

Spectroscopic Investigations of the Ternary System $\text{Cu}(\text{OAc})_2/\text{NH}_4\text{OAc}/\text{HOAc}$

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Solutions of copper acetate in anhydrous acetic acid containing ammonium acetate have been investigated by means of UV-VIS, ESR and ^{14}N NMR spectroscopy. The influence of temperature and ammonium acetate concentration has been studied and some solid addition compounds have been isolated and spectroscopically characterized. On the basis of these results, some conclusions can be drawn with respect to the molecular species present in the system, and to the reasons of the thermochromic behaviour of these solutions. It has been shown that in contrast to former investigations, copper acetate is present in acetic acid in both the monomeric and dimeric form.

Introduction

The thermochromic behaviour of the ternary system $\text{Cu}(\text{OAc})_2/\text{NH}_4\text{OAc}/\text{AcOH}$ was first observed 50 years ago [1] and the change of greenish blue to a blue-violet colour at a temperature of 110 °C was first attributed to the formation of a copper–amine complex $\text{Cu}(\text{NH}_3)_n^{2+}$. This assumption was accepted in the literature until 1967, when Hardt and Streit [2] investigated the system by means of UV-VIS spectroscopy, finding no evidence for the formation of an amine complex. Two peaks were observed only, which have to be assigned in accordance with other investigations [3] to the d–d transition of copper and to the dimeric species $\text{Cu}_2(\text{OAc})_4$. Solid addition compounds can be also isolated from this system, but they have not been characterized spectroscopically so far [2]. In the work presented here, several methods of spectroscopy have been employed in order to obtain a more detailed analysis of the thermochromic behaviour within the full temperature range up to 120 °C, and in order to obtain some more information about the composition of the system depending on temperature and salt concentration.

Method

ESR

ESR spectra of solutions and the solid addition compound $\text{Cu}(\text{OAc})_2 \cdot 4\text{NH}_4\text{OAc} \cdot 4\text{HOAc}$ were

recorded, since any change in the composition of the solution, especially a change in the coordination of the copper ion should be accompanied by a change in the magnetic behaviour and thus by a change of the ESR spectra.

UV-VIS

The absorption spectra and their dependence on temperature could be regarded as the most promising tool for the observation of new species responsible for the thermochromic behaviour. They also should enable the observation of equilibria between different molecular species being formed according to the salt concentration.

NMR

Recording of the NMR spectra of the nitrogen nucleus should allow a rather doubtless decision, whether any interaction between the copper ion and the nitrogen atoms of the ammonium- or amino-groups takes place, and if temperature influences this interaction. Proton NMR spectra have also been recorded, but their information content is rather poor and hence not discussed below.

Experimental

Solutions

Anhydrous acetic acid was prepared by boiling 24 hours with acetic acid anhydride and fractional distillation over a column. Reagent grade copper acetate was dried at 98 °C to obtain the anhydrous form. Ammonium acetate was recrystallized from ethanol/ether, the anhydrous form dried *in vacuo*. All further operations have been carried out under nitrogen atmosphere. The UV-VIS spectra have been recorded with a Pye-Unicam SP 1700/1800 spectrometer, the ESR spectra with a Varian E-104A spectrometer and the ^{14}N NMR spectra with a Bruker WP 80 FT-spectrometer using aqueous NaNO_3 solution as standard.

Solids

$\text{Cu}(\text{OAc})_2 \cdot 4\text{NH}_4\text{OAc} \cdot 4\text{HOAc}$ was prepared from a 0.04 M solution of copper acetate in anhydrous

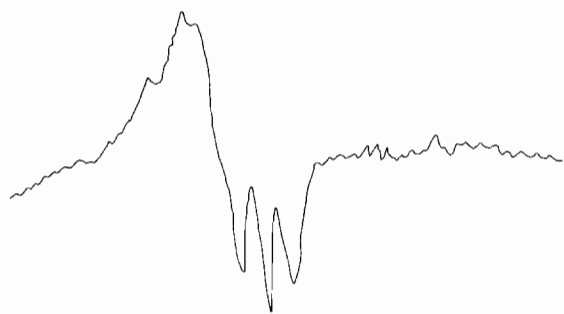


Fig. 1. ESR spectrum of 0.005 *M* copper acetate solution in anhydrous acetic acid.

acetic acid by addition of 40 g ammonium acetate per 100 ml solution and crystallization after cooling. After filtration and washing with HOAc/ether and ether, the compound is dried *in vacuo*. Elemental analysis (theoretical values in parenthesis): Cu 8.8% (8.7%), C 32.7% (32.9%), H 6.9% (6.9%), N 7.6% (7.6%).

A DTA analysis of this compound was performed. In contrast to former results leading to a linear loss of weight [2], we observed a clear plateau between 140 and 200 °C, which can be attributed to the formation of the species $\text{Cu}(\text{OAc})_2 \cdot \text{NH}_4\text{OAc}$.

Dissolving the compound in polar solvents leads to the precipitation of a deep violet compound, identified as $\text{Cu}(\text{NH}_2)_2(\text{OAc})_2$. This copper diamino-diacetato complex can be synthesized also by dissolving 1 g copper acetate and 0.42 g ammonium acetate in 150 ml anhydrous acetone and precipitation of the complex by addition of another 0.42 g ammonium acetate. Elemental analysis (theoretical values in parenthesis): Cu: 29.5% (29.7%), C 22.3% (22.3%), H 5.6% (5.6%), N 12.8% (13.0%).

Results

ESR Spectra

In contrast to the literature [2, 3] stating that solutions of copper acetate in anhydrous acetic acid do not give any observable ESR signal, we obtained a well resolved spectrum of the 0.005 *M* solution (the same concentration was used also for the UV-VIS spectroscopy). The ESR spectrum is shown in Fig. 1. In contrast to former assumptions – based on the non-existence of an ESR signal – we have to assume that copper acetate is not only present in its dimeric form, but also as monomer in such solutions. The UV/VIS spectra discussed below give some more support to this assumption.

Raising the temperature leads to a broad signal without hyperfine structure. In the ternary system, containing also ammonium acetate, a decrease of the *g* values can be observed, which can be interpreted by

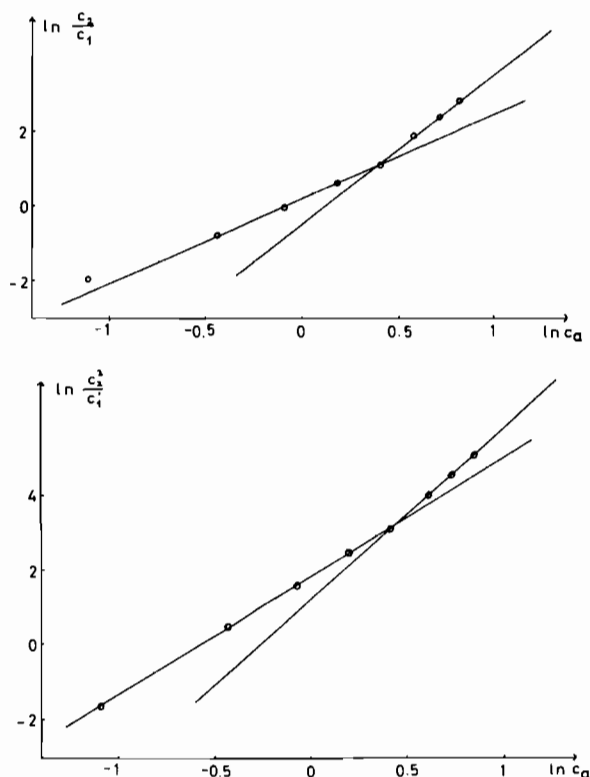


Fig. 2. Graphic evaluation of UV/VIS spectroscopic data according to equations (1) (Fig. 2a) and (2) (Fig. 2b).

the formation of adducts of copper acetate and ammonium acetate with a lower *g* value. The increase of the *g* value with increasing temperature supports this interpretation, since less adducts should be present at elevated temperature, and hence the *g* value again more closed to that of the pure copper acetate solution.

In addition to the solutions, the ESR spectrum of the solid addition compound $\text{Cu}(\text{OAc})_2 \cdot 4\text{NH}_4\text{OAc} \cdot 4\text{HOAc}$ has been recorded (Fig. 2). Two *g* values ($g_{\parallel} = 2.318$, $g_{\perp} = 2.058$) can be taken from the spectrum. It can be concluded therefore, that the copper atom is present as monomeric and in a coordination with D_{4h} symmetry [4]. The average *g* value corresponds to that of copper acetate solutions with a high excess of ammonium acetate, indicating thus the presence of similar adducts in the solutions and supporting the interpretation of the dependence of *g* values on concentration and temperature of the solution as given above.

UV/VIS Spectra

The spectrum of the pure copper acetate solution in acetic acid shows two bands at 687 and 366 nm, which have been assigned to the d-d transition and to dimeric copper acetate, respectively [3]. Addition of ammonium acetate to this solution weakens both

TABLE I. Absorption and Molar Extinction Coefficients for the Ternary System Cu(OAc)₂/NH₄OAc/HOAc, (c_{tot} = Cu(OAc)₂ concentration, c_A = NH₄OAc concentration, R = molar ratio, A = absorption at 687 nm, e = extinction coefficient).

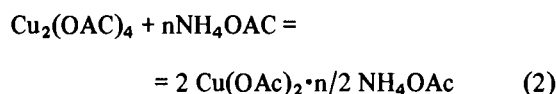
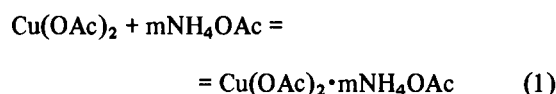
c_{tot} (mM)	c_A (M)	R	A	e
5.48	0.000	0	1.207	220
5.33	0.328	62	1.071	201
5.42	0.637	117	0.937	173
5.32	0.916	181	0.782	147
5.19	1.210	233	0.641	123
4.97	1.500	302	0.532	102
5.03	1.833	365	0.449	89
4.94	2.054	416	0.400	81
4.88	2.290	470	0.370	76
4.74	2.547	538	0.328	70
4.61	2.792	606	0.317	69
4.50	3.110	691	0.297	66
4.39	3.262	743	0.289	66

bands; the main influence is observed, however, at the peak at 366 nm, which disappears at a 300 fold excess of ammonium acetate compared to Cu(OAc)₂ concentration. This change in the spectrum is accompanied by a change from greenish-blue to deep blue colour. We therefore conclude that disappearance of dimeric copper acetate and formation of addition compounds with single copper atoms takes place upon addition of ammonium acetate. The influence of ammonium acetate is given quantitatively in Table I.

Heating the ternary system in all concentrations being investigated (*i.e.* molar ratio of ammonium acetate: copper acetate from 0 to 700) up to 120 °C does not lead, however, to any observable new absorption band indicating a new species being formed. It is very likely, however, that a change in the monomer/dimer equilibrium of copper acetate favouring the monomer as indicated also by the ESR spectra, leads to a more intensive blue colour being thus the main reason of the thermo-chromic behaviour. The only copper amine complex showing a violet colour is Cu(OAc)₂(NH₂)₂ [5]. The UV/VIS spectrum of this complex shows an absorption maximum at 615 nm, which is clearly different from the maximum of copper acetate. If such a compound was formed in the ternary system as postulated formerly [1], the concentration should be very low and hence not the main reason for the visible colour change. The question whether N-coordinated copper atoms are present in such solutions cannot be answered, therefore, by UV/VIS spectroscopy and will be discussed later in connection with the NMR results.

Unfortunately, ESR and UV/VIS spectra do not allow any quantitative estimation of the monomer/

dimer equilibrium of pure copper acetate solutions and its being affected by ammonium acetate. One can try, however, to obtain a qualitative estimation by means of a formal treatment of the equilibria starting from the assumptions that either the monomeric or dimeric form of copper acetate is the dominant species. The change in the absorption corresponding to the d-d transition due to the adduct formation is a suitable measure for this evaluation [6]. For the ternary system Cu(OAc)₂/LiOAc/HOAc this has been done [6] assuming that only the dimeric form is present in Cu(OAc)₂/HOAc solutions. In the present study, we have investigated the agreement of the spectroscopic data with both assumptions, represented by the equations (1) and (2) respectively:



Application of Lambert-Beer's law leads – with the simplifying assumption, that only one kind of addition compound is formed – to the following expressions:

$$c_1 = (A - e_2 \cdot c) / (e_1 - e_2),$$

corresponding to (1) (3)

$$c_2 = (A - 0.5 c \cdot e'_1) / (e_2 - 0.5 e'_1),$$

corresponding to (2) (4)

where c = total copper concentration, c_1 = equilibrium concentration of monomeric copper acetate, c'_1 = equilibrium concentration of dimeric copper acetate, c_2 = equilibrium concentration of the addition compound, e_1 = extinction coefficient of monomeric copper acetate, e'_1 = extinction coefficient of dimeric copper acetate = $2 e_1$, e_2 = extinction coefficient of the addition compound, A = measured absorption of the solution. The extinction coefficients can be taken from the limiting values of Table I. Considering the equilibrium constants according to the reactions (1) and (2) leads to the logarithmic eqns. given in (5) and (6),

$$K = c_2 / (c_1 \cdot c_A^m), \ln(c_2/c_1) = m \cdot \ln c_A + \ln K \quad (5)$$

$$K' = c_2^2 / (c_1' \cdot c_A^n), \ln(c_2^2/c_1') = n \cdot \ln c_A + \ln K', \quad (6)$$

where c_A corresponds to the equilibrium concentration of ammonium acetate, which for the given system is to a good approximation equal to the total

TABLE II. Temperature Dependence of ^{14}N NMR Line Width (for solution 0.01 M $\text{Cu}(\text{OAc})_2$, 3.5 M NH_4OAc).

T °C	LW (Hz)
40	40
50	51
60	65
70	135
80	*

*No peak observable.

concentration of ammonium acetate. The diagrams of $\ln c_A$ versus $\ln(c_2/c_1)$ and $\ln(c_2^2/c_1')$ should thus display a straight line with slopes m and n , respectively, if either eqn. (1) or (2) gives a correct description of the equilibrium of adduct formation. These diagrams are shown in Fig. 2a and b. For both cases straight lines are not observed, but – according to the concentration range – two different linear relations can be defined. In the case corresponding to eqn. (1) (Fig. 2a), the values for m are 2.1 and 4.0, respectively, indicating that eqn. (1) gives a correct description for high concentrations of ammonium acetate, *i.e.* that under such conditions copper acetate is present in its monomeric form. At lower ammonium salt concentration, both dimeric and monomeric forms seem to be present. For the case corresponding to eqn. (2), no reasonable interpretation can be given for the resulting values of n , being 3.0 and 4.4, respectively. In accordance with the ESR spectra it can be stated, therefore, that monomeric copper acetate is always present in acetic acid solutions and probably the most important species involved in reactions.

^{14}N NMR Spectra

0.005 M copper acetate solutions with varying ammonium acetate concentration (0.6–2.7 M) have been investigated, but no influence of the concentration on the chemical shift could be observed. The

line width is also constant within the range of 10–25 Hz. Significant changes of the chemical shift cannot be observed also at elevated temperature, the line widths however grow continuously (Table II) until the peak cannot be observed any longer at 80 °C. In order to exclude the possibility that this effect is due to dissociation of ammonium acetate, we recorded the same spectra for solutions of ammonium acetate only. In this case, no broadening of the peaks can be observed. It is to be concluded therefore, that the increase of line widths in the ternary system is due to an interaction of the paramagnetic copper ion with nitrogen, which does not take place at room temperature. This indicates the intermediate formation of some species, where copper can interact directly with the nitrogen atoms. Since from the known compounds only $\text{Cu}(\text{OAc})_2(\text{NH}_2)_2$ is formed readily and also has a violet colour, it might be possible that formation of this species in very low concentrations causes the NMR effects and contributes to a small extent to the thermochromic behaviour of the ternary system.

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