Grateful acknowledgment is made for an appropriation from the Milton Fund of Harvard University for the expenses of this investigation.

Summary

Wien has shown experimentally that deviations from Ohm's Law amounting to more than 50% in some cases occur in electrolytes at very high field strengths (3000 to 300,000 volts per centimeter). It is demonstrated in this paper that if adequate experimental precautions are taken to avoid errors due to heating, to polarization, and to the secondary effects of inductance and capacitance, there is no measurable variation of the real resistance of electrolytes with variation of the applied voltage throughout the range of voltages and frequencies suitable for use in the Kohlrausch method of measuring electrolytic conductance. Ohm's law may, therefore, be regarded as valid for electrolytes under these conditions.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE GEORGE HERBERT JONES AND THE KENT CHEMICAL LABORATORIES OF THE UNIVERSITY OF CHICAGO]

THE STRUCTURE OF FERRIC THIOCYANATE AND THE THIOCYANATE TEST FOR IRON

BY H. I. SCHLESINGER AND H. B. VAN VALKENBURGH[1]

RECEIVED DECEMBER 15, 1930 PUBLISHED APRIL 6, 1931

The usual explanation of the thiocyanate test for ferric ions assumes that the red color is due to the formation of un-ionized ferric thiocyanate, but there is no convincing evidence that dilute aqueous solutions of ferric thiocyanate are only very slightly ionized. Even if they were, it seems unlikely that the union of slightly colored ferric ion with colorless thiocyanate ion should produce a highly colored molecule, since simple ionic dissociation is usually not accompanied by marked color changes. On the other hand, it has been known for a long time that the action of an excess of ammonium or alkali thiocyanate on ferric salts leads to the formation of highly colored substances of the type $Me_3[Fe(CNS)_6]$.[2] That the formation of the complex ion $[Fe(CNS)_6]^{\equiv}$ has not been generally accepted as an explanation of the reaction is due to two causes. In the first place, the solid salts do not appear to have a color exactly identical with that of the solutions in question. In the second place, these salts are not soluble in dry ether, which, as is well known, extracts the colored substance from

---

[1] This article is taken from a thesis presented by H. B. Van Valkenburgh to the Ogden Graduate School of Sciences in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Krüss and Moraht, *Ann.*, **260**, 193 (1890); Rosenheim and Cohn, *Z. anorg. Chem.*, **27**, 280 (1901).

aqueous solutions. The ethereal solutions thus obtained do not contain either ammonium or alkali salts.

Both of these objections to the hypothesis that the color of the solutions is due to the complex ferric thiocyanate ion $[Fe(CNS)_6]^{\equiv}$ can be easily met. Solid salts frequently exhibit shades of color which differ from those of their solutions. Furthermore, the absorption spectra[3] of aqueous solutions of salts of the type $Me_3Fe(CNS)_6$ of ethereal extracts of these solutions, of aqueous solutions of ferric thiocyanate and of solutions of anhydrous ferric thiocyanate in anhydrous ether exhibit practically identical absorption spectra,[4] as shown in Figs. 1 and 2. These facts indicate that the light-absorbing substances are the same in these three types of solutions, and

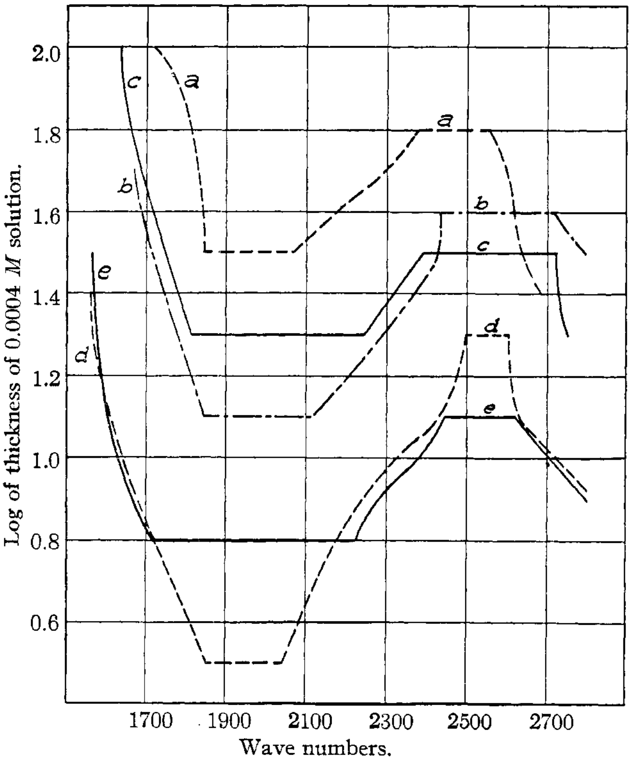

Fig. 1.—Absorption spectrum of $Fe(CNS)_3$: a, 0.0004 *M*, c, 0.0008 *M*, in water; d, 0.0002 *M*, e, 0.0004 *M*, in ether; of $Na_3Fe(CNS)_6$: b, 0.0004 *M* in water.

---

[3] The absorption spectra were photographed with a Hilger quartz spectrograph. A description of the apparatus and experimental procedure will be found in an article by Schlesinger and Salathe, This Journal, **45**, 1871 (1923).

[4] The slight differences in the absorption spectra are due to the addition of thiocyanic acid to the aqueous solutions of ferric thiocyanate to prevent hydrolysis, and to unavoidable differences in the unknown concentration of the actual absorbing substance.

therefore exclude the possibility that the red color is due, as might be otherwise imagined, to an ether-soluble, non-ionizable aquo compound, $\left[\mathrm{Fe}\begin{matrix}(\mathrm{CNS})_3\\(\mathrm{H_2O})_3\end{matrix}\right]$. The latter conclusion is corroborated by the finding that electrolysis of aqueous solutions of ferric thiocyanate causes the red color to migrate toward the anode, while ferric ions pass toward the cathode.

The identity of the absorption spectra of solutions of hexathiocyanate salts and of ferric thiocyanate, as well as the ionic migration experiment, suggest that solutions of the supposedly simple salt also contain the complex ion. If that is the case the formula $\mathrm{Fe[Fe(CNS)_6]}$ should be assigned to ferric thiocyanate. That this assumption is correct is borne out by the fact that in anhydrous ethereal solutions, as well as in benzene, its molecular weight is practically twice that corresponding to the simple salt. In aqueous solutions, unless a large excess of thiocyanate ion is present, the complex ion is more or less dissociated; thus are explained the slight differences in absorption spectra noted above.[4] Furthermore, if a large excess of thiocyanate ions is added to the aqueous solutions, all of the ferric ion is converted into the complex ion and ether can no longer extract $\mathrm{Fe[Fe(CNS)_6]}$ from the solutions. These conclusions are in agreement with the facts.

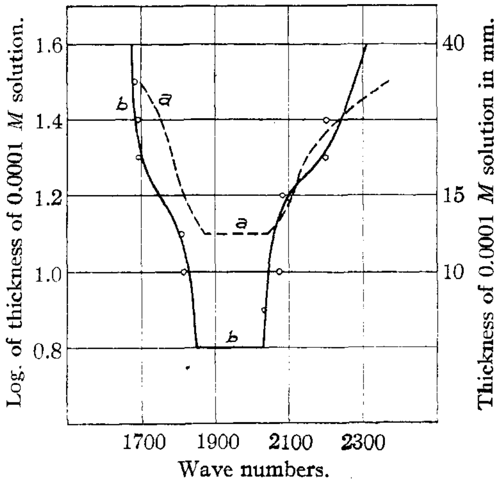

Fig. 2.—Absorption spectra of ethereal extracts: a, 0.0004 *M* $\mathrm{Na_3Fe(CNS)_6}$; b, 0.0001 *M* $\mathrm{(NH_4)_3Fe(CNS)_6}$.

Only one point remains to be discussed. The effect of ammonium chloride in decreasing the color of ferric thiocyanate solutions was formerly explained as being due to the reaction: $\mathrm{3NH_4Cl + Fe(CNS)_6 \rightleftharpoons 3NH_4CNS + FeCl_3}$. A more logical explanation is the reaction represented by the equation: $\mathrm{[Fe(CNS)_6]^{=} + 6Cl^- \rightleftharpoons [FeCl_6]^{=} + 6CNS^-}$. The existence of a hexachloroferric ion is not unwarranted in view of the well-established existence of the corresponding fluoro ferric ion; furthermore, addition of chloride ions to ferric salt solutions alters the absorption spectra of the latter, indicating complex ion formation, as is described below.

Experimental

Preparation of Ferric Thiocyanate.—The preparation of anhydrous ferric thiocyanate proved very troublesome until it was discovered that the products of decomposition of the substance in solution could be excluded from the crystals only if crystallization was carried out very slowly. Equivalent quantities of solutions of barium thiocyanate and ferric sulfate were mixed, and the solution, after standing for some time, was filtered to remove barium sulfate, and placed over sulfuric acid in a brown desiccator until a small crop of crystals had formed. The crystals were removed by decantation of the solution, which was again allowed to evaporate. This process was repeated several times until crystals of constant composition were obtained. Various samples of such material gave an iron content of 24.49 ± 0.02%; calculated for $Fe(CNS)_3$, 24.29%.

Preparation of Sodium Ferric Hexathiocyanate.—This salt was obtained according to the directions of Rosenheim and Cohn.[2] It was found that the compound $Na_3Fe(CNS)_6 \cdot 12H_2O$, described by them, loses water over sulfuric acid, yielding a trihydrate.

The absorption spectra of the various thiocyanates in aqueous and ethereal solutions have already been adequately described. Figure 3 shows the effect of the addition of ammonium chloride to 0.02 and 0.002 *M* solutions of ferric chloride, acidified with a small amount of hydrochloric acid to prevent hydrolysis. It is seen that the addition of the chloride shifts the end absorption markedly toward the longer wave lengths.[5] Such changes indicate the formation of a new compound, presumably a complex ion.

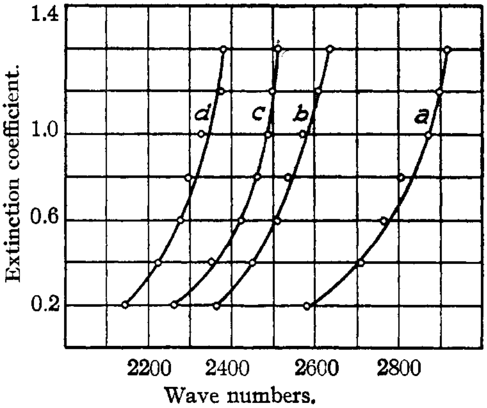

Fig. 3.—Absorption spectrum of aqueous solutions of $FeCl_3$: a, 0.002 *M;* b, 0.002 *M* $FeCl_3$ + 2.0 *M* NH_4Cl; c, 0.02 *M;* d, 0.02 *M* $FeCl_3$ + 1.0 *M* NH_4Cl.

Determinations of the molecular weight of ferric thiocyanate in benzene were made by the freezing point method and in ether by the boiling point method. The apparatus of Menzies, as well as that of Washburn–Cottrell, was used in the latter. The benzene was carefully distilled twice and showed a constant freezing point. The ether was purified in the usual manner and finally distilled twice from sodium. It had a constant boiling point. The results of the molecular weight determinations are shown in Table I. Both in benzene and in ethereal solutions ferric thiocyanate undergoes moderately rapid spontaneous decomposition as already described by Rosenheim and Cohn.[2] Among the products of decomposition are polymerized derivatives of thiocyanic acid. It is therefore not surprising that the results are on the whole somewhat higher than values corresponding to twice the molecular weight of $Fe(CNS)_3$. The agreement of individual values is as good as is to be expected in view of the instability of the solutions.

---

[5] The measurements were made with the Hilger spectrograph and sectorphotometer.

TABLE I

MOLECULAR WEIGHT OF FERRIC THIOCYANATE

In ether

Subs., g.	Soln., cc.	Elevation of b. p., °C.	Molecular weight Found	Molecular weight Calcd. for $Fe[Fe(CNS)_6]$
0.3400	32.2	0.0730	483	460
.1806	32.0	.0411	458	
.2045	32.1	.0452	471	
	Ether, g.			
.1770	70.443	.011	482	
		Average	473	

In benzene

Subs., g.	Benzene, g.	Lowering of f. p., °C.	Molecular weight Found	Molecular weight Calcd. for $Fe[Fe(CNS)_6]$
0.021	24.397	0.010	448	460
.027	23.658	.012	495	
.018	20.153	.010	465	
		Average	469	

This research is one of a series of investigations carried out with the aid of a grant from the Bache Fund of the National Academy of Sciences.

Summary

1. In aqueous solutions of ferric thiocyanate the red color migrates to the anode during electrolysis.

2. The red color of these solutions is shown by their absorption spectra to be identical with that of aqueous solutions of salts containing the complex ion $[Fe(CNS)_6]^{\equiv}$ and with ethereal solutions of anhydrous ferric thiocyanate.

3. In the latter as well as in benzene, ferric thiocyanate has a molecular weight approximately twice that corresponding to the formula of the simple salt. On the basis of these results it is concluded that the red color observed in the thiocyanate test for iron is due to the ion $[Fe(CNS)_6]^{\equiv}$, and that ether extracts the compound $Fe[Fe(CNS)_6]$, from aqueous solutions. The diminution in color caused by ammonium chloride is ascribed to the formation of a hexachloro ferric ion.

CHICAGO, ILLINOIS