## 66. *The Ferric Thiocyanate Complex in Ethyl-alcoholic Solution.*

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It is proved by conductometric measurements that only one complex compound between $Fe^{+++}$ and $SCN^-$ exists in alcoholic solution, the ratio being 1 Fe : 3 SCN. The most probable structure is that of a polynuclear complex compound. The cation complexes $Fe(SCN)^{++}$ and $Fe(SCN)_2^+$, which have recently been proved to exist in aqueous solution, do not occur in ethyl-alcoholic solution.

VARIOUS theories have been put forward concerning the structure of the ferric thiocyanate complex whose intense red colour is used for the photometric determination of iron. For a long time this red colour was thought to be due to undissociated $Fe(SCN)_3$ molecules. In 1931 Schlesinger and van Valkenburgh (*J. Amer. Chem. Soc.*, **53**, 1212) concluded that the colour was due to the anion complex $Fe(SCN)_6^{---}$; and Brintzinger and Ratanarat (*Z. anorg. Chem.*, 1935, **223**, 106) assumed, on the basis of their dialysis coefficient measurements, that the compound was an anion complex. However, recent workers (Møller, *Kem. Maanedsblad*, 1937, **18**, 138; Bent and French, *J. Amer. Chem. Soc.*, 1941, **63**, 568) proved conclusively (especially by photometric measurements) that in the reaction between ferric and thiocyanate ions the complex cations $[Fe(SCN)]^{++}$ and $[Fe(SCN)_2]^{+}$ were formed. The author's conductometric measurements confirmed their existence in aqueous solution only. In ethyl alcohol, on the other hand, the measurements show that there exists only one complex compound, and this in the ratio 1 Fe : 3 SCN.

Since it is known that ferric thiocyanate in alcoholic solution has a molecular weight corresponding to $Fe_2(SCN)_6$, and that it exhibits the properties of polynuclear complexes (*e.g.*, high solubility in organic solvents), the most probable formula for this substance is that proposed by Schlesinger (*ibid.*, 1941, **63**, 1765) (see inset), and this is in complete analogy to the now generally accepted structure of ferric chloride.

## EXPERIMENTAL.

The conductometric measurements were not carried out by titrations, since the insufficient solubility of the titrant reagent in alcohol would impair the accuracy owing to the dilution effect; instead, separate conductivity measurements at different concentrations were taken. Since we wished to work with concentrated solutions we used a special cell for which only 2 c.c. of solution were required. This cell consisted essentially of two parallel platinised platinum electrodes 2 cm. apart contained in a Pyrex tube of 5 mm. diameter. The conductivity was measured by means of a Wheatstone bridge with end-coils and a Leeds & Northrup a.c. galvanometer as null-point instrument. The experimental error in these conductometric measurements was within $\pm$ 0·2%. Table I shows the specific conductivity ($\kappa$) of solutions of constant concentration of ammonium thiocyanate (0·5M) and various concentrations of ferric nitrate (nonahydrate). The solvent was 96% (by vol.) ethyl alcohol. The experiments were carried out in a thermostat at 30°. The conductivities were measured immediately after the preparation of the solutions to avoid errors which might be caused by the slow oxidation of the ethyl alcohol to acetaldehyde by ferric ions. It is evident from the values given in Table I that the conductometric curve has a break at 1Fe : 3SCN. The measurements shown in Table II were at 0° and with a constant concentration (0·1M) of ferric nitrate and varied concentrations of ammonium thiocyanate, the solvent being the same as before. Here, too, where the concentration ratio changes in the opposite direction, the results show only the one break at 1Fe : 3SCN and do not indicate the existence of any cation complex. The structure of the compound is satisfactorily explained by Schlesinger's formula.

TABLE I.

*Conductivity measurements at* 30° *in ethyl alcohol* (96% *vol.*) *at a constant concentration of* 0·5M-$NH_4SCN$.

| $Fe(NO_3)_3$, M. | $\kappa \times 10^3$. | $Fe(NO_3)_3$, M. | $\kappa \times 10^3$. | $Fe(NO_3)_3$, M. | $\kappa \times 10^3$. | $Fe(NO_3)_3$, M. | $\kappa \times 10^3$. |
|---|---|---|---|---|---|---|---|
| 0·0 | 11·25 | 0·0750 | 9·79 | 0·1375 | 8·76 | 0·30 | 10·31 |
| 0·0125 | 10·99 | 0·0875 | 9·55 | 0·1500 | 8·70 | 0·35 | 11·12 |
| 0·0250 | 10·73 | 0·1000 | 9·32 | 0·1750 | 8·66 | 0·40 | 11·94 |
| 0·0375 | 10·48 | 0·1125 | 9·10 | 0·20 | 8·76 | 0·45 | 12·66 |
| 0·0500 | 10·27 | 0·1250 | 8·92 | 0·25 | 9·52 | 0·50 | 13·34 |
| 0·0625 | 10·03 | | | | | | |

TABLE II.

*Conductivity measurements at* 0° *in ethyl alcohol* (96% *vol.*) *at a constant concentration of* 0·1M-$Fe(NO_3)_3$.

| $NH_4SCN$, M. | $\kappa \times 10^3$. | $NH_4SCN$, M. | $\kappa \times 10^3$. | $NH_4SCN$, M. | $\kappa \times 10^3$. | $NH_4SCN$, M. | $\kappa \times 10^3$. |
|---|---|---|---|---|---|---|---|
| 0·0 | 1·904 | 0·100 | 2·275 | 0·200 | 2·647 | 0·50 | 4·792 |
| 0·025 | 2·004 | 0·125 | 2·367 | 0·25 | 2·831 | 0·60 | 5·724 |
| 0·050 | 2·098 | 0·150 | 2·461 | 0·30 | 3·026 | 0·70 | 6·698 |
| 0·075 | 2·185 | 0·175 | 2·558 | 0·40 | 3·899 | 0·80 | 7·581 |

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