on the curve, but there are no definite break points to indicate the formation of complexes.

The change of colour from blue to green is indicative of the transformation of the copper(II) formate solvocomplex to copper(II) chloride complex.

On adding bromide ions to the blue solution containing copper(II) ions first the solution turns green then a black precipitate is formed, which is

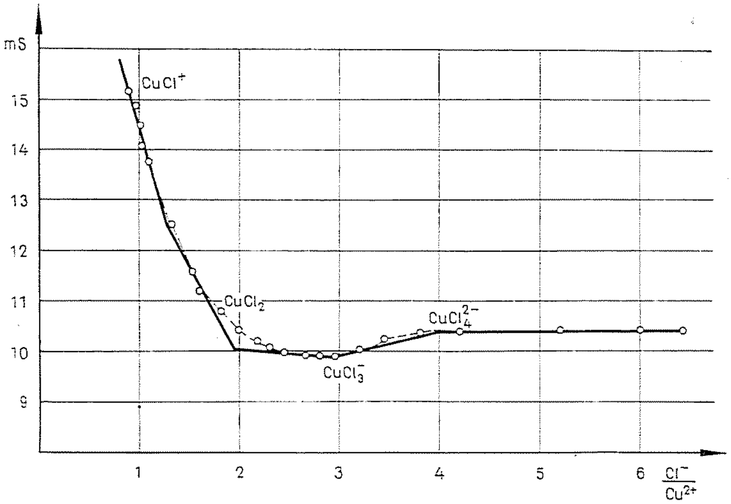

Fig. 1

dissolved by excess reagent while the solution turns wine-red. As shown by Fig. 2, the sections between different Br : Cu^{2+} ratios are curved, but the conductivity decreases on adding bromide in increasing amount, indicative of complex formation. The ratios belonging to the break points correspond to co-ordination numbers 1, 2 and 3. At the concentrations used, no break point corresponding to co-ordination number 4 can be observed.

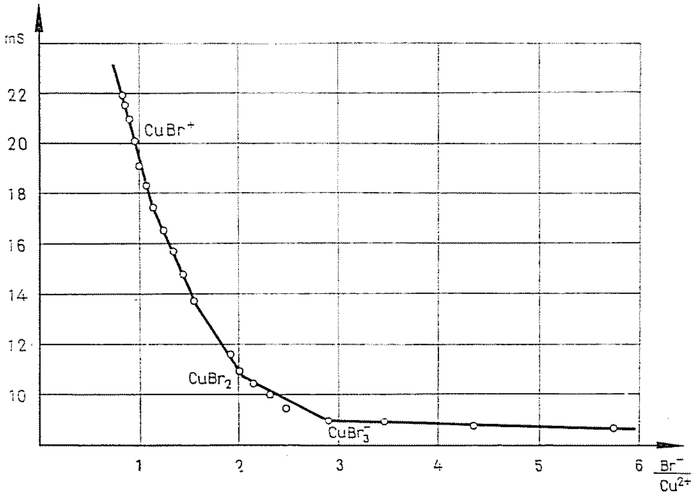

Fig. 2

b) Reaction of cadmium(II) ions with chloride ions

Cadmium(II) ions form a white precipitate with chloride ions which is soluble in excess reagent. In Fig. 3 the conductivity of solution is plotted against the $Cl^- : Cd^{2+}$ ratio. At the first section of the curve the conductivity decreases. The first break point corresponds to composition $CdCl^+$. The next section corresponds to the formation of white $CdCl_2$ precipitate. The lowest minimum is at a ratio corresponding to $CdCl_2$. In the third section the conductivity increases up to a third break point at a $Cl^- : Cd^{2+}$ ratio of 3 : 1, indicative of the presence of the ion $CdCl_3^-$, while the fourth break point at 4 : 1, is showing the formation of $CdCl_4^{2-}$. After this break point the conductivity increases.

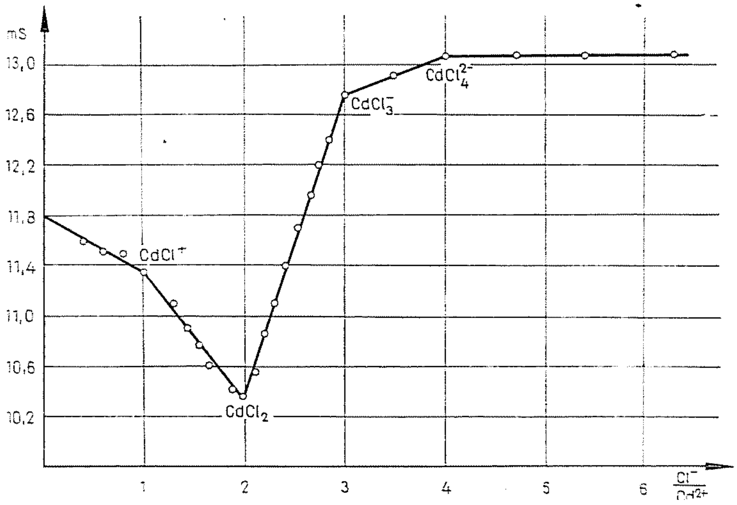

Fig. 3

Whereas the conductivity curve of copper(II) ions consisted of curved sections, that of cadmium(II) ions of straight ones.

c) Reaction of zinc(II) ions with chloride ions

No change can be observed when chloride ions are added to the solution of zinc(II) ions in formic acid. Still, a complex formation reaction must proceed, since zinc sulphide which quantitatively precipitates from chloride-free solution cannot be precipitated from the solution of zinc ions also containing chloride ions.

The break points of the curve in Fig. 4 are at ratios corresponding to co-ordination numbers 2, 3 and 4, respectively. No break point appears at co-ordination number 1.

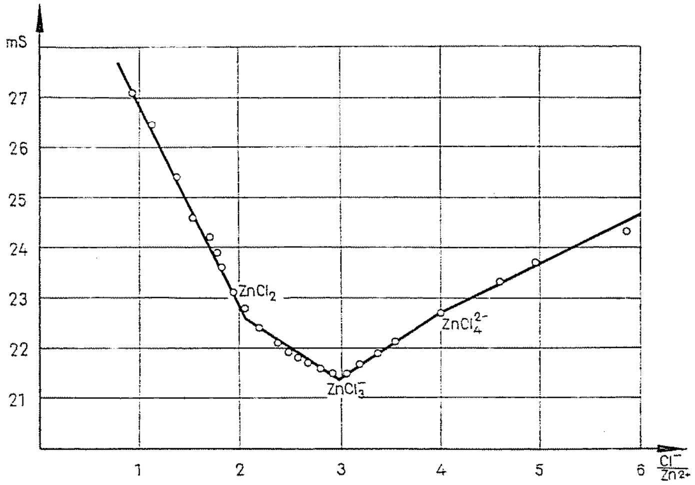

Fig. 4

d) Reaction of cobalt(II) ions with chloride ions

The pink solution of cobalt(II) perchlorate in formic acid turns deep blue on adding chloride ions, but no precipitate is formed.

In Fig. 5 the titration curve of the titration of cobalt(II) perchlorate with chloride ions is presented. The $Cl^- : Co^{2+}$ ratio belonging to the first break point corresponds to composition $CoCl_2$, while the second break point corresponds to $CoCl_3^-$ and the third to $CoCl_4^{2-}$. The blue colour is due to the presence of $CoCl_4^{2-}$ complex ions, while the cobalt(II) formate solvocomplex is pink.

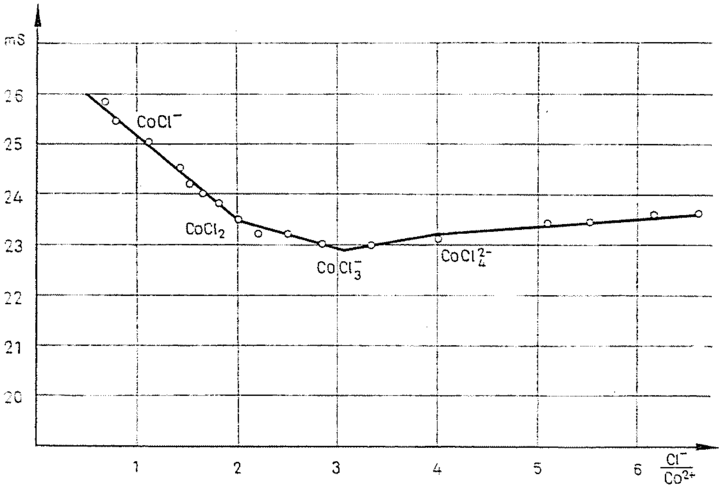

Fig. 5

e) Reaction of iron(II) ions with chloride and iodide ions

Iron(II) ions form a complex with chloride ions in formic acid medium. The break points on the titration curve in Fig. 6 correspond to compositions $FeCl_2$ and $FeCl_3^-$, respectively. There appears no break point at the composition $FeCl_4^{2-}$, while the break point characteristic of $FeCl^+$ is not accurately at the $Cl^- : Fe^{2+}$ ratio of 1 : 1. Iron(II) ions form a black precipitate with iodide ions which is dissolved in excess reagent with wine-red colour. The titration curve obtained in the conductometric titration of iodide ions with iron(II) perchlorate is presented in Fig. 7. Mol ratios at the break points correspond to compositions FeI^+, FeI_2, FeI_3^- and FeI_4^{2-}, respectively. The lowest conductivity was measured at a composition corresponding to the formation for FeI_2 precipitate.

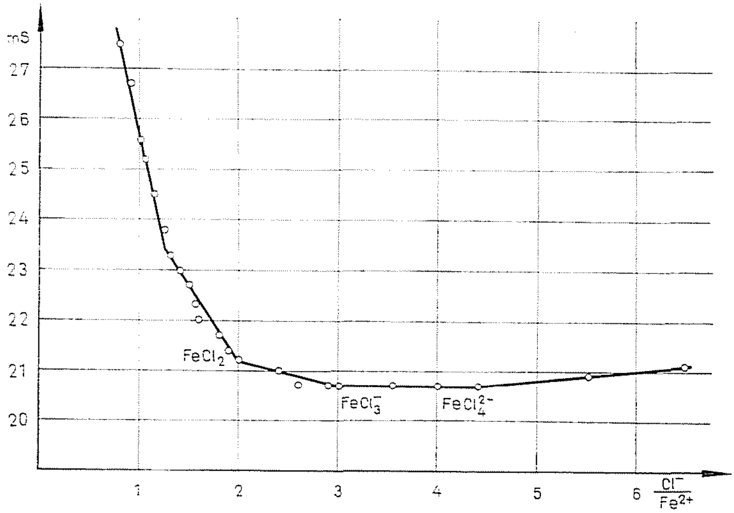

Fig. 6

In the figures the conductivity is plotted against the anion to cation ratio. The reduction in conductivity during titration is indicative of the formation of a precipitate or a slightly dissociated compound or complex. In the cases studied, conductivities were found to decrease in the initial portion of the curves. When precipitation or complex-forming reactions had ended the conductivities increased in cases where the concentration of titrating solution was greater than the initial concentration. Since the mobilities of different complex ions formed during titration are different, the titration curve consists of portions of different slopes.

The portions between break points may be straight or curved depending on the stability of the complex or the solubility of the precipitate formed.

It may occur that a sufficiently stable neutral or uncharged complex molecule or ionic associates are formed during titration. In this case lowest conductivity is measured at a mole ratio corresponding to this complex.

Very often more complexes are formed in succession. At the concentrations used and under the conditions of titration in some cases no break point was obtained at ratios 1 : 1 and 1 : 4.

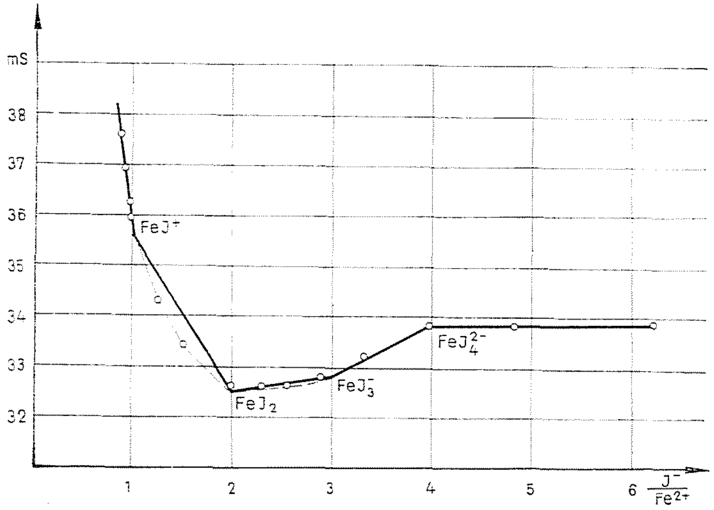

Fig. 7

Summary

The formation and stoichiometry of the halide complexes of Cd(II), Cu(II), Fe(II), Co(II) and Zn(II) ions in formic acid were studied by conductometric titration.

The stability of the halides of Cd and Zn ions was found to be so high that their sulphides could not be precipitated in the presence of halide ions. On the basis of the break points on the titration curves, the following complexes were found to exist in formic acid under the given conditions: $CuCl^+$, $CuCl_2$, $CuCl_3^-$, $CuCl_4^{2-}$; $CuBr^+$, $CuBr_2$, $CuBr_3^-$, $CdCl^+$, $CdCl_2$, $CdCl_3^-$, $CdCl_3^{2-}$; $ZnCl^+$, $ZnCl_2$, $ZnCl_3^-$, $ZnCl_4^{2-}$, $FeCl^+$, $FeCl_2$, $FeCl_3^-$, FeI^+, FeI_2, FeI_3^-, FeI_4^-.

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