Comparison of ESR Spectra of Two Cu(II) Salts in Some Amide Solutions

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Dedicated to Professor Dr. E. Wicke

X-band ESR spectra of liquid solutions of Cu(II)nitrate and Cu(II)chloride in N-methylformamide and four N,N-disubstituted amides are reported and discussed with respect to the occurrence of ion pairs or higher ionic aggregations. Nitrate solutions allow to distinguish two complex types of moderate asymmetry at most. Chloride solutions indicate a succession of at least three complex types with strongly increasing asymmetry.

Introduction

In a previous paper [1] concerned with dielectric relaxation spectroscopy of liquid electrolyte solutions we reported, among others, on copper(II) salts in N,N-diethylacetamide (DEA) solution. At sufficiently high concentration the salts studied, Cu(II)nitrate and Cu(II)chloride, exhibit a lower frequency spectral component which, as in the case of other salts, can be ascribed to ion pairs or other ionic aggregations, the relative intensity of these contributions being different for both solutes. The dielectric data, however, did neither allow to distinguish (possibly) different species nor to elucidate their nature. In order to gather further information in that respect, it seems worthwhile to consider the electron spin resonance (ESR) of the paramagnetic Cu^{2+} ion. With the aim of discriminating, if possible, amongst different species (which are observed on the same time scale by both methods), the present paper regards the ESR of the two above-mentioned salts dissolved in some amides. For direct comparison with the dielectric behaviour, high concentrations had to be measured. However, since in the case of ESR measurements the dipole-dipole interactions would complicate the discussion of spectra, we restrict ourselves to moderate Cu^{2+} concentrations but study also some solutions with an excess of the respective anion as obtained by addition of a non-paramagnetic salt.

The salts $Cu(NO_3)_2 \cdot 3H_2O$ (CuN) and $CuCl_2 \cdot 2H_2O$ (CuC) were both used in hydrated form; for comparison, however, also solutions of (nonhydrated) $CuCl_2$ and solutions with additional water content were measured. A series of amides was employed as solvents, namely N-methylformamide (MFA), N,N-dimethylformamide (DMF), N,N-diethylformamide (DEF), N,N-dimethylacetamide (DMA) and N,N-diethylacetamide (DEA). Solutions in DMF and DEA as typical representatives of diamides were studied in particular.

Experimental

The ESR measurements were carried out with an X-band spectrometer Bruker ESP 300, equipped with a Hall probe ER032M and a NMR-Gaussmeter ER035M for field measurement. Picein was used as standard for field as well as intensity determination [2]. The sample temperature was controlled by a gas flux system; measurements were done within the liquid range only.

Salts and solvents from Aldrich and Fluka were used as obtained.

Formal Description of the ESR Spectra

The Cu^{2+} ion in liquid solution exhibits usually an ESR quartet, the four more or less resolved hyperfine (HFS) lines resulting from the nuclear spin $I = 3/2$. It is well established experimentally as well as theoretically that under rapid motion conditions (i.e. not too high viscosity) these HFS components are of

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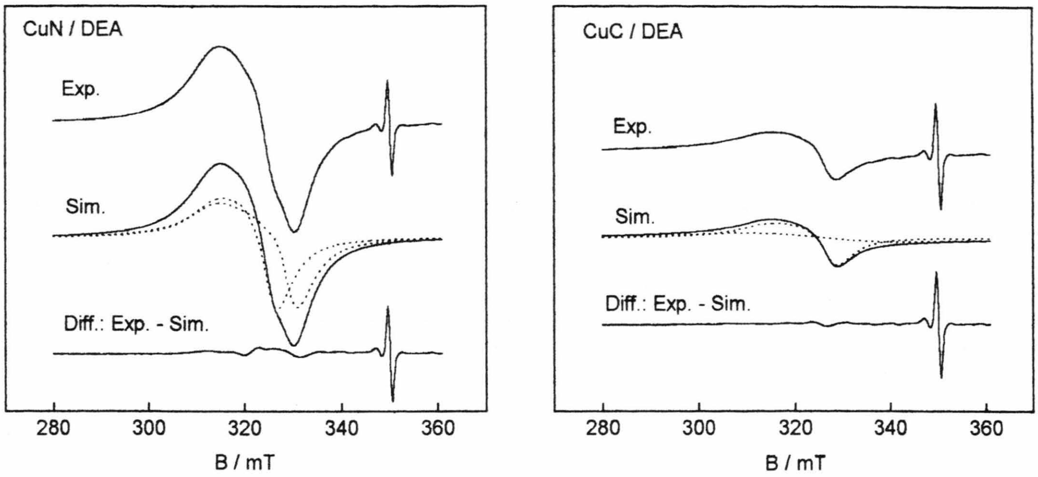

Fig. 1. Two examples of experimental ESR spectra and their simulatioin using 4-Lorentzian components (dotted lines). Fit parameters as given in Table 1 (for left spectrum, types **S** and **N**; for right spectrum, types **S** and **C''**). The signal on the high field side is due to the standard (picein). Salt concentration $c = 0.05$ mol/l, temperature 20 °C in both cases. No additional chloride.

Lorentzian shape [3]. In fact, the spectra of various well-defined species of different size in solvents of different viscosity have been found to be describable within experimental uncertainties by four Lorentzians [3, 4]. The viscosities of the solutions studied here are moderate ($\eta = 0.8 \ldots 1.7$ mPa s), corresponding conditions can thus be assumed to hold. Additional measurements with homologous diamides have demonstrated that 4-Lorentzian spectra are even found at increased viscosities (N,N-dibutylformamide, $\eta = 3.6$ mPa s), only at still higher viscosities a tendency toward spectra resembling powder patterns is revealed (N,N-diethyl-*m*-toluamide, $\eta = 21$ mPa s). With the five amides considered here we have observed the 4-Lorentzian shape for a number of examples, even those (regarded in the discussion section) where other data suggest more than one species to be present. On the other hand, we have found examples with significant deviations. It seems permissible to conjecture that the latter finding is a sufficient, though not necessary, indication that the spectra originate in more than one well-defined kind of complexes rather than assuming inhomogeneity effects in the lineshape of one and the same species. It was possible to describe those spectra as superposition of components of the 4-Lorentzian type, characterized by individual magnetic parameters, in particular by notably different g factors and/or linewidths. With respect to the introductory question we presume that these spectral components are due to "chemically" distinguishable species.

The analysis of spectra is illustrated in Figure 1. Its left part represents a typical unresolved spectrum which already at a first glance indicates deviations from the 4-Lorentzian character. As shown in the figure, it can be simulated as the sum of two spectra, both broadened and differing mainly in their g factor. The spectrum in the right part of Fig. 1 is broadened, too. In comparison to the first one, its intensity is reduced, as may be seen in relation to the standard signal. The fit requires a very broad background signal in that case.

The numerical simulation of the spectral shape was carried out under visual control of the fit quality. It was possible in all cases by use of one or two (in a few cases three) 4-Lorentzian components. It yields for each component the following parameters:

(I) g as determined from the center of gravity of the four lines,
(II) $\bar{A}$, the mean distance of HFS lines (the simulation uses individual distances but the HFS lines were found to be approximately equidistant),
(III) ΔH_{pp}, the linewidths of the four HFS lines (usually decreasing with increasing field); for easy comparison, the mean width $B = \overline{\Delta H_{pp}}$ will be considered,
(IV) I/I_0, the relative intensity of the respective spectral component, based on the numerical double inte-

gration of the experimental spectrum after normalization relative to the standard signal. Here I_0 is calibrated by comparison with Cu salt solutions in various solvents (including aqueous solutions) for which it can reasonably be assumed that *all* spins contribute to the spectrum observed. Consequently the possible I/I_0 values vary between 0 and 1.

Table 1. Classification of the 4-Lorentzian spectral components occuring in the fits of the experimental ESR spectra. The different types are denoted by capitals (**F** etc.). The parameters given are the g factor, the mean distance $\bar{A}$ of HFS lines (in mT) and the mean linewidth $B = \overline{\Delta H_{pp}}$ (in mT) as found for low Cu^{2+} concentrations ($c \approx 0.05$ mol/l) at 20 °C. Uncertainties are in the last digit given. Salts: CuN = $Cu(NO_3)_2 \cdot 3H_2O$; CuC = $CuCl_2 \cdot 2H_2O$.

Type (species)	Parameter	Salt	Solvent MFA	DMF	DEF	DMA	DEA
F	g	CuN	2.202	2.200	2.194		
		CuC	2.201	2.196	2.190		
	$\bar{A}$	CuN	3.8	4.0	3.8		
		CuC	3.9	4.1	4.1		
	B	CuN	2.2	2.4	2.7		
		CuC	2.3	2.3	2.3		
S	g	CuN	2.190	2.183	2.186	2.190	2.185
		CuC	2.180	2.182	2.184	2.193	2.186
		[a]		(2.180)			
	$\bar{A}$	CuN	3.7	3.7_5	3.6	3.4	3.8
		CuC	3.8	3.8_5	3.9	3.5	3.4
		[a]		(4.0)			
	B	CuN	5.0	4.9	6.7	6.6	7.8
		CuC	5.3	7.4	7.4	6.8	7.6
		[a]		(4.9)			
N	g	CuN					2.168
	$\bar{A}$	CuN					3.6
	B	CuN					7.0
C′	g	[a]		(2.162)			
		[b]		2.161			
	$\bar{A}$	[a]		(4.2)			
		[b]		4.4			
	B	[a]		(7.2)			
		[b]		7.8			
C″	g	CuC					2.156
	$\bar{A}$	CuC					3.6
	B	CuC					30

[a] CuC/DMF component **S** with c dependent B decomposed into two components **S** and **C′** with constant B (parameters in parentheses).
[b] CuN/DMF with chloride excess, *cf.* Figure 3.

Results and Discussion

By arranging the 4-Lorentzian components found for each system in the order of decreasing g and cross-comparing the parameters (I) to (III) of the different systems, the spectral components required for fitting can tentatively be classified as shown in Table 1. (The capital letters used for the designation of the component types refer to their interpretations as discussed in the following.) That classification shall serve here merely as means of distinguishing between spectral components.

Systems with DMF and DEA as solvent have been studied in two concentration series, either by dissolving only the Cu salt ($c = 0.05$ to 0.8 mol/l) or by keeping the Cu^{2+} concentration at a low value (≈ 0.05 mol/l) and adding NaCl in increasing concentration to study the effect of chloride excess. It turned out that the parameters (I) to (III) of the spectral components as recorded in Table 1 were practically independent of concentration in both series. An exception is the system CuC/DMF where for component **S** the linewidth B was found to increase with increasing c (up to 12 mT at $c = 0.8$ mol/l), provided one attempts to fit the spectra with the minimum number of components. This variation, however, can formally be described in an alternative manner by keeping the linewidth B unaltered and introducing an *additional* spectral component with smaller g. Both possibilities are included in Table 1. Is should be stressed in that context that generally the description of the spectra by a minimum number of discrete components is simple but not compelling and that a more structured distribution of parameters, even a continuous one, is feasible as well.

Parameter (IV), that is the relative intensity I/I_0, shows a pronounced concentration dependence which will be helpful in assessing the respective components. It shall therefore be regarded in the first instance. In Figure 2, I/I_0 is displayed as function of salt concentration, and in Fig. 3 it is given for the CuN/DEA and CuN/DMF systems with added Cl^-.

Before discussing these results, a remark should be made on the influence of the water content. The parameters given in Table 1 stay practically unchanged if nonhydrated CuC is used or if the water content of the solvent is increased. Even the mean linewidth B is only little altered; at most the *ratio* of

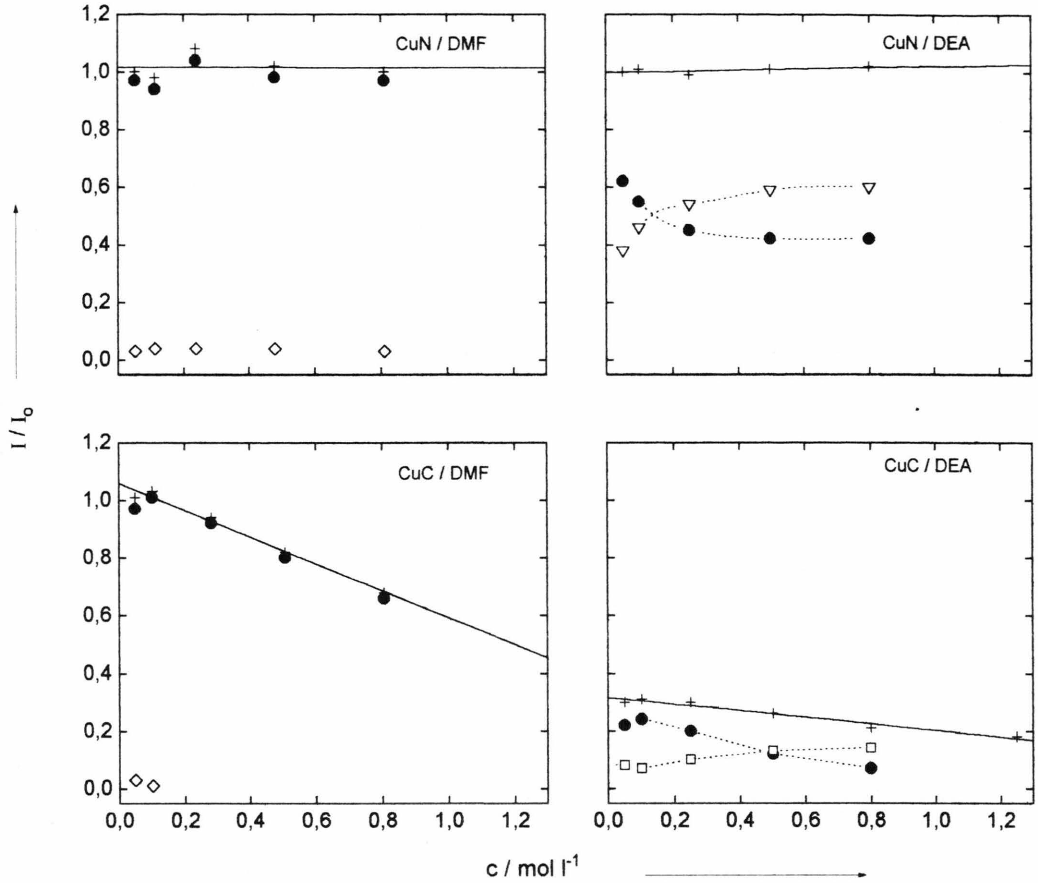

Fig. 2. Relative intensities I/I_0 of fitted spectral components against concentration c of salt solutions (no additional chloride), 20 °C. The lines are guides to the eye only. Symbols for spectral components (*cf.* Table 1): ◇ **F**, ● **S**, ▽ **N**, □ **C″**. Sum of intensities of components detected: +.

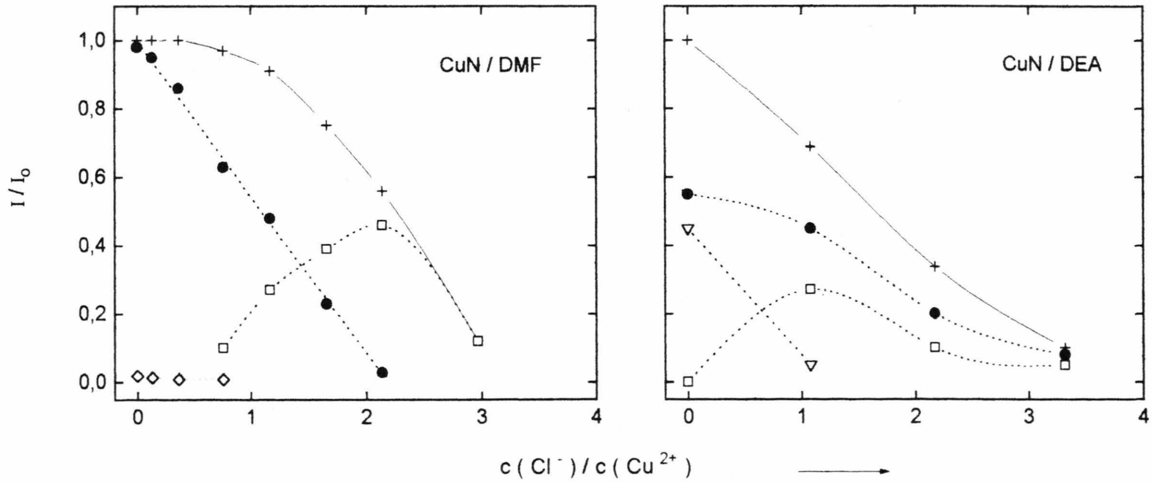

Fig. 3. Relative intensities I/I_0 of fitted spectral components for CuN ($c = 0.05$ mol/l) with added NaCl in DEA and DMF solution, 20 °C. Symbols as Fig. 2, except for: □ **C′** (Table 1).

widths of the four HFS lines decreases toward unity. This behaviour is probably due to the well known solvent-solvent interactions in diamide-water mixtures which result in a preferential solvation rather than hydration of ions as far as the water content is not too high [1, 5, 6]. Water effects can therefore be left out of consideration.

It is expedient to start the discussion with the spectral component termed **S** since this is common for all systems studied. In particular for CuN/DMF (Fig. 2), it accounts for nearly the whole intensity ($I/I_0 \approx 1$) over the salt concentration range studied. On addition of chloride (Fig. 3), component **S** is reduced in its relative intensity. These findings suggest that **S** might originate in solvated Cu^{2+} ions which do not interact with counterions. However, such a general assumption is not tenable. First, the conductivity of CuN in the diamides DMF to DEA is clearly less than expected for a completely dissociated salt [7–10]. To take into account the different viscosities η, one may regard the Walden type product $\Lambda\eta$, where Λ is the 'equivalent conductivity'. At moderate concentrations ($c \approx 0.5$ mol/l), its value is $<30\%$ of the expected one in any case, and it decreases in the order DMF, DMA, DEF, DEA [10]. Second, the dielectric relaxation spectra of CuN/diamide systems [1] exhibit a contribution which, at least at moderate and higher concentrations, indicates the existence of polar "ion pair" species (using that term in a broad sense for moieties involving cations and anions). This leads to the conclusion that component **S** represents not only solvated Cu^{2+} ions but also certain "ion pair" species, *viz.* complexes including the NO_3^- ion. Dielectric relaxation data point to solvent shared ion pairs. Perhaps this is the reason for only insignificant changes of the ESR parameters in comparison to solvated ions.

For CuN/DEA, the system which presumably contains the largest fraction of "ion pair" species, there appears an additional ESR spectral component termed **N** which differs from component **S** mainly by its smaller g factor (Table 1). This component **N** is suppressed (as also S) when chloride is added (Fig. 3), which shows as well that it is related to an "ion pair" species involving NO_3^-.

Altogether, the solutions of CuN can entirely be characterized by these spectral components **S** and **N**. There is no "missing" fraction in the the sum of relative intensities. Thus it is sufficient to take into consideration the occurrence of two types of "ion pair" species at most. Since the parameters of **N** are consistent with the assumption of tetragonally distorted symmetry, this may relate to $[Cu(NO_3)_2]$ with anions in axial position, as proposed for glassy Cu(II)nitrate solutions [11]. According to the dielectric results, the species with properties corresponding to **S** should then be polar, thus it may be $[CuNO_3]^+$ in the form of a solvent shared ion pair.

The situation is different for the solutions of CuC. It is interesting to note that on addition of chloride to CuN solutions, in particular in the case of the solvent DEA, one finds for the ratio $c(Cl^-)/c(Cu^{2+}) \approx 2$ just the same spectrum as with a solution of solely CuC (Figure 3). This means that complexes involving Cu^{2+} and Cl^- ions are formed which are preferred in competition with NO_3^- involvement. Moreover it may be noticed that on increasing concentration, both of solely CuC as well as excess Cl^-, there is an increasing fraction of I/I_0 "missing". This may be ascribed to a species **X** which evades detection possibly because of too broad an ESR signal. With increasing concentration, the different spectral components appear in the sequence **S**, **C′ + C″**, **X**. Here **C′** and **C″** are written in combination since it cannot be excluded that they represent equivalent circumstances which exhibit different linewidth B in analogy to the above-mentioned concentration dependence of component S. Together with an "ion pair" species probably contributing to **S** also in the case of CuC solutions, one has thus to take into consideration three magnetically distinguishable "ion pair" species at least.

This finding is in qualitative accord with the inferences drawn from other investigations, which have shown that complexes $[CuCl]^+$, $[CuCl_2]$, $[CuCl_3]^-$ and $[CuCl_4]^{2-}$ may occur in DMF [12–14] and other aprotic solvents [15–17]. The latter complex is likely to be formed only to a minor amount [12].

We have not yet referred to the spectral component of type **F** (Table 1). It is peculiar in appearing only with formamide derivatives as solvent. In comparison to the other components, it is distinguished by rather narrow HFS lines and the highest g value, similar to that of aqueous solutions (2.200 [18]). This is indicative of a complex of cubic symmetry, perhaps a CuF_6 solvation complex, where F stands for the formamide. Such a complex is unlikely in acetamide solutions due to steric reasons [19]. The relative intensity of component **F** is very small (it is noticeable in the spectra only due to beginning HFS resolution).

Lastly some inferences may be drawn from the linewidths B which, however, must remain qualitative in character since B is influenced by various structural and dynamical properties. It has been shown [3] that Cu(II) spectra of solutions are well described by the Kivelson theory [20] according to which B contains different contributions. These consist of structural factors depending on the anisotropies Δg of the g tensor and ΔA of the HFS tensor, and dynamical factors depending on the rotational tumbling correlation time τ_c. Moreover, in the case of small anisotropies, the stochastic distortion of the ligand arrangement rather than rotational motion may govern the relaxation. Also, exchange between two species may contribute to the linewidth. For many situations the contribution with a dynamical factor proportional to the rotational correlation time is estimated to be predominant [18]. Adopting this also for the present systems, let us assume that in a *qualitative* sense $B \sim f(\Delta g, \Delta A) \cdot \tau_c$.

Dielectric measurements [1] did not give any hint at spectral components with considerably different rotational tumbling correlation times. For the species observable by this method, that is for the polar ones, but possibly also for others, it is thus unlikely that the appreciable differences in ESR linewidths B are due to large differences in τ_c. Rather they will relate to the anisotropies Δg and/or ΔA, that is qualitatively to the electrical asymmetry of the respective complexes. In that regard CuN and CuC solutions again differ clearly. For CuN, the linewidths observed do not exceed $B \approx 7 \ldots 8$ mT, indicating complexes of moderately distorted symmetry. For CuC, on the other hand, the linewidths increase beyond the detectable limit, which is not implausible for higher complexes such as $[\mathrm{CuCl_3}]^-$. In qualitative accord with this inference, the dielectric relaxation behaviour of CuN is indicative of more polar species than that of CuC.

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