A Spectrophotometric Study of Ferric Thiocyanate in Isodielectric Mixtures of Various Aqueous–non-Aqueous Solvent Pairs[1]

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Woods and Mellon[2] recently made a spectrophotometric study of ferric thiocyanate in acetone–water solutions at various volume concentrations. Their work showed that as the volume per cent. of acetone in the solution was increased, the corresponding absorption curve, plotted as per cent. transmittancy *versus* wave length, had a consistently deeper minimum. This decrease in transmittancy with increasing concentration of acetone was attributed to the lower dielectric constant of the solution.

The present study was undertaken in order to clarify the role of the dielectric constant of the medium in the ferric thiocyanate system. It would seem that if the intensity of color is solely a function of the dielectric constant of the solvent, with the other variables, such as concentrations and temperature kept constant, the absorption curves for this system should be identical in all isodielectric mixtures, regardless of the solvent pair. Accordingly, the absorption spectra of ferric thiocyanate was investigated at various fixed dielectric constants in the following solvent pairs: acetone–water, methanol–water, ethanol–water, isopropyl alcohol–water, ethylene glycol–water and dioxane–water.

Materials

Nitric Acid.—J. T. Baker Analyzed nitric acid was distilled from an all-glass apparatus, collecting the middle 50%. The distillate was allowed to remain twenty-four to thirty-six hours under a hood to remove dissolved nitrogen dioxide. A nitric acid solution, 6.04 N, was prepared from the distillate. The standardization was with sodium tetraborate decahydrate, using methyl red as an indicator; d^{25}_4 1.1933. The solution was stored in a dark, cool place.

Ferric Nitrate.—J. T. Baker Analyzed (99.8% pure) iron wire (0.1 g.) was dissolved in about 10 ml. of the 6.04 N acid. Hydrogen peroxide (30%) was added to insure complete oxidation to ferric ion. The solution was evaporated to dryness on a steam-bath. The residue was dissolved in exactly 10 ml. of 6.04 N nitric acid and diluted to 1 liter. A 100-ml. aliquot portion of this solution was diluted to 250 ml., giving a solution containing 40 p. p. m. of iron in 0.024 N nitric acid. The solution was stored in a cool, dark place; d^{25}_4 1.0015.

Ammonium Thiocyanate.—J. T. Baker Analyzed salt was used without further purification: 100 g. of ammonium thiocyanate was dissolved in 400 g. of water. The resulting solution contained 20% of ammonium thiocyanate by weight; d^{25}_4 1.0452. It was stored in a cool, dark place.

Methyl Alcohol.—A liter of Mallinckrodt acetone-free methanol was refluxed[3] over 15–20 g. of magnesium turnings for three hours. The methanol was then fractionally distilled through a 50-in. Fenske column. The middle

500-ml. portion was collected: n^{20}D (obsd.) 1.3285, n^{20}D (lit.) 1.3288.

Ethyl Alcohol.—A liter of U. S. Industrial commercial absolute alcohol was refluxed[4] over 7 g. of sodium and 27.5 g. of diethyl phthalate for one hour. It was then fractionally distilled, collecting the middle 500-ml. portion, n^{20}D (obsd.) 1.3610, $n^{20.5}$D (lit.) 1.3610.

Acetone.—About 2.5 liters of J. T. Baker Analyzed acetone was treated[5] with 100 ml. of 85% phosphoric acid. The acetone was distilled through an 18-in. Vigreux column, collecting the middle 2-liter portion. This portion was dried for forty-eight hours over anhydrous potassium carbonate and then fractionally distilled, collecting the middle 1500-ml portion: n^{20}D(obsd.) 1.3586; n^{20}D (lit.) 1.3591.

Dioxane.—About 2 liters of U. S. Carbon and Carbide dioxane was purified by a standard procedure.[4] The middle 1-liter portion was collected after fractionation: n^{20}D(obsd.) 1.4215; n^{20}D(lit.) 1.4221.

Isopropyl Alcohol.—About 2 liters of Eastman Kodak Co. (98–99%) isopropyl alcohol was fractionally distilled, collecting the middle 80%. This was then dried for eighteen hours over anhydrous sodium sulfate in a refrigerator. It was then refractionated; n^{20}D(obsd.) 1.3768, n^{20}D(lit.) 1.3776.

Ethylene Glycol.—About 2 liters of Eastman Kodak Co. Technical grade was fractionated. The fraction boiling between 197–198° was collected and dried over sodium sulfate for a week in a refrigerator. This portion was then vacuum-distilled and the fraction boiling between 107–108° at 9.5 mm. pressure was collected: n^{20}D (obsd.) 1.4309; n^{20}D (lit.) 1.4318.

Experimental Method

The weight percentage of water at 25°, corresponding to dielectric constants of 30, 40, 50, 60 and 70, were obtained from the literature.[5] From calculations involving density data, the correct volumes of organic solvent and water required to give the desired dielectric constant were determined.

After the reagents had attained thermal equilibrium in a thermostat, the following procedure was used in preparing a solution: five ml. of ferric nitrate solution, 5 ml. of nitric acid solution and 2 ml. of ammonium thiocyanate solution were placed, in the order listed, in a thermostated, calibrated, 50-ml. volumetric flask. Allowing for the water already present in the reagents used, the calculated volumes of organic solvent and water required to give a definite dielectric constant were added to the flask. Dilution, to the mark, was made by a previously prepared mixture of the solvent-pair having the desired dielectric constant. The above procedure allowed the maintaining of a constant iron concentration of 4 p. p. m. in all cases and also kept the pH of the solution within the desirable limits[2] of 0.70 to 0.25. The solution was thoroughly mixed and the absorption data were obtained within one-half hour after development of the color. Very little fading was observed in that time limit. The blank consisted of a solution of the same solvent-pair made up to the same dielectric strength.

All absorption measurements were made with a Beckman Model D U Quartz Spectrophotometer, using specially matched corex cells. These cells, 0.998 cm. in depth, were thoroughly rinsed 3 or 4 times with the solution to be measured, and the faces wiped dry with a lintless cloth. Per cent. transmittancy values were read at 10 mμ inter-

(1) Part of a thesis submitted by Sidney Baldwin to the Graduate School of the University of Maryland in partial fulfilment of the requirements for the degree of Master of Science.

(2) Woods and Mellon, *Ind. Eng. Chem., Anal. Ed.*, **13**, 551 (1941).

(3) Bjerrum and Zechmeister, *Ber.*, **56**, 894 (1923).

(4) Fieser, "Experiments in Organic Chemistry," D. C. Heath & Co., Boston, Mass., 1941.

(5) Åkerlöf, THIS JOURNAL, **54**, 4132 (1932).

vals from 400 to 540 mμ and at 20 mμ intervals from 540 to 700 mμ. The instrument was operated at maximum sensitivity and at narrow slit width (0.02 mm.). Two runs were made at each dielectric strength for each solvent pair. If the values checked within 1–2% at each wave length, no further runs were made. The average of the two runs was used.

A Coleman Model 4D pH meter was used for measuring the acidity of the solutions after the transmittancy curves were taken in order to check the pH.

The wave length scale of the spectrophotometer was not calibrated. The photometric scale was checked using a solution of potassium chromate in 0.05 N potassium hydroxide. The values obtained checked very well with those reported by previous workers.[6]

During absorption measurements, the cuvettes were not temperature controlled, due to conditions not under our control. The room temperature was essentially constant during each run. The temperature range, in which all the measurements were made, was $28.0 \pm 1.2°$. The calculated volumes of non-aqueous solvent and water used in the various mixtures, gave the desired dielectric constant at 25°. It was realized that, owing to the dissolved electrolytes and to the difference in temperatures, the value of the existing dielectric constant would differ from the desired value. Nevertheless, it was assumed that, since the same concentrations of reagents were used in all the determinations, and since the experimental temperatures in all except a few cases were reasonably close
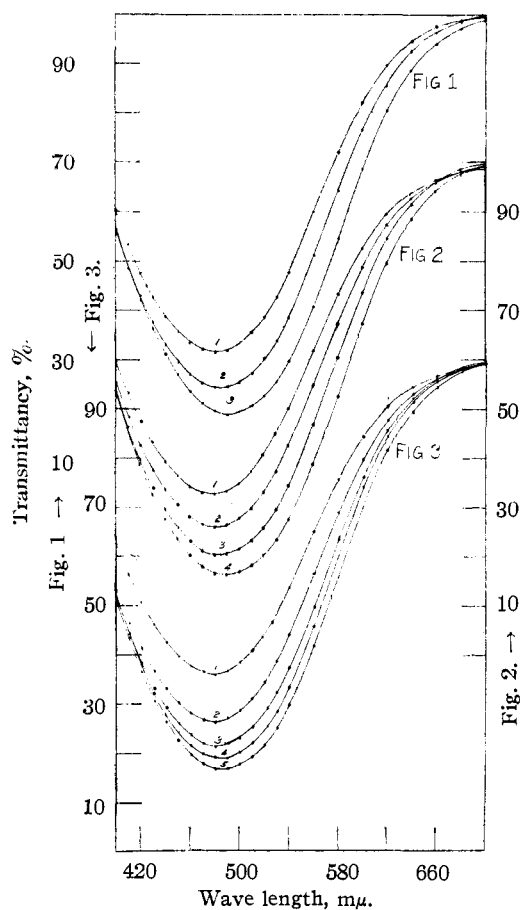

Fig. 1.

Fig. 1.—Methanol– water solutions	Curve	Dielectric constant	° C.
	1	70	29.0
	2	60	28.0
	3	50	28.0

Fig. 2.—Ethanol– water solutions	Curve	Dielectric constant	° C.
	1	70	27.2
	2	60	26.8
	3	50	26.8
	4	40	27.2

Fig. 3.—Isopropyl alcohol–water solutions	Curve	Dielectric constant	° C.
	1	70	27.5
	2	60	27.8
	3	50	27.8
	4	40	27.4
	5	30	27.5
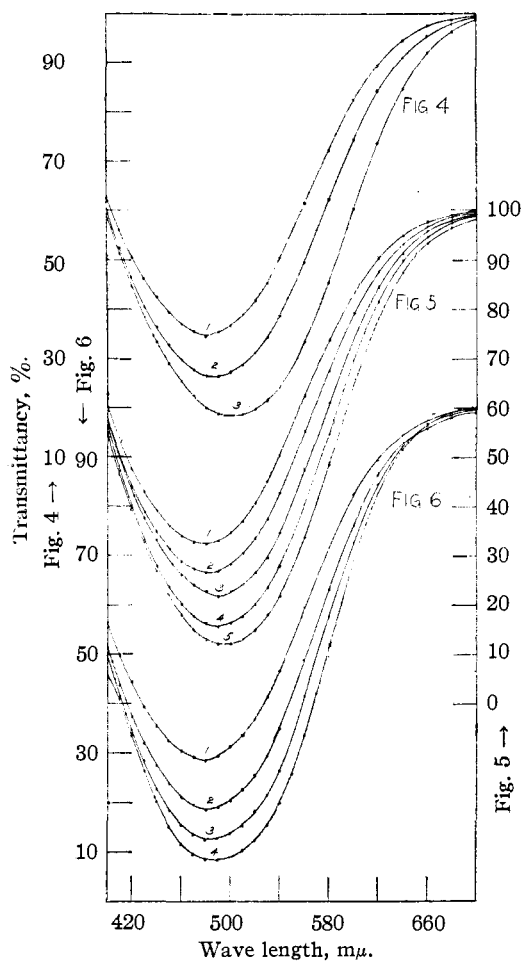
Fig. 4.—Ethylene glycol–water solutions	Curve	Dielectric constant	t °C.
	1	70	28.3
	2	60	28.1
	3	50	29.2

Fig. 5.—Dioxane– water solutions	Curve	Dielectric constant	t °C.
	1	70	28.4
	2	60	28.6
	3	50	29.1
	4	40	28.6
	5	30	28.6

Fig. 6.—Acetone– water solutions	Curve	Dielectric constant	t °C.
	1	70	28.1
	2	60	28.1
	3	50	28.3
	4	40	29.0

Wave length, mμ.

(6) Von Halban and Siedentopf, Z. physik. Chem., **100**, 208 (1922).

to 28°, both effects would cause almost an equal variation in any fixed, calculated, dielectric constant. Consequently, the solutions prepared should have the same relative dielectric strength even if the absolute values referred to in our data are not strictly valid.

Discussion of Data

The spectrophotometric curves for the six solvent pairs are shown in Figs. 1–6. In all cases, the absorption decreases as aqueous conditions are approached. In general, there is a larger difference between the minima at the higher dielectric constant values than at the lower values. Figures 1–6 also show that there is a slight hypsochromic effect, i. e., there is a shift in the peak of the absorption band toward lower wave lengths as aqueous conditions are approached. This is in agreement with the work of Woods and Mellon[2] in acetone–water solvents. It contradicts the observa-

TABLE I

WAVE LENGTHS WHERE MINIMA OCCUR

Solvent pairs	30	40	50	60	70
		Dielectric constant			
Acetone–water		490	483	480	480
Methanol–water			492	483	480
Ethanol–water		490	487	485	480
Isopropanol–water	485	485	480	480	480
Ethylene glycol–water			503	488	480
Dioxane–water	495	490	490	483	480

Our data for the hypsochromic effect are summarized in Table I.

An examination of the transmittancy curves for the various isodielectric mixtures also shows that acetone–water mixtures have lower per cent. transmittancy values than any of the other corresponding isodielectric media. Furthermore, reference to Table I shows that the minima did not usually occur at the same wave length in the various isodielectric media. Thus it is evident that specific solvent effects are also in operation in addition to any operating dielectric effect.

Before attempting to explain the above observations, we would like to call attention to Table II, which is a summary of conclusions concerning the nature of the species causing the color in the ferric thiocyanate system. In regard to absorption work, the following observations have been made. Frank and Ostwalt[7g] showed that the positive complex $Fe(SCN)^{++}$ had an absorption minimum at about 447.5 mμ. Woods and Mellon[2] observed that as the ammonium thiocyanate added was increased from 0.5 to 5.0 ml., (SCN^-/Fe^{+3} changed from 76 to 765), the intensity increased and the peak of the absorption band shifted from 460 to 480 mμ. They also observed that the absorption band of a solution obtained by extracting the ferric thiocyanate com-

TABLE II

SUMMARY OF CONCLUSIONS CONCERNING NATURE OF COLORED SPECIES

Reference 7	Solvent	Fe^{+3} (M)	SCN^{-1} (M)	$\frac{SCN^{-1}}{Fe^{+3}}$	Nature of colored species
a	Aqueous				$Fe(SCN)_6^{-3}$
a	Ether or benzene				$Fe[Fe(SCN)_6]$
b	Aqueous				$Fe(SCN)^{++}$, $Fe(SCN)_2^+$, $Fe(SCN)_3$ and possibly $Fe(SCN)_4^-$ at high thiocyanate concn.
c	Aqueous	0.003582	0.000109 to 0.6322	0.03–176	$Fe(SCN)^{++}$, $Fe(SCN)_2^+$
d	Non-aq.				Dimer, $Fe_2(SCN)_6$
d	Aqueous	.1	4	40	$Fe(SCN)_4^-$
e	96% Ethanol	.1	0 to 0.80	0–8	Dimer, $Fe_2(SCN)_6$
e	96% Ethanol	0–0.50	.5	0–1	Dimer, $Fe_2(SCN)_6$
f	Aqueous	.002	.01–0.02	5–10	Positive complexes $Fe(SCN)^{++}$, $Fe(SCN)_2^+$
f	Aqueous	.002	.2–0.4	100–200	Negative complexes $Fe(SCN)_4^-$ to $Fe(SCN)_6^{-3}$
g	Aqueous	.001–0.008	.0003	0.3–0.0375	$Fe(SCN)^{++}$
g	Aqueous	.0003	.003	10	Higher complexes
h	Organic solvent–water mixture	.0716 × 10⁻³	.11	1540	Probably $Fe_2(SCN)_6$ and negative complexes

tions of Schlesinger and Van Valkenburgh,[7a] who claim that there is no difference in the absorption spectra of aqueous solutions of ferric thiocyanate and of non-aqueous solutions of ferric thiocyanate.

(7) (a) Schlesinger and Van Valkenburgh, THIS JOURNAL, **53**, 1212 (1931); (b) Møller, *Kem Maanedsblad*, **18**, 138 (1937); *C. A.*, **33**, 9179 (1939); (c) Bent and French, THIS JOURNAL, **63**, 568 (1941); (d) Schlesinger, *ibid.*, **63**, 1766 (1941); (e) Uri, *J. Chem. Soc.*, 336 (1947); (f) Babko, *J. Gen. Chem.* (*U. S. S. R.*), **16**, 1549 (1946); *C. A.*, **41**, 4732 (1947); (g) Frank and Ostwalt, THIS JOURNAL, **69**, 1321 (1947); (h) present study.

plex with a mixture of equal volumes of amyl alcohol and ethyl ether had about the same intensity as that of an acetone solution of the same concentration of iron. However, the peak of the absorption band of the extract was at 500 mμ. Since in non-aqueous solvents[7a,e] the iron exists as the dimer, $Fe_2(SCN)_6$, one concludes that the absorption maximum at 500 mμ must be due to the dimer. Absorption maxima between 447 mμ and 480 mμ depend on the nature of the complex ion present.

TABLE III

Compound	450 mμ Regression equation[a]	δest_T[b]	480 mμ Regression equation[a]	δest_T	520 mμ Regression equation	δest_T
Acetone	$\log T = 0.0117D + 0.700$	0.74	$\log T = 0.0177D + 0.216$	0.51	$\log T = 0.0161D + 0.446$	0.31
	$T = 8.56 \times 10^{-7}D^4 + 13.2$	.57	$T = 9.47 \times 10^{-7}D^4 + 6.29$	.26	$T = 11.6 \times 10^{-7}D^4 + 10.1$	1.33
Ethanol	$\log T = 0.00641D + 1.10$	.81	$\log T = 0.010D + 0.808$	.39	$\log T = 0.0103D + 0.893$	0.50
Methanol	$\log T = 0.00617D + 1.12$	1.07			$\log T = 0.0116D + 0.774$	0.54
	$T = 5.04 \times 10^{-7}D^4 + 23.5$	0.56	$T = 6.52 \times 10^{-7}D^4 + 15.5$	.10		
Glycol	$\log T = 0.00671D + 1.12$	.82	$\log T = 0.0121D + 0.699$	.32	$\log T = 0.0162D + 0.498$	1.87
	$T = 5.92 \times 10^{-7}D^4 + 25.2$	.10				
Dioxane	$\log T = 0.00549D + 1.17$	.90	$\log T = 0.0101D + 0.818$	1.30	$\log T = 0.0109D + 0.862$	1.06
Isopropanol	$T = 7.24 \times 10^{-7}D^4 + 21.8$	.82	$T = 7.96 \times 10^{-7}D^4 + 16.4$	0.57	$T = 9.50 \times 10^{-7}D^4 + 21.7$	0.67

[a] Where D = dielectric constant. T = per cent. transmittancy; [b] δest_T = unbiased standard error of estimate of T found from the regression equation.

Therefore, based on the hypsochromic effect, in light of the conclusions of other investigators concerning the nature of the colored species, we can conclude that in this investigation (the ratio of thiocyanate to iron was 1540) the color forming species is mainly a mixture[8] of $Fe_2(SCN)_6$ and various negative complex ions. On approaching non-aqueous conditions, $Fe_2(SCN)_6$ predominates,[7d,e] while on approaching aqueous conditions, the negative complexes, in particular $Fe(SCN)_6^{-3}$ become more important.

If one assumes that the following equilibrium reaction exists $Fe(SCN)_6^{-3} + Fe^{+3} \rightleftarrows Fe_2(SCN)_6$, (1) then the increase in color intensity on approaching non-aqueous conditions is explainable if the color of $Fe_2(SCN)_6$ is assumed to be more intense than that of the negative complex. Furthermore, the equilibrium serves to explain the specific solvent effects. If there is a tendency for the solvent to donate a free electron pair to Fe^{+3}, then a strong electron donating solvent would favor the dissociation of $Fe_2(SCN)_6$ into ions, while a weaker electron donating solvent would favor association into $Fe_2(SCN)_6$, thereby producing a greater color intensity. Acetone, according to this study, thus would have a weak electron donating tendency compared to the other organic solvents used. The concept that acetone is a poorer electron donor is tantamount to saying that it is a weaker base than the other organic solvents used in this study. Measurements of Koch[9] based on solvation activity coefficients of Ag^+ in various solvents, placed the solvents in the following order of decreasing basicity: methanol, ethanol and acetone. The same order holds equally well for the basicity with respect to H^+ and it seems reasonable to expect it to hold also for Fe^{+3}. Although there are no values listed for the other organic solvents used in this study, it appears likely that they should have electron donating tendencies not too far different from methanol and ethanol. Thus, acetone should favor the equilibrium in reaction (1) to the right to a much greater extent than any of the other solvents used.

In trying to correlate per cent. transmittancy with some property of the solvent, we obtained two general empirical relations, if the dielectric constant was treated as the independent variable, namely

$$T = mD^4 + b \qquad (1)$$
$$T = a10^{cD} \text{ or } \log T = \log a + cD \qquad (2)$$

where T is the per cent. transmittancy, D is the dielectric constant and m, b, a and c are empirical constants which were evaluated by the method of least squares. The results are given in Table III. We would like to state, however, that it is impossible to distinguish between specific solvent effects and dielectric effects. These equations serve to generalize the data. No trend was observed when either weight per cent. or mole-fraction of water was used as the independent variable.

Summary

1. The absorption curves for ferric thiocyanate at an iron concentration of 4 p. p. m., at relative dielectric constants of 30, 40, 50, 60 and 70 have been measured in the range of 400 to 700 mμ in the following solvent pairs: methanol–water, ethanol–water, isopropyl alcohol–water, ethylene glycol–water, dioxane–water, and acetone–water. The work was carried out at about 28° with a Beckman Model DU Spectrophotometer.

2. In general, on approaching aqueous conditions a decrease in intensity of color and a shifting of the absorption peak to a lower wave length are observed. These experimental observations are accounted for by postulating that $Fe_2(SCN)_6$ and $Fe(SCN)_6^{-3}$ are the species causing the color and that the former has a more intense color than the latter.

3. The increased intensity in acetone–water solutions compared to other solvent–water mixtures is attributed to the feeble, basic character of acetone compared to the other organic solvents used.

4. Equations have been obtained empirically showing the correlation of per cent. transmittancy with the dielectric strength of the solution.

(8) The possibility of existence of other complex ions is not denied. In light of the work summarized in Table II, it appears that in our case the highly negative complexes would be the most important.

(9) Koch, *J. Chem. Soc.*, 269 (1928); *Phil. Mag.*, [7] **11**, 579 (1931).

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