

## Dimer/Monomer Equilibrium of Copper(II) Acetate in Mixtures of Acetic Acid, Ethanol and Water from Optical and Magnetic Measurements

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The dimer/monomer equilibrium of copper acetate in solutions,  $\text{Cu}_2(\text{CH}_3\text{COO})_4 \rightleftharpoons 2\text{Cu}(\text{CH}_3\text{COO})_2$ , has been studied, using data from visible and UV spectrophotometry, ESR spectrometry, magnetic susceptibility, and electrolytic conductivity. The various methods give consistent results, except for ethanol/water solutions where a precipitate is slowly formed. In dry acetic acid, the dissociation constant  $K_D$  is less than  $5 \times 10^{-6}$  M at 25°C, and the enthalpy  $\Delta H$  for the process is positive and greater than 5 kcal/mol. Addition of water reduces  $\Delta H$ , and  $K_D$  increases as  $\log K_D = -4.85 + 3.7 \log C_{\text{H}_2\text{O}}$  between 2 and 25 M  $\text{H}_2\text{O}$  at 25°C. The equilibrium shows that acetic acid is preferred as dimer ligands, while water is preferred on monomers. Saturated copper acetate solutions in this water concentration range have constant dimer concentrations.

In dry ethanol  $K_D \leq 5 \times 10^{-4}$  M and  $\Delta H \geq 7$  kcal/mol. Small additions of acetic acid will replace the ethanol ligands and stabilize the dimeric molecules. We suggest that the stabilizing effect of acetic acid ligands on copper acetate dimers is a result of an extra bond from the hydroxyl group.

**H**ydrated copper(II) acetate  $\text{Cu}_2(\text{CH}_3\text{COO})_4 \cdot 2\text{H}_2\text{O}$  (hereafter we write Ac for  $\text{CH}_3\text{COO}$ ) crystallizes with the copper ions arranged in pairs.<sup>1</sup> In acetic acid, ethanol and many other solvents, the copper acetate is also mainly in dimeric form<sup>2-7</sup> with only small dissociation to monomers ( $\text{CuAc}_2$  with solvent ligands) and very few free ions ( $\text{CuAc}^+$  and  $\text{Cu}^{2+}$ ). A  $\text{Cu}^{2+}$  ion lacks one electron in the  $3d$  shell. Hence, it has a magnetic moment with  $S = 1/2$ , and optical transitions are possible between the  $3d$  states, if the ion is in an asymmetric environment. The dimer-monomer dissociation of copper acetate in solutions can be determined, since the copper pair structure influences the magnetic and optical properties in the following ways:

(a) Overlap of the  $\text{Cu}^{2+}$  wave functions gives an antiferromagnetic coupling between the two spins, resulting in a lowest non-magnetic singlet state and a magnetic triplet state with  $S = 1$ , some  $\Delta/hc \approx 300 \text{ cm}^{-1}$  higher in energy,<sup>8</sup>

where  $h$  is Planck's constant, and  $c$  is the velocity of light. Hence, the static susceptibility  $\chi_d$  of the dimers is reduced relative to the susceptibility  $\chi_m$  of the monomers or the ionized dissociation products by <sup>9</sup>

$$\chi_d/\chi_m = \frac{S_d(S_d+1)}{2 S_m(S_m+1)} \frac{3}{(3 + \exp(\Delta/kT))} \quad (1)$$

$$= 4(3 + \exp(\Delta/kT)) \approx 1/2 \text{ at } T \approx 300^\circ\text{K}$$

if we neglect possible small differences in magnetic  $g$ -values and Van Vleck temperature independent paramagnetism.

Electron spin resonance (ESR) transitions between the dimer triplet states are possible. However, we expect the dimeric molecules to have a triplet zero-field splitting of the same order as in copper acetate crystals,<sup>8</sup> where  $D/hc = 0.34 \text{ cm}^{-1}$ . This will result in a solution ESR line, several thousand gauss wide, too broad to be observed, unless the molecular motion correlation time  $\tau$  is much less than  $\hbar/D$ . For dimers in ethanol, we have found from PMR<sup>10</sup> that  $\tau \approx 10^{-10} \text{ s}$ , and the condition for line narrowing by averaging is not fulfilled. The monomers with  $S = 1/2$ , however, will have a line width comparable to that of  $\text{Cu}^{2+}$  in water, where  $\Delta H \approx 150 \text{ gauss}$ , if the motion is fast enough to average out the  $g$ -value anisotropy. We require  $\tau \approx \hbar/\Delta g \beta H_0$  where  $\beta$  is the Bohr magneton, and  $H_0$  is the resonance field. Since  $\tau$  is shorter for the smaller monomeric molecules, this condition is just fulfilled for  $\Delta g \approx 0.3$  and  $H_0 \approx 3000 \text{ gauss}$ . Hence, the intensity of the ESR line of copper acetate solutions is proportional to the concentration of monomers and ionized dissociation products.

(b) In solvated  $\text{CuAc}_2$ ,  $\text{CuAc}^+$  and  $\text{Cu}^{2+}$ , the copper ion is surrounded by a somewhat distorted octahedron of 6 neighboring negative ions, giving an electrostatic field of mainly cubic symmetry on the copper site. In the dimer, however, each copper ion "sees" a field, where the inversion symmetry is destroyed by the presence of the other  $\text{Cu}^{2+}$  as a nearest neighbor. Therefore, the copper acetate dimers show considerably stronger optical absorption than the dissociation species, and the absorption peaks are shifted in frequency. While octahedrally coordinated  $\text{Cu}^{2+}$  ions in water show vibrationally allowed absorption around  $8000 \text{ \AA}$  with molar extinction coefficient  $\epsilon \approx 10$ , the dimer spectrum is similar to that of copper acetate crystals, which has a strong line at  $7000 \text{ \AA}$  ( $\epsilon \approx 200$ ), with a shoulder at  $9000 \text{ \AA}$  ( $\epsilon \approx 20$ ), and another line at  $3700 \text{ \AA}$  ( $\epsilon \approx 50$ ). There have been many attempts to interpret the dimer spectrum.<sup>11-18</sup> The X-ray structure of copper acetate and the difference between  $g_x$  and  $g_y$ , show that the local symmetry in the solid, as seen by the  $\text{Cu}^{2+}$  ion, is not higher than  $C_{2v}$ . The polarization of the absorptivity then favors the assignment proposed by Kokoszka *et al.*<sup>17,19</sup> in the hole formalism: ground state  $d_{x^2-y^2}$ ; transitions at  $7000 \text{ \AA}$  to states  $d_{xx}$  and  $d_{yy}$ ; at  $3700 \text{ \AA}$  to state  $d_x$ , and at  $9000 \text{ \AA}$  to state  $d_{xy}$ . The last transition is allowed only in the lower symmetry group  $C_2$ . The crystal  $9000 \text{ \AA}$  line is weak at room temperature, but much stronger at  $77^\circ\text{K}$ , which indicates a greater distortion of the lattice at low temperature.

Recently Cheng and Howald<sup>7</sup> reported data for the dimer/monomer equilibrium of copper acetate in acetic acid/water solutions, based on photometric and potentiometric measurements. They assumed the molar optical

absorption of the dimer to be independent of the type of its axial ligands. *A priori* we would not expect this to be necessarily true, since the optical absorption is allowed only to the extent that the  $\text{Cu}^{2+}$  wave functions deviate from inversion symmetry. We expect that the asymmetry will depend on the type of ligand. To avoid this uncertainty, we have repeated the spectrophotometric measurements, using constant ratios acetic acid/water and varying the copper acetate concentrations. Then the ligand composition should stay constant for each acetic acid/water ratio. To check the results we have also done some ESR and susceptibility measurements. From conductivity measurements in solvents like ethanol we have obtained additional information about the dissociation to  $\text{CuAc}^+$  and  $\text{Cu}^{2+}$ . While data on susceptibilities of copper acetate solutions have been reported before by Kondo and Kubo,<sup>4</sup> and qualitative ESR measurements by Kochi and Subramanian,<sup>6</sup> we are not aware of dimer-monomer dissociation constant derived from magnetic experiments. We have used these various methods to study the dissociation of copper acetate in acetic acid/water, in ethanol, and in acetic acid/ethanol. Slow precipitation, probably of basic copper acetate in ethanol/water solutions, led to inconsistent results for this system.

### EXPERIMENTAL

Most of the spectrophotometric data were measured on a Perkin-Elmer 137 UV spectrophotometer, equipped with a temperature controlled cell mount. Above 7500 Å, a Beckman DK spectrophotometer was used.

The ESR spectra were recorded at 9.5 GHz on a Varian V-4502 spectrometer with a variable temperature liquid sample cell. The absorption depends on the cavity  $Q$ -value, and it is very important for quantitative work that the dielectric losses do not change from run to run. Therefore, the solutions were changed, while the sample tube was permanently mounted in the cavity to insure its unchanged position. The change in the dielectric constant of the liquids made slight adjustments of the microwave bridge necessary when the solvent was changed. The field modulation and the recording of the absorption line derivative gave a signal amplitude proportional to  $(\Delta H)^{-2}$  for equal number of spins. For a copper concentration of 0.016 M, we estimate that the sensitivity was adequate to detect ESR lines of width  $\Delta H \lesssim 700$  gauss.

The static susceptibility was measured by the Gouy method at room temperature, using a 12" Varian Fieldial magnet. A double-ended high precession Gouy tube with inner diameter 16 mm was used to eliminate solvent corrections. A Sartorius balance 2442 accurate to 0.1 mg was used.

The conductivity measurements were carried out with a Mullard conductivity bridge E 7566/3, equipped with a Mullard conductivity cell E 7591/3 with platinum blackened electrodes.

The copper acetate used was the hydrated salt Merck zur Analyse. The acetic acid was 99–100%, and the ethanol was > 99.1%, both Merck zur Analyse. The water content was determined by gas chromatography to be about 0.2 and 0.1 M, respectively, for the acetic acid and the ethanol used. The solutions were prepared by first mixing the solvents in the given volume percentage ratios, then dissolving the copper acetate monohydrate, and stirring for an hour. No change in optical absorption was detected after longer periods of stirring, and the absorption would return to the initial values after warming to 70°C and cooling again.

### RESULTS

*a. Optical spectrophotometric measurements.* To determine the copper acetate dimer/monomer equilibrium in solution, we need to know the molar absorptivities  $\epsilon(\lambda)$  at some wavelength  $\lambda$ . We chose to work at 7000 Å, where

the dimer has an absorption maximum and the dissociation products absorb little. Following the procedure by Cheng and Howald,<sup>7</sup> we found  $\epsilon_{\text{Cu}^{2+}}(7000) = 5.1$  from measurements on copper nitrate in water solution. Using the published dissociation data for copper acetate in water<sup>20-25</sup> we found  $\epsilon_{\text{CuAc}^+}(7000) = 14.5$ , and  $\epsilon_{\text{CuAc}_2}(7000) = \epsilon_m = 31$ . This value for  $\epsilon_m$  is in good agreement with the result reported by Cheng and Howald at 6700 Å, but since we have found that the dimer absorption  $\epsilon_d$  varies with the solvents and the ligands, we have no assurance that the monomer absorption will be exactly the same in acetic acid or ethanol as in water. Fortunately,  $\epsilon_m$  is relatively small, and slight errors in its value are not very important for the final result.

For solutions where only dimers and monomers are present in significant concentrations, the fraction of copper in the dimeric state is given by

$$x = (\bar{\epsilon} - \epsilon_m) / (\epsilon_d - \epsilon_m) \quad (2)$$

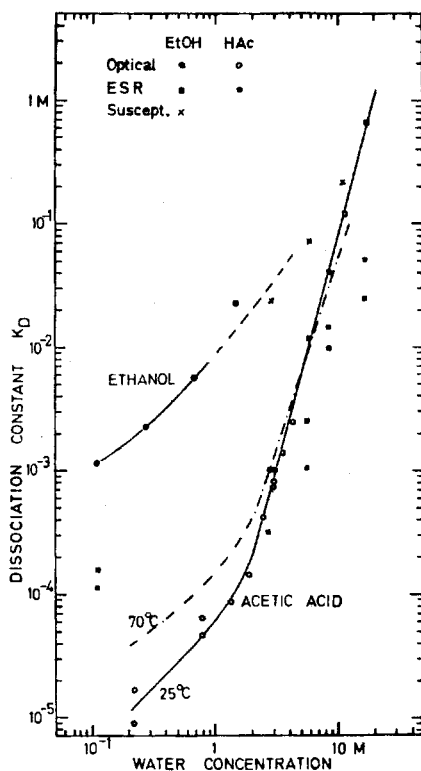


Fig. 1. Dimer/monomer dissociation constants for acetic acid and ethanol solutions of copper acetate as functions of water content. Points and full lines are for 25°C; dash-dot line shows changes at 70°C.

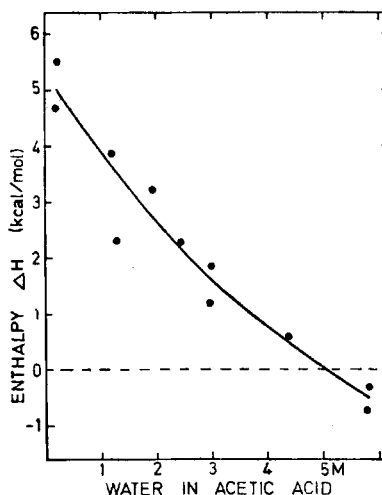


Fig. 2. Enthalpy change  $\Delta H$  for dimer/monomer dissociation as a function of water content in acetic acid.

where  $\bar{\epsilon}$  is the mean absorptivity at 7000 Å per molar copper in solution, regardless of whether the molecules are in monomeric or dimeric form. The dimer-monomer dissociation constant for  $\text{Cu}_2\text{Ac}_4 \rightleftharpoons 2\text{CuAc}_2$  is

$$K_D = 2C_T(1-x)^2/x \quad (3)$$

where  $C_T$  is the total copper concentration. We measured  $\bar{\epsilon}$  as a function of  $C_T$  for a series of acetic acid/water and ethanol/water solutions with  $C_T$  varied in the range  $10^{-4}$  to  $10^{-2}$  M at temperatures 25°C and 70°C. The data were fitted to eqns. (2) and (3), to give a constant value for  $\epsilon_d$  and a concentration independent  $K_D$  for each solvent. The resulting values for  $K_D$  at 25°C as a function of water concentration are shown in Fig. 1. We also show the average  $K_D$  at 70°C in acetic acid/water by a dash-dot line. At water concentrations higher than 5 M, the effect of monomer dissociation to  $\text{CuAc}^+$  may begin to introduce errors in the derived  $K_D$  values. But no correction for further dissociation has been applied, since it is difficult to determine the fraction of  $\text{CuAc}^+$  in the acid. For dry ethanol solutions we estimate from electrical conductivity measurements that the dissociation constant  $K_M = C_{\text{CuAc}^+}C_{\text{Ac}^-}/C_{\text{CuAc}_2}$  is only of the order  $10^{-5}$  M, but it increases when water is added.

The dissociation constant can be written

$$K_D = \exp(-\Delta H/RT + \Delta S/R) \quad (4)$$

In Table 1 we list the results for  $\epsilon_d$  and  $K_D$  for the driest solvents used, and also the values for the enthalpy change  $\Delta H$ , the entropy change  $\Delta S$ , and the free energy change  $\Delta G = \Delta H - T\Delta S$  derived with the use of eqn. (4). We see that  $\epsilon_d$  decreases with increasing temperature in both solvents. We also found that  $\epsilon_d$  is independent of the water content up to 5 M water in acetic acid.

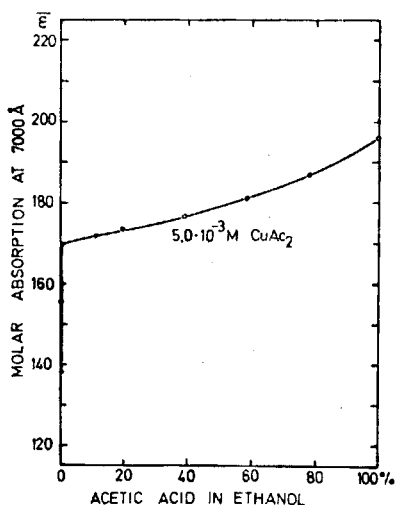


Fig. 3. Mean 7000 Å absorptivity at 25°C of copper acetate in acetic acid/ethanol solutions.

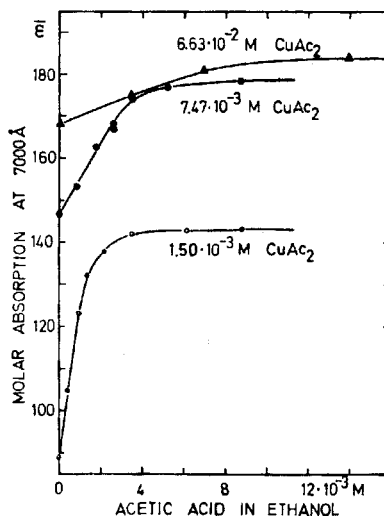


Fig. 4. Same as Fig. 3, expanded scale.

The monomer fraction increases rapidly with the addition of water.  $K_D$  is temperature independent, and  $\Delta H=0$  in acetic acid with 5 M water. The enthalpy change as a function of water content in acetic acid is shown in Fig. 2.

Additions of acetic acid to ethanol solutions of copper acetate give striking changes in optical absorption, as shown in Figs. 3 and 4. The acetic acid replaces ethanol as ligands and stabilizes the dimers. As can be seen from Table 1, both  $K_D$  and  $\epsilon_d$  in the mixtures have values intermediate to those for pure acetic acid and ethanol. The first sharp increase in  $K_D$  as reflected in  $\bar{\epsilon}$  must be caused by ligand replacement, while the increase in  $\bar{\epsilon}$  towards 100 % acetic acid is probably caused by the reduced dielectric constant of the mixture.

Table 1. Spectral data and dissociation constants for copper acetate in solutions.

Solvent	T (°C)	$\epsilon_d$ at 7000 Å	$K_D$ (M)	$\Delta H$ (kcal/mol)	$\Delta G$ (kcal/mol)	$\Delta S$ (cal/mol)
HAc with 0.2 M H <sub>2</sub> O	25	201 ± 3	1 × 10 <sup>-5</sup>	5 ± 1	7	- 6
	70	182 ± 3	3 × 10 <sup>-5</sup>			
EtOH with 0.1 M H <sub>2</sub> O	25	183 ± 3	1.0 × 10 <sup>-3</sup>	7 ± 2	4	+ 11
	70	166 ± 3	5 × 10 <sup>-3</sup>			
EtOH with 5 % HAc	25	192 ± 3	2 × 10 <sup>-4</sup>			
EtOH with 10 % HAc	25	196 ± 3	1.5 × 10 <sup>-4</sup>			

The acetic acid reaction with ethanol to ethyl acetate is too slow to influence the equilibrium in freshly prepared samples.

*b. UV measurements.* The copper acetate solutions show very strong UV absorption around 2500 Å with molar absorptivities of the order  $\bar{\epsilon} \approx 5000$ . This is probably caused by charge transfer. The peak is close to the cut-off point of acetic acid, but in ethanol solutions it can be studied without interference. Here, the UV absorption shows considerable temperature change with an isosbestic point at 2700 Å, as shown in Fig. 5. The temperature effect is most pronounced for solutions with about the same concentration of dimers and monomers, and we interpret it as caused by different UV absorption for these two species. The dimer/monomer ratio changes with temperature, and with the equilibrium data given in Table 1 we derive the pure dimer and pure monomer charge transfer absorptions (dashed in Fig. 5). Copper acetate concentrations from  $1.25 \times 10^{-4}$  to  $4.16 \times 10^{-4}$  M in ethanol give consistent results for  $\epsilon_m(\lambda)$  and  $\epsilon_d(\lambda)$  in support of our values for  $K_D$  and  $\Delta H$ .

The maximum dimer UV absorption is about twice that of the monomer, but the monomer line is broader, so that the integrated absorption is about the same for the two species. The peak is slightly shifted from 2470 Å for the dimer to 2570 Å for the monomer. Small additions of acetic acid increase the dimer fraction and  $\bar{\epsilon}_{\max}$ .

*c. ESR measurements.* The ESR spectra of copper acetate in acetic acid/water and ethanol/water solutions were studied, and relative line intensities were found by integrating the recorded line derivatives. Results for  $1.66 \times 10^{-3}$

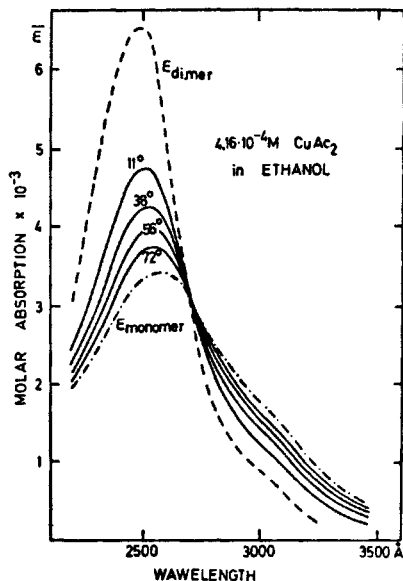


Fig. 5. Mean UV absorptivity of copper acetate in ethanol as a function of wavelength and temperature. Deduced  $\epsilon_d$  and  $\epsilon_m$  dashed.

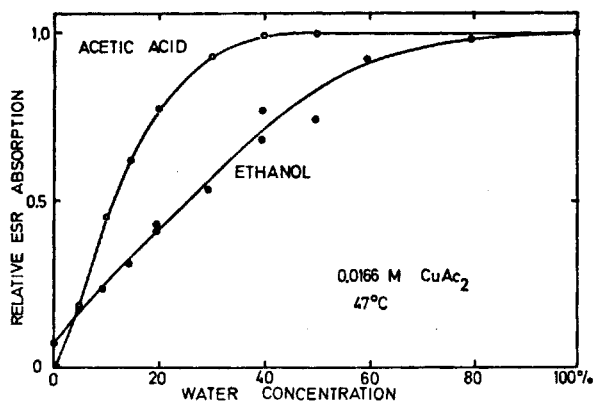


Fig. 6. Relative ESR absorption of copper acetate in acetic acid and ethanol as a function of water content.

M solution run at 47°C to increase solubility are shown in Fig. 6. The loss of intensity relative to water solution gives the dimer fraction  $\alpha$ . Resulting values of  $K_D$  determined with eqn. (3) and reduced to 25°C with eqn. (4), and values for  $\Delta H$  from Fig. 2, are plotted in Fig. 1. For acetic acid solutions the agreement with optical data is very good, but for ethanol solutions the apparent ESR intensity is only about half of the expected value.

The mean magnetic  $g$ -value from the center of gravity of the lines is 2.17 in water solution (mainly  $\text{CuAc}^+$ ) and 2.16 in pure ethanol solution ( $\text{CuAc}_2$ ).

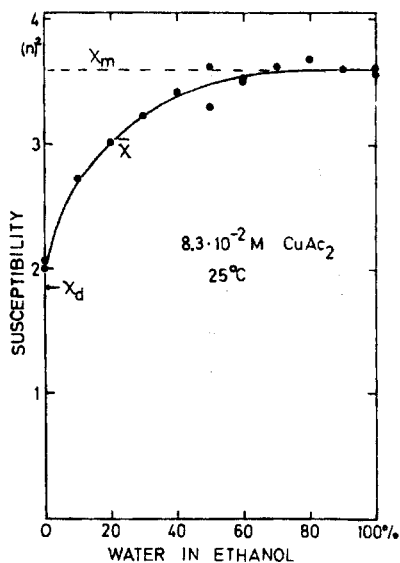


Fig. 7. Static susceptibility of copper acetate in ethanol/water solutions, expressed in squared number of Bohr magnetons per copper atom.

This shift is in qualitative agreement with the slightly higher frequency for optical absorption of the monomers than for the ions. Solutions with a fairly large fractions of monomers showed some hyperfine structure in the ESR lines. This gives information on the copper electron-nucleus coupling and on correlation times for the monomers, as will be discussed in another article.

*3d. Static susceptibility measurements.* As a check on the magnetic properties of the ethanol solutions, the static susceptibility  $\bar{\chi}$  was measured at  $1.66 \times 10^{-2}$  and  $8.3 \times 10^{-2}$  M and  $25^\circ\text{C}$ . The results of one series are shown in Fig. 7, with  $\bar{\chi}$  given as the square of  $n$  effective Bohr magnetons per Cu ion. The dimer fraction  $x$  is

$$x = (\chi_m - \bar{\chi}) / (\chi_m - \chi_d) \quad (5)$$

The monomer susceptibility  $\chi_m$  was assumed to be the same as that of water solution, where the copper is also in the form  $\text{CuAc}^+$  and  $\text{Cu}^{2+}$ . The dimer susceptibility  $\chi_d$  was found from the driest ethanol solutions, where  $x$  was taken from our optical work. Then  $K_D$  was calculated from eqn. (3). The results are plotted in Fig. 1. There is a fair agreement with the optical data, but the susceptibility and the ESR data are inconsistent.

Our susceptibility results for water and ethanol solutions are in good agreement with the data given by Kondo and Kubo.<sup>4</sup> We find the ratio  $\chi_d/\chi_m = 0.52$  at  $25^\circ\text{C}$ , and using eqn. (1), we compute the singlet-triplet energy splitting  $\Delta = hc \times 320 \text{ cm}^{-1}$ . This is close to the value for copper acetate crystals, where Figgis and Martin<sup>9</sup> found  $\Delta/hc = 286 \text{ cm}^{-1}$ .

*e. Conductivity measurements.* Some conductivity measurements were done in ethanol/water solutions. As expected from the high dimer fraction, the conductivity in dry ethanol solution is very low, only about 1/500 of that of the same amount of copper acetate dissolved in water. The conductivity



increases in the normal way with the square root of the copper acetate concentration. The conductivity in methanol solution is about 20 times greater than in ethanol, which is partly caused by greater dimer to monomer dissociation in this solvent.

The stabilizing effect of acetic acid on copper acetate dimers is strikingly demonstrated by adding small amounts of HAc to ethanol solutions. As shown in Fig. 8, the conductivity first decreases by additions of acetic acid. Normally,

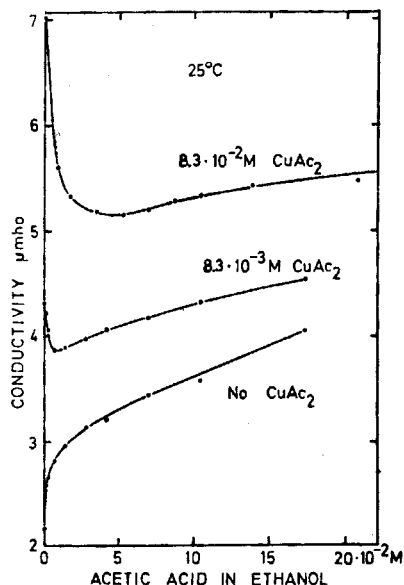


Fig. 8. Electrolytic conductivity of copper acetate in ethanol with small additions of acetic acid.

we would expect greater conductivity when acid is added to a solution, because of the mobile  $H^+$  ions. But here, the tendency of small concentrations of the HAc to dissociate is counteracted by its tendency to coordinate to monomers and pair them off to dimers. The reduced monomer fraction means that less can dissociate to  $CuAc^+$  and  $Ac^-$ . The conductivity minima occur for approximately the HAc concentrations that correspond to the initial  $CuAc_2$  monomer concentration. The stabilizing effect of HAc on dimers is not large enough, however, to give a conductivity minimum when the acid is added to water solutions of copper acetate.

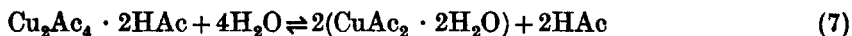
## DISCUSSION

*a. Acetic acid/water solutions.* The spectrophotometric and the ESR methods give the same results for copper acetate dimer/monomer dissociation in acetic acid/water solutions to within the experimental errors. The ESR method is most suitable for high water contents, while the spectrophotometric method is most accurate for rather dry acetic acid. Our  $K_D$  values in Fig. 1 show much

less scatter than the data reported by Cheng and Howald,<sup>7</sup> and above 2 M H<sub>2</sub>O they can be fitted by the equations

$$\begin{aligned} \log K_D &= -4.85 + 3.7 \log C_{\text{H}_2\text{O}} && \text{at } 25^\circ\text{C} \\ \log K_D &= -4.35 + 3.1 \log C_{\text{H}_2\text{O}} && \text{at } 70^\circ\text{C} \end{aligned} \quad (6)$$

This indicates that the dimer/monomer equilibrium is given mainly by



as already suggested by Cheng and Howald.<sup>7</sup> Eqn. (7) implies that the dimeric molecules have acetic acid axial ligands, while the monomers have water axial ligands. The decrease of the measured exponent from a value slightly higher than 4.0, if we also take into account the effect of  $C_{\text{HAc}}$  on  $K_D$ , to 3.7 at 25°C and to 3.1 at 70°C, show that while acetic acid is preferred as dimer ligands, some dimers with water ligands may also be found, and *vice versa* for the monomers. Higher temperature will give more even distribution of the ligand species on monomers and dimers, and thus reduce the measured power of  $C_{\text{H}_2\text{O}}$  in  $K_D$  as observed. But since the dielectric constant of the solutions varies greatly with the water content, we cannot exclude the possibility that this may cause the rapid variation of  $K_D$  with  $C_{\text{H}_2\text{O}}$  and not the equilibrium (7).

For low water concentrations, much less than four H<sub>2</sub>O are sufficient to break the dimer copper-copper bond, and obviously  $K_D$  must have a finite value even for completely water-free acetic acid. Only an upper limit for  $K_D(C_{\text{H}_2\text{O}}=0) \leq 5 \times 10^{-6}$  M at 25°C can be extrapolated from these measurements. At very low water concentrations, the deviation from Beer's law becomes too small for accurate measurements.

It is puzzling that HAc is more strongly attached to dimers than H<sub>2</sub>O molecules are, while H<sub>2</sub>O appears to replace HAc on monomers. The structure of HAc suggests that its hydroxyl group may perhaps form an additional hydrogen bond to the oxygen of one of the dimer acetate bridges. This is indicated in Fig. 9 a, where two of the four bridges are shown with the dimensions as in solid copper acetate.<sup>1</sup> Here, a hydrogen bond can have a reasonable length and can be in the Cu—O—C plane with about 120° angles Cu—O···H and C—O···H. But for a ligand on a monomer as shown in Fig. 9 b, such a bond is impossible, since it would be perpendicular to the Cu—O—C plane. Without the extra bond, water is probably preferred on the monomers. The extra bond hypothesis would also explain the fact that acetic acid replaces ethanol as dimer ligands.

Sandved<sup>26</sup> has measured the solubility of copper acetate in acetic acid/water mixtures. His data are given in Fig. 10, where the total copper acetate concentration is divided into dimers and monomers, using our  $K_D$  values for 25°C. From the solubility minimum at 2.5 M H<sub>2</sub>O to nearly 25 M ( $\approx 50\%$ ) H<sub>2</sub>O, the copper-as-dimer concentration in saturated solution is approximately  $8 \times 10^{-3}$  M and constant, while the monomer concentration varies by two orders of magnitude. This shows that the tendency of the dimers to crystallize is independent of the solvent and of whether the solid phase contains ligands H<sub>2</sub>O·HAc or 2H<sub>2</sub>O. Thus, the stronger tendency of HAc to form dimer ligands is counteracted by the stronger intermolecular bonds formed by H<sub>2</sub>O ligands.

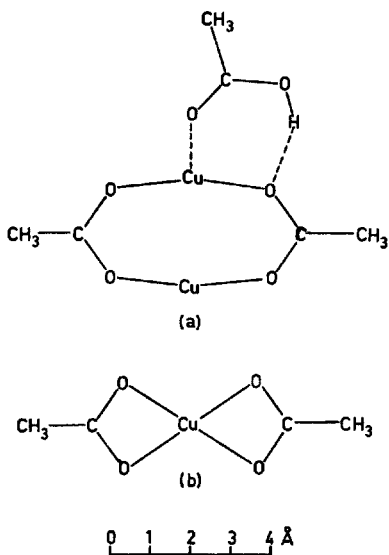


Fig. 9. Assumed structure of (a) copper acetate dimeric molecule (only two bridges shown) with one HAc ligand, and (b) copper acetate monomeric molecule with ligands (not shown) above and below the plane of the paper.

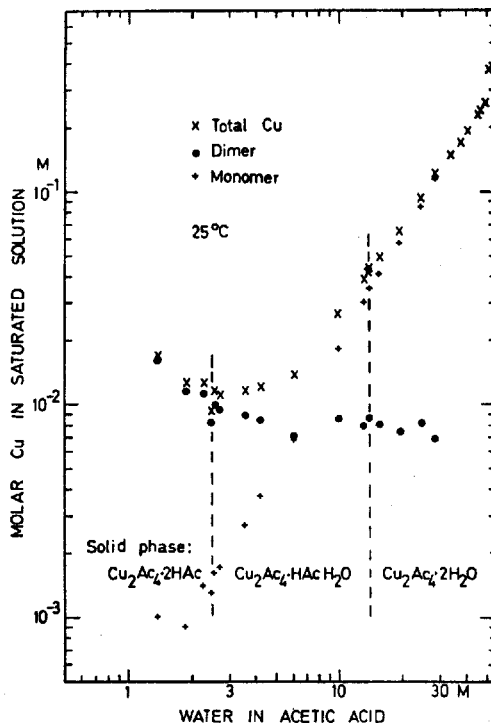


Fig. 10. Solubility of copper acetate in acetic acid/water (after Sandved<sup>26</sup>) divided in dimers and monomers.

The higher solubility in dry acetic acid may perhaps be explained by the inability of the strongly bound HAc ligand in Fig. 9 a to form any intermolecular bond. First, either the  $\text{O}-\text{H} \cdots \text{O}$  or the  $\text{O} \cdots \text{Cu}$  bond must be broken. With a slight addition of water, which increases the ionization,<sup>27</sup> this happens more often, and thus the solubility is reduced.

The dimer molar absorption of the lines at 7000 Å and 3700 Å decreases with increasing temperature while there appears a line at 9000 Å. This is in qualitative agreement with the  $d-d$  transitions assignment by Kokoszka *et al.*,<sup>17,19</sup> if we assume that each  $\text{Cu}^{2+}$  ion of the dimers in solution "sees" a crystal field of mainly  $C_{2v}$  symmetry, and that vibration introduces field components of  $C_2$  symmetry. Higher temperature and thus greater  $C_2$  perturbation would give more intense  $d_{x^2-y^2} = d_{xy}$  absorption, while the other transitions from  $d_{x^2-y^2}$  would decrease in intensity, because admixing of new states would reduce the amount of the original wavefunctions. There is a slight shift of the 7000 Å line to longer wavelength with temperature, which shows that the

thermal vibrations reduce the average crystal  $z$ -field. A reduced crystal field is likely to have less  $z$ -asymmetry, and thus less of  $4p$ -states would be mixed into the  $3d$ -states. This would also reduce with increasing temperature the intensity of the transitions allowed in the  $C_{2v}$  symmetry.

The 7000 Å line decreases with temperature about proportionally with the dimer fraction in the singlet state, while the 9000 Å line increases as the triplet fraction. But since the 9000 Å line is strong in copper acetate at liquid nitrogen temperature<sup>17</sup> it cannot be ascribed to a triplet-triplet transition only, although Ross<sup>11</sup> has predicted a singlet-triplet separation of roughly  $2500\text{ cm}^{-1}$  in the  $d_{xz}$  and  $d_{yz}$  states.

*b. Ethanol/water solutions.* As seen in Fig. 1, the ESR results are inconsistent with the optical and the susceptibility data for ethanol/water solutions. Furthermore, a visible precipitate was slowly formed in solutions with more than about 2 M of water. Most probably, the precipitate is basic copper acetate,<sup>28</sup> where the copper ions "see" a crystal field of the monomeric form. When small crystallites are formed in the solutions, they rotate slower with increasing size, and when  $\omega < \Delta g\beta H_0/\hbar$ , the rotation frequency  $\omega$  is too small to average out the anisotropy in the  $g$ -values of the copper ions. Then, these crystallites will give an ESR line of width  $\Delta H \approx \Delta g\bar{H}/\bar{g} \approx 400$  gauss for  $\Delta g \approx 0.3$ ,  $\bar{g} \approx 2.2$  and  $H \approx 3000$  gauss. Such a line can probably be detected, but the low intensity in the wings make quantitative work very difficult, and we are likely to seriously underestimate the line intensity. Already for complexes consisting of only a few molecules, we expect the rotation frequency to be too slow for good averaging. Aggregation, however, will not influence the static susceptibility. Hence, we believe that the deviations in the ESR results show that considerable aggregation of copper acetate molecules in mononuclear form exist even in freshly made and perfectly clear ethanol/water solution. Because of the aggregation, we have not attempted to derive accurate values for the  $\text{CuAc}_2 \rightleftharpoons \text{CuAc}^+ + \text{Ac}^-$  dissociation constant  $K_M$  from our conductivity measurements.

However, dry ethanol solutions appear to be stable, and the optically determined values for  $K_D$  up to 1 M  $\text{H}_2\text{O}$  seem to have some significance. By extrapolation we estimate  $K_D(C_{\text{H}_2\text{O}} = 0) \lesssim 5 \times 10^{-4}$  M at  $25^\circ\text{C}$ . The enthalpy difference is greater than for dry acetic acid solution, and a color change towards yellow can be seen in ethanol solutions when the temperature is raised from  $25^\circ$  to  $70^\circ\text{C}$ .

*c. Acetic acid/ethanol solutions.* Optical absorption and electrolytic conductivity show that acetic acid replaces ethanol ligands and stabilizes the copper acetate dimers in ethanol solutions. PMR shifts confirm that acetic acid is preferred as dimer ligands.<sup>29</sup> The initial very sharp rise in  $\bar{\epsilon}$  shows that the difference  $E$  in affinity is great.

With concentrations  $C_{\text{HAc}}$  and  $C_{\text{EtOH}}$ , the ratio of ligand formation probabilities are

$$p_{\text{HAc}}/p_{\text{EtOH}} = (C_{\text{HAc}}/C_{\text{EtOH}}) \exp(E/RT) = 10^3(C_{\text{HAc}}/C_{\text{EtOH}}) \quad (8)$$

for  $E \approx 4$  kcal/mol. This appears to be the order of magnitude preference shown for HAc ligands, and it leads to a reasonable estimate for the binding energy of the proposed hydrogen bond. But it is surprising that an approximate-

ly constant  $\bar{\epsilon}$  is reached for considerably less than one HAc added per  $\text{CuAc}_2$  in the more concentrated solutions. Then all dimers cannot have only HAc ligands, and we expect the dimers with ethanol ligands to establish an equilibrium with the monomers appropriate for almost pure ethanol. However, our data do not seem to fit such an equilibrium.

The extra bond hypothesis is supported by our observation of a similar and even stronger dimer stabilizing effect, when propionic acid, butyric acid and higher homologues of acetic acid are added to ethanol solutions. Formic acid also stabilizes copper acetate dimers in ethanol, but less than acetic acid does.

The molar absorptivity  $\epsilon_d$  for dimers with solvent ligands is about 10 % different in acetic acid and ethanol, and also  $\epsilon_d$  for dimers with only HAc ligands seems to vary with the acetic acid/ethanol ratio. This, as well as the variation in the equilibrium constant  $K_D$ , is probably a function of the dielectric properties of the mixtures. Solvents with higher dielectric constants will try to pull the complexes apart and increase  $K_D$ , while the pull on the ligands will reduce the dimer axial field asymmetry which determines the absorptivity.

### CONCLUSIONS

The dimer/monomer equilibrium of copper acetate in mixtures of acetic acid, ethanol and water has been derived, using data from visible and UV spectrophotometry, ESR intensity, magnetic susceptibility, and electrolytic conductivity. The various methods give consistent results except for ethanol/water solutions, where aggregation probably occurs and a precipitate is slowly formed.

In acetic acid, we interpret the equilibrium as a function of water content to mean that acetic acid ligands are preferred on dimers, while water ligands are preferred on monomers. Higher temperature will tend to give more even distribution of ligands.

Saturated copper acetate solutions seem to have a constant dimer concentration in acetic acid with 2 to 25 M of water.

Acetic acid will replace ethanol as ligands and will stabilize the dimers. We believe that the geometry favours acetic acid dimer ligands by offering the possibility of an extra hydrogen bond.

The dissociation constant  $K_D$  and the dimer absorptivity  $\epsilon_d$  vary with the acetic acid/ethanol solvent ratio, although here the dimers seem to have only HAc ligands. This shows that we cannot *a priori* assume  $\epsilon_d$  to be a constant independent of the solvent, and the variation is probably caused by the dielectric properties of the mixtures. But  $\epsilon_d$  for up to 5 M of water in acetic acid appears to be constant.

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