THE PHYSICAL PROPERTIES

OF

CUPRIC NITROSYL COMPLEXES

by

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PREFACE

Absorption of nitric oxide, by non-aqueous solutions of cupric salts, to form a deep-violet solution, was first observed by Kohlschütter in 1904. Because the complexes had never been isolated from solution - and, indeed, are unstable even in solution - their composition was not elucidated for some time. The cupric salts that had been observed to react were: cupric sulphate in concentrated sulphuric acid; cupric fluoride, chloride and bromide in a range of organic, electron-donating solvents. These solutions are all sensitive to traces of air and moisture. No solid cupric salt undergoes reaction.

Early work on gas-absorption measurements, to determine the Cu:NO ratio, and ion-migration experiments, which suggested an ionic compound of the type $CuNOX_2^{(n-2)-}$, presented some extremely conflicting results. The empirical formula was settled in 1960 by Fraser and Dasent, with the assignment of the covalent formula CuX_2NO.

Evidence obtained from spectroscopic and further ion-migration experiments suggested the complex dissociated into colourless ions, according to the equilibrium:

$$CuX_2NO \rightleftharpoons NO^+ + CuX_2^-$$

Study of $CuCl_2NO$ in a wide range of alcoholic solvents showed that the reaction:

$$CuCl_2 + NO \longrightarrow CuCl_2NO$$

goes to completion only in solvents of high molecular weight. In methanol and ethanol, for example, absorption of nitric oxide is a function of cupric chloride concentration, which suggested the equilibrium:

$$CuCl_2 + NO \rightleftharpoons CuCl_2NO$$

The equilibrium constants for these reactions were measured; and an attempt to relate stability directly to the dielectric constant of the solvent was made. This is not possible, and results obtained suggested that solvation of the complex might take place, and that stability was a function of both dielectric constant and solvent molecule size.

This thesis is presented in continuation of the work of Dr. R. T. M. Fraser in order to:

1) Make a further study of the behaviour of the cupric chloride nitrosyl in methanol.

2) To investigate the possibility of preparing further nitrosyl complexes of cupric salts.

3) To investigate the nitrosyl complex of o-hydroxy benzylamine copper (II).

4) To detect, and determine, the degree of solvation (if any).

5) To isolate and analyse the solid state.

Acknowledgments:

I should like to thank Dr. R. T. H. Fraser for his many helpful discussions, and encouragment throughout.

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ABSTRACT

The reaction between cupric chloride and nitric oxide in methanol has been studied by measuring the absorption of nitric oxide per mole copper as a function of initial cupric chloride concentration. The results were interpreted by the equilibria:

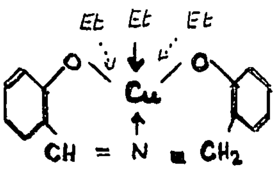
$$CuCl_2 + NO \rightleftharpoons CuCl_2NO$$

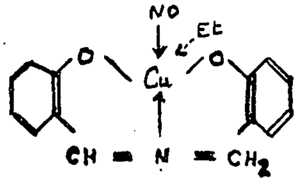
$$CuCl_2NO \rightleftharpoons CuCl_2^- + NO^+$$

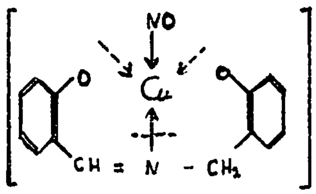
$$NO^+ + CH_3OH \rightleftharpoons CH_3NO_2 + H^+$$

Over the concentration range 0.016 - 0.2 M, dissociation of the nitrosyl to NO-containing species is estimated to be 85%. As the concentration is decreased further, this dissociation tends to completion.

The nitrosyl of salicylal o-hydroxybenzylamine copper (II) was prepared, and the number of molecules of associated solvent determined by the mole ratio method.







The nitrosyl complexes of cupric iodide, cyanide, thiocyanate and pyridine thiocyanate have been prepared

in solution. The nitrosyls of cupric iodide, cyanide and thiocyanate are extremely unstable, with a life-time of the order of two minutes. The nitrosyl of cupric pyridine thiocyanate is stable in solution for several hours. Spectrophotometric evidence is presented for their existence. Further investigations covered cupric nitrate, hydroxide, iodate, salicyaldoximate and dithio-oxamide. None of these compounds were observed to form nitrosyls.

Consideration of the conditions under which nitrosyls may be formed has led to the suggestion that NO requires to be able to attain the fourth co-planar position.

The solid nitrosyls of cupric bromide and chloride have been isolated by precipitation with petroleum ether. On drying, the solid loses associated solvent, and it is suggested that dimerisation could be expected to $(CuCl_2NO)_2$. Analysis of the solid shows that it may be isolated with one molecule of solvent attached.

Solvation determination by I.R. spectra on $CuCl_2NO$ shows that one molecule of solvent is attached, with some indication of a second less strongly held.

INTRODUCTION

The first mention of nitrosyl complexes with cupric halides appeared in 1904, in a paper by V. Kohlschütter and M. Kutscheroff.[1] They were investigating the electrolysis of cupric chloride solutions, in concentrated hydrochloric acid, according to the reaction:

$$CuCl_4^{--} \rightleftharpoons CuCl_3^{-} + Cl^{-} \rightleftharpoons CuCl_2 + 2Cl^{-} \rightleftharpoons$$
$$CuCl^{+} + 3Cl^{-} \rightleftharpoons Cu^{2+} + 4Cl^{-}$$

These complex ions decompose, in the order shown, with increasing dilution. The authors sought to estimate the quantity of $CuCl_4^{--}$ present by reaction with nitric oxide.

The quantity of nitric oxide absorbed was not very great, and decreased rapidly with dilution. The green solutions became dark and opaque. However, the predominant absorption was not observed in the region expected, namely when the complex negative ions were present, as indicated by the abnormal migration of copper to the anode. It ceased before normal dissociation was observed, passing through a maximum value; at this intermediate stage the solution became a deep blue-violet colour. The conductivity measurements were of the same order before and after absorption; but fell slightly after absorption had taken place. In the light of present knowledge, nitric oxide reacts with the covalent cupric chloride molecule, to form a neutral violet complex, as the fore-going evidence does actually indicate.

The deep violet colouration was observed in alcoholic solvents e.g. methanol and ethanol; also in acetone, glacial acetic and formic acids. A similar colouration was given by cupric bromide in ethanol. Again, the absorption of nitric oxide is reported as being a function of the concentration of the cupric salt, increasing on dilution. Electrolysis of these solutions seemed to indicate that nitric oxide was being absorbed by a complex ion; the purple colour moved towards the anode. In alcoholic solutions, the specific conductivity, which was of the order of 5 x 10^{-4} ohms^{-1} $\mathrm{cm.}^{-1}$, increased slightly after absorption. Kohlschütter explained his results on the basis of the equilibrium:

$$(CuCl_4)Cu \rightleftharpoons CuCl_4^{--} + Cu^{++}$$

$$+$$

$$NO \rightleftharpoons (NO)_x(CuCl_4^{--})_y$$

However, in formic acid, the specific conductivity drops after absorption; and the red-violet colour of the complex migrates to the cathode. Kohlschütter considered that the predominant ion reacting in this instance was $CuCl^+$.

He concluded: that the blue solutions, containing Cu^{2+} ions never absorb nitric oxide; and that the brown or green solutions, containing complex ions, do absorb nitric oxide; and that the nitric oxide is attached either to the anion or cation as a complex ion. On exposure to air, or dilution with water, the reaction is reversed, nitric oxide is regenerated, and the solutions are indistinguishable from the original. No solid cupric salt undergoes reaction with nitric oxide.

It is difficult to obtain any useful quantitative information from this paper, as the authors have omitted to state the temperature, at which their results were taken; or, although aware of the effect of water in decomposing the complex formed, have made no reference to any attempt to dry, or even purify their solvents. Furthermore, there is no mention of any correction for the amount of nitric oxide absorbed by the solvent.

Further work on nitrosyl complexes was by W. Manchot[3] in 1910, who set out to determine quantitatively the amount of nitric oxide taken up per mole copper; he worked first with solutions of cupric sulphate in concentrated sulphuric acid, and found that formation of the complex commenced at 73.8%, and at 97.6%, one mole of nitric oxide per mole copper was absorbed. This amount cannot be increased, either by increasing the acid strength, or by variation with pressure.

Temperature 0°C			
Molarity $CuSO_4$	Moles NO per mole Cu	Pressure mms.	% Acid
0.0058-0.0265	1 - 0.96	752	97.6
0.0179	0.99	1603	97.6
0.175	1.0	329	97.6
0.0266	0.063	759	88.0
0.0241	0.75	752	90.0

On repeating the earlier measurements made on solutions of cupric chloride in ethanol, Manchot was unable to attain this limit, except by using increased pressure. He decided that this could probably be accounted for by the sensitivity of the complex to water, and that the water content of the crystalline compound employed had become important. We are unable, however, to obtain anhydrous cupric chloride pure, but concluded that the limiting amount of nitric oxide absorbed would again, by analogy, be one mole per mole copper. The results obtained are shown in Figs. 1 and 2.

Other solvents were employed, and the highest value obtained was in ethyl acetate, where the absorption was 0.893 moles NO per mole copper at 0°C. In acetone, no discernible limit was reached.

Manchot attempted to isolate the solid complex, by treating the alcoholic solution with toluene. Pale-blue oily drops separated, followed by solid masses. These decomposed so quickly that an investigation was not possible.

The conclusion, which is essentially correct, was that: one mole of nitric oxide combines with one mole of cupric salt, in various solvents, to form a somewhat dissociated compound. This dissociation is considerably increased by the presence of water. On adding sulphuric acid to the aqueous solution, the dissociation is suppressed in proportion to this addition, and is prevented completely in 97.6% sulphuric acid. This may also be taken to indicate that the acid molecule forms a constituent of the complex.

Manchot[3] continued his work, with the publication in 1914, of a paper in which he investigated whether this reaction of cupric chloride and bromide is a general characteristic of cupric salts. A wide series of salts was investigated, including the fluoride, nitrate, acetate,

Figure 1

EFFECT OF WATER ON ABSORPTION OF NITRIC OXIDE

BY $CuCl_2 \cdot 2H_2O$ IN ETHANOL[a]

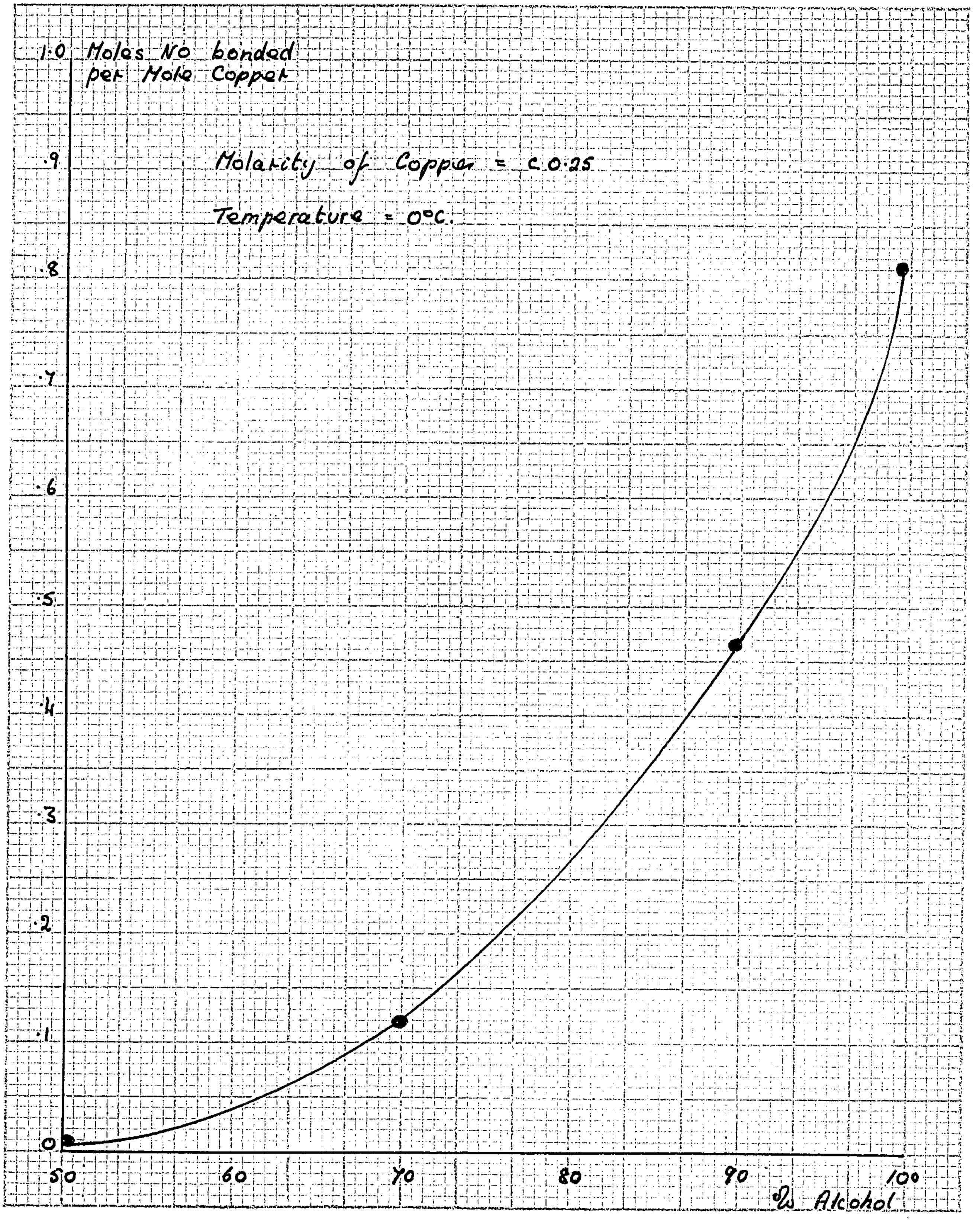
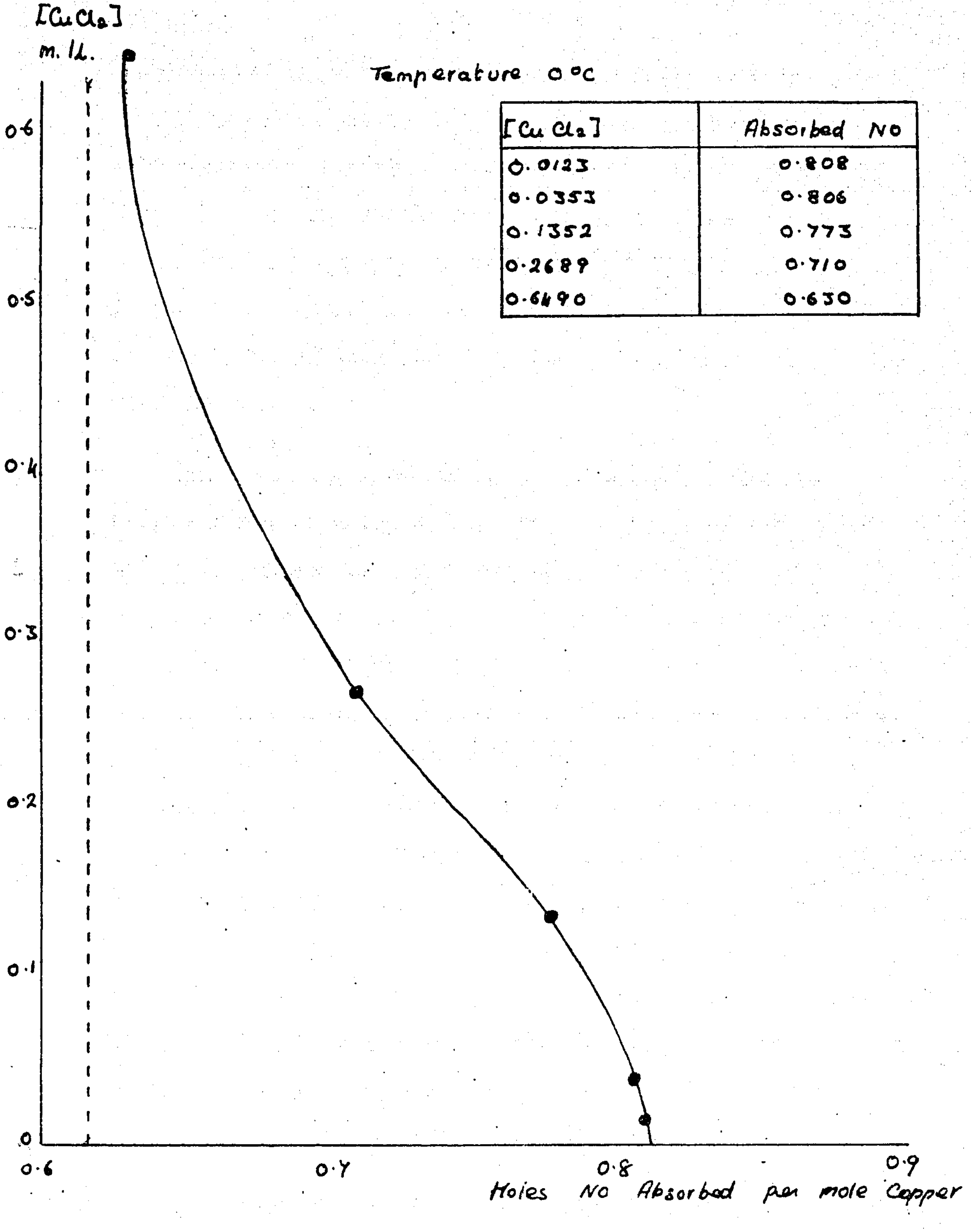

1·0
Moles NO bonded per Mole Copper
·9
·8
·7
·6
·5
·4
·3
·2
·1
0
50
60
70
80
90
100
% Alcohol
Molarity of Copper = c 0·25
Temperature = 0°C.

Figure 2

VARIATION OF NITRIC OXIDE ABSORPTION
WITH CONCENTRATION BY $CuCl_2 \cdot 2H_2O$ IN ETHANOL[2]



$[CuCl_2]$	Absorbed NO
0.0123	0.808
0.0353	0.806
0.1352	0.773
0.2689	0.710
0.6490	0.630

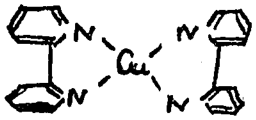
tartrate, benzoate and formate. In no case were these salts observed to form a compound with nitric oxide. This could be due to the insolubility of the salts in alcohol, and the sensitivity of the nitrosyl to traces of water; but appears surprising, particularly in the first case. Complete dehydration of the alcohol by the addition of anhydrous sodium sulphate did not alter the results.

The quantitative addition of nitric oxide to cupric bromide indicated a maximum value of one mole of nitric oxide per mole copper is attained. At atmospheric pressure, the reaction is virtually complete over the concentration range 5 x 10^{-3} – 5 x 10^{-1} moles copper. The interpretation was in the use of anhydrous cupric bromide. Manchot pointed out that the values are consistently higher than when the hydrated chloride is used, and considered that the water of crystallisation was essentially responsible for the difference in results. It will be shown later that this view is not wholly correct. The reversibility of the reaction is demonstrated by passing hydrogen through the solutions, when all the nitric oxide is given up:

$$CuX_2 + NO \rightleftharpoons CuX_2.NO$$

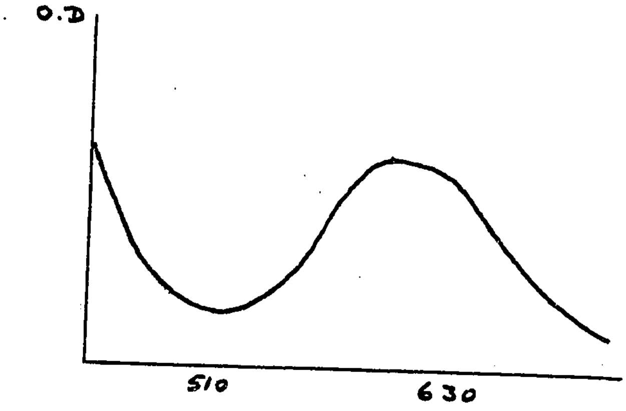
On treatment of the solutions after absorption with

$\alpha\alpha'$-dipyridyl, all the nitric oxide was driven off, and precipitation of the dipyridyl complex occurred:



Another interesting fact established by Manchot was that cupric sulphate nitrosyl in concentrated sulphuric acid – the most stable of the nitrosyl solutions – was inert to electric currents, suggesting that the largest part of the complex was present in the neutral form. Considering all these facts, he gave his opinion that addition of nitric oxide was to the whole molecule; that ionisation to nitric oxide containing ions occurred subsequently, and could be regarded as of secondary importance.

Manchot and Linkh[4] examined the absorption spectra of the nitrosyls of cupric chloride in ethyl alcohol and acetate. The absorption curves obtained were all of the same form:



and Manchot concluded that the colour was due to CuX_2NO alone, and that the solvent played no part in the composition of the complex.

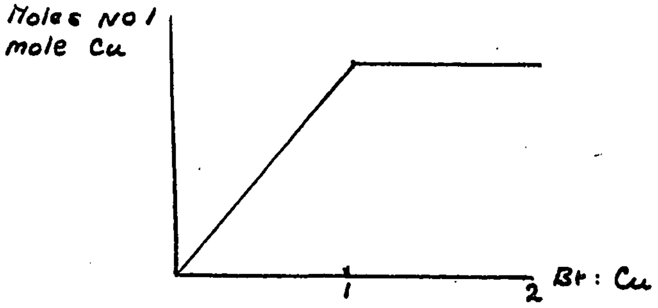
Investigations have shown that the compound formed between nitrosyl chloride and cuprous chloride gave solutions identical with those formed from cupric chloride and nitric oxide.[5] The freshly prepared sample appeared to be diamagnetic, with rapidly increasing paramagnetism, ascribed to its decomposition to cupric chloride and nitric oxide. The diamagnetism corresponds either to $CuCl_2^-NO^+$ or $CuCl_2NO$.

It is perhaps, not too surprising, in view of the apparently conclusive evidence of the ion-migration experiments[1] that the ionic nature of the complex was accepted. Measurements[6] on what was assumed to be the ion $Cu(C_2H_5OH)_3NO^{2+}$ showed that its solution in ethanol was diamagnetic. The solvation factor of three was based on no measured evidence, but simply inferred by analogy with aqueous copper complexes. An unsuccessful attempt was made to relate the variation in absorption of nitric oxide, by cupric chloride, in ethanol, to pressure. While variation in pressure should have some effect on the equilibrium position, it is possible that traces of water have a far greater effect on lowering the absorption of nitric oxide.

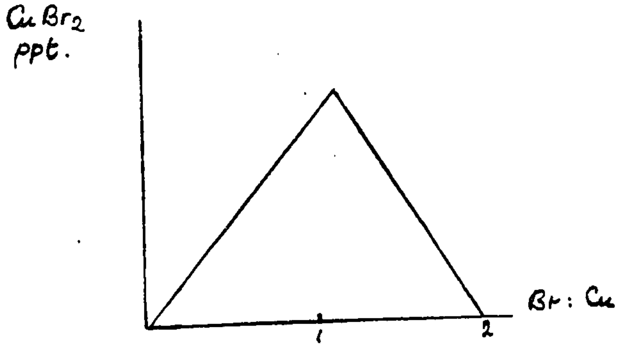
The most striking feature of the early work is probably the remarkable lack of agreement on the quantity of nitric oxide absorbed per mole copper. Kohlschütter had reported values varying from 0.5 to 3.6 for the NO:Cu ratio. And in spite of Manchot's more careful measurements, the extraordinary value of 3.6 was accepted, apparently uncritically, by Sidgewick.[7]

The stoichiometric composition of the nitrosyls was established conclusively by Fraser and Dasent[8] in 1960. The nitric oxide : copper ratio was re-determined. Measurements were made on cupric bromide in ethanol, where the ratio was constant at 1:1, and on anhydrous cupric chloride in ethanol, where the value approached a limit of 1:1 at low concentrations.

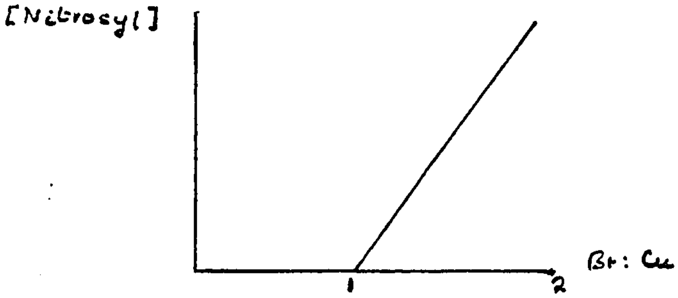
The effect of increasing the chloride:copper ratio by the addition of lithium chloride was examined. If the absorbing species was a complex cupric anion, the absorption of nitric oxide would be expected to rise above one mole per mole copper, as the halide content was increased. This was not found; the nitric oxide: copper ratio did not rise above one, even when the chloride:copper ratio was as high as twenty-seven. It is clear that the complex contains no more than two chloride ions. The possibility that the absorbing species was a complex cation, of the type $CuXNO^+$, was examined, by studying the effect of reducing the halide: copper ratio. Silver perchlorate was added to precipitate some of the bromide content as silver bromide, and the precipitate filtered off. The variation of nitric oxide absorbed with bromide:copper ratio was:



This gave the first appearance that the absorbing species in bromide solutions was $CuBrNO^+$. However, at all ratios of bromide:copper less than two, absorption of nitric oxide was accompanied by precipitation of cuprous bromide. The maximum precipitation occurred at bromide:copper = 1, and fell off linearly to zero as bromide:copper → 2.



The actual concentration of nitrosyl present was determined by measurement of the optical density at 575 mu. This was observed to fall linearly from bromide: copper = 2, and reached zero at bromide:copper = 1.



The explanation of these results was that: cupric copper in the presence of bromide in alcoholic solution is reduced by nitric oxide to insoluble cuprous bromide, and oxidation of the nitric oxide occurred, presumably to NO^+.

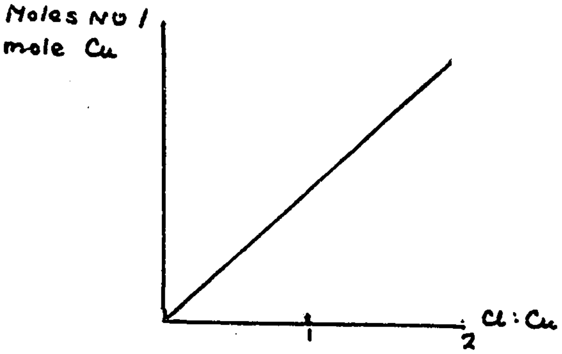
$$Cu^{2+} + Br^- + NO \rightleftharpoons CuBr + NO^+ \quad ......(1)$$

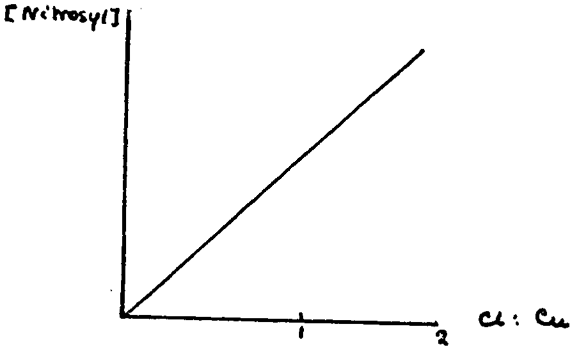
This reaction is prevented if two bromides are available, when the reaction taking place is:

$$Cu^{2+} + 2Br^- + NO \rightleftharpoons CuBr_2NO \quad ....(2)$$

The reversibility of reaction (1) was demonstrated by removing nitric oxide from solution, by passing through a stream of purified nitrogen: - the cuprous bromide immediately re-dissolved.

The behaviour of cupric chloride is different. In no case was cuprous chloride precipitated as the chloride: copper ratio was decreased. The absorption of nitric oxide fell linearly to zero from chloride:copper = 2 to chloride:copper = 0, with nitric oxide absorption.





The conclusion was that the absorbing species was covalent CuX_2 in both cases; but the chloride nitrosyl was evidently the more stable of the two, showing no tendency to decompose to the cuprous halide. Thus on the evidence produced so far, two possibilities for the structure of the nitrosyls has been presented:

i) CuX_2NO ii) $NO^+CuX_2^-$

Structure i) does not account for the conductivity of the solutions. Structure ii) does not account for the colour, as neither ion absorbs in the visible region of the spectrum.

Spectrophotometric evidence for the equilibrium

$$CuX_2NO \rightleftharpoons NO^+ + CuX_2^-$$

was presented. By decreasing the dielectric constant of the solution by adding carbon tetrachloride, it was found that a definite increase in optical density accompanied the addition, owing to the suppression of the formation of ionic species.

Because of the conflict with Kohlschütter's results the ion migration experiments were repeated. Migration of the colour does occur, and was explained by saying that the colourless ions migrate. At the anode, CuX_3^- was discharged. The neutral molecule immediately reacts with nitric oxide to form the violet nitrosyl around the anode. NO^+ is discharged at the cathode as a gas. The whole process gives an apparent colour migration towards the anode.

The continuation of this work[9] led to the determination of molecular extinction co-efficient for cupric bromide and chloride in a variety of alcoholic solvents. They were determined at a carbon tetrachloride concentration of 95%, where it was found that dissociation to ionic species was completely repressed.

Table 2 - Molecular Extinction Coefficients

	Solvent	λ max.	ε
$CuBr_2$	CH_3OH	570	1002
"	C_2H_5OH	570	1035
$CuCl_2$	CH_3OH	560	1200
"	C_2H_5OH	560	1000

The stability constants of the nitrosyls were measured in a series of alcohols. With cupric bromide, absorption of nitric oxide is complete, and the reaction to be considered is:

$$CuBr_2NO \underset{}{\overset{K_c}{\rightleftharpoons}} CuBr_2^- + NO^+$$

With cupric chloride, there is, in addition, the equilibrium:

$$CuCl_2 + NO \overset{K_f}{\rightleftharpoons} CuCl_2NO$$

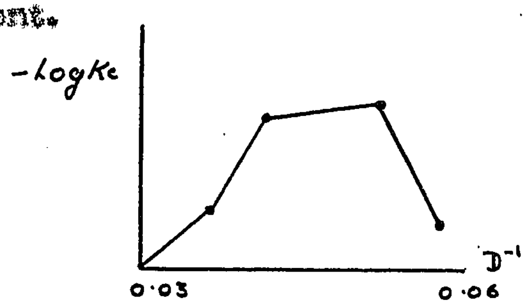
to be taken into account.

Table 3 - Values of K_c for Cupric Bromide		
Solvent	Temperature °C	K_c
Methanol	25	9.7×10^{-3}
Ethanol	20	1.88×10^{-2}
n-Propanol	25	5×10^{-4}
n-Butanol	25	2×10^{-4}
t-Butanol	25	2.2×10^{-4}

Table 4 - Values of K_f and K_c for Cupric Chloride			
Solvent	Temperature °C	K_f	K_c
Methanol	20	5.8	1.55×10^{-2}
Ethanol	22	1.18×10^{2}	6.2×10^{-3}
n-Propanol	23.4	2.3×10^{2}	2.8×10^{-5}
n-Butanol	23.4	1.9×10^{2}	2.3×10^{-5}
n-Pentanol	22	-	6.2×10^{-4}
t-Butanol	23.5	-	2.2×10^{-3}

The concentration of nitrosyl was measured spectrophotometrically. It was impossible to take readings at concentrations greater than 10^{-2} molar; and the values given above were taken in the region of 10^{-3} molar.

The Born equation, $\Delta G = (1 - 1/\varepsilon)e^2/r$, predicts that a plot of $-\ln K_c$ against the inverse of the dielectric constant should yield a straight line, if the variation in dissociation constant is due solely to the change in dielectric constant of the solvent, and provided the radii of ions formed is independent of the nature of the solvent.



Both series of nitrosyls dissociate least in n-Butanol This result could be accounted for by assuming that solvation takes place, and that the size of the alcohol molecule also affects the stability of the complex.

Consideration of these facts led to the preparation of cupric fluoride nitrosyl[10] in n-butanol. The instability of the fluoride nitrosyl may be presumed due to the instability of the CuF_3^- ion, formed by the reaction:

$$CuF_3NO + ROH \rightleftharpoons H^+ + RONO + CuF_3^-$$

The complex was stabilized by the addition of hydrofluoric acid to the solution. The absorption spectra is similar to that of the other nitrosyls. The solution of cupric fluoride nitrosyl in formic acid was quite stable. Absorption measurements gave the NO:Cu ratio 0.94 - 0.98. It would appear, therefore, that the complex is CuF_2NO.

THE BEHAVIOUR OF CUPRIC CHLORIDE NITROSYL IN ETHANOL[11]

Table 5

Temperature °C	Concentration moles per litre	$\log_{10}C$	Moles NO absorbed per mole copper
15.3	0.355	-0.450	0.638
	0.216	-0.665	0.642
	0.121	-0.917	0.677
	0.0436	-1.360	0.729
	0.0209	-1.610	0.769
	0.00436	-2.360	0.874
26.2	0.500	-0.301	0.546
	0.209	-0.680	0.584
	0.105	-0.979	0.629
	0.0288	-1.541	0.729
	0.0125	-1.903	0.842
	0.0063	-2.201	0.868
	0.00504	-2.298	0.854
	0.00416	-2.381	0.895
	0.00363	-2.440	0.896
30.0	0.0502	-1.398	0.577
	0.0240	-1.620	0.668
	0.0010	-2.000	0.779
	0.000525	-3.280	0.881

Treatment of the Data

The stability constants, determined in previous work, have depended upon the assumption that the behaviour of the nitrosyl in alcohol may be adequately described in terms of two equilibria, one for the formation of the complex:

$$CuX_2 + NO \xrightleftharpoons{K_f} CuX_2NO$$

and one for its subsequent ionisation:

$$CuX_2NO \xrightleftharpoons{K_c} CuX_2^- + NO^+$$

In case where cupric chloride is the absorbing species, and absorption of nitric oxide is not complete, it may be assumed that K_f and K_c alone are sufficient to describe the system. Then:

$$\begin{array}{ccccc} CuCl_2 & + & NO & \overset{K_f}{\rightleftharpoons} & CuCl_2NO \\ C(1-x) & & [NO] & & (1-\alpha)xC \end{array}$$

where C is the initial concentration of cupric chloride, x is the amount of nitric oxide absorbed per mole of copper salt, NO is the solubility of nitric oxide in the solvent alone; and α is the degree of ionisation of the nitrosyl.

$$\begin{array}{ccccc} CuCl_2NO & \overset{K_c}{\rightleftharpoons} & CuCl_2^- & + & NO^+ \\ (1-\alpha)xC & & \alpha xC & & \alpha xC \end{array}$$

giving:

$$K_f = \frac{(1-\alpha)x}{[NO]\,(1-x)}$$

$$K_c = \frac{\alpha^2 xC}{1-\alpha}$$

Eliminating α :

$$C = \frac{K_cK_f[NO]\,(1-x)}{\{x-K_f[NO]\,(1-x)\}^2}$$

which reduces to the form:

$$C = \frac{A(1-x)}{(Dx-B)^2}$$

where $A = K_cK_f\ NO$ $\quad B = K_f\ NO$ $\quad D = B + 1$

thus: $\log_{10}C - \log_{10}A = \log_{10}(1-x) - 2\log_{10}(Dx-B)$

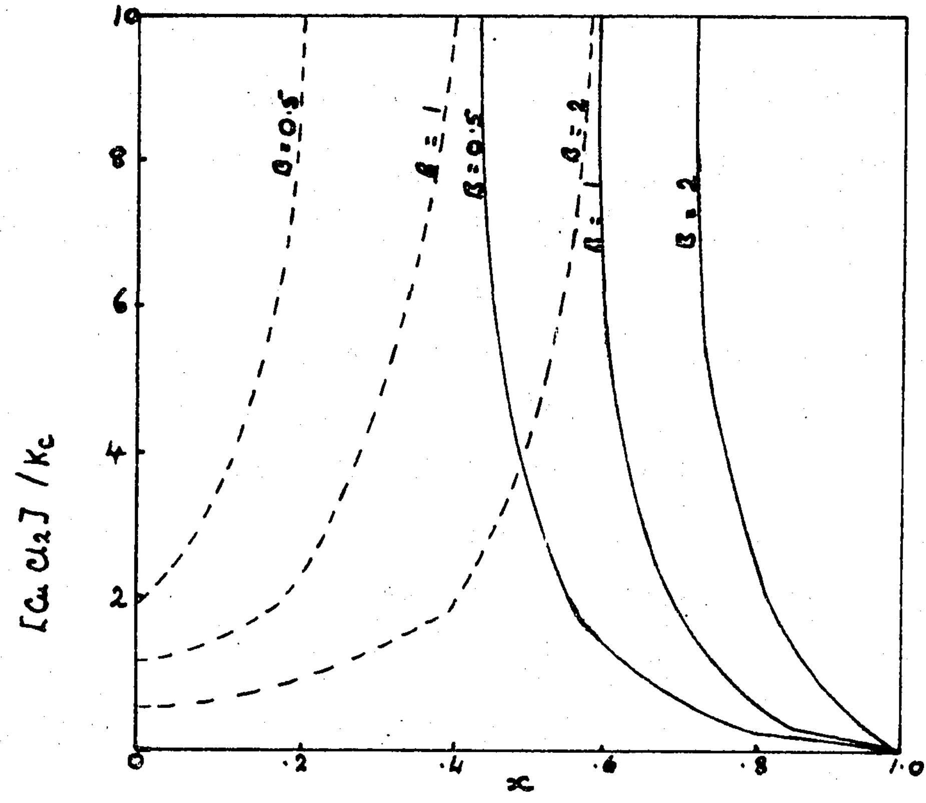
Fig. 3 shows the graph of i) C against x ii) log C - log A against x.

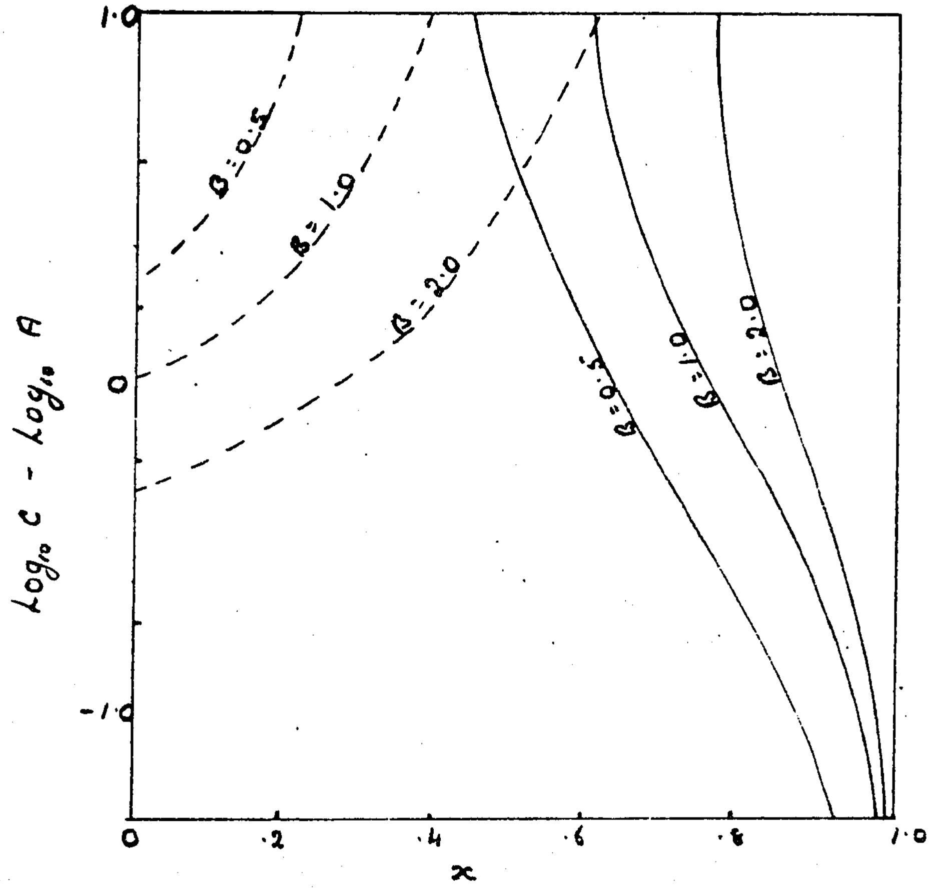
Figure 3

THEORETICAL GRAPHS DERIVED FROM THE EQUILIBRIA:

$$CuCl_2 + NO \rightleftharpoons CuCl_2NO$$

$$CuCl_2NO \rightleftharpoons CuCl_2^- + NO^+$$


[Cu Cl2] /Kc
x
0
·2
·4
·6
·8
1·0
2
4
6
8
10
B = 0·5
B = 1
B = 0·5
B = 2
B = 1
B = 2


Log10 C - Log10 A
x
0
·2
·4
·6
·8
1·0
-1·0
0
1·0
B = 0·5
B = 1·0
B = 2·0
B = 0·5
B = 1·0
B = 2·0

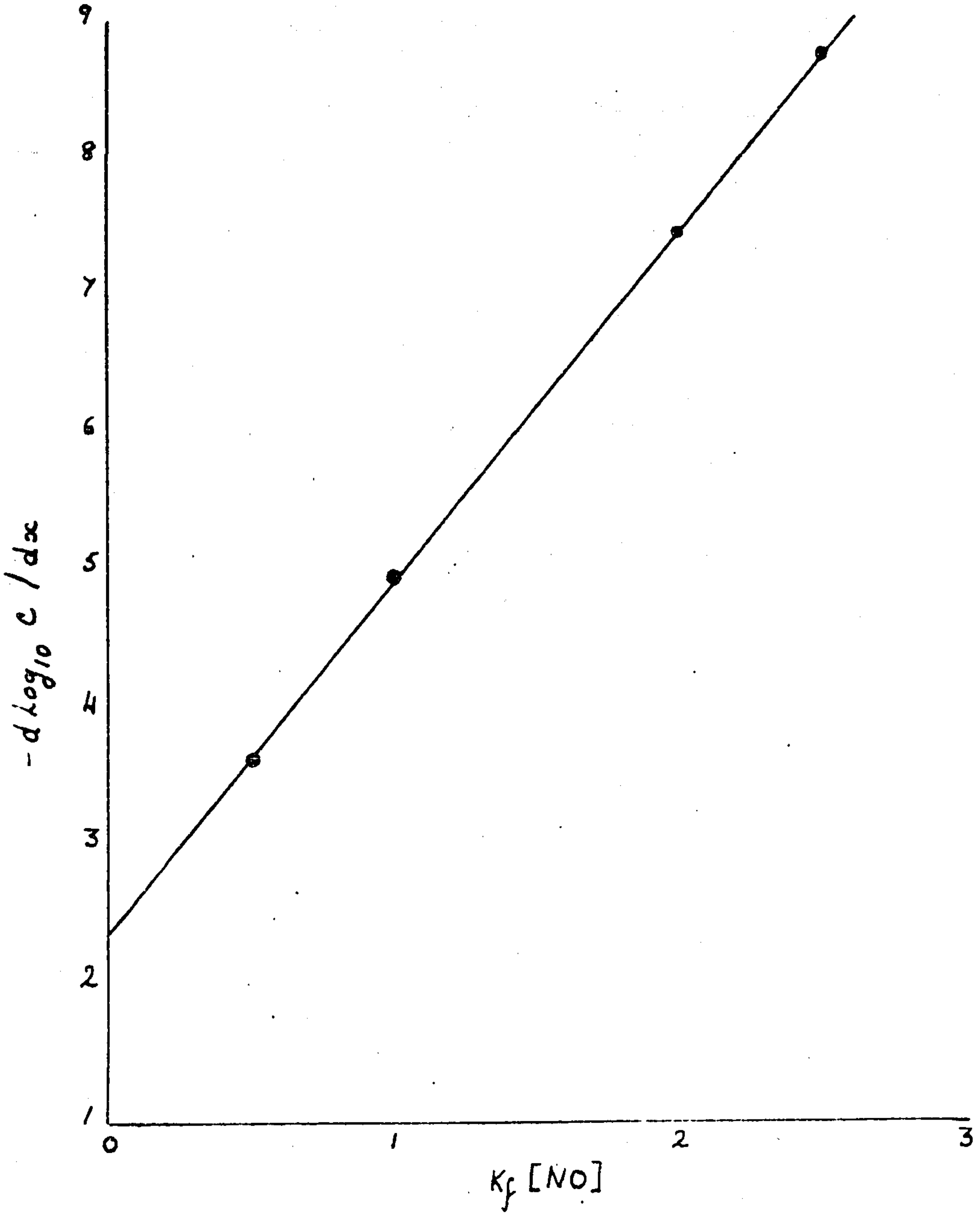
For any particular solvent at a given temperature, K_c, K_f and [NO] must all be constant, hence it should be possible to evaluate K_f and then K_c from a plot of log C against x. It is not necessary to measure the optical density in order to determine $[CuCl_2NO]$ and hence K_f and K_c; thus investigations can be extended to more concentrated solutions than has been done before. As shown in Fig. 3, the theory predicts that x has an upper limit of 1 as the cupric chloride concentration tends to zero; and tends asymptotically to a lower limit of B/D as the concentration increases. Values obtained from the negative square root would not be observed in practice. Further, over much of its length, the graph of log C against x is linear; it should, therefore, be possible to plot values of -dlog C/dx against B, and, thus, from the slope determined experimentally, obtain a value for K_f. Fig 4 shows the relation between this slope and B.

Under conditions where interaction of the nitrosonium ion with the solvent becomes important, a more complex expression is obtained:

$$\begin{array}{ccccc} CuCl_2 & + & NO & \overset{K_f}{=\!=\!=} & CuCl_2NO \\ (1-x)C & & [NO] & & x(1-\alpha)C \end{array}$$

Figure 4

CALIBRATION FOR K_f VALUES



9
8
7
6
5
4
3
2
1
0
1
2
3
$-d \log_{10} c \,/\, dx$
$K_f\,[NO]$

$$\begin{array}{ccccc} CuCl_2NO & \xrightleftharpoons{K_c} & CuCl_2^- & + & NO^+ \\ x(1-\kappa)C & & x\kappa C & & x(\kappa-\beta)C \end{array}$$

$$\begin{array}{ccccccc} NO^+ & + & ROH & \xrightleftharpoons{K_s} & H^+ & + & RNO_2 \\ x(\kappa-\beta)C & & S & & x\beta C & & \beta xC \end{array}$$

from which :

$$K_f = \frac{x(1-\kappa)}{(1-x)[NO]} \qquad \cdots\cdots\cdots\cdots\cdots (1)$$

$$K_c = \frac{x\alpha(\alpha-\beta)C}{1-\alpha} \qquad \cdots\cdots\cdots\cdots\cdots (2)$$

$$K_s = \frac{x\beta^2 C}{S(\alpha-\beta)} \qquad \cdots\cdots\cdots\cdots\cdots (3)$$

From (3):

$$x\beta^2 C = R(\alpha-\beta) \qquad \text{where } R = K_s \cdot S$$

$$\beta^2 xC + \beta R - \kappa R = 0$$

$$\text{and} \quad \beta = \frac{-R + \sqrt{R^2 + 4xC\kappa R}}{2xC}$$

Substituting in (2):

$$K_c = \frac{x\kappa C}{1-\alpha}\left[\kappa + \frac{R - \sqrt{R^2 + 4xC\alpha R}}{2xC}\right]$$

$$= \frac{\kappa}{1-\kappa}\left[\frac{2\alpha xC + R - \sqrt{R^2 + 4xC\kappa R}}{2}\right]$$

$$(R^2 + 4xC\kappa R)^{\frac{1}{2}} = R + 2\kappa xC - \left[\frac{\kappa^2 x^2 C^2}{4R}\right]$$

$$K_c = \frac{\kappa}{2(1-\kappa)} \frac{\kappa^2 x^2 C^2}{4R}$$

From (1):

$$\kappa = \frac{x - K_f[NO](1-x)}{x}$$

$$1-\kappa = \frac{K_f[NO](1-x)}{x}$$

Substituting:

$$K_c = \frac{[x - B(1-x)]^3 x^2 C^2 x}{x^3\ 2\ B(1-x)\ 4R}$$

$$C^2 = \frac{8 K_o K_f [NO] R (1-x)}{[x - K_f[NO](1-x)]^3}$$

$\log C = \frac{1}{2}\log 8 K_o K_f [NO] R + \frac{1}{2}\log (1-x) - 3/2 \log (x(1+K_f[NO]) - K_f[NO])$

The theoretical curves derived from this expression are shown in Figs. 5 and 6. It will be observed that, while it is still possible to evaluate K_f, the possibility of evaluating any further stability constant has been lost. The curves again tend asymptotically to a limiting value of R/S.

The results obtained experimentally are shown in Fig. 7. The result of plotting C against x is as predicted.

Table 6

°C	x_{lim}	R exp	Predicted Slope	Observed Slope	K_f	K_o
30.0	.38	0.6	i)2.9 ii)2.6	2.8	5 x 10	-
26.2	.37	1.5	i)5.7 ii)5.0	5.0	1×10^2	1.35×10^{-2}
16.3	.33	1.7	i)6.7 ii)5.3	6.85	1.13×10^2	5.8×10^{-3}

The last two results show very good agreement with previous values obtained on the assumption that the reaction could be expressed adequately in terms of two equilibria only. As the temperature increases, this

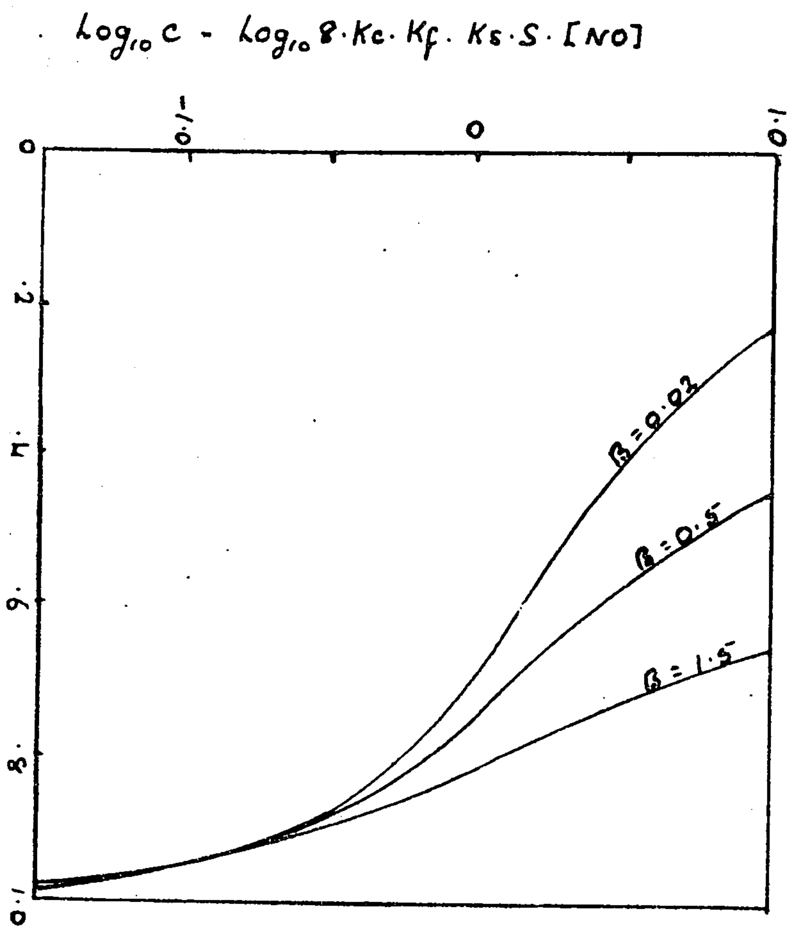
Figure 5

THEORETICAL GRAPHS DERIVED FROM THE EQUILIBRIA

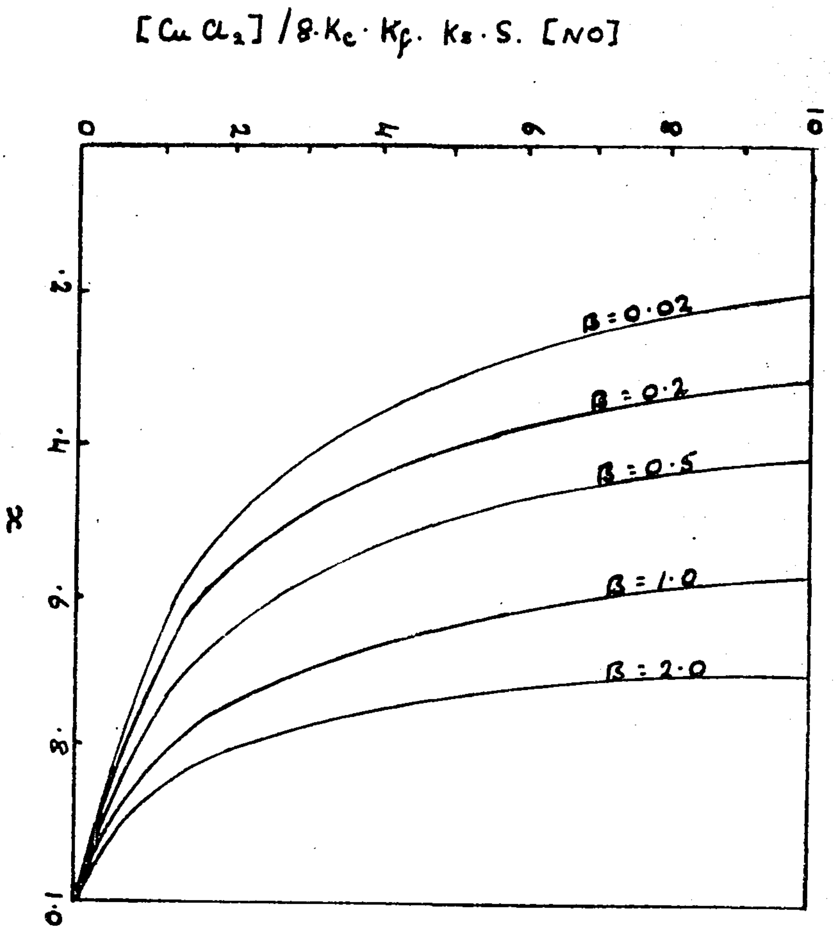
$$CuCl_2 + NO \rightleftharpoons CuCl_2NO$$

$$CuCl_2NO \rightleftharpoons CuCl_2^- + NO^+$$

$$NO^+ + ROH \rightleftharpoons H^+ + RNO_2$$



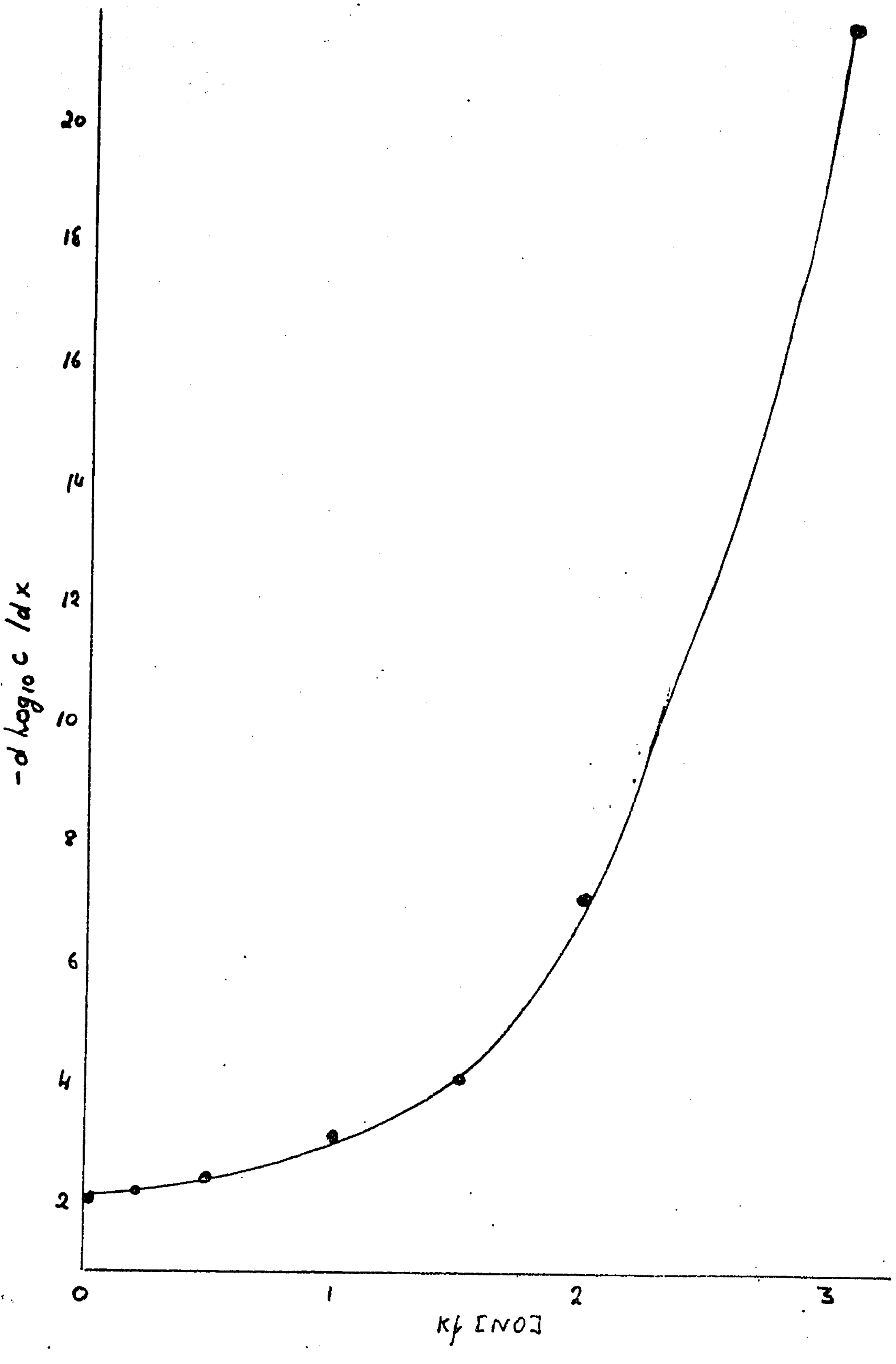
$\log_{10} C - \log_{10} 8 \cdot K_c \cdot K_f \cdot K_s \cdot S \cdot [NO]$
0
·2
·4
·6
·8
1·0
-1·0
0
1·0
B = 0·02
B = 0·5
B = 1·5



$[CuCl_2] / 8 \cdot K_c \cdot K_f \cdot K_s \cdot S \cdot [NO]$
x
·2
·4
·6
·8
1·0
0
2
4
6
8
10
B = 0·02
B = 0·2
B = 0·5
B = 1·0
B = 2·0

Figure 6

CALIBRATION FOR K_f VALUES INCLUDING SOLVENT INTERACTION



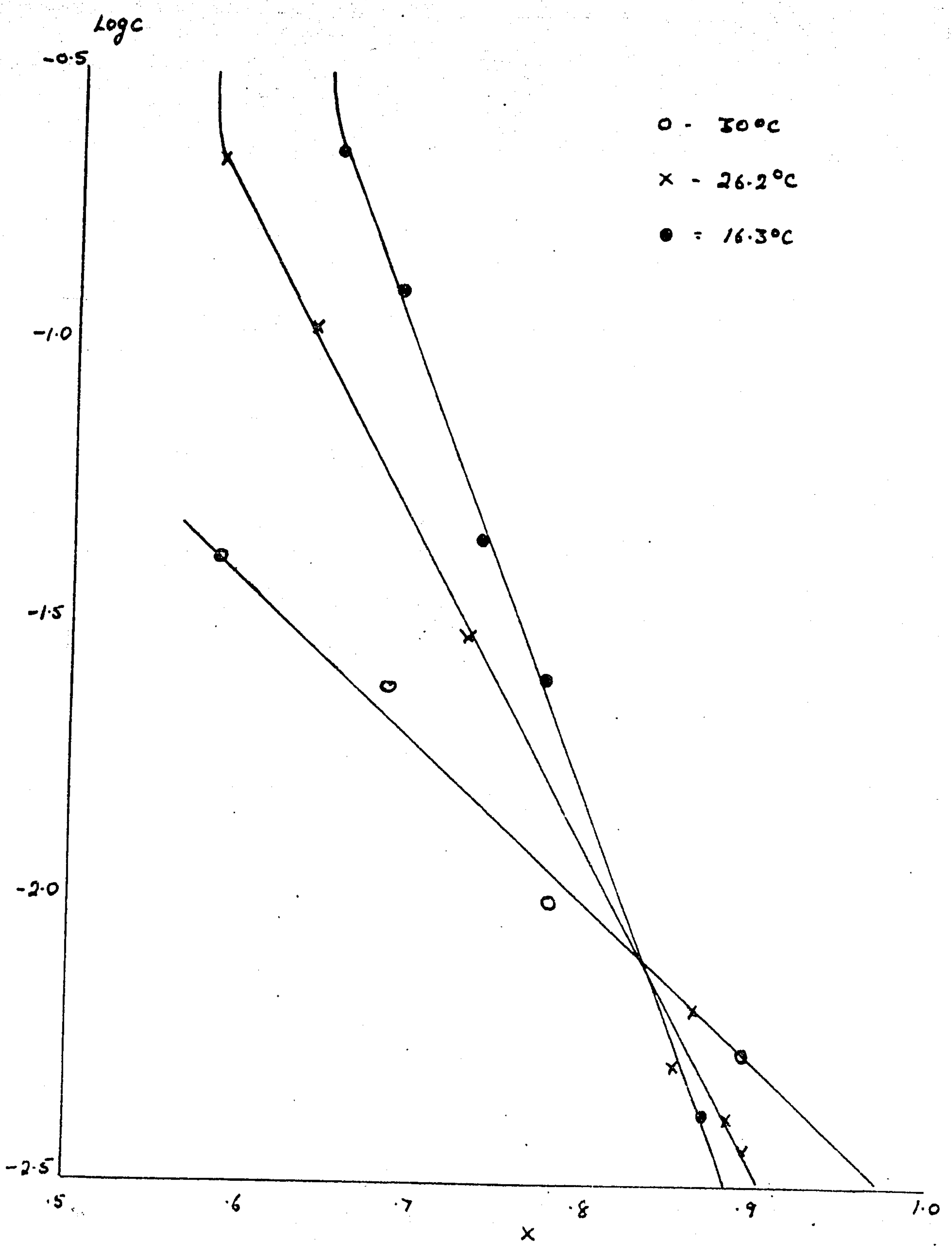
$-d\log_{10}c\ /dx$
20
18
16
14
12
10
8
6
4
2
0
1
2
3
K_f [NO]

assumption is no longer valid, and results obtained at 30.0°C indicate clearly that considerable solvent interaction with NO^+ is taking place.

Figure 7

CUPRIC CHLORIDE IN ETHANOL

Plot of log C v. x



Log c
-0.5
-1.0
-1.5
-2.0
-2.5
·5
·6
·7
·8
·9
1.0
x
o - 30°C
× - 26.2°C
● = 16.3°C

THE BEHAVIOUR OF CUPRIC CHLORIDE NITROSYL IN METHANOL.

EXPERIMENTAL.

Preparation of Anhydrous Cupric Chloride[12,13].

Fisher Grade anhydrous and hydrated cupric chloride were dehydrated by passing a stream of dry hydrogen chloride over them. The dehydrating apparatus was kept at a temperature of approximately 150°C in an atmosphere of refluxing bromobenzene. The product was stored in a vacuum dessiccator over concentrated sulphuric acid and potassium hydroxide pellets. Dry hydrogen chloride was prepared by dropping concentrated sulphuric acid into concentrated hydrochloric acid. The mixture of acids was stirred continuously throughout the addition.

Later, it was found sufficient to dry the chloride by heating to 120°C for forty-eight hours.

Analysis of Anhydrous Cupric Chloride[14]

The product was analysed in 0.2g. samples for copper and chloride.

Copper was estimated as its pyridine thiocyanate This compound was used for further investigation of nitrosyl formation (see next section)

Theoretical % Cu = 47.250   Found: 47.25 - 47.42%

Chloride was estimated by titration with silver nitrate solution, using dichlorodifluoroescein as indicator. This was prepared by dissolving 0.1g. dichlorodifluoroescein in 100 mls. 65% ethanol.

Theoretical % Cl = 52.750   Found 52.40 - 52.84%

It was observed that where cupric chloride had been dried in the oven slight traces of cuprous chloride were present, but this was not sufficient to affect the results.

Purification of Alcohols

Absolute alcohol was first refluxed with 1.5g. silver nitrate, 5g. potassium hydroxide per litre, for several hours, to remove aldehydes.

Two methods were used for the removal of water:

i) The alcohol was distilled, and refluxed with 5g. magnesium turnings, 0.5g. iodine per litre for three hours.

ii) The alcohol was distilled directly into a flask containing Drierite (calcium sulphate), and left standing for at least twenty-four hours. Drierite takes up 6.6% by weight of water, and for complete dehydration of the alcohol, an excess of 25% is required. The use of this method brought the water content down to below 0.003%.

The product was distilled directly into the 100 ml. volumetric flasks, used to make up the solutions and used immediately.

Preparation of Solutions

The anhydrous salt was transferred into a small glass specimen tube, without removing the salt from the oven. The polythene cap of the tube made a satisfactorily air-tight closure; and the tube was kept in a dessicator, while not actually being weighed. The neck of the tube fitted exactly into the opening of the volumetric flasks, and exposure of the contents to atmospheric moisture was thus kept to a minimum.

Estimation of Water Present[15]

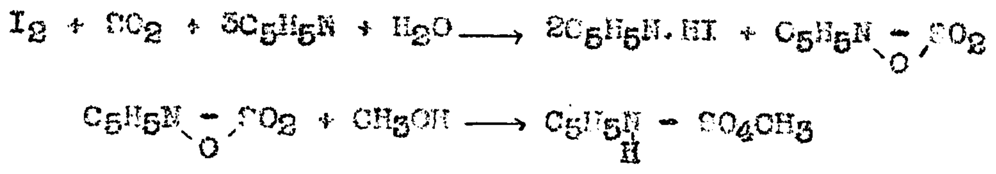
Karl Fisher reagent was used to determine the percentage of water present in the solutions used. Titrations were effected on 5 or 10 ml. portions of solution, both before and after absorption of nitric oxide had taken place. In general, there was no detectable increase in the water content in the latter case.

The reagent provided consisted of two stock solutions:

i) sulphur dioxide in pyridine

ii) iodine in methanol

For use, i) was added to ii), and the mixture left standing overnight. The reagent was standardised against a 'standard water solution' containing a weighed quantity of water. The solvent was absolute methanol, dried with Drierite, containing e.g. 7.5818(2)g. water in 500 mls. methanol. As the reagent gradually decomposes, the standardisation was repeated daily. The reaction taking place may be represented as:



$$I_2 + SO_2 + 3C_5H_5N + H_2O \longrightarrow 2C_5H_5N.HI + C_5H_5N\underset{O}{-}SO_2$$

$$C_5H_5N\underset{O}{-}SO_2 + CH_3OH \longrightarrow C_5H_5\underset{H}{N} - SO_4CH_3$$

The end-point was detected visually, by the first appearance of unused iodine. The titrations were carried out in a closed system, protected from atmospheric moisture by calcium chloride drying tubes.

Preparation of Nitric Oxide[16]

$$2NaNO_2 + 2FeSO_4 + 3H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + 2NaHSO_4 + 2H_2O + 2\ NO$$

Two stock solutions were made up:

i) 278g. $FeSO_4.7H_2O$ + 55 mls. 36N H_2SO_4 per Litre.

Nitric oxide was produced by mixing equal volumes of these two solutions. Generation of the gas was slow, however, on adding 1g. calcium sulphate per 25 ml. solution to ii) before mixing, evolution of the gas was almost instantaneous.

Preferably, nitric oxide was obtained from a cylinder supplied by the Matheson Co., Inc. New Jersey.

APPARATUS

Description of the Absorption Apparatus (Fig. 8)

The gas absorption apparatus consisted of three sections:

i) Source of nitric oxide - resevoir (A,B) and purifying tubes (C,D)

ii) The gas burette (R,S,T)

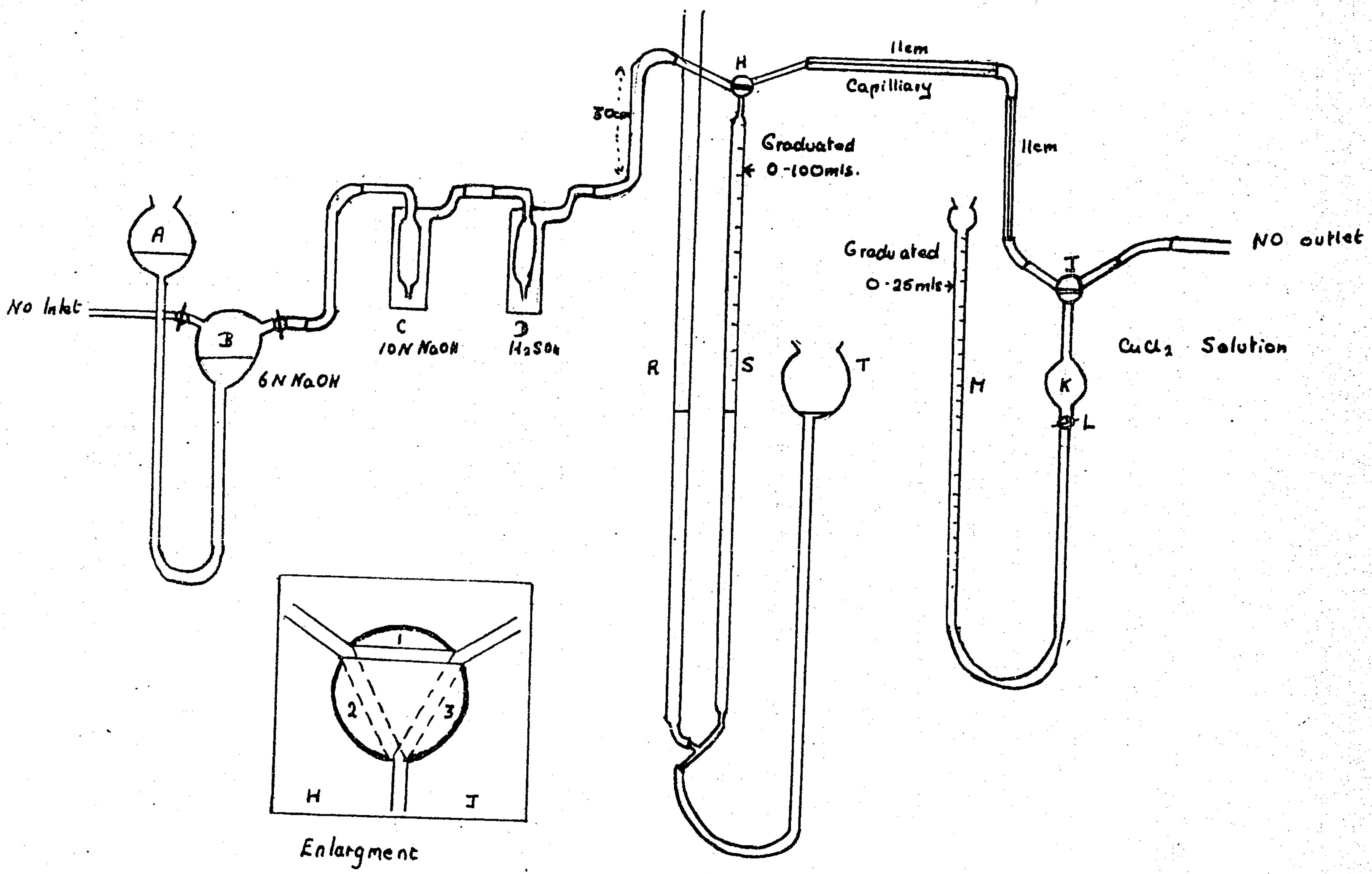
iii) The absorption bulb and burette (K,M)

Nitric oxide was stored in the flask B. The volume of gas in this resevoir could be varied by raising or lowering the forcing bulb C, containing 6N sodium hydroxide solution, which also served as an absorbent for any acidic oxides of nitrogen. The nitric oxide was then passed through a bubbler C, containing 10N sodium hydroxide solution, coloured with a few drops of universal indicator; next, through a second bubbler D, containing concentrated sulphuric acid. These solutions were changed frequently - the solution in (A,B) was changed every four weeks; the sodium hydroxide in C was changed when the indicator showed a pH of about 8; the sulphuric acid in D was changed after every twenty-five absorptions, or once a week.

In order to reduce the possibility of acid spray

Figure 8

GAS ABSORPTION APPARATUS


11cm
H
Capilliary
30cm
Graduated
0-100mls.
11cm
A
No Inlet
B
6N NaOH
C
10N NaOH
D
H_2SO_4
R
S
T
Graduated
0-25mls
M
NO outlet
I
$CuCl_2$ Solution
K
L
1
2
3
H
I
Enlargment

being carried over into G, the inlet to H was set about 30 cm. above the outlet of the bubbler D.

The gas burette G was calibrated in 0.1 ml. from 0.04 - 100 ml. (0.74 cm. length = 1.00 ml.). All connections were made of polythene, heat-sealed to the glass, and bound with wire; giving a perfectly gas-tight flexible joint. The taps were greased with Apiezon Regd. grease. Connection between the two high vacuum, three-way taps H and J, was by means of two lengths of capilliary glass tubing, each 11 cm. long; flexibility was ensured by three short links of polythene tube.

The thermostat surrounding the bulb Z consisted of a 1-litre beaker containing a brass ring. The temperature of the ring was under remote control from a colora ultra-thermostat. In order to maintain temperatures more than 5 °C below room-temperature, the beaker was replaced by a 2-litre double-walled vacuum flask. The temperature of this thermostat was continuously monitored by means of a Y.S.I. 80 Recorder, connected to a Telethermometer fitted with a stainless steel probe. Manual adjustment of the temperature of the circulating water kept the variation of the temperature of the reactants below ± 0.25°C, Stirring was supplied by means of a jet of nitrogen.

Purification of Mercury[17]

Impurities were removed by allowing the mercury to run in a fine stream, through a long length of glass tubing, containing 10% nitric acid. The process was repeated a second time; and the mercury finally passed through a column of water. The mercury was dried; and dust removed by passing it through a folded filter-paper, with a pin-hole in the apex.

Operation of the Apparatus

The mercury resevoir T was raised until the gas-burette filled with mercury to H, which was then turned to connect C with J. On lowering T, any residual gas in the burette collected below H could be simply removed. At the commencement of a series of experiments a slow stream of nitric oxide was passed into the system; the gas burette was filled and emptied several times to remove traces of air. Subsequently, an atmosphere of nitric oxide was maintained in the apparatus.

To perform an absorption:- a stream of warm air, dried by passing through a tube containing calcium chloride, was sucked through H and K. This was accomplished by connecting J to a vacuum pump; and was continued until both M and K were completely dry, and free from traces of nitric oxides.

The tap J was closed, the solution under test poured into M; the tap opened until K was filled to the level of J; and then both J and L (the tap at the bottom of K) closed. F was connected by H through J to the outlet, T was raised until the gas burette filled with mercury, then H rotated to connect D to the outlet Nitric oxide was passed through the system to remove any traces of alcohol vapour from the capilliary tubes; then H was turned to connect F to D, and the reservoir lowered so that F filled with nitric oxide. To ensure that this enclosed volume of gas was at atmospheric pressure, the tap H was rotated to connect F momentarily to the atmosphere. H was then turned to connect D with the outlet, and more nitric oxide passed through to ensure only this gas remained between F and J. H and J were then shut; readings of F, K, temperature in E and T, and barometric pressure were noted. T was raised about ten centimetres, tap H opened to connect F to J, J opened to link F to K, and L opened, so that about 10 - 15 mls. of solution ran back into M. L was closed, and the new reading in F noted. H was then further isolated from the system by a screw-clip. As absorption proceeded, K was placed in the thermostat, removed every five minutes for shaking, replaced, and, if necessary, the mercury levels in E and G were adjusted. Throughout the absorption, the pressure of nitric oxide in G was kept at about five centimetres above atmospheric pressure. Otherwise, the test solution tended to suck back through J. After absorption was complete, the pressure in G was adjusted to atmospheric, the bulb shaken to allow any excess nitric oxide in the solvent to adjust to the slight pressure change. The barometric pressure, the temperature in K and G, and the volume remaining in G were read.

The volume of nitric oxide absorbed by the solution was calculated from the expression:

$$V = \frac{273}{760}\left[\frac{y \cdot P_1}{T_1} - \left\{\frac{z \cdot (P_2 - f)}{T_2} + \frac{x(P_2 - f')}{T_{th}}\right\}\right]$$

where: y - volume of gas in G at start, at T_1°A and P_1mm. pressure.

z - volume of gas in G at end, at T_2°A and P_2 mm. pressure.

f - vapour pressure of the solvent at T_2°

f'- " " " at the thermostat temperature.

x - volume of solution was run out of K.

T_1 and T_2, the temperature in the gas burette at the beginning and end of the absorption respectively, were determined by taking the average of the temperatures in R and T - the mercury levelling tubes.

Preliminary Determinations

i) The volume of the bulb K was measured between the taps L and J, by filling it with mercury and weighing.

Result: volume of K = 55.26 mls.

ii) As a check of the measuring system, a mass of gas was enclosed in the gas burette; its volume at atmospheric pressure and room temperature noted. The pressure was then increased by 10 - 20 cm. mercury, and the system left for twelve hours. Checks were made from S to J, and from S to B. The apparatus appeared to be perfectly gas-tight throughout.

iii) The dead spaces between the zero graduation of the gas burette and the tap H; and between H and J were determined by enclosing a mass of gas in the burette and measuring its volume at different pressures, both above and below atmospheric pressure, by raising or lowering the measuring tube.

From the set of equations: $P(V+x) = P'(V'+x)$, where P and P' were the pressures, V and V' the volumes read off the gas-burette, the value of x, the particular dead space being measured, was determined. The total dead space was of the order of 3 mls.

iv) A series of determinations made on the rate of absorption of nitric oxide by the solvent or solution, showed that, in all cases, uptake of nitric oxide proceeded rapidly during the first twenty minutes; and that the reaction was always complete within ninety minutes.

v) Effect of Dissolved Salts on the Vapour Pressure of the Solvent

Since the vapour pressure of the solvent, both at the temperature of the gas-burette, and of the thermostat, occurs in the formula for the quantity of nitric oxide absorbed; an estimate was made of the effect of the dissolved copper salt on the lowering of the vapour pressure.

The solutions used were 0.001M - 0,2M

Raoult's law: $$\frac{P_o - P}{P_o} = x$$

where $P_o - P$ is the lowering of the vapour pressure; and P_o the vapour pressure of the solvent, at the temperature considered, x - is the mole fraction of copper salt in solution.

In a 0.2M solution, it may be seen that the lowering of vapour pressure is of the order:

$$1.2 \times 10^{-2} p_o$$

vi) <u>Effect of Dissolved Salts on the Solubility of Nitric Oxide in the Solvent</u>

No correction was made for this effect. It becomes significant only at concentrations of cupric salts greater than 0.25M, which is outside the region considered.

MEASUREMENT OF ABSORPTION SPECTRA[10]

Since the usual silica cells could not be filled with nitrosyl solutions without exposure to air, and nitric oxide could not be bubbled through easily, a special cell was used. It was constructed from precision rectangular-bore borosilicate glass-tubing, approximately 1 cm. square; and fitted with a standard 19/38 taper socket, so that various bubbling heads could be used. The dimensions of the cell are shown in Fig. 9.

When spectrophotometric measurements were taken in conjunction with absorption measurements on the gas-line, the nitrosyl solution was forced, under an atmosphere of nitric oxide, from the bulb K into the cell, after the reaction was complete. Nitrosyls could also be prepared directly in the cell. Two types of bubbling head were used: Fig. 9.

a) was used for general preparative work.

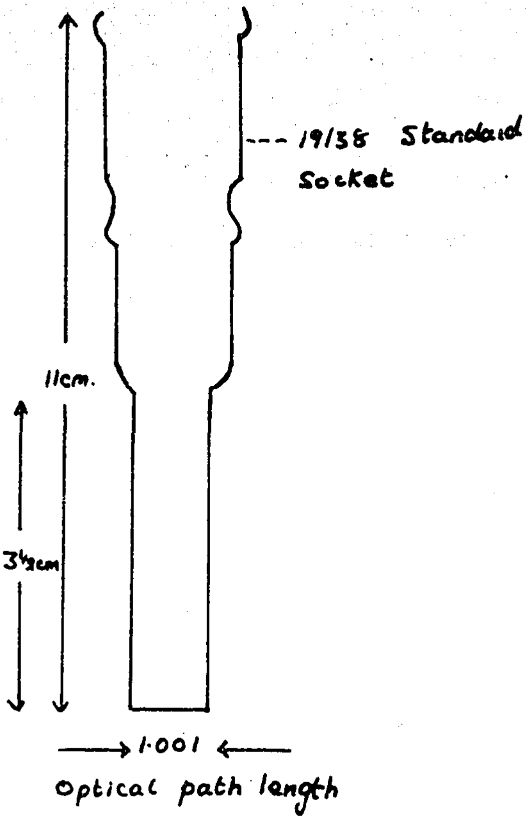
b) incorporated a thermistor (Yellow Springs Instrument Co., Inc. Probe no. 404) and was used for quantitative measurements, where the solution temperature was monitored throughout the spectrophotometric readings.

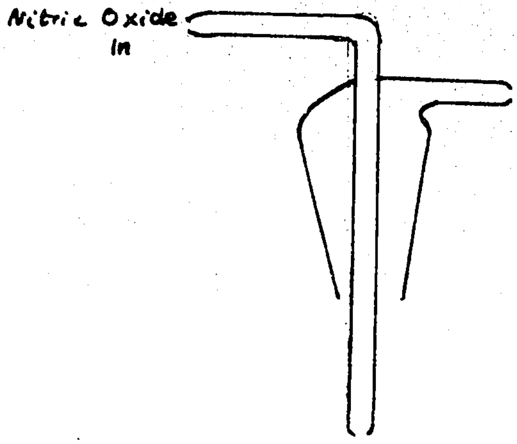
The spectra were determined on a Beckman DK2

Figure 9

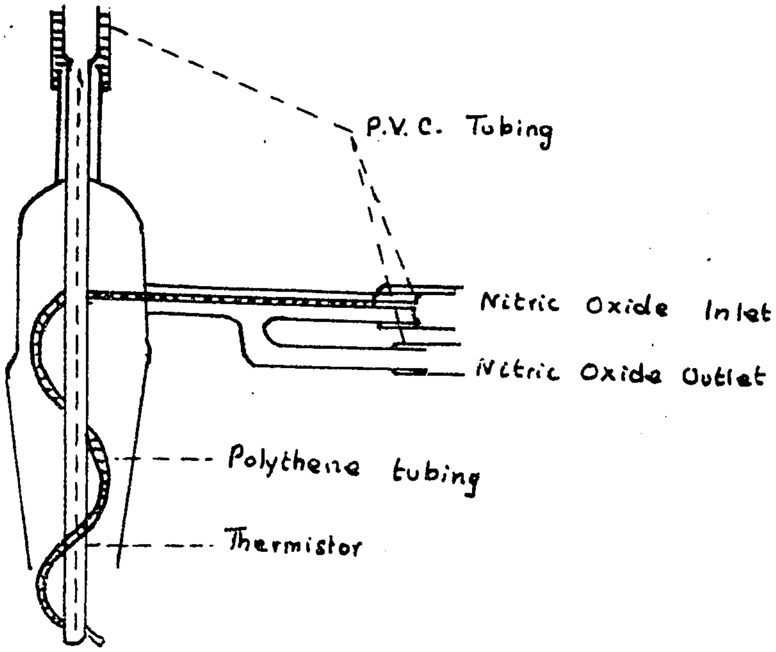
CELL AND BUBBLING HEADS USED IN

DETERMINATION OF ABSORPTION SPECTRA





Bubbling head (a)



Bubbling head (b)

Recording Spectraphotometer. The quantitative determinations on cupric chloride nitrosyl in methanol were taken on a Perkin-Elmer 350 Spectrophotometer. The solutions of chloride nitrosyl are reasonably stable; no change in the quantitative values of the absorption spectra were observed, when the solutions were kept in the cell, for periods of up to twenty minutes.

RESULTS AND DISCUSSION

Calculation of Vapour Pressure

For substitution as f and f' in the formula for the volume of nitric oxide absorbed, vapour pressures were calculated from the expression:

$$\log_{10}P = \frac{-0.05223a}{T^{\circ}A} + b$$

For methanol: a = 38,324 b = 8.8017

Solubility of Nitric Oxide in the Solvent

Absorption measurements on the purified solvent were carried out at temperatures ranging from 8 - 45°C.

Table 7

Temperature	Mls. NO per 100 mls. Solvent
8	54.96
14	49.97
20	45.92
26.8	42.78
35	35.59
45	32.27

Calculation of Results

Sample calculation - readings taken:-

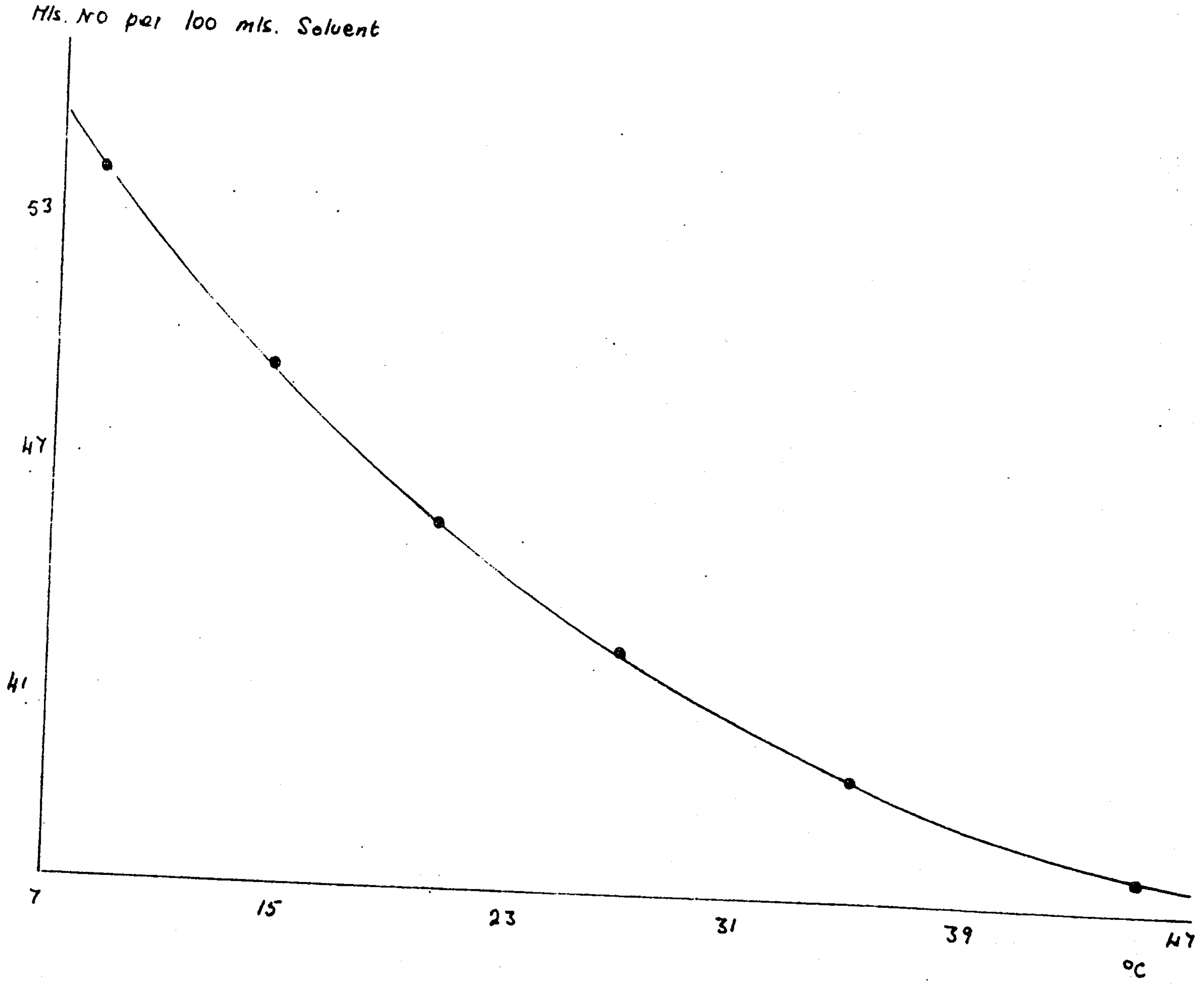
Molarity of cupric chloride solution = 0.1693

Dead space volume between S and J = 2.86 mls.

Level in S: initial - 90.40 final - 24.48

Figure 10

SOLUBILITY OF NITRIC OXIDE IN METHANOL


Mls. NO per 100 mls. Solvent
53
47
41
7
15
23
31
39
47
°C

Level in M: initial 18.21 final 1.22

Temperature in S: 24.9°C 24.9°C

Barometric pressure 747.9mm. 747.1mm.

Thermostat: 25.0°C throughout

Vapour pressure of solution: 121.9 at 24.9°C

122.5 25.0°C

Volume of gas absorbed at N.T.P. =

$$\frac{273.1}{760}\left\{\frac{(90.40+2.86)\times747.9}{273.1+24.9}-\left\{\frac{(24.48)(747.1-121.9)}{273.1+24.9}+\frac{(18.21-1.22)(747.1-122.5)}{273.1+25.0}\right\}\right\}$$

$$\frac{273.1}{760}\left\{\frac{93.26\times747.9}{298.0}-\left\{\frac{27.34\times625.2}{298.0}+\frac{16.99\times622.1}{298.1}\right\}\right\}$$

$$\frac{273.1}{760}\left(234.1-(57.36+35.48)\right)$$

$$\frac{273.1\times141.3}{760}$$

Volume of solution absorbing this =

Volume of bulb K - amount run into M

55.26 - 16.99 = 38.27

Mls. NO absorbed per 100 mls. solution:

$$\frac{273.1\times141.3\times100}{760\times38.27}=132.6$$

Mls. NO absorbed per 100 mls. solvent = 43.4 mls. at 25°C

∴ Mls. NO absorbed by copper salt = 89.2

$$\text{Moles NO absorbed per mole copper} = \frac{89.2}{0.1693\times10^{2}\times22.41}$$

$$= 0.23(5)$$

The initial investigation was carried out on solutions where copper concentration varied from 0.01 - 0.2M. Reproducibility was not good. There are two reasons for this: i) the low value of nitric oxide absorbed by the copper salt ii) extreme sensitivity to traces of water. The latter is by far the more important. Titration by Karl Fisher reagent showed the water content was 0.2 - 0.3%. Fig. 11 shows the plots of C against x - c is the initial concentration of cupric chloride and x is the total quantity of nitric oxide absorbed by the salt. In this case the points showed a general tendency to drift towards zero as C decreases.

Table 8 (i)

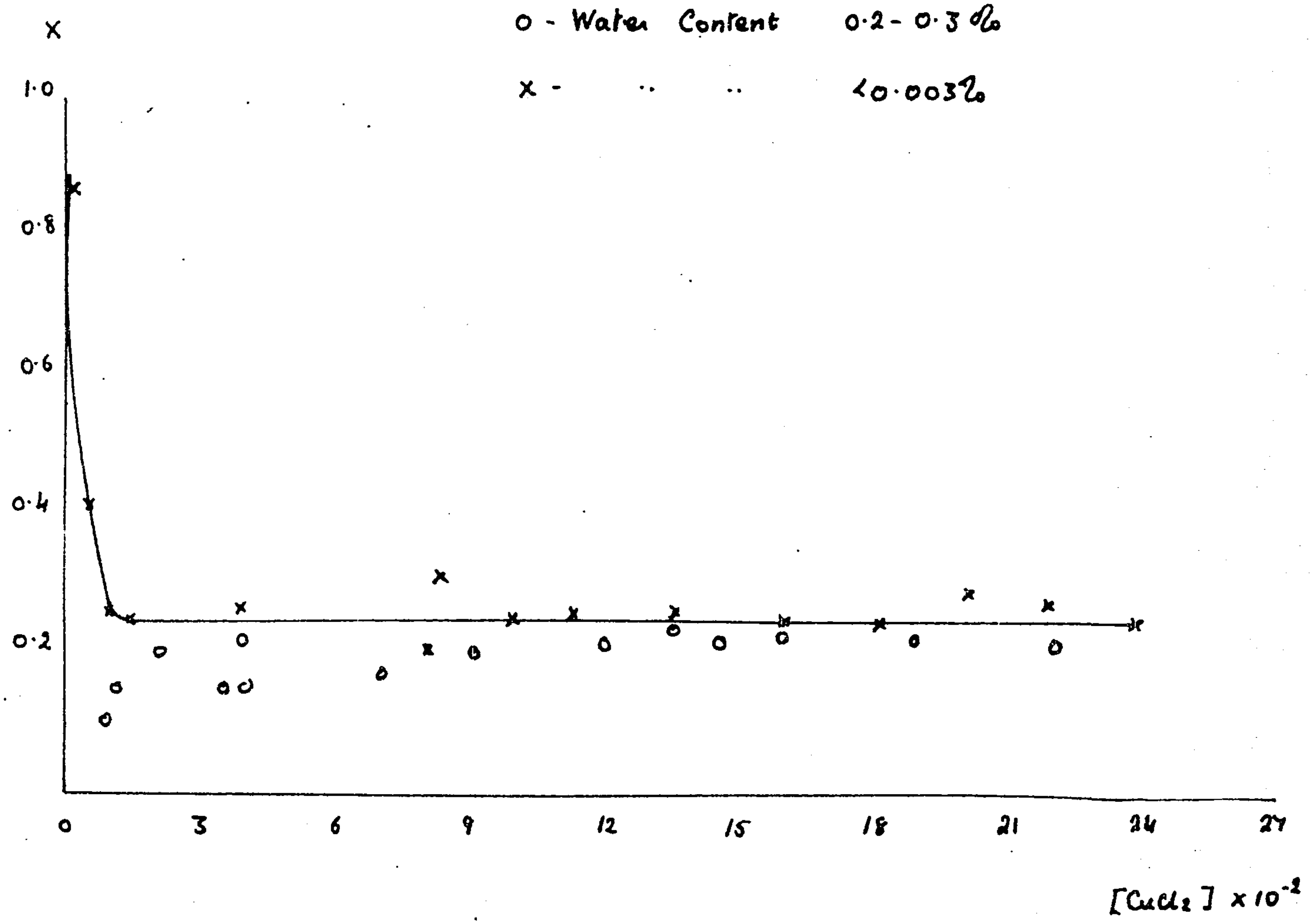
Temperature = 25°C (±0.05) Water Content = 0.2 - 0.3%

$CuCl_2$ Moles per litre	Moles NO Absorbed per mole copper
0.008	0.10
0.0105	0.15
0.04	0.15
0.02	0.20
0.039	0.22
0.035	0.15
0.07	0.17
0.092	0.20
0.12	0.20
0.137	0.23
0.144	0.21(5)
0.16	0.22
0.18	0.22
0.19	0.21
0.22	0.20

Figure 11

BEHAVIOUR OF CUPRIC CHLORIDE NITROSYL IN METHANOL (1)

Plot of c v. x


o - Water Content 0·2 - 0·3 %
x - .. .. <0·003%
X
1·0
0·8
0·6
0·4
0·2
0
3
6
9
12
15
18
21
24
27
[CuCl₂] x 10⁻²

Water affects the results by i) replacing the associated methanol ii) by partially replacing the nitric oxide. Manchot's work on $CuCl_2.2H_2O$ in ethanol showed that 50% water content was required, before nitrosyl formation was completely inhibited, at a copper concentration of 0.25M.

The water content of the solvent was cut down to less than 0.005% by the use of Drierite. This also marks the range limit of the Karl Fisher reagent. Absorbtion of nitric oxide increased slightly. Good reproducibility of results at concentrations below 0.02M was still not attained.

Table 8 (ii)

Temperature = 25°C (±0.05) Water Content = 0.005%

$CuCl_2$ moles per litre	Moles NO Absorbed per mole copper
0.00195	0.375
0.0030	0.405
0.01	0.26
0.015	0.25
0.04	0.26
0.06	0.20
0.08	0.30
0.10	0.25
0.11	0.25
0.13	0.36
0.16	0.25
0.18	0.24
0.20	0.28
0.22	0.26
0.24	0.24

The graph is approximately constant over the greater part, and tends to $x = 1.0$ as C decreases. This is qualitatively in accordance with the theory discussed previously. In order to investigate the non-constant region, complete dehydration of the alcohol was necessary. This was accomplished by adding trace quantities of anhydrous sodium sulphate to each solution. The results are shown in Fig. 12. and 13.

Table 8 (iii)

Temperature 25°C (±0.05) Water Content 0

$CuCl_2$ Moles per litre	$Log_{10}C$	Moles NO Absorbed per mole copper
0.0005	-3.301	1.0(5)
0.002	-2.699	0.65
0.2236	-2.444	0.56
0.0059	-2.230	0.47(6)
0.0098	-2.008	0.34
0.0127	-1.896	0.29
0.0196	-1.707	0.25(6)
0.0157	-1.755	0.27(7)

Table 9

$x_{lim.}$	$B_{obs.}$	Predicted Slope	Observed Slope	K_r	K_c
0.2	0.25	i) 2.9 ii) 2.5	2.2(6)	1.28x10	-

Figure 12

BEHAVIOUR OF CUPRIC CHLORIDE NITROSYL IN METHANOL (ii)

Plot of C v. x

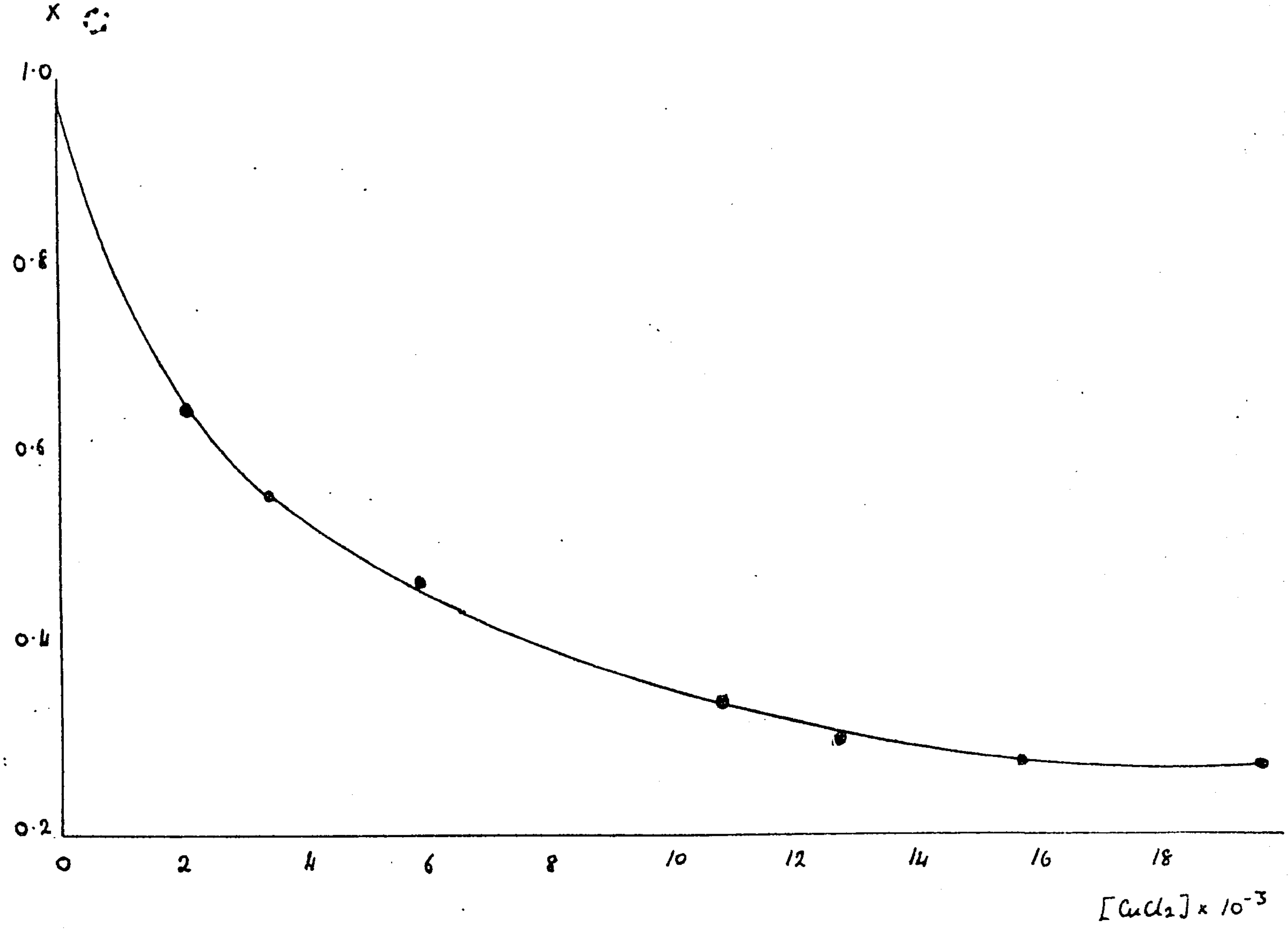
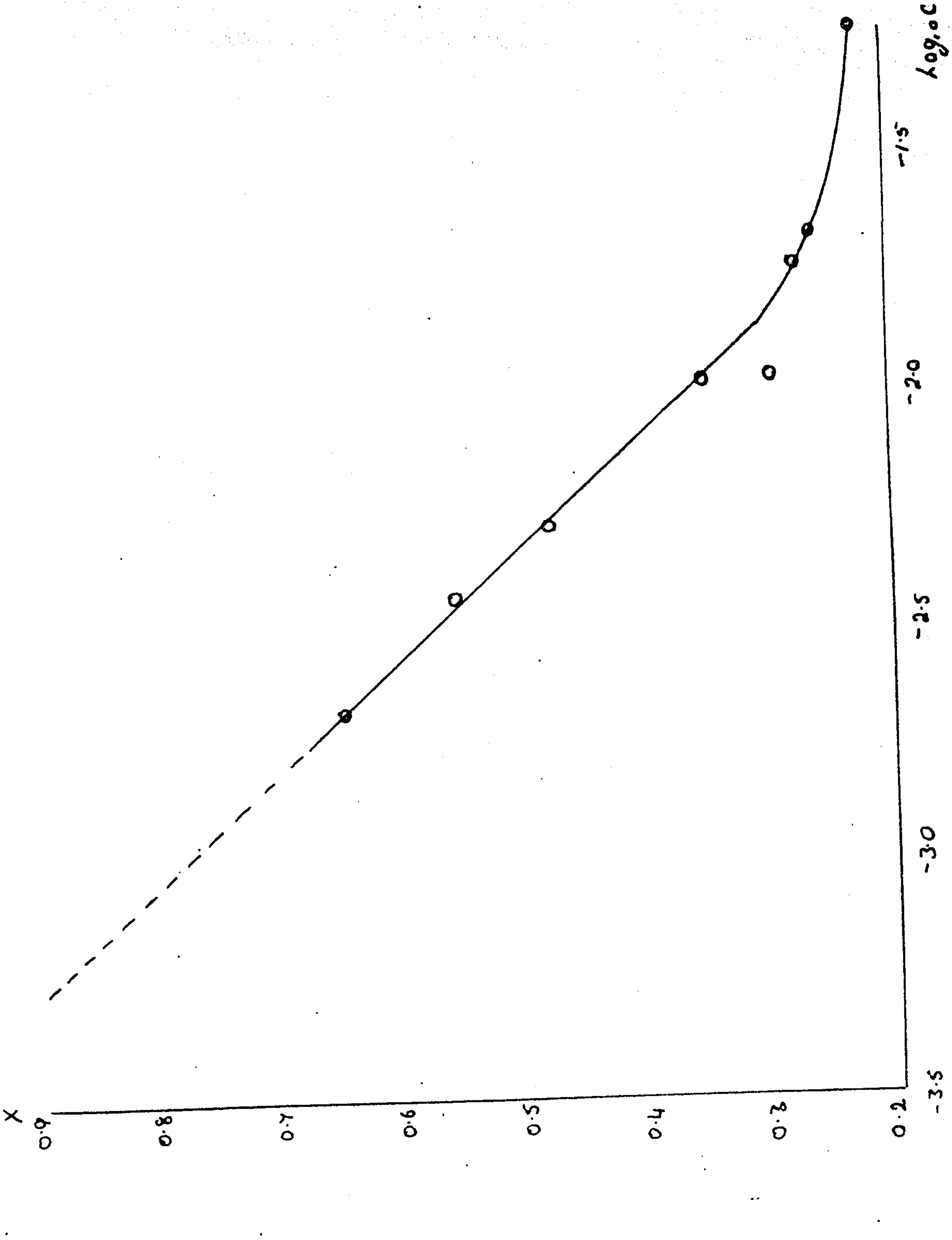

X
1·0
0·8
0·6
0·4
0·2
0
2
4
6
8
10
12
14
16
18
[CuCl$_2$] x 10^{-3}

Figure 13

BEHAVIOUR OF CUPRIC CHLORIDE NITROSYL IN METHANOL

Plot of $\mathrm{Log}_{10}C$ v. x


X
0·9
0·8
0·7
0·6
0·5
0·4
0·3
0·2
-3·5
-3·0
-2·5
-2·0
-1·5
log₁₀c

In the case of methanol, there is no question of ignoring interaction of the nitrosonium ion with the solvent. The reaction taking place must be described by all three steps:

$$CuCl_2 + NO \xrightleftharpoons{K_f} CuCl_2NO$$
$$CuCl_2NO \xrightleftharpoons{K_c} CuCl_2^- + NO^+$$
$$NO^+ + ROH \xrightleftharpoons{K_s} RNO_2 + H^+$$

Although values for K_c and K_s cannot be separated general comparison with the theoretical curves shows that dissociation of the nitrosyl must be considerable. As $B = [CuCl_2NO] / [CuCl_2]$ the nitrosyl concentration could be calculated using Fig. 11. Over the linear portion of the graph, $C > 0.016$ the dissociation to nitrosyl-containing species can be estimated as 35%; with concentration of the nitrosyl falling to zero as C tends to zero.

In view of the very good agreement with the theoretical graphs of the results obtained, only a quick check was made to determine the nitrosyl concentration by spectrophotometric measurement. Measurements were made at a wavelength of 550 mμ; the value 1200 for the extinction coefficient[9] was used to calculate the concentration. Nitrosyls were prepared directly in the cell.

Table 10

Temperature °C	$CuCl_2$ init. Moles per litre	O.D.	Moles $CuCl_2NO$ per mole copper
27	0.02	1.524	0.0635
27	0.015	1.360	0.0702
24.8	0.01	0.744	0.0618
27	0.008	0.465	0.0491
27	0.006	0.342	0.0475
26.5	0.004	0.187	0.0390
26.5	0.002	0.065	0.0231
26	0.001	0.042	0.0350
25	0.0002	0.0025	0.0104

This leads to an average value for $K_f[NO] = 0.112$, followed by $K_f = 6.0$. Qualitative agreement is good. The value for K_f is of the right order

Summary

A theory has been put forward to account for the behaviour of cupric chloride and nitric oxide in solvents where complete reaction of cupric chloride does not take place. It has been found to hold for ethanol and methanol; and would be expected to apply to n-propanol and n-butanol.

The difference in behaviour noted by Manchot Fig. 2, is presumably due to the presence of two molecules of water in the hydrated salt.

PREPARATION OF NEW NITROSYLS IN SOLUTION

EXPERIMENTAL : PREPARATION OF CUPRIC SALTS

Cupric Iodide

Cupric iodide was prepared on the suggestion by M. Treube[18], that the compound was stable in very dilute solution, for periods of up to an hour or more; provided the temperature did not rise above 24°C.

0.05 - 0.2g. anhydrous cupric sulphate was added to 100 mls. solvent. The solubility is extremely low, and the resulting mixture was used as a suspension. A solution containing not more than 0.02g. potassium iodide per 100 mls. solvent, was added in sufficient quantity to produce cupric iodide. At this dilution, the solution was colourless. The temperature of the solution was kept at 0°C. The nitrosyl complex was prepared directly in the cell used to take the spectrum, by bubbling nitric oxide through the solution. Spectra were recorded immediately. Condensation on the wall of the cell was nullified by coating the outside with glycerol.

Cupric Cyanide and Cupric Thiocyanate

These were prepared by the standard reactions:

i) $CuSO_4 + 2KCN \longrightarrow Cu(CN)_2 + K_2SO_4$

$2Cu(CN)_2 \longrightarrow 2CuCN + (CN)_2$

ii) $CuSO + 2KCNS \longrightarrow Cu(SCN)_2$

$2Cu(CNS)_2 \longrightarrow 2CuCNS + (CN)_2 + 2S$

Reactions were carried out at 0°C, as described for cupric iodide. The thiocyanate solutions deposited a white precipitate of cuprous thiocyanate almost immediately after passing nitric oxide, which appeared to have the effect of rapidly accelerating the decomposition. The final concentration of copper (II) salts was estimated to be $10^{-4} - 10^{-5}M$, but the exact concentration at any instant was not easy to determine. This also led to the difficulty that a value for ε_{max} could not be estimated. Spectra were recorded at fifteen second intervals on the cyanide solutions.

Cupric Nitrate

i) The tri-hydrate was prepared by treating cupric oxide with nitric acid; filtering off excess cupric oxide, and crystallising from the solution formed. The solid obtained was readily soluble in methyl acetate; trace quantity of nitric acid was added, and nitric oxide bubbled through the solution.

ii) Anhydrous cupric nitrate was prepared by the method of Addison. Copper metal was treated with a mixture of ethyl acetate and nitrogen dioxide, and the compound $Cu(NO_3)_2 \cdot N_2O_4$ crystallised from the solution. On heating in a vacuum at 150-200°C, the solid sublimed, leaving a 100% anhydrous product.

Cupric Hydroxide

Anhydrous cupric hydroxide was prepared by dissolving cupric oxide in concentrated ammonia solution, and leaving in a dessiccator, over concentrated sulphuric acid. The product consisted of a mixture of cupric oxide and a white powder, assumed to be the hydroxide. Its solubility in alcohol appeared to be negligible.

Cupric Iodate

Cupric iodate was prepared by treating cupric sulphate solution with potassium iodate.

Cupric Dithio-oxamide

Cupric dithio-oxamide formed as a dark green precipitate , when a solution of aqueous cupric sulphate was treated with dithio-oxamide reagent.

Cupric Salicyaldoximate[19]

A solution of 0.2g. cupric chloride in 100 mls. water was prepared, and 2N sodium hydroxide added until a slight permanent precipitate was formed. Dilute acetic acid was added to dissolve this. The resulting mixture was at a pH of 2.6, which gives the optimum conditions for precipitation of the copper complex. 1g. salicyaldoxime was dissolved in 5 mls. 95% ethanol, and poured into 95 mls. of water at a temperature not exceeding 80°C. This solution was added to the cupric chloride solution. The precipitate was dried at 100°C.

Cupric Pyridine Thiocyanate[20]

This was prepared in conjunction with the analysis of copper. Four standard solutions were made up.

i) 0.8g. ammonium thiocyanate + 0.5mls. pyridine in 100mls. water.

ii) 80 mls. 95% ethanol + 19.2 mls. water + 0.8 mls. pyridine + 0.05g. ammonium thiocyanate.

iii) 10 mls. absolute alcohol + 2 drops pyridine

iv) 20 mls. sodium dried ether + 2 drops pyridine.

The weighed sample was dissolved in 100 mls. water; pyridine added dropwise until the solution turned deep-blue; 0.5g. ammonium thiocyanate added, and the mixture stirred vigorously. It was transferred to a weighed F. Grade sintered glass crucible with the aid of solution i); washed six times with solution ii); and the walls of the crucible were washed with 1.5 ml. portions of solution iii); and dried between each washing. The final washing was with 1-2 ml. portions of solution iv). The precipitate was dried in a vacuum dessiccator for 15 mins. before weighing. Methyl acetate was used to form the nitrosyl. The complex is very nearly insoluble in the solvent but the nitrosyl formed is soluble, and the reaction was satisfactorily carried out by leaving the solid complex in contact with the solvent, and passing nitric oxide for some time. This was the only nitrosyl prepared that was at all stable.

RESULTS

Cupric Iodide

The first solvents tried were the alcohols n-butanol and n-propanol, as dissociation of the other halide complexes is least here.[9] In n-propanol a very transient violet colour was observed. Attempts to stabilise the complex by the addition of trace quantities of hydriodic acid were not effective. Formation of the iodide complex was clearly visible in acetone and ethyl acetate. It was most stable in the latter, where the colour lasted 10-15 secs.

In general, absorption spectra of nitrosyl solutions in the visible region show three maxima:

i) strong band in the region of 300 mu, which is due to nitric oxide dissolved in the solvent.

ii) medium-weak band around 550 mu, which is characteristic of the nitrosyl.

iii) weak band at 950 mu, which is due to copper (II).

Spectra, in acetone, were recorded immediately. The spectra obtained are shown in Fig. 14. The peak at 450 mu is identified as due to the α-iodo derivative

$$I_2 + (CH_3)_2CO \longrightarrow ICH_2\text{-}C\text{-}CH_3$$[21]

Some stabilization of the nitrosyl was effected by adding hydriodic acid to the solution in trace quantity.

Interference from the iodo-complex was prevented by using a reference solution of iodine in acetone at a similar concentration.

Methyl acetate proved to be the most satisfactory system with which to work. Initial experiments without the addition of trace H^+ were similar to 1, 2, and 3 of fig. 14. Fig. 15 shows the spectra with acid stabilization. 1 - where the reference cell contains solvent, shows some tendency to split into two maxima - one due to iodine, the other at $\lambda = 580$ (∓ 10) is due to the nitrosyl. The shift in $\lambda_{max.}$ on substitution of iodine in the nitrosyl is consistent with the general trend of the halides, where $\lambda_{max.}$ for $F < Cl < Br < I$. All trace of nitrosyl had disappeared when the spectra were run for the second time - 20 secs. later.

Owing to the extreme instability of the cupric iodide, no quantitative measurements were practicable.

Figure 14

FORMATION OF CuI_2NO IN ACETONE

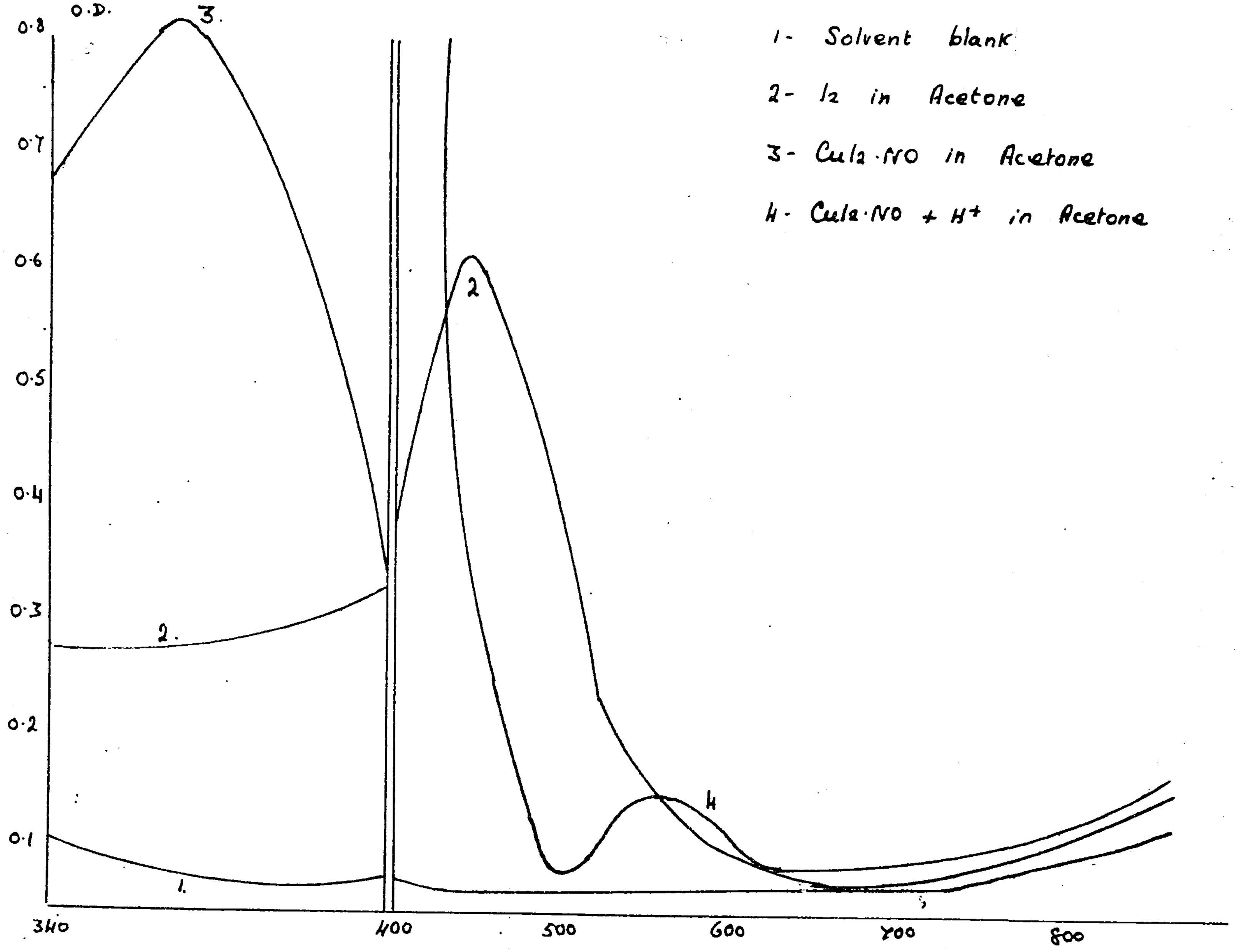
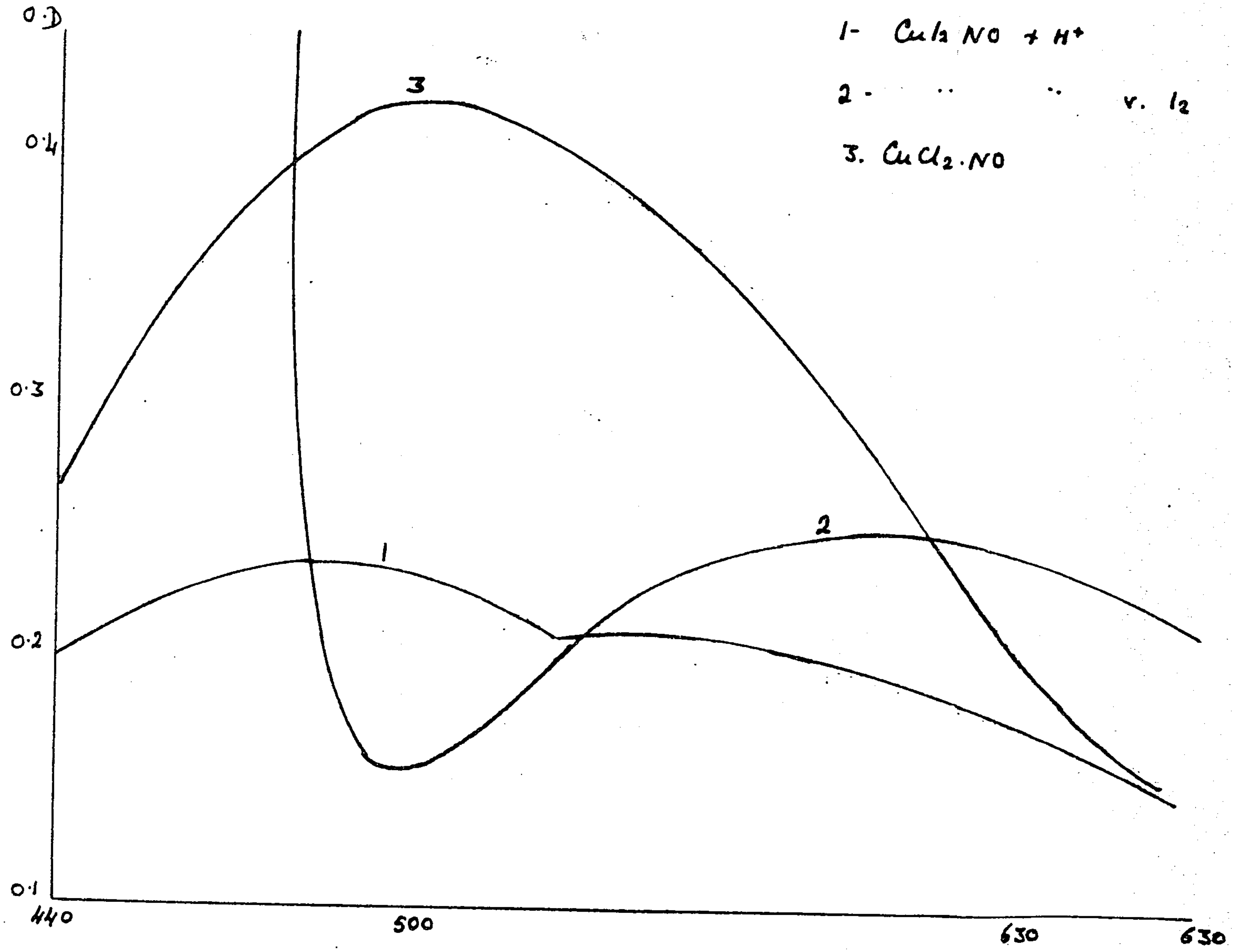

1- Solvent blank
2- I_2 in Acetone
3- $CuI_2 \cdot NO$ in Acetone
4- $CuI_2 \cdot NO + H^+$ in Acetone
O.D.
0·8
0·7
0·6
0·5
0·4
0·3
0·2
0·1
340
400
500
600
700
800
1.
2.
2
3.
4

Figure 15

FORMATION OF CuI_2NO IN METHYL ACETATE


O.D
0·4
0·3
0·2
0·1
440
500
630
630
1
2
3
1- CuI2 NO + H+
2- .. .. v. I2
3. CuCl2.NO

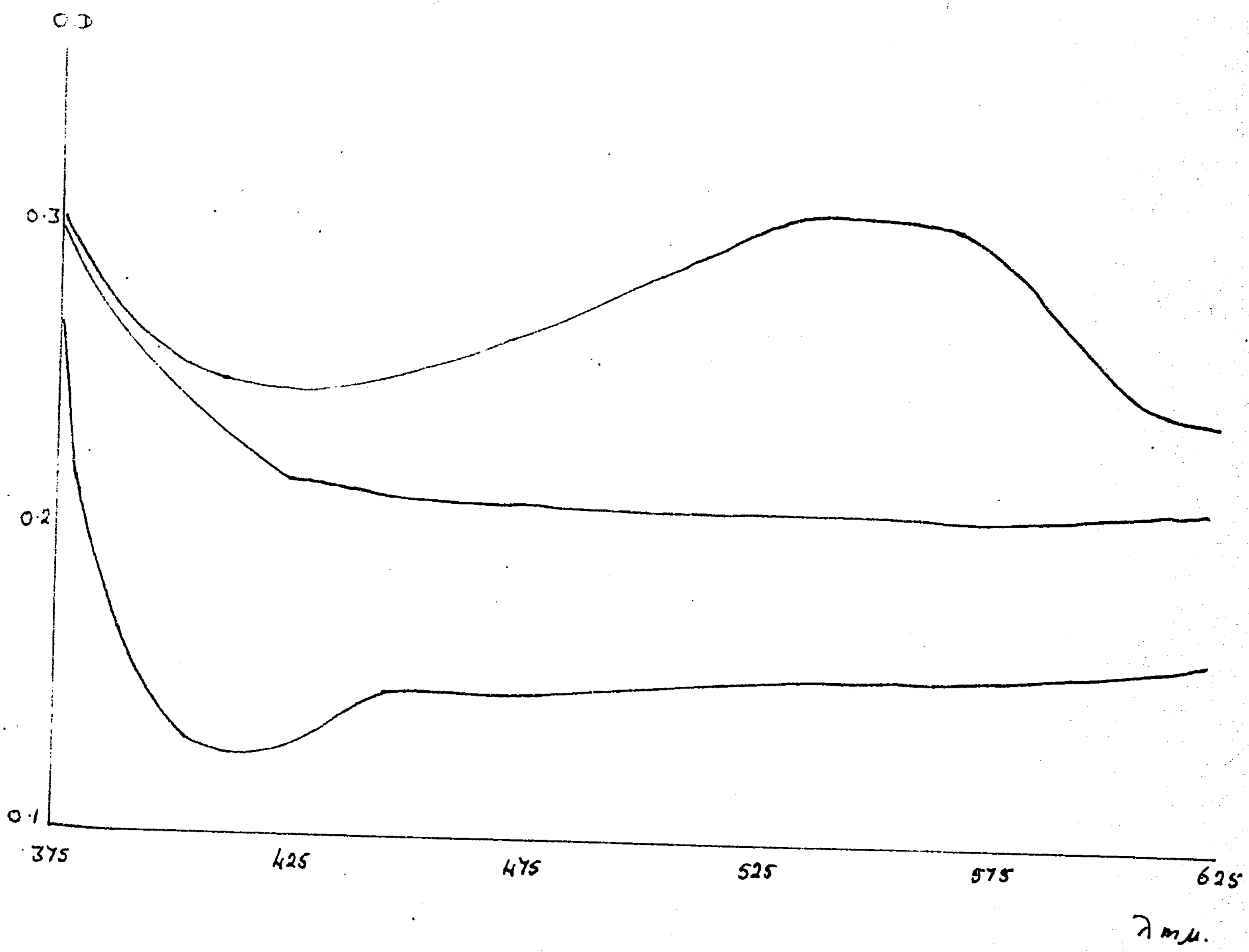
Cupric Cyanide and Cupric Thiocyanate

Two solvents were employed: i) 10% methanol : 90% carbon tetrachloride. ii) methyl acetate. Cyanogen appeared to be producing a similar type of interference to that of iodine. Maxima are recorded as 470 mμ and 545 (±10) mμ for $Cu(CN)_2NO$ in solvent i). Fig. 16 shows a series of spectra of cupric cyanide nitrosyl in methyl acetate, taken consecutively at intervals of 15 secs. It will be observed that only the first one, taken within five secs. of passing nitric oxide through the solution, showed clearly the characteristic band of a nitrosyl. After six minutes absorption at 545 mμ had dropped to zero.

Fig. 17 shows the spectra of $Cu(CNS)_2NO$ in methyl acetate, stabilized by acid. Separation of the experimentally determined curve into two bands is implied by the sharp maxima at 475 mμ and the shoulder on its right.

Figure 16

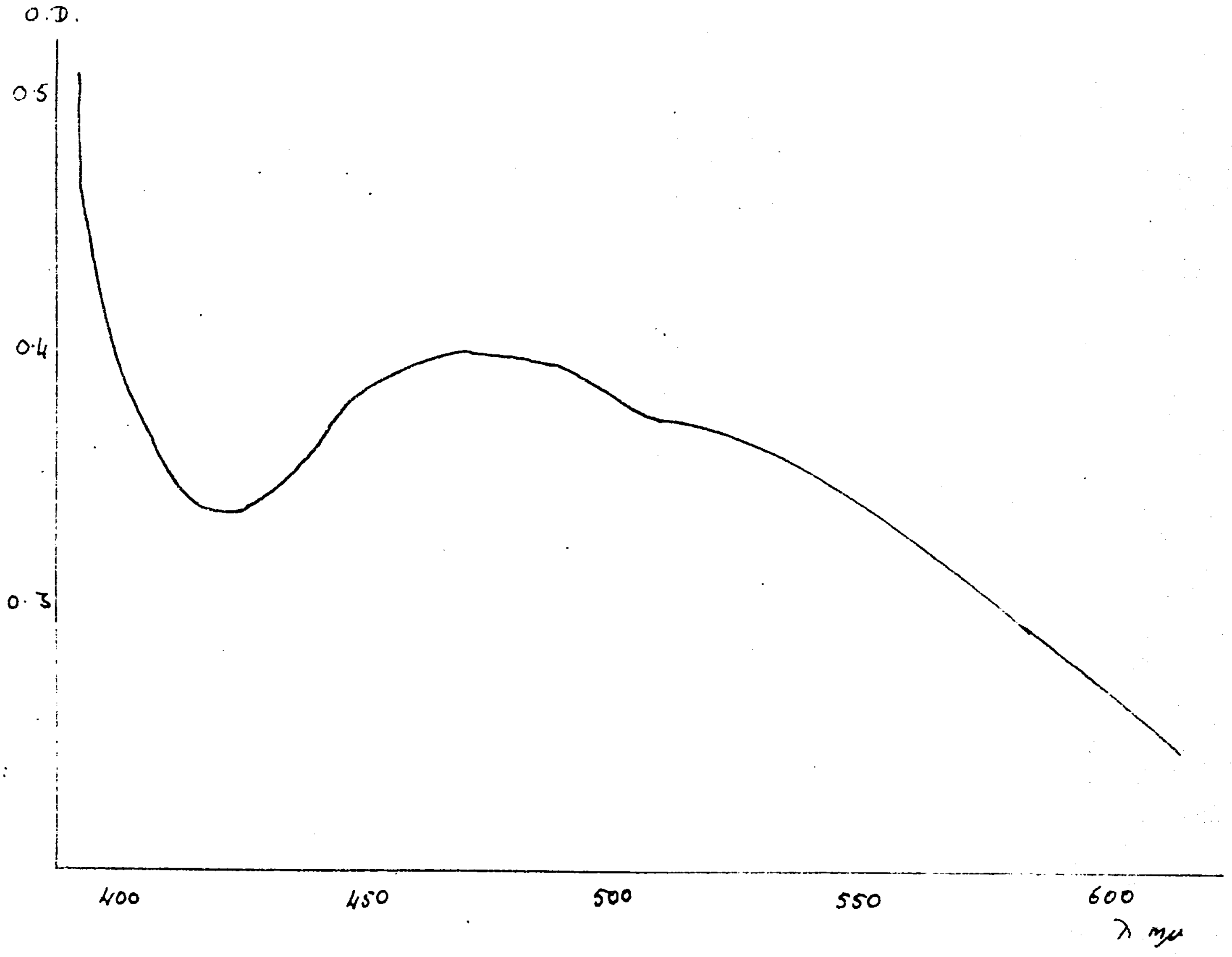
FORMATION OF Cu(CN)$_2$NO IN METHYL ACETATE



O.D
0·3
0·2
0·1
375
425
475
525
575
625
λ mμ.

Figure 17

FORMATION OF $Cu(SCN)_2NO$ IN METHYL ACETATE


O.D.
0.5
0.4
0.3
400
450
500
550
600
λ mμ

Cupric Nitrate

Neither the hydrate, nor the anhydrous salt form nitrosyls. The solvents considered were methyl acetate, ethanol and n-butanol.

Cupric Hydroxide

Cupric hydroxide was not observed to form a nitrosyl. This might be due to extreme insolubility.

Cupric Iodate

Cupric iodate does not form a nitrosyl.

Cupric Dithio-oxamide

Cupric dithio-oxamide does not form a nitrosyl. Fig. 18 ii).

Cupric Salicyaldoximate

Cupric Salicyaldoximate does not form a nitrosyl. Solubility in the solvents tried e.g. methyl acetate is good.

The possibility of further co-ordination to copper salicyaldoximate was investigated by studying the I.R. spectra. Three spectra were compared:

i) cupric salicyaldoximate - Nujol
ii) triethyl phosphate - solvent blank
iii) cupric salicyaldoximate in triethyl phosphate phase mull.

The P=O stretching frequency give a band at 1280 cm^{-1} Co-ordination P=O→Cu will cause the main band to shift or split. In case iii) bands at 1200cm^{-1} and 1230cm^{-1} were attributed to this effect. It is assumed that two molecules of solvent are attached; the first being more strongly bound than the second.

Cupric Pyridine Thiocyanate

The spectrum of the nitrosyl obtained is shown in Fig. 18 i). The reversibility of the reaction was demonstrated by passing nitrogen through the nitrosyl solution; when the starting material precipitated out. Ion-migration experiments, which require over-night stability, were not successful

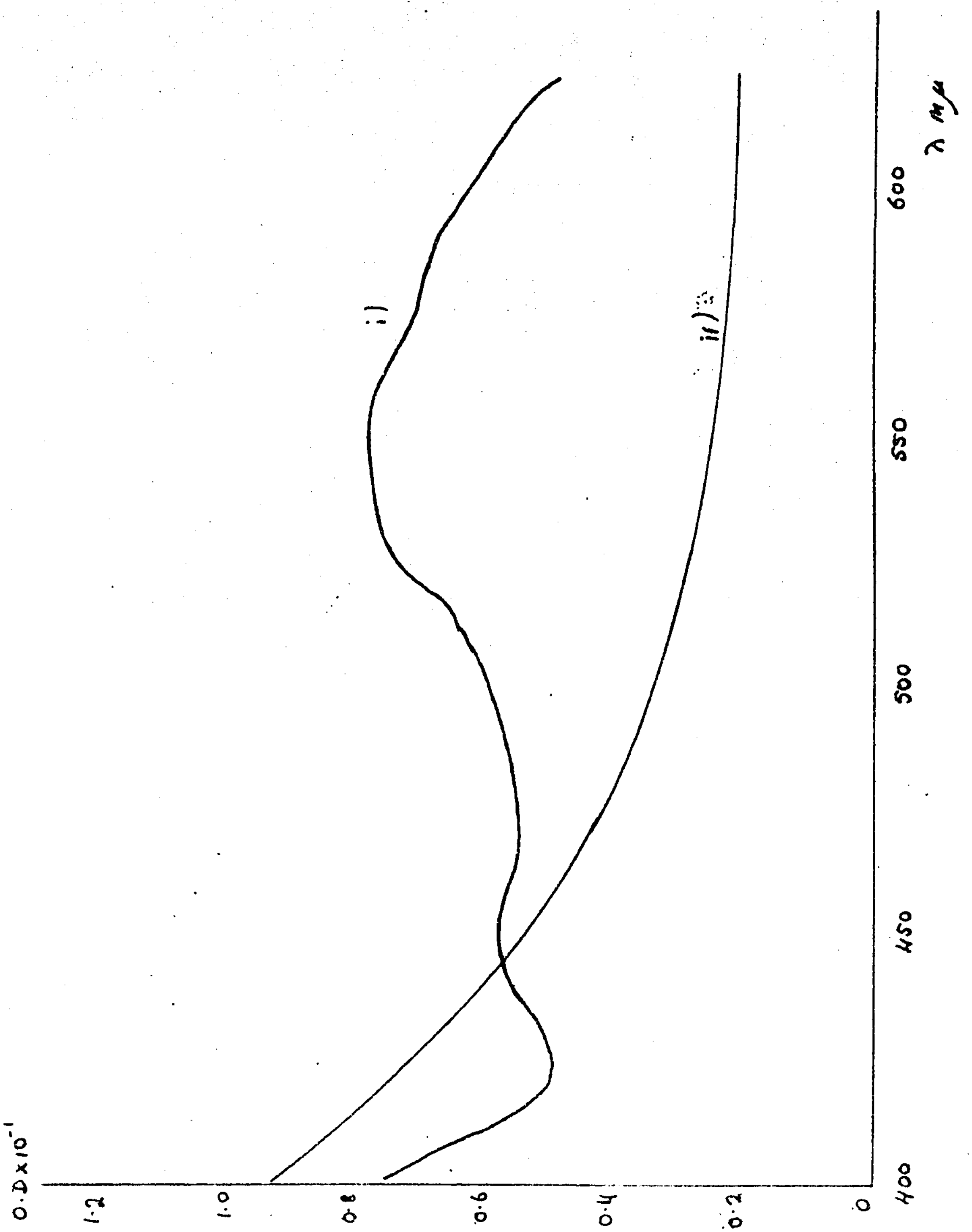
Cupric Sulphate

In view of the fact that cupric sulphate is present in several of the cases where nitrosyl formation is assigned to other species; a check was made in each instance, that cupric sulphate in the solvent does not form a nitrosyl. It would appear that sulphuric acid is the only solvent where this occurs.

Figure 18

FORMATION OF $CuPy_2(SCN)_2NO$ IN METHYL ACETATE

CUPRIC DITHIO-OXAMIDE + NO IN METHYL ACETATE


O·D x10⁻¹
1·2
1·0
0·8
0·6
0·4
0·2
0
400
450
500
550
600
λ mμ
i)
ii)

Summary of $\lambda_{max.}$ Values

Table 11

Nitrosyl	Solvent	max.
CuI_2NO	MeAc	550 (±10)
$Cu(CN)_2NO$	CH_3OH/CCl_4	545 (±10)
"	MeAc	545 (± 5)
$Cu(SCN)_2NO$	"	540 (±10)
$Cu(SCN)_2Py_2NO$	"	540

SALICYLAL O-HYDROXYBENZYLAMINE COPPER (II) NITROSYL

EXPERIMENTAL

Preparation of Salicyaldoxime[22]

General reaction:

R.CHO + $NH_2OH.HCl$ + NaOH ⟶ R.CH=NOH + H_2O + NaCl

17g. hydroxylamine hydrochloride were dissolved in 30 ml. water, and neutralised by a solution containing 20g. sodium hydroxide in 60 ml. water. The reaction mixture was kept in an ice-bath. 26 ml. salicyaldehyde in 200 ml. alcohol were added to the cold solution. Sodium chloride and some oxime crystallised out. The mixture was warmed under reflux for two hours, after adding sufficient alcohol to dissolve the oxime. The alcohol and most of the water was removed by distillation under reduced pressure. The aqueous residue was extracted with ether; and the extract dried with anhydrous sodium sulphate. The greater part of the ether was removed by distillation, and the residue allowed to crystallise. The product was purified by treatment of its chloroform solution with petroleum ether.

Yield = 46.5% m.pt. 57°C

Preparation of Sodium Amalgam[22]

25g. sodium, in small pieces, was added to 975g. purified mercury, covered by 400 mls. toluene in a one l. beaker, and the mixture stirred constantly. The sodium was forced under the surface of the mercury with a pointed glass rod. The toluene was decanted, and the mixture heated until it melted. It was freed from slag by filtering through paper with a hole in the apex of the cone, while still hot. The product was broken up and placed in a stoppered container.

Preparation of O-Hydroxybenzylamine from Salicyaldoxime[23]

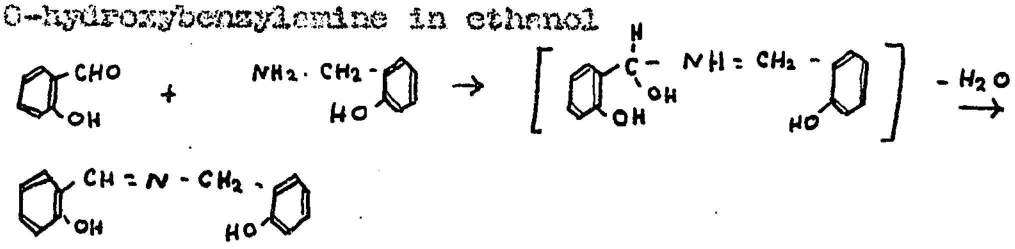
20g. salicyaldoxime were dissolved in 300 mls. 50% ethanol; and the Na/Hg amalgam added to the mixture. The temperature was kept below 55°C, by cooling the flask in ice, and excess alkali continuously neutralised by adding concentrated hydrochloric acid. The reaction was kept at pH 7+, universal indicator having been added to the solution. Complete reaction was indicated by the copious evolution of hydrogen. The solution was acidified and separated from the mercury. It was distilled under reduced pressure until the sodium chloride began to crystallise out. The solution was re-diluted and distilled until sodium chloride was crystallised out, as before. The mixture was diluted to 600 mls. and transferred to a flask containing 25 mls. ether. The amine crystallised out on adding ammonium hydroxide. The crude product was removed by filtration.

The yield was improved by evaporating the mother liquor to dryness, shaking the residue with alcohol, and treating the filtrate with petroleum ether. The product was purified by recrystallisation from absolute alcohol, plus treatment of the solvent with petroleum ether.

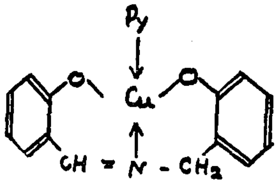
Yield = 79%

Preparation of Salicylal O-hydroxylamine Copper (II)[23]

Salicylaldehyde was condensed for one hour with O-hydroxybenzylamine in ethanol



The resulting Schiff's base was separated, and the mixture treated with cupric acetate in water. The crude product precipitated out, was filtered and dried. Purification was by dissolving the crude product in a minimum of pyridine and filtering. The dimer breaks to form a 1:1 complex with pyridine:



The addition of water causes precipitation of the pyridinate. The mixture was left standing over-night; the water decanted, and the crude pyridinate heated at 70°C, which removed almost all the pyridine. To ensure complete removal, the residue was boiled in ether for 30 mins.; filtered, and re-precipitated by adding water. The pure chelate was dried at 70°C; then recrystallised from bromobenzene. It decomposed on standing, and was kept in a dessicator at 5°C.

RESULTS

Preparation of the Nitrosyl

Solvents considered for the preparation of the nitrosyl were;

i) 10% methanol : 90% carbon tetrachloride. Solubility of the chelate is approx. 10^{-3}M to give a green solution. On passing nitric oxide the solution became first colourless, then violet. On exposure to air the violet colour persisted for several minutes; indicating the formation of a stable nitrosyl. The absorption spectrum had a maximum at 585 ($\pm$5)mμ.

ii) Inert solvents e.g. carbon tetrachloride, benzene, cyclohexane. The solubility was greatest in benzene - 3.013 x 10^{-4}M, giving a green solution. Nitric oxide was passed for over an hour in each case. No nitrosyl formation could be detected.

iii) A mixture of 10% pyridine : 60% methanol : carbon tetrachloride. The green solution remained quite unchanged on passing nitric oxide, indicating the pyridinate does not form a complex.

iv) The chelate did not form a complex in triethyl phosphate. Cupric bromide in this solvent formed a nitrosyl immediately, $\lambda_{max.}$ = 590mμ, indicating that the solvent is a suitable medium for nitrosyl formation.

The infra-red spectra considered were:

i) chelate phase mull

ii) triethyl phosphate

iii) chelate : triethyl phosphate phase mull

The strong band due to P=O at 1260 cm.$^{-1}$ had shifted 10 cm.$^{-1}$ in the presence of the chelate, indicating that solvent association to the copper takes place.

Infra-red spectra of:

i) chelate in methanol : carbon tetrachloride

ii) chelate nitrosyl in methanol : carbon tetrachloride

were taken. A weak band at 1840 cm.$^{-1}$ in ii) was identified as due to nitric oxide co-ordination.

Determination of the number of Associated Solvent Molecules a) to the chelate alone b) to the nitrosyl

The method used in each case was Job's mole ratio method. A 2.928 x 10^{-4}M solution of chelate in benzene was made up. A solution of ethanol in benzene, at the same concentration was added. The volume in each case was made up to 30 ml. Spectra were taken in a 10 cm. cell. The results obtained at a wavelength of 550mμ are shown in Fig. 19. It is apparent that solvent association takes place with the consecutive addition of three associated ethanol molecules.

The same solutions were used to determine association to the chelate nitrosyl. The results are shown in Fig. 20 The wavelength is 550 mu. Nitrosyl formation is at a maximum in the presence of one molecule of solvent. The addition of further solvent causes some dissociation of the nitrosyl.

If solutions with more than four molecules of ethanol available were left standing for several days, decomposition of the chelate occurred, leaving a brown precipitate. The solution had become a deep violet, the colour intensifying from colourless or pale violet to dark purple.

Figure 19

MOLE RATIO METHOD FOR DETERMINING SOLVATION TO CHELATE

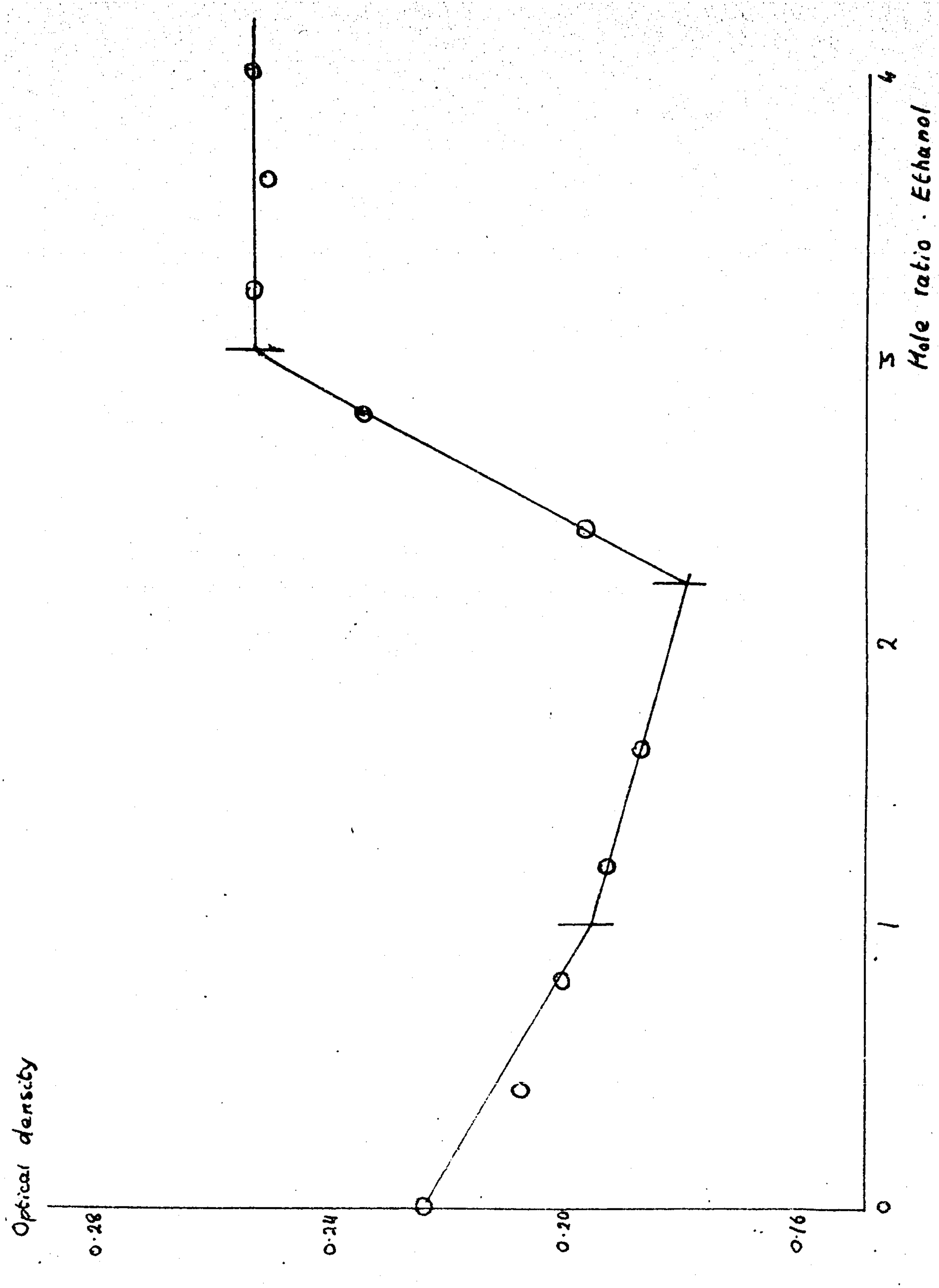
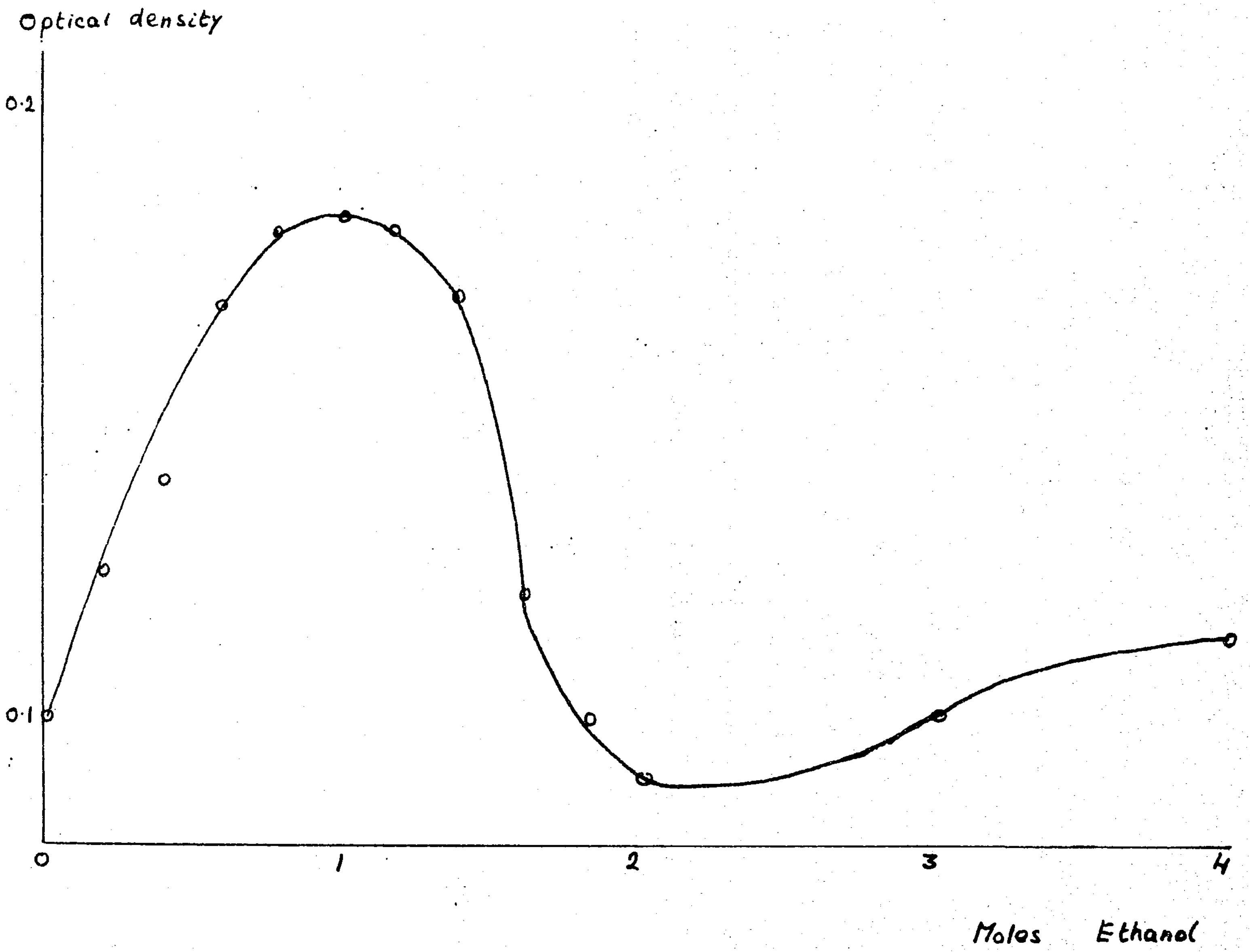

Optical density
0·28
0·24
0·20
0·16
0
1
2
3
4
Mole ratio . Ethanol

Figure 20

MOLE RATIO METHOD FOR DETERMINING SOLVATION TO CHELATE NITROSYL


Optical density
0·2
0·1
0
1
2
3
4
Moles Ethanol

DETERMINATION OF SOLVATION BY I.R. SPECTRA

EXPERIMENTAL

The solvent used was 10% methanol : carbon tetrachloride. The nitrosyl was prepared in a 50 ml. round-bottomed flask, fitted with a 19/38 glass stopper, incorporating a nitric oxide inlet and outlet. The outlet led directly to the I.R. sodium chloride cell, and the solution was transferred unchanged under an atmosphere of nitric oxide. Alternatively, the nitrosyl solution was transferred by hypodermic syringe, which was first filled with nitric oxide. Transfer was effected so that the cell was swept out with nitric oxide before the nitrosyl went in. The spectra were run on a Perkin-Elmer infra-cord spectrophotometer.

The spectra were run as:

Sample	Reference	
CH_3OH/CCl_4	$CuCl_2/CH_3OH/CCl_4$	..A
CH_3OH/CCl_4	$CuCl_2NO/CH_3OH/CCl_4$	.B

in order to get the methanol absorption positive.

Table 12

Absorption bands $cm.^{-1}$	Assignation
*3500	O-H stretching (strong)
2962	CH_3 "
2872	" "
1840	NO "
1750	NO bonded to complex
1460	H on CH_3 bending
1109	O-H "
*1034	C-OH stretching (strong)

* shifted 10 $cm.^{-1}$ indicating bonding from the oxygen a) to cupric chloride b) to cupric chloride nitrosyl. The band at 1034 $cm.^{-1}$ was used to determine quantitatively the number of molecules of solvent associated to copper.

Let the no. of molecules of methanol attached to cupric chloride be S. Then consider that one molecule of solvent is replaced by NO in the complex, giving a solvation factor of S-1.

Consider A:

$$O.D. = t(\varepsilon_{s}\cdot C\cdot S + \varepsilon_{m}\cdot[M]\cdot C\cdot S + \varepsilon\cdot[CCl_4]) - t(\varepsilon_{m}\cdot[M] + \varepsilon\cdot[CCl_4])$$

where t is the cell thickness, ε_s is the extinction coefficient of solvated cupric chloride, ε_m is the extinction coefficient of methanol; [M] is the initial concentration of methanol, which is 10% and the same in each cell, and C is the initial concentration of cupric chloride.

$$\text{O.D.} = t(\varepsilon_a . C.s. - \varepsilon_m . C.s)$$

$$t.C.s(\varepsilon_a - \varepsilon_m)$$

Consider B: Let the concentration of nitrosyl be x; the extinction coefficient ε_c.

$$\text{O.D.} = t(\varepsilon_a . (C-x)s + \varepsilon_c . x(s-1) + \varepsilon_m . [\,[M] - (C-x)s - x(s-1)]$$

$$+ \varepsilon . [CCl_4]) - t(\varepsilon_m . [M] + \varepsilon . [CCl_4])$$

$$= t(C.s(\varepsilon_a - \varepsilon_m) - x.s(\varepsilon_a - \varepsilon_m) + x.\varepsilon_c(s-1) - x.\varepsilon_m(s-1))$$

$$= t[s(\varepsilon_a - \varepsilon_m)(C-x) + x(s-1)(\varepsilon_c - \varepsilon_m)]$$

The assumption is made that $\varepsilon_a \simeq \varepsilon_c$. Writing $x = f.c$ where f is constant, which is true over the range considered:

$$\text{O.D.} = t[C(\varepsilon_a - \varepsilon_m)(s-f)]$$

The plot of O.D. against C yields two straight lines of slope ratio A:B = s:s−f. The results are shown in Fig. 21.

Table 13

CuCl$_2$ moles per litre	Optical Density x 10^{-2} A	B
0.02	5.0	3.2
0.03	8.1	4.8
0.05	11.6	7.4
0.07	15.8	10.0
0.09	20.8	13.2
0.12	27.6	–

f – determined by absorption measurements = 0.88

From the graphs s = 2.5. The fractional value may be interpreted by suggesting that <u>at least</u> two solvent molecules are attached to cupric chloride; and one to the cupric chloride nitrosyl.

(Note)

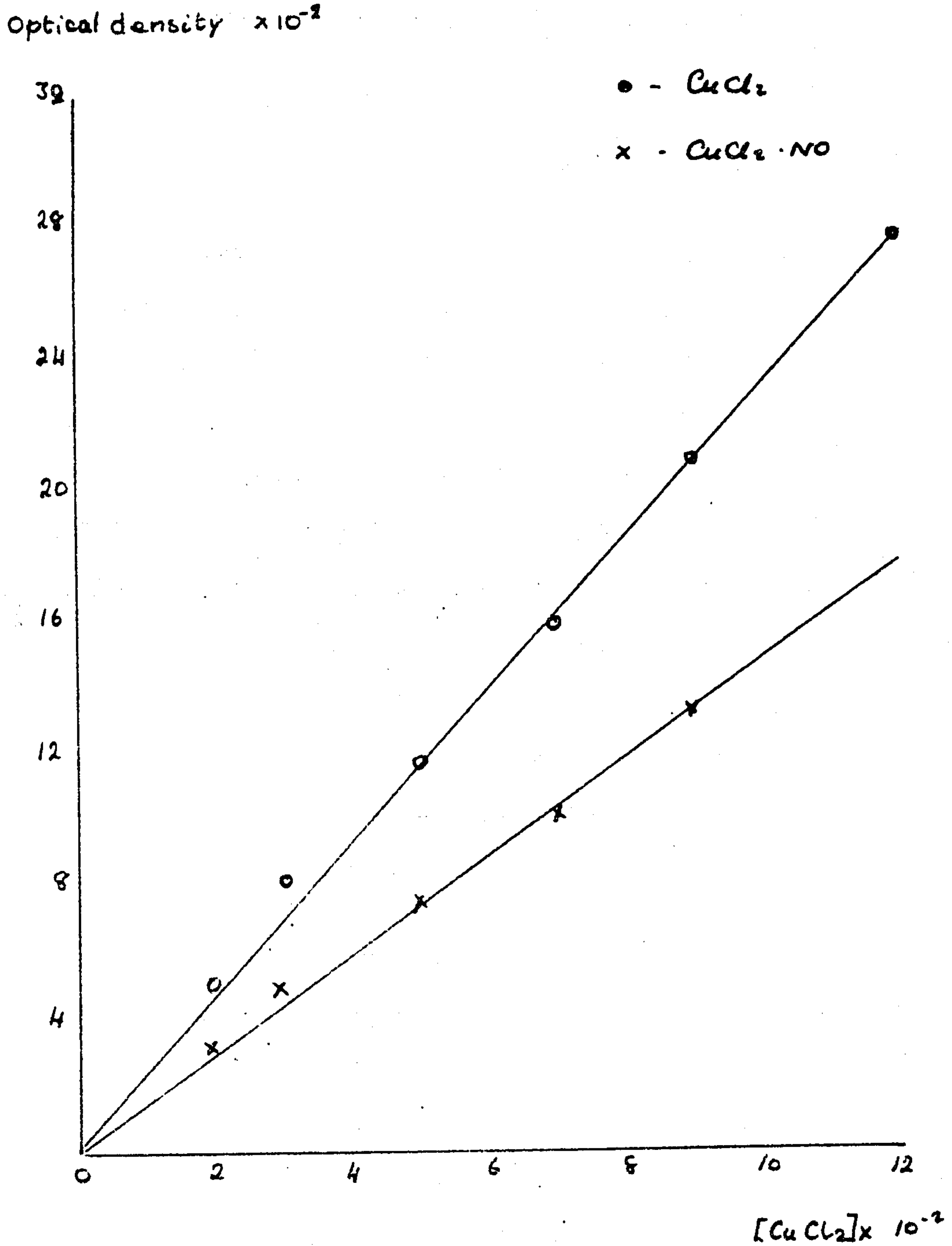
The Perkin Elmer Spectrophotometer is not usually considered to be accurate enough for this type of quantitative work.

Owing to the large quantity of unsolvated methanol present, the solvated quantity being measured is subject to error from this source.

It is, therefore, possible that the agreement with the other results obtained here is somewhat fortuitous.

Figure 21

DETERMINATION OF SOLVATION BY I.R. SPECTRA


Optical density ×10⁻²
● - CuCl₂
× - CuCl₂·NO
32
28
24
20
16
12
8
4
0
2
4
6
8
10
12
[CuCl₂]× 10⁻²

ISOLATION OF THE SOLID NITROSYLS

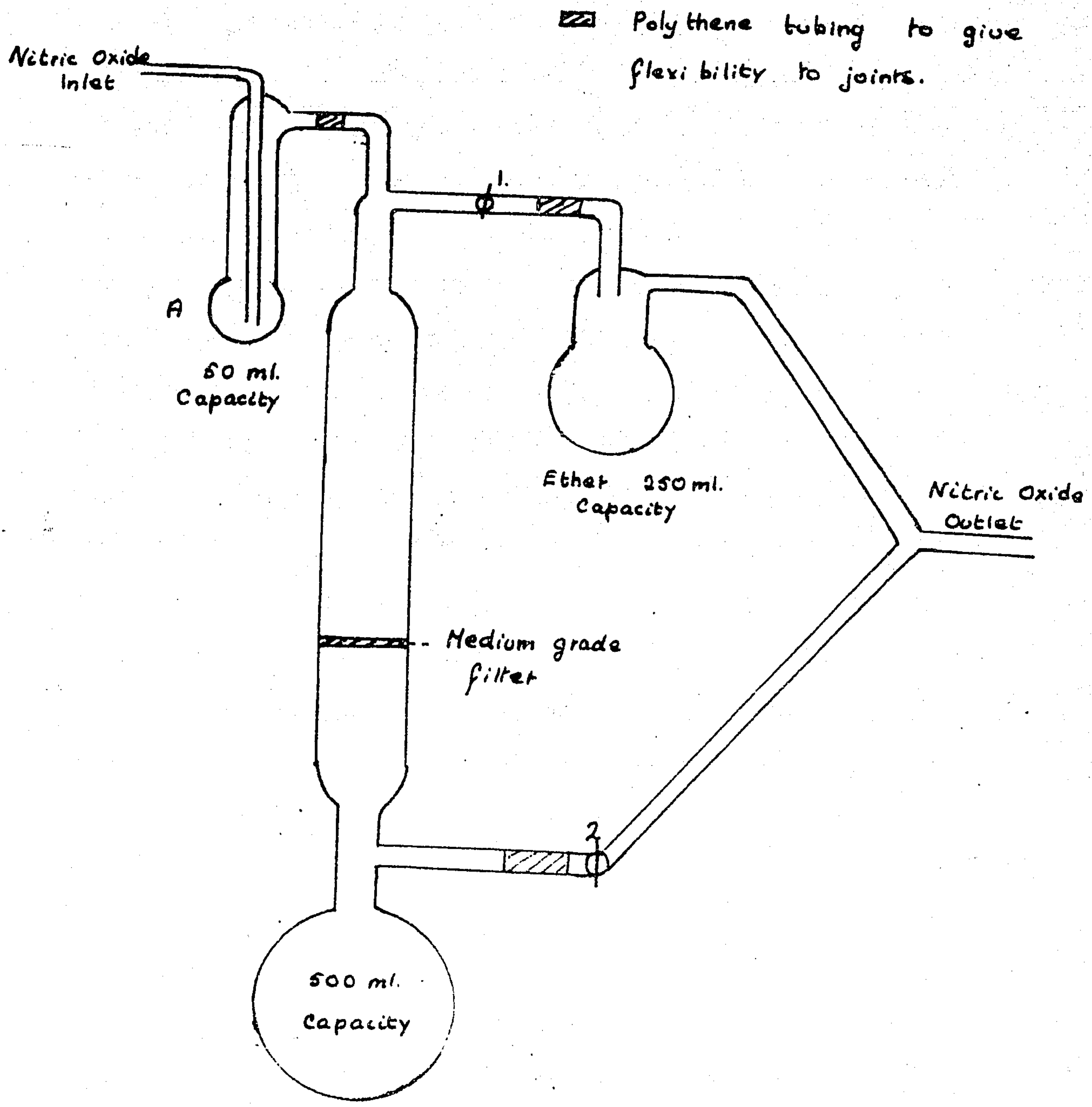
EXPERIMENTAL

Manchot [2] reported in 1910, that addition of toluene to the complex solution caused the precipitation of pale blue crystals, and that these were too unstable to be examined. A solution of cupric chloride nitrosyl was made up in ethanol, cooled in liquid air, and toluene added. No precipitate was obtained. It was found that toluene and nitric oxide, in the presence of traces of air, produced blue crystals that decomposed immediately. The complex was made up in 10% methanol/carbon tetrachloride and toluene added; traces of a black precipitate were obtained. It was observed that this was stable up to 55°C, when it decomposed.

Enst and Huckemann,[24] investigating the structure of nitrosyl-bis(salicyaldehyde)-iron-pyridine reported that precipitation was effected by petroleum ether. On the strength of this observation, this was the next reagent tried. The apparatus used to isolate the solid is shown in Fig. 22. Passage of solution through the filter is regulated by taps 1 and 2. A saturated solution of cupric bromide in 10% methanol/carbon tetrachloride was made up in the flask A, and nitric oxide bubbled through for ninety minutes when the reaction was assumed

Figure 22

ISOLATION OF THE SOLID - APPARATUS


▨ Polythene tubing to give flexibility to joints.
Nitric Oxide Inlet
A
60 ml. Capacity
1.
Ether 250 ml. Capacity
Nitric Oxide Outlet
Medium grade filter
2
500 ml. Capacity

to be complete. The solution was transferred to the filter, and petroleum ether, saturated with nitric oxide, added. The solid complex appeared as a black precipitate. It was found to be stable, provided it remained in contact with the solvent, but started to decompose after drying completely. Decomposition was immediate on exposure to air. In order to obtain a reasonable yield, 5 g. cupric bromide or chloride in 25 mls. solvent was used. Although this is in excess of the solubility of the cupric salt in the solvent, it went into solution as the nitrosyl formed. Any excess was filtered off before the addition of petroleum ether. Cyclohexane was also used as a precipitating reagent, but was not as effective. The precipitate was dried under a stream of nitric oxide, and washed with petroleum ether or cyclohexane to remove unattached solvent. The complex was decomposed by water, and the resulting solution analysed for copper:methanol ratio.

Analysis of Copper

Was by titration against standard sodium thiosulphate solution. The solution was standardised against potassium iodate, using starch indicator.

Analysis of Methanol

Was by the method of Boos,[25] 0.4 mls. of a solution of 5g. potassium permanganate dissolved in 200 mls. 15% phosphoric acid, was added to 1 ml. test solution. After five minutes enough sodium bisulphite was added to decolourise the solution, then 200 mg. chromotropic acid was added, and the solution cooled in an ice-bath. 5 mls. concentrated sulphuric acid added, and the mixture shaken and left in ice for two minutes. The absorbance at 570 mμ measured, the reagent blank subtracted, and the alcohol content determined by comparison with standard curves.

RESULTS

In case where the solid nitrosyl was dried under a fast stream of nitric oxide for 40 mins. no trace of methanol was found in the complex. This result was obtained for both chloride and bromide, at all concentrations analysed. Concentration of copper in the test solution varied between 0.004 - 0.1 M.

In case where the solid nitrosyl was precipitated from solution, and analysed after washing, but not treated to extensive drying by a stream of gas, the amount of methanol found in the solid varied. Values indicating a 1:1 complex were consistently reproducible; but were observed to rise as high as 3:2.

ATTEMPTED PREPARATION OF SILVER NITROSYLS

Preparation of Nitrosyl Chloride[26]

This was prepared on a semi-micro scale, adapting the method of Martin and Wilcox, from concentrated hydrochloric acid and sodium nitrite. The gas was purified by passing over solid sodium nitrite, moist potassium chloride, and calcium chloride, and collected in a 5 ml. round-bottomed flask, cooled in a mixture of acetone and dry ice.

The product was used in an attempt to prepare silver nitrosyls in a manner analagous to the reaction:

$$CuCl + NOCl \longrightarrow CuCl_2NO$$

Freshly prepared silver chloride was treated with nitrosyl chloride. The experiment was repeated in the presence of ethanol. No reaction was observed. Treating silver iodide in the same way resulted in the immediate production of iodine.

DISCUSSION

Copper (II) Complexes

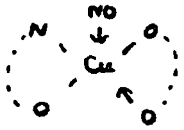
Copper (II) forms a very few tetrahedral complexes, e.g. K_2CuCl_4, but for the most part occurs in octahedral or planar environments. In the octahedral complexes there are usually four short co-planar bonds, and two long bonds. Planar complexes may be regarded as the limiting case of the distorted octahedron, where the two more weakly bound ligands have been removed completely.

Some recent examples have also been described where 5 - co-ordinate copper is known, e.g. copper acetyl acetonate adds pyridine in non-polar solvents.[27]

Discussion of Experimental Results

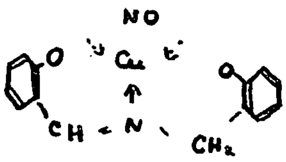
The crystalline structure of o-hydroxybenzylamine copper (II) is given by Barclay[28] as a dimer, where the two copper atoms have different environments. One atom is in a square planar configuration; the other is a distorted square pyramid. On the approach of ligands capable of co-ordinating with copper, the dimer breaks immediately.

In inert solvents, approach of NO produces no no reaction; hence a nitrosyl pictured as:

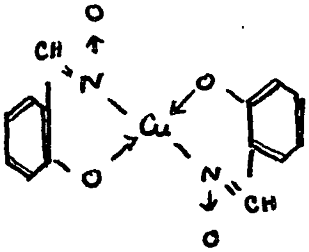


is not formed. Nor does the dimer break to form a 4 co-ordinate nitrosyl. The pyridinate with copper held in the square planar configuration does not form a nitrosyl. In methanol, copper has three strong bonds in a planar configuration, the fourth planar bond to methanol is relatively weak. Nitrosyl formation reaches a maximum at a 1:1 ratio of methanol:copper. This seems to indicate that nitrosyl formation is only possible, when the fourth co-planar position is vulnerable to attack by nitric oxide, and, presumably, one methanol remains on the complex.

The nitrosyl formed on leaving the chelate nitrosyl solution standing for several days presumably has one if not two, of the copper - oxygen bonds broken.

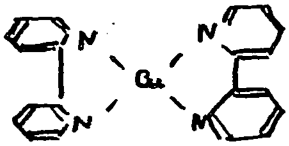


The idea is further illustrated by the use of cupric salicyaldoximate:



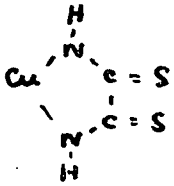
where copper forms four strong bonds in a trans planar configuration. Although triethyl phosphate co-ordinates readily in the 5th and 6th positions, nitric oxide cannot attack.

Further, on adding αα'dipyridyl complex nitrosyl is precipitated out as:



with four planar bonds, and all the nitric oxide off.

Another point of interest is provided by the attempt to form a nitrosyl from a bi-dentate copper group:

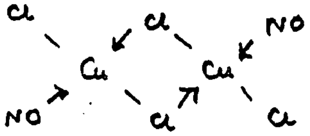


It could be inferred from its lack of co-operation that nitrosyl complexes have the trans configuration.

Solvation determination by I.R. spectra giving the value of 1.5 is interpreted by suggesting that one solvent molecule goes into the fourth co-ordinate position, with possibly a second weakly attached. Analysis of the solid tends to confirm this.

The formation of a nitrosyl by $Cu(py)_2(TCM)_2$ is indicative of 5 co-ordinate copper.

As three co-ordinate copper is unknown, the dry solid may be assumed to dimerise.



<u>Summary of Nitrosyl Bond Types</u>[89]

The unique features in the properties and reactions of nitric oxide arise from its ability to exist in three forms, NO^+, NO and NO^-. The modes of complex formation are:

i) $NO-X$	sharing the electron pair
ii) $NO^+\ X^-$	donation of one electron
iii) $M^+\ NO^-$	acceptance of one electron
iv) $NO^+\ \dot{X}$	one electron bond
v) $M \leftarrow \dot{N}O$	electron pair donated to metal atom
vi) $M \leftarrow \overset{+}{N}\equiv O$	three electron donation
vii) $\overset{+}{M} \leftarrow N{=}O^-$	electron pair bond, but one electron is donated by the metal to NO group.

Infra Red Spectra[30]

The range of frequencies that have been observed in nitrosyls is 1940 cm.$^{-1}$ - 1045 cm.$^{-1}$ Complexes discussed involve change in the N-O stretching frequency for NO. NO absorbs at 1878 cm.$^{-1}$ 2330 cm.$^{-1}$ for NO^+ The change is consistent with the removal of an electron from the anti-bonding orbital in NO and concomitant with increase in bond strength of NO. NO^- frequency is 1170 - 1045 cm.$^{-1}$

The cupric nitrosyls are diamagnetic. Therefore, the lone electron on NO has paired with the unpaired electron on copper, giving a π-bond to the d-orbital. The band at 1720 cm.$^{-1}$ has been assigned by Wilkinson[6] studying what he assumed was $[Cu(C_2H_5OH)_5NO]^{2+}$ to three electron donation by NO. If this is the case, back donation by the copper must be considerable, so $\bar{M}$=N=O has been assigned to the region 1400 - 1500 cm.$^{-1}$ by Lewis[31]. Or possibly case 4 would give a band in this position. No information is obtainable concerning the bond length. The complex is too unstable to permit X-ray study of its structure.

Visible Spectra

Colour of the nitrosyls in general is either blue or red. The colour depends on the electron shift induced by the group or atom X. NO^+ does not absorb in the visible region.[29] The band at 550 nm is assigned to charge transfer between Cu and N.

CLAIMS TO ORIGINAL RESEARCH

1. Detailed study of absorption measurements pertaining to cupric chloride in methanol.

2. The nitrosyls of cupric iodide, cyanide, thiocyanate and cupric pyridine thiocyanate have been prepared for the first time.

3. The nitrosyl of O-salicylal hydroxybenzylamine Copper (II) has been prepared. Solvent association has been determined a) to the chelate alone b) to the chelate nitrosyl.

4. Preparation of the Solid Nitrosyls of Cupric Bromide and Chloride - and their analysis.

5. The solvation to cupric chloride nitrosyl has been investigated by I.R. spectra.

6. Consideration has been given to the conditions required for nitrosyl formation.

BIBLIOGRAPHY

1. V. Kohlschutter and M. Kutscheroff, Ber. 37 3044 (1904).
2. W. Manchot, Annalen, 375 308 (1910).
3. W. Manchot, Ber. 47 1601 (1914).
4. W. Manchot and H. Linch, Ber. 59 406 (1926).
5. A. Burg and D. McKenzie, J. Amer. Chem. Soc. 74 3143 (1952).
6. W. P. Griffith, J. Lewis and G. Wilkinson, J. Chem. Soc., 3993 (1958).
7. N.V. Sidgwick, The Chemical Elements and their Compounds Oxford University Press (1950).
8. R.T.M. Fraser and W.E. Dasent, J. Amer. Chem. Soc., 82 348 (1960).
9. R.T.M. Fraser, J. Inorg. Nucl. Chem., 17 265 (1961).
10. R.T.M. Fraser, Nature, 186 730 (1960).
11. R.T.M. Fraser, Unpublished results.
12. L. Vanino, Handbuch der Preparativen Chemie, 3rd. Edn. 1 612
13. D. Meek, D.K. Straub and R.S. Drago, J. Amer. Chem. Soc., 82 6013 (1960).
14. A.I. Vogel, Quantitative Inorganic Analysis, Longman's (1951) pps. 453, 252.
15. Reference 14, p. 699
16. Inorganic Syntheses, 1st. ed. Vol. II p. 126, McGraw-Hill

17. A.I. Vogel, Reference 16, p. 783.

18. T. Traube, Ber. <u>17</u> 87 (1889).

19. A.I. Vogel, Reference 16, p. 608.

20. A.I. Vogel, Reference 16, p. 608.

21. F.H.Getman, J. Amer. Chem. Soc., <u>50</u> 2883 (1928).

22. [illegible] Belford and [illegible], J. Amer. Chem. Soc. <u>42</u> 1740 (1920).

23. H. Nishida, Y. Saito and [illegible] Sato, J. [illegible] Chem., 238 (1957).

24. [illegible] Kent and H. Reichenau, Zeit. fur anor. und all. chemie, 209 (1931).

25. [illegible] Boos, Anal. Chem., <u>20</u> 964 (1948).

26. A. Martin and [illegible] Wilcox, Inorganic Syntheses Vol. IV, p. 63, McGraw Hill Book Co. Inc.

27. D.P. Graddon, Nature, <u>187</u> 1010 (1960).

28. J. Barclay, Proc. Royal Soc., 604 (1961).

29. [illegible] Wilkins and J. Lewis, Quart. Rev., IX 115 (1955).

30. J. Lewis, R.J. Irving and G. Wilkinson, J. Inorg. Nucl. Chem., <u>7</u> 32 (1958).

31. J. Lewis, Rec. of Chem., Prog., <u>22</u> 147 (1961).