290. *Ferric Thiocyanate. Part I. Molecular Weight in Organic Solvents.*

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The molecular weight of ferric thiocyanate has been determined in ether and alcohol. Contrary to the results of Schlesinger and Van Valkenburgh, only the monomer, $Fe(CNS)_3$, is found to be present. The substance is not soluble in pure benzene.

As the result of investigation of the constitution of ferric thiocyanate Schlesinger and Van Valkenburgh (*J. Amer. Chem. Soc.*, 1931, **53**, 1212) considered that the substance was a dimer, $Fe_2(CNS)_6$, in organic solvents, dissociating in water to give the anion $Fe(CNS)_6{}^{3-}$. Their main evidence was ebullioscopic and cryoscopic measurements in ether and benzene, and electrical migration experiments in aqueous solution. In so far as the organic solvents are

concerned, this work seems to have been generally accepted (Baldwin and Svirbely, *ibid.*, 1949, **71**, 3326; Uri, *J.*, 1947, 336), but a number of workers (Møller, *Kem. Maanadsblad*, 1937, **18**, 138; Bent and French, *J. Amer. Chem. Soc.*, 1941, **63**, 568; Edmunds and Birnbaum, *ibid.*, p. 1471; Babko, *Compt. rend. (Doklady) Acad. Sci. U.R.S.S.*, 1946, **52**, 37; Frank and Ostwalt, *J. Amer. Chem. Soc.*, 1947, **69**, 1321) have since produced conclusive evidence for the existence of the ion $FeCNS^{2+}$ in dilute aqueous solution, and have measured its stability constant $K_1 = [FeCNS^{2+}]/[Fe^{3+}][CNS^-]$ at various ionic strengths.

That higher complexes also exist is shown by the fact that solvents such as ether can extract the red colour from aqueous ferric thiocyanate solutions (thus proving the existence of at least traces of a neutral complex $[Fe(CNS)_3]_x$) and by the fact that in certain solutions migration to the anode can occur (Babko, *loc. cit.*; Schlesinger, *loc. cit.*; *J. Amer. Chem. Soc.*, 1941, **63**, 1765), indicating negatively charged complexes. Babko has postulated a series of complexes of the type $Fe(CNS)_x^{(3-x)+}$, carrying $(3 - x)$ positive charges, where x varies from 0 to 6. He gives stability constants for these complexes, but only the first of these ($x = 1$) seems to be based on experimental evidence.

The main object of our work, which will be described in Part II, is to study the equilibrium between the various possible complexes by measuring the distribution of the substance between ether and water. For this purpose, it is essential to know the molecular complexity of the ferric thiocyanate in ethereal solution, and, as preliminary distribution experiments indicated that the thiocyanate was monomeric, a special investigation of the molecular weight in ether, alcohol, and benzene was undertaken. Our results being in direct conflict with those of Schlesinger and Van Valkenburgh, they are reported in detail.

EXPERIMENTAL.

Preparation of Solutions.—Repeated attempts were made to prepare pure crystalline ferric thiocyanate by Schlesinger and Van Valkenburgh's method, *i.e.*, slow evaporation of a solution made from barium thiocyanate and ferric sulphate, or from thiocyanic acid and ferric hydroxide. In no case was a pure product obtained. The only analysis which Schlesinger and Van Valkenburgh give is for total iron (= 24·49%). Gravimetric determinations as Fe_2O_3 on three of our samples gave 21·1, 22·25, and 24·1%, which approach this value. Parallel determinations of thiocyanate (by addition of excess of silver nitrate and back-titration with potassium thiocyanate) gave only 5·0, 4·6, and 4·95%, respectively [Calc. for $Fe(CNS)_3$: CNS, 75·8%], and titrations with titanous sulphate and with permanganate showed that nearly all the iron was in the ferrous condition. A typical analysis of three crops of crystals from the same preparation is given below :

	CNS, %.	Fe(III), %.	Fe(II), %.
1st crop (large crystals)	10·1	2·25	—
2nd crop	16·5	2·7	—
3rd crop (small crystals)	29·3	2·6	23·6
Theory (anhydrous)	75·8	24·2	0·0

An insoluble residue which seemed to contain sulphur or polysulphides was always present. It is evident that internal oxidation–reduction was taking place. The evaporation was carried out in the dark and extended over several weeks, as recommended by Schlesinger and Van Valkenburgh.

Evaporation of the ethereal extract also did not prove satisfactory, as difficulty was experienced in drying the extract. Large quantities of sodium sulphate always decolorised the extract, and phosphoric oxide and metallic sodium also decomposed the solute. On addition of the ethereal extract to a large amount of benzene, water droplets separated and could be removed by filtration. On removal of the ether by distillation under reduced pressure, a solid separated which had the composition : CNS^- 23·6; Fe^{3+} 5·5; Fe^{2+} 19·0%. As molecular-weight determinations on preparations of such variable and uncertain composition, which were not completely soluble, would have had no significance, attempts to prepare the crystalline solid were abandoned, and solutions were prepared as follows.

(1) An aqueous solution of potassium thiocyanate, ferric sulphate, and sulphuric acid was extracted with AnalaR ether, and the wet extract used directly in the ebulliometer, its composition being determined by analysis. The extract was found to contain thiocyanic acid in considerable quantity, but to be free from sulphate. (2) An alcoholic solution of ferric sulphate was prepared indirectly by shaking a solution of ferric chloride in alcohol for some hours with solid silver sulphate. The solution contained exactly equivalent amounts of Fe^{3+} and SO_4^{2+}. This solution was then shaken for 4 hours with the exact equivalent of barium thiocyanate, and the gelatinous precipitate which formed was separated in the centrifuge. The solution again contained free thiocyanic acid, but no sulphate and only a trace of barium could be detected. (3) It was not found possible to prepare solutions in benzene at all. Benzene did not extract ferric thiocyanate from aqueous solutions of any composition tried, and when ethereal extracts were added to benzene and the ether was removed by vacuum distillation, a solid was thrown out of solution and an almost colourless filtrate was obtained. It is concluded that ferric thiocyanate is insoluble in pure benzene, though it forms a purple solution if small amounts of ether are present.

Method.—The apparatus used was Swietoslawski's differential ebulliometer (" Ebulliometry," Chem. Pub. Co., N.Y., 1945, Fig. 7), but arranged for electrical heating, a small platinum coil immersed directly in the liquid being in series with external windings. In this method, the boiling liquid is pumped over

one thermometer, while the vapour condenses on a second; the difference in the reading of the two thermometers gives the elevation and is independent of fluctuations in atmospheric pressure. When mixed solvents are used (*e.g.*, moist ether) a certain amount of fractionation is bound to occur between the two thermometers, and this was found to give rise, in the case of ether saturated with water, to a difference of 0·023°. In the experiments quoted, the Beckmann thermometers were calibrated in the apparatus, the solvent being used in the same condition as it was to be used in the final experiment, and it was assumed that the degree of fractionation occurring in the two experiments would be nearly the same.

Results.—The thermodynamic ebullioscopic constants for dry ether is 2·24, but moisture will lower this. Values for the constant given in I.C.T. for salicylic acid and for thiocyanic acid, and those calculated from our own experiments, are shown in the following table. Values marked * were made with

Salicylic acid.

Concn. (moles/1000 g.)	0·0767	0·1	0·2	0·237	0·287	0·287	0·3	0·441
K (I.C.T.)	—	2·16	2·18	—	—	—	2·22	—
K (obs.)	2·06$_5$ *	—	—	2·16	2·03 *	2·12	—	2·20

Thiocyanic acid.

Concn. (moles/1000 g.)	0·1	0·2	0·3$_5$	0·5
K (I.C.T.)	—	1·917	—	1·926
K (obs.)	2·075 *	—	2·08 *	—

ether saturated with water. These results served to check the apparatus, and showed that thiocyanic acid has its normal molecular weight in this solvent. A value of 2·06 was chosen for the ebullioscopic constant of moist ether.

The following are the results of two experiments. In the calculations, the elevation due to the thiocyanic acid was worked out and subtracted from the observed elevation. The difference is assumed to be due to the ferric thiocyanate whose molecular weight is being determined. The theoretical molecular weight for single molecules is 230.

$Fe(CNS)_3$, g./1000 g.	HCNS, g./1000 g.	Total elevation.	M.	$Fe(CNS)_3$, g./1000 g.	HCNS, g./1000 g.	Total elevation.	M.
7·866	1·04	0·112°	214	35·75	7·06	0·569°	228

The value chosen for the ebullioscopic constant of alcohol was 1·14, this being the mean of three determinations with benzoic acid in our apparatus and four from I.C.T. (maximum deviation, 3%). The results of two experiments are as follows :

$Fe(CNS)_3$, g./1000 g.	HCNS, g./1000 g.	Total elevation.	M.	$Fe(CNS)_3$, g./1000 g.	HCNS, g./1000 g.	Total elevation.	M.
22·1	1·244	0·144°	210	36·7	0·466	0·221°	197

[*Added, November 10th*, 1950.] After this paper had been submitted, Meyer, Metzler, and Swift (*J. Amer. Chem. Soc.*, 1950, **72**, 3765, 3772, 2776) showed that ferric chloride, which it might have been thought would behave in a similar manner to ferric thiocyanate, shows considerable complexity in ethereal solutions. Not only does it associate with hydrochloric acid to give the compound $HFeCl_4$, but in concentrations greater than 0·001M. it polymerises. It was therefore thought advisable to obtain independent confirmation of the monomeric character of the thiocyanate solutions.

It will be shown in Part II that if the thiocyanate concentration is kept constant (and in excess), the proportion of $Fe(CNS)_3$ to other complexes in the aqueous solution is also constant. Such solutions can therefore be considered as consisting of single molecules of the thiocyanate. If they are extracted with ether, then a constant partition coefficient will indicate that the molecules in ether are also monomeric. In an experiment at room temperature, 40 ml. of ether, previously saturated with water, were shaken with 40 ml. of aqueous solutions of composition NH_4CNS, 0·45M., $HClO_4$, 0·675N., $Fe(ClO_4)_3$, xM. The results are given below :

x	0·025	0·0083	0·001	0·0005	0·00025
Fe in ether/Fe in water	8·9	8·45	9·1	8·45	7·8

The concentration of iron in the ethereal layer was not very different from x. That of the thiocyanate in the aqueous layer was reduced to 0·21M. by extraction of thiocyanic acid. These figures may be compared with those given by Meyers *et al.* (*loc. cit.*), who report that, over the same range, the coefficient for ferric chloride varies from 1·070 to 0·317.

DISCUSSION.—It will be seen from the tables above that there is no simple stoicheiometric relationship between the iron and the acid in ethereal and in alcoholic solutions (such as is found with ferric chloride). Thiocyanic acid is quite strongly extracted from its aqueous solution by ether, and the presence of iron does not noticeably increase the extraction ratio. These facts, together with the additive nature of the ebullioscopic elevation, show that the compound $HFe(CNS)_4$ is not formed at the concentrations studied. The slightly low value of the molecular weight found ebullioscopically is probably due to slight decomposition, the solutions being rather unstable. Conductivity measurements show that ferric thiocyanate in moist ether is not ionised, the very small conductivity being attributable to thiocyanic acid. It is therefore

concluded that ferric thiocyanate exists in solution in ether, alcohol, and similar solvents in the form of single molecules only. The results of Schlesinger and Van Valkenburgh's ebullioscopic experiments can be explained if it is assumed that they were misled by an analysis for total iron into believing that a solid product, similar to that obtained by us, was in fact a pure substance. We are at a loss, however, to explain their results in benzene, for in our experience ferric thiocyanate is insoluble in this solvent.

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