840. *Solution Properties of Anhydrous Copper Nitrate in Ethyl Acetate, Methyl Cyanide, and Nitromethane.*

By C. C. Addison, B. J. Hathaway, N. Logan, and A. Walker.

The solubility of anhydrous copper nitrate in ethyl acetate, nitromethane, and methyl cyanide is compared with values for anhydrous silver and zinc nitrates. Molecular-weight measurements indicate that copper nitrate is present as the monomer, but that on dilution below 0·1M, there is a sharp decrease in apparent molecular weight. Three different types of molar conductivity–concentration curves are obtained in the three media. Ultraviolet spectra show high $\varepsilon_{\text{max.}}$ values, of the order of 2000, for absorption in the nitrate region in pure solvents. Absorption spectra in methyl cyanide–water mixtures have also been examined.

The various physical properties reported are consistent with one another if it is assumed that stepwise dissociation $Cu(NO_3)_2 \rightleftharpoons Cu(NO_3)^+ + NO_3^- \rightleftharpoons Cu^{2+} + 2NO_3^-$ can occur.

In recent years extraction from aqueous solution into organic solvents has become important for separation and purification of heavy-metal nitrates, and the nature of the species in solution in the organic solvents has been extensively investigated. However, in such systems the water molecules which may be present in the co-ordination sphere of the metal can profoundly influence the behaviour of the nitrate group. Certain anhydrous metal nitrates are now known to exhibit high solubility in organic solvents, and in these solutions the physical properties of the nitrate group can be studied in the complete absence of water. Copper nitrate solutions were of interest since this compound forms a monomeric gas and preliminary experiments[1] indicated that it is also monomeric in solution in ethyl acetate.

---

[1] Addison and Hathaway, *Proc. Chem. Soc.*, 1957, 19; *J.*, 1958, 3099.

The solvents chosen represent media of low dielectric constant (ethyl acetate), high dielectric constant but poor complex-forming properties (nitromethane), and high dielectric constant with high complex-forming properties (methyl cyanide). In addition to solubility values, the molecular weights, electrical conductivities, and ultraviolet absorption spectra of the solutions have been determined over the same concentration ranges so that direct comparison is possible.

RESULTS AND DISCUSSION

(1) *Solubilities.*—The solubility of copper nitrate is compared in Table 1 with corresponding values for silver and zinc nitrates. Solubilities in methyl cyanide are considerably higher than in nitromethane; this reflects the complex-forming powers of methyl cyanide, and each salt crystallises from solution in the latter as an addition complex with it. The most noteworthy feature is the very high solubility of copper and zinc nitrate in ethyl acetate. The infrared spectrum[3] of each compound indicates covalently bonded nitrate groups, and since the solubility of silver nitrate (in which no covalency exists) in ethyl acetate is low, it was at first inferred that high solubility in ethyl acetate was a consequence of covalent metal–nitrate bonding. However, anhydrous cadmium nitrate, which is clearly ionic in the solid state,[3] is also very soluble in ethyl acetate. The readiness with which the metal ion is solvated is obviously a contributory factor. Copper and zinc form many stable complexes in which oxygen is the donor atom; silver co-ordinates more readily with the nitrogen atom, and this is reflected in its different solubility characteristics. Other anhydrous transition-metal nitrates are being examined to define these solubility effects more precisely.

TABLE 1. *Solubilities of anhydrous nitrates (at 20° except where otherwise stated).*

	Solubility (g. per 100 g. of solvent)		
Solvent	$Cu(NO_3)_2$	$AgNO_3$	$Zn(NO_3)_2$
H_2O	150 (25°)	228	128 (25°)
EtOAc	151 (25°)	2·7	>136
$MeNO_2$	5·1	Negligible	0·45 [2]
MeCN	33·7	112	71

Expressed in molecular units, copper nitrate is much more soluble in ethyl acetate than in water, 1 mole dissolving in 7·0 moles of water, but in only 1·41 mole of ethyl acetate. The colour of the blue-green solution in ethyl acetate is much more intense than that of an aqueous solution of the same concentration. The heats of solution of the anhydrous salt in a large excess of water or ethyl acetate are 17·2 ± 0·1 and 15·9 ± 0·3 kcal. mole^{-1}, respectively.[4]

Solubility of copper nitrate in ethyl acetate by extraction of solvent. The solubility value (Table 1) was determined by shaking ethyl acetate with excess of solid for one week. The saturated solution is viscous, and the solubility was therefore confirmed by an independent method.

When copper nitrate is added to a mixture of ethyl acetate and light petroleum, separation into two liquid phases occurs. A solution of copper nitrate in ethyl acetate was therefore treated with varying quantities of light petroleum (b. p. 40—60°), and the equilibrium composition of the ethyl acetate phase determined (Table 2). As the ratio

TABLE 2.

Ratio (w/w) light petroleum : EtOAc	0	0·98	2·31	2·86	5·37	10·51	15·87
Mol. composition of EtOAc phase $[EtOAc/Cu(NO_3)_2]$	7·27	2·88	2·32	2·14	1·74	1·48	1·42

---

[2] Addison and Hodge, *J.*, 1954, 1138.

[3] Addison and Gatehouse, *J.*, 1960, 613.

[4] Greenwood and Perkins, unpublished results.

light petroleum : ethyl acetate was increased, progressively larger amounts of ethyl acetate were extracted into the petroleum phase. In the limit, the colourless upper phase consisted of ethyl acetate in light petroleum, and the lower phase was a saturated solution of copper nitrate in ethyl acetate, with a negligible content of light petroleum. The limiting composition of the ethyl acetate phase (Table 2) is in good agreement with the molar composition of the saturated solution [$\text{EtOAc}/\text{Cu(NO}_3)_2 = 1{\cdot}41$] determined by direct addition (Table 1).

Addition compound with ethyl acetate. The saturated solution may be regarded as a liquid addition compound $\text{Cu(NO}_3)_2,1{\cdot}5\text{EtOAc}$, in which a little anhydrous copper nitrate is dissolved. Copper nitrate also forms an addition compound $\text{Cu(NO}_3)_2,1{\cdot}5\text{C}_4\text{H}_8\text{O}_2$ with 1,4-dioxan.[5] The formation of a stable addition compound between copper nitrate and ethyl acetate is supported by the following observations: (*a*) When cooled to —70°, the saturated solution solidifies to a glass, and crystallisation from the solution has never been achieved. (*b*) Copper nitrate does not dissolve in benzene, yet when a solution in ethyl acetate containing less copper nitrate than is indicated by the formula $\text{Cu(NO}_3)_2,1{\cdot}5\text{EtOAc}$ is diluted by a large volume of dry benzene, no precipitation occurs.

In the presence of water, however, there is no evidence of solvation of copper nitrate by ethyl acetate. If a solution of copper nitrate in ethyl acetate is shaken with water, the salt is completely extracted into the aqueous phase. This unusual behaviour resembles that of silver perchlorate, which has a high solubility in benzene but is also completely extracted into water.

(2) *Molecular Weights.*—Molecular-weight values in the three organic solvents, determined ebullioscopically, are shown in Fig. 1. At the higher concentrations in ethyl acetate and nitromethane, the molecular weight is precisely that of the monomer. In methyl cyanide a constant but rather smaller molecular weight of 157 is observed. The electrical conductivity (Fig. 2) of methyl cyanide solutions is higher than that of solutions in nitromethane (which has similar dielectric constant) so that the lower molecular weight probably does represent some ionic dissociation, even at higher concentrations. However, the molecular weight in methyl cyanide in concentrations above 0·1M is independent of concentration, which would be surprising if ionisation was appreciable. The values in Fig. 1 were calculated by using the elevation constant $K_b = 1{\cdot}30°$ per mole per 1000 g. of solvent;[6] this was determined for organic solutes and it is possible that it may not be the exact value applicable to systems of this type.

The behaviour on dilution in all solvents is unusual; at a critical concentration of about 0·1M there is a sharp fall in molecular weight in each case. This is illustrated by comparison of the curves for methyl cyanide solutions of copper nitrate and silver nitrate (Fig. 1). The latter is typical of the variation in molecular weight which results from increasing ion association with increasing concentration. Measurements were extended to the lowest concentrations consistent with accuracy; from the shape of the curves it appears that at infinite dilution dissociation into three ions is possible:

$$\text{Cu(NO}_3)_2 \longrightarrow \text{Cu(NO}_3)^+ + \text{NO}_3^- \longrightarrow \text{Cu}^{2+} + 2\text{NO}_3^-$$

but that the sudden decrease in molecular weight below 0·1M may well represent the first stage in this dissociation.

Provided that the solvents were scrupulously dried, solutions in boiling methyl cyanide and ethyl acetate remained clear and stable. Solutions of copper nitrate in nitromethane are stable indefinitely at room temperature, but reaction occurs if the solution is boiled for some time. After a delay the clear solution suddenly evolves dinitrogen tetroxide copiously, and a green solid is deposited. Reactions of copper nitrate with organic compounds will be discussed elsewhere, but it is of interest here that such reaction is primarily a property of the monomer. With an 0·135M solution (Fig. 1) the b. p. elevation indicated

---

[5] Addison and Logan, unpublished results.

[6] Walden, *Z. phys. Chem.*, 1906, **55**, 281.

a monomer in solution, but reaction occurred within two minutes of addition of copper nitrate. For this reason measurements could not be made at higher concentrations.

(3) *Electrical Conductivities.*—Three quite different types of conductivity–concentration curve are obtained in the three media (Fig. 2). The curve showing electrical conductivity in methyl cyanide indicates that even in this medium copper nitrate is a very weak electrolyte. The general form of the curve is normal, but molar conductivity is small. The molar conductivity of tetraethylammonium nitrate in methyl cyanide at 20° varies from 128 ohm^{-1} cm.^{2} at 0·0455M to 77 ohm^{-1} cm.^{2} at 0·182M. Over the same molar concentration range, the conductivity of copper nitrate solutions varies between 15·0 and 12·6 ohm^{-1} cm.^{2}. (The molar conductivity of silver nitrate in methyl cyanide[7] is 155.2 ohm^{-1} cm.^{2} at 228·3 × 10^{-5}M.) In these solutions the methyl cyanide will compete with the nitrate group as ligand for the copper ion; molecular weights do not reach the monomer value, so that some ionic dissociation no doubt occurs. However, since the dielectric constant of methyl cyanide is 37·5, this dissociation must be small at concentrations above 0·1M. The vertical line *A* (Fig. 2) represents the concentration below which molecular-weight values fall rapidly, and the increase in conductivity below this concentration is therefore in accord with the molecular-weight data. It should be emphasised that the latter represent the condition of the solution at the boiling point, whereas conductivities were determined at 20° or 25°. However, the broad correlation between molecular weight and conductivity data suggests that the temperature difference is not of major significance.

FIG. 1. *Molecular weight of copper nitrate in non-aqueous solvents.*

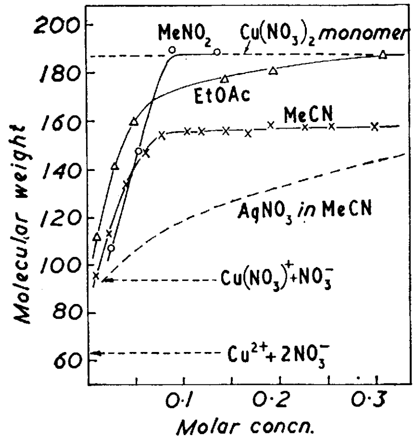
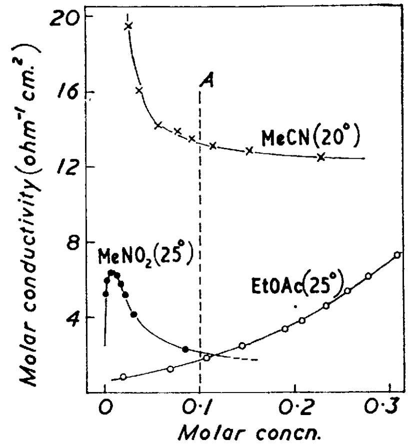


FIG. 2. *Molar conductivity of copper nitrate solutions.* (*The conductivity values for ethyl acetate solutions have been multiplied by* 100.)



The conductivity values in ethyl acetate are extremely low, all measured values lying below 0·1 ohm^{-1} cm.^{2}. The dominant factor here is the low dielectric constant (6·02), so that conductivity at low concentrations would not be expected to reflect with any sensitivity the change in species in solution. The main feature of interest is the steady increase in molar conductivity with increasing concentration. Such increases have been observed following a conductivity minimum, as in the classical measurements of Fuoss and Kraus[8] on solutions of tetraisopentylammonium nitrate in water–dioxan mixtures, but even with very dilute solutions of copper nitrate in ethyl acetate no minimum has been detected. In the higher concentration range, no interpretation based on a major change

---

[7] Walden and Birr, *Z. phys. Chem.*, 1929, **144**, 269.

[8] Fuoss and Krauss, *J. Amer. Chem. Soc.*, 1933, **55**, 21.

in species in solution is acceptable, since conductivity continues to increase over the concentration range for which, according to molecular-weight measurements, the species present is precisely the monomer. We consider that the dissolution of appreciable amounts of polar copper nitrate molecules increases the effective dielectric constant of the ethyl acetate solution; if it is accepted that ionic dissociation can occur to a minute extent under these conditions, then the increase in conductivity may be attributed to a small but regular increase in the effective dielectric constant.

The low molar conductivity values observed in nitromethane indicate that copper nitrate is virtually a non-electrolyte in this medium. Electrolytes of the type $M^{2+}(X^-)_2$ give molar conductivities[9] in M/1000-solution and at 25° in the range 200—240 ohm^{-1} cm.^{2}. The maximum value found for copper nitrate is 6·5 ohm^{-1} cm.^{2}, and above the monomer concentration (line *A*, Fig. 2) the value is <2 ohm^{-1} cm.^{2}. The difference between the conductivity values at high concentrations in nitromethane and methyl cyanide is readily attributable to the greater ligand strength of the latter. At concentrations below line *A*, conductivity increases; this resembles the behaviour in methyl cyanide and is again consistent with molecular-weight data. However, in high dilution the behaviour is quite abnormal. Three aspects must be considered here: (*a*) the copper nitrate molecule dissociates into ions in this range; (*b*) the solutions at 25° are quite stable; their absorption spectra over the available wavelength range[10] compare closely with those in other solvents, and neither the spectra nor the electrical conductivity changes with time; (*c*) the dielectric constant of nitromethane (35·9) is near to that of methyl cyanide (37·5).

It would be expected therefore that, as concentration decreases, the molar conductivity should increase rapidly to values comparable with those of methyl cyanide solutions. Instead, the conductivity increases only slightly, and passes through a maximum at M/100-concentration. There thus exists some superimposed physical effect which produces a decrease in molar conductivity with decreasing concentration. Curves of this type are obtained with anhydrous zinc nitrate and anhydrous cobalt nitrate, and also with nitromethane solutions of the addition compounds $Cu(NO_3)_2,N_2O_4$ and $Fe(NO_3)_3,N_2O_4$[5] and appear to be characteristic of solutions of anhydrous metal nitrates in nitromethane. No satisfactory interpretation can be offered at this stage; it is possible that the nitrate ion may be solvated by nitromethane to a sufficient extent to reduce its mobility, but no supporting evidence for this is available and solvent absorption prohibits the study of the ultraviolet spectrum in the 250—350 mμ range.

(4) *Absorption Spectra.*—Ultraviolet absorption spectra for ethyl acetate and methyl cyanide solutions are given in Fig. 3, together with curves for dioxan and ethyl alcohol for comparison. Extinction coefficients in the first three solvents are of the order of 2000, compared with $\varepsilon = 12$ in aqueous solution. Ethyl alcohol solutions show intermediate behaviour. $\lambda_{max.}$ is 302·5 mμ for the NO_3^- ion in water; in the two oxygen-containing solvents dioxan and ethyl acetate, $\lambda_{max.}$ is changed only slightly to 294 mμ. In contrast, $\lambda_{max.}$ is increased to 323 mμ in methyl cyanide solutions. Methyl cyanide therefore causes an appreciable modification in the spectrum of both the NO_3^- and Cu^{2+} ions; in the visible range $\lambda_{max.}$ lies in the limits 785—820 mμ for water, nitromethane, ethyl acetate, and dioxan solutions, but in methyl cyanide $\lambda_{max.}$ is displaced to 750 mμ, with $\varepsilon_{max.} = 47$.

The factors responsible for the high absorption by the nitrate group in non-aqueous solvents are not yet properly defined. Katzin[11] found high ε values (of the order of 1000) for nitrate absorption in solutions of hydrated copper nitrate in t-butyl alcohol, and attributed this to the distortion suffered by the electronic orbitals of the nitrate group on entering the co-ordination sphere of the metal ion. With solutions of anhydrous copper nitrate in the absence of water, the ε values (Fig. 3) are higher than any previously observed. This is consistent with Katzin's interpretation, but since the copper and nitrate

[9] Nyholm and Parish, *Chem. and Ind.*, 1956, 470.

[10] Addison and Hathaway, *J.*, 1960, 1468.

[11] Katzin, *J. Chem. Phys.*, 1950, **18**, 789; *J. Inorg. Nuclear Chem.*, 1957, **4**, 187.

ions show an unusually strong tendency for covalent bonding, the distortion of the nitrate group from planar to pyramidal may also be a contributory factor.[12] On these arguments, high absorption is to be expected at concentrations where copper nitrate is monomeric in solution. However, if complete dissociation into three ions occurs on dilution, there should be a marked decrease in ε; this has been examined for methyl cyanide and ethyl acetate solutions (see Table 3).

TABLE 3. *Influence of copper nitrate concentration on ultraviolet absorption spectra.*

(*a*) In methyl cyanide.

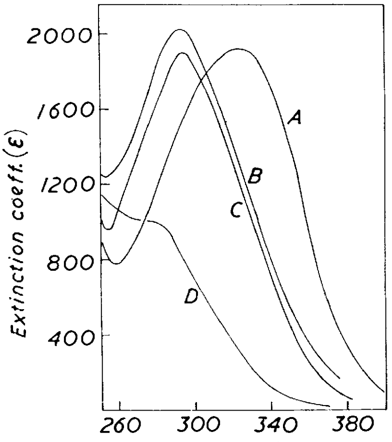
Molar concn.	ε	$\lambda_{max.}$ (mμ)
0·00055	1775	325
0·00111 *	1900	323
0·00222	1905	320
0·00444	1930	320
0·00888	1860	318
0·01292	1860	318

(*b*) In ethyl acetate.

Molar concn.	ε	$\lambda_{max.}$ (mμ)
0·00060	1960	294
0·00120 *	2010	294
0·00965	2180	294
0·1068	2400	294

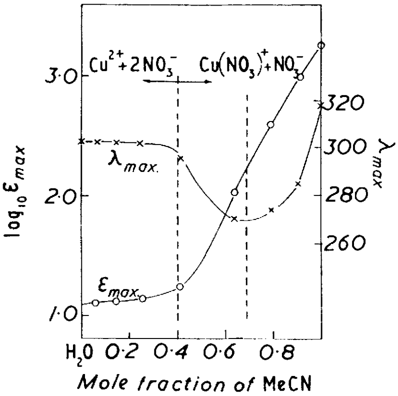
* Curves given in Fig. 3.

FIG. 3. *Ultraviolet absorption spectra of copper nitrate solutions.*



A, MeCN. *B*, EtOAc. *C*, Dioxan. *D*, EtOH.

FIG. 4. *Absorption spectra of copper nitrate in methyl cyanide–water mixtures.*



In methyl cyanide, a 25-fold change in concentration introduces only a small variation in $\varepsilon_{max.}$. It should be noted that the concentrations used in this case fall in a range in which dissociation is appreciable (Fig. 1) and in which the molecular weight is approximately half that of the monomer. If we continue the assumption that the high absorption results from a nitrate ion which is covalently bonded rather than present in an ion pair, all observations can be correlated on the basis that the first-stage dissociation is

$$Cu(NO_3)_2 \longrightarrow Cu(NO_3)^+ + NO_3^-$$

and that the species $Cu(NO_3)^+$ is responsible for the high absorption. This conclusion is supported by the results on ethyl acetate solutions (Table 3). The concentrations used cover a wider range, including the high concentration at which the solute is present as a monomer, and the variation in $\varepsilon_{max.}$ is consequently greater. Nevertheless, all values of $\varepsilon_{max.}$ are high. There is reason to believe that in the solid state[13] and the gaseous state[14]

[12] Holleck, *Z. phys. Chem.*, 1944, **194**, 140.
[13] Wallwork, *Proc. Chem. Soc.*, 1959, 311.
[14] Bauer and Addison, *Proc. Chem. Soc.*, 1960, 251.

the two nitrate groups in copper nitrate are bonded differently so that stepwise dissociation is feasible.

Since methyl cyanide and water are miscible in all proportions, it was of interest to study the variation in the absorption spectrum of copper nitrate with solvent composition (see Fig. 4). Neither $\varepsilon_{max.}$ nor $\lambda_{max.}$ varies regularly with mole-fraction of methyl cyanide; three stages can be discerned, which can again be interpreted on the basis of stepwise dissociation. Up to 0·4 mole-fraction of methyl cyanide, absorption characteristics are similar to those in water; $\lambda_{max.}$ is unchanged at 302·5 mμ and $\varepsilon_{max.}$ increases only slightly (from 12 in water to 18·0 in 0·407 mole-fraction of methyl cyanide). The solute may be regarded as fully dissociated into $Cu^{2+} + 2NO_3^-$ ions. Thereafter, ε increases rapidly, and this solvent composition coincides with that at which $\lambda_{max.}$ decreases. This is believed to be the composition at which association to $Cu(NO_3)^+ + NO_3^-$ begins. The third stage, beginning at about 0·7 mole-fraction of methyl cyanide, is revealed by a slight change in direction of the $\varepsilon_{max.}$ curve, and a minimum in the values for $\lambda_{max.}$. The formation of some monomer may occur here, but this effect is more probably related to changes in the solvation shell of the $Cu(NO_3)^+$ ion.

All measurements shown in Fig. 4 were made at the same copper nitrate concentration (0·0118M). $\varepsilon_{max.}$ in water is independent of concentration, and in methyl cyanide (Table 3) varies only slightly with concentration. In view of the postulated change in species in the mixed solvent, the influence of concentration on $\varepsilon_{max.}$ was also examined in a region (0·791 mole-fraction of methyl cyanide) where $\varepsilon_{max.}$ might be particularly sensitive to concentration. Results are as tabulated.

Molar concn. of $Cu(NO_3)_2$ in 0·791 mole-fraction MeCN ...	0·0118	0·0236	0·0354
$\varepsilon_{max.}$	410	422	460
$\lambda_{max.}$	275	275	275

The variation is somewhat larger than with the pure solvents, but does not invalidate the general conclusions to be drawn from Fig. 4.

Experimental.—Copper nitrate was prepared as already described.[1]

Solvents were dried and purified scrupulously by standard methods. Ethyl acetate was finally purified by distillation from a copper nitrate solution.

Molecular weights were determined in Cottrell's apparatus, suitably guarded against entry of moisture. Ultraviolet spectra were determined with the Unicam S.P. 500 spectrophotometer, with matched fused silica cells and ground stoppers. Electrical conductivites were measured by using the circuit described by Greenwood and Worrall,[15] and a conductivity cell of the type designed by Groeneveld and Zuur.[16]

One of us (A. W.) is indebted to the Department of Scientific and Industrial Research for a Maintenance Grant.

THE UNIVERSITY, NOTTINGHAM.
[*Received, April 11th*, 1960.]

[15] Greenwood and Worrall, *J. Inorg. Nuclear Chem.*, 1957, **3**, 357.
[16] Groeneveld and Zuur, *Rec. Trav. chim.*, 1953, **72**, 617.