to the ion–dipole bonds between oxygen and metal cations in hydrates. The formation of these bonds results in steric repulsion between the methylene groups of dioxane and the halogen atoms, forcing the mercury to assume a valence angle less than 180°. This steric effect is greatest for mercuric iodide; this molecule has the smallest mercury valence angle and therefore the largest electric moment. Further evidence for this type of bonding will be presented in a paper on the electric moments of some organomercuric halides to be published[5] shortly.

Experimental

The refractive indices listed in Table I were determined with a Pulfrich refractometer. The densities were measured with an Ostwald–Sprengel pycnometer of approximately 5 ml. capacity. Commercial 1,4-dioxane was refluxed over sodium and distilled through a Widmer column in an all-glass still. Merck U. S. P. mercuric iodide was heated to remove moisture before making up solutions. The concentrations were limited by the low solubility of mercuric iodide in dioxane. This solvent was used because, with the exception of methylene iodide, it is better than any of those listed by Bell.[6]

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[5] Presented before the Physical and Inorganic Division at the Cincinnati Meeting of the American Chemical Society, April, 1940.

[6] Bell, *J. Chem. Soc.*, 1381 (1931).

DEPARTMENT OF CHEMISTRY
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Ferric Thiocyanate

BY SYLVAN M. EDMONDS AND NATHAN BIRNBAUM

For some time we have been conducting a photometric study of the equilibrium involved in a ferric thiocyanate solution. Unaware of the work of Bent and French,[1] we have duplicated many of their measurements using a high precision balance type photoelectric colorimeter similar to that described by Withrow, Shrewsbury and Kraybill.[2] It seems worth while, nevertheless, to record here some of our results and to call attention to a rather striking series of experiments which differ from those of Bent and French and also point rather conclusively to the existence of the $FeCNS^{++}$ ion. Measurements were made at unit ionic strength (1 *M* perchloric acid) of mixtures of ferric perchlorate and ammonium thiocyanate. In this way the effect of hydrolysis can be ignored and the complicating factor of chloride ion is absent. Writing the equation for the reaction between ferric ion and thiocyanate in the general form

$$\underset{a - x}{Fe^{+++}} + \underset{b - nx}{nCNS^-} \rightleftarrows \underset{x}{Fe(CNS)_n^{3-n}}$$

we have

$$\frac{(a - x)(b - nx)^n}{x} = K \tag{1}$$

By confining measurements to conditions where $b \gg a$ or x this simplifies to

$$\frac{(a - x)b^n}{x} = K$$

For a fixed cell length and concentration of ferric ion a, K may be evaluated from any two measurements of the transmission by simultaneous solution of the two equations

$$(a - x)b^n/x = (a - y)d^n/y$$

and

$$y/x = \log I_y/\log I_x$$

whence

$$K = \frac{b^n d^n(\log I_y - \log I_x)}{d^n \log I_x - b^n \log I_y}$$

By selecting $n = 1$, reasonably reproducible values for K were obtained, *viz.*, $K = 0.0079 \pm 0.0006$. This is as good as can be expected considering the difference method employed in its calculation. Higher values for n yield values for K which vary by several hundred per cent. for small changes in a or b.

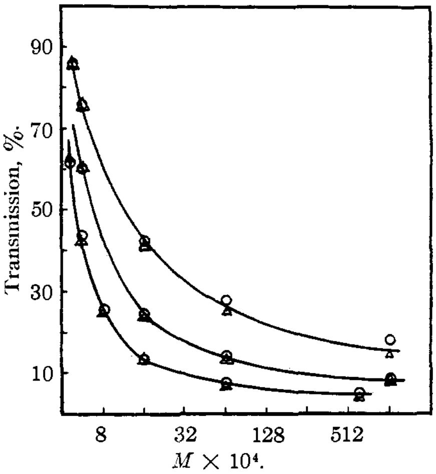

Fig. 1.—Circles indicate CNS^- and triangles Fe^{+++} when the other ion concentration is 5×10^{-4} for upper curve, 10^{-3} for middle curve and 2×10^{-3} for the lower.

In Fig. 1 are shown three series of measurements wherein at a given fixed concentration of ferric or thiocyanate ion the per cent. transmission for a constant cell length is plotted against the other ion concentration. It will be noted that

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[1] Bent and French, THIS JOURNAL, **63**, 568 (1941).

[2] Withrow, Shrewsbury and Kraybill, *Ind. Eng. Chem., Anal. Ed.*, **8**, 214 (1936).

over a considerable range of concentration below and above the stoichiometric requirements for the possible constituents, FeCNS^{++}, Fe(CNS)$_2^+$, Fe(CNS)$_3$, Fe(CNS)$_6^{\equiv}$, the pairs of curves (fixed thiocyanate–variable ferric ion; fixed ferric ion–variable thiocyanate) overlap. For solutions of identical color intensity, x in equation (1) must be the same, if we ascribe the color to the one complex Fe(CNS)$_n^{3-n}$. For any point on any pair of overlapping curves then $(a - x)(b - nx)^n = (b - x)(a - nx)^n$. This equation is satisfied for all values of x only if $n = 1$, that is, if the complex is Fe(CNS)$^{++}$.

Another interesting confirmation may be noted by considering identical values of x (*i. e.*, per cent. transmission) for any two points lying on two different series of curves. For these points we would have the relation $(a - x)(b - nx)^n = (c - x)(d - nx)^n$, where a and c are the two concentrations of ferric ion and b and d the corresponding thiocyanate concentrations producing the identical color. As a first approximation this may be written as $ab^n = cd^n$, since x is relatively small. The experimental points all satisfy this equation only for $n = 1$; that is, $ab = cd$ for any two points on different curves where the color is the same.

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The Fungistatic Properties of Binary Fatty Acid Mixtures

BY CHARLES HOFFMAN, T. R. SCHWEITZER AND GASTON DALBY

The fungistatic properties of the fatty acids containing 1 to 14 carbon atoms have been reported.[1] This earlier study was made with each individual acid in as pure state as possible. In testing the fungistatic properties of a binary mixture it was found that the inhibiting power of the fatty acids was not additive, and that on the contrary there was a definite subtractive effect especially marked if the mixture consisted of a weak and strong fungistatic acid.

The method used was exactly as previously reported.[1] In the tables the inhibiting concentrations of the mixture are compared with the respective inhibiting concentrations of the pure acids at each *p*H value. Since a definite subtractive effect exists at *p*H 8 it is difficult to attribute this effect to any variation in the respective concentrations of non-ionized and ionized acid molecules. At *p*H 8 the acids are essentially in the form of the salts.

Acetic and caprylic acids form an interesting mixture in that acetic is a weak fungistat and caprylic a strong one.

TABLE I

THE FUNGISTATIC PROPERTIES OF MIXTURES OF ACETIC AND CAPRYLIC ACIDS

Case 1, 50% acetic and 50% caprylic (all percentages are molar). Case 2, 25% acetic and 75% caprylic. Case 3, 75% acetic and 25% caprylic.

*p*H	Molar concn.[a] of mixture for inhibition	Calcd. molar concn.[a] of each acid present in inhibiting mixture		Molar concn.[a] of pure acid for inhibition		% Effectiveness of caprylic
		Acetic	Caprylic	Acetic	Caprylic	
			Case 1			
2	0.0049	0.0025	0.0025	0.035	0.0012	48
5	.0069	.0035	.0035	.0875	.0018	51
6	.0294	.0147	.0147	ineff.	.0080	54
7	.0784	.0392	.0392	ineff.	.0196	50
			Case 2			
2	.0020	.0005	.0015	.0350	.0012	80
5	.0032	.0008	.0024	.0875	.0018	75
7	.0320	.0080	.0240	ineff.	.0190	79
8	.090	.022	.067	ineff.	.048	72
			Case 3			
2	.0049	.0037	.0012	.0350	.0012	100
5	.0111	.0083	.0028	.0875	.0018	64
7	.135	.101	.034	ineff.	.0190	56

[a] The molar concentration is the total concentration and includes both the dissociated and undissociated fatty acid molecules.

When acetic and caprylic acids are present in equimolecular proportions approximately 50% of the stronger fungistat, caprylic, is inactivated. Where caprylic is present in 75% molar concentration, approximately 25% is inactivated. In case 3, where acetic acid is present in greater concentration than caprylic, the per cent. of caprylic inactivated is not so regular over the various *p*H values.

TABLE II

THE FUNGISTATIC PROPERTIES OF AN EQUIMOLECULAR MIXTURE OF ACETIC AND PROPIONIC ACIDS

*p*H	Molar concn.[a] of mixture for inhibition	Calcd. molar concn.[a] of each acid present in inhibiting mixture		Molar concn.[a] of pure acid for inhibition		% Effectiveness of propionic
		Acetic	Propionic	Acetic	Propionic	
2	0.0164	0.0082	0.0082	0.0350	0.0054	65
5.5	0.1190	0.0595	0.0595	ineff.	0.0405	68

[a] The molar concentration is the total concentration and includes both the dissociated and undissociated fatty acid molecules

The subtractive effect of a weak fungistat on a

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[1] Hoffman, Schweitzer and Dalby, *Food Research*, **4**, 539 (1939).