(23) There is not a large difference between ratios of Γ which is proportional to $\int A(\nu)\, d \ln \nu$ and A' which is proportional to $\int A(\nu)\, d\nu$, but since $\Gamma \simeq A'/E_{max}$, the correction was easily applied. $A(\nu) = -\log T(\nu)$ and $T(\nu) = I(\nu)/I_0(\nu)$ where E_{max} is the energy at the peak maximum, A is absorbance, T is transmittance, and I and I_0 are the intensities of the incident radiation at each frequency with and without absorption by the sample.

(24) By analogy to chlorobenzene, one would expect to find four bands (two A_1 and two B_2 for C_{2v} symmetry) near 1580 (two bands), 1480, and 1450 cm^{-1} which shift upon perdeuteration to 1560, 1540, 1350, and 1320 cm^{-1}. These all are loosely assignable to the in-plane modes corresponding to C–C vibrations; see T. R. Nanney, R. T. Bailey, and E. R. Lippincott, *Spectrochim. Acta*, **21**, 1495 (1965). A band at 1480 cm^{-1} appears in chlorobenzene and in triphenylphosphine, but it is not observed in the diazonium salts, nor could it be observed in the complexes owing to interfering absorptions. L. S. Gray, V. A. Fassel, and R. N. Kniseley, *Spectrochim. Acta*, **19**, 514 (1960), reported a band at 1500 cm^{-1} which shifts upon ^{15}N substitution in KBr pellets of benzenediazonium chloride, but we cannot detect this band in mulls of the hexafluorophosphate salts.

(25) W. E. Carroll, F. A. Deeney, and F. J. Lalor, *J. Chem. Soc., Dalton Trans.*, 1430 (1974).

(26) This cyclic ether complex is especially useful from a synthetic standpoint since it is quite soluble in chloroform and methylene chloride, whereas the free diazonium salt is insoluble in these solvents.

(27) We are considering the conditions under which the diazo ligand is monodentate.

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Thermodynamics of Solvation of the Copper(II) Acetate Dimer[1]

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The potential difference between Cu(Hg) and Hg–$Hg_2(OAc)_2$ electrodes has been measured for a wide range of $Cu(OAc)_2$–H_2O–HOAc solutions. $E° = 0.2917 \pm 0.0003$ V for the cell reaction $2Cu(Hg) + 2Hg_2(OAc)_2(s) + 2H_2O(l) = Cu_2(OAc)_4{\cdot}2H_2O(s) + 4Hg(l)$. This corresponds to $G° = -447.35$ kcal mol^{-1} for the solid $Cu_2(OAc)_4{\cdot}2H_2O$. Similarly measurements for solid $Cu_2(OAc)_4{\cdot}2H_2O{\cdot}2HOAc$ give $E° = 0.2983 \pm 0.0007$ V and $G° = -634.36$ kcal mol^{-1}. Extensive spectrophotometric measurements of the solubility of $Cu_2(OAc)_4{\cdot}2H_2O{\cdot}2HOAc$ give $G° = -329.12 - 0.293(H_2O) + 0.0365(H_2O)^2 - 0.00183(H_2O)^3$ for the free energy of the $Cu_2(OAc)_4$ dimer in acetic acid solutions as a function of the water concentration. Approximate enthalpies and entropies are calculated for the various solids and for the monomeric and dimeric forms of copper acetate in solution. In both solids and in solution the copper acetate dimer shows a clear preference ($\Delta G° = -0.9 \pm 0.3$ kcal mol^{-1}) for the coordination of water as opposed to acetic acid. New equations are given for the activities in the system water--acetic acid.

There are three solid species present in equilibrium with acetic acid–water solutions saturated with copper acetate at 25°. Over the range from 14.97 *M* water to pure water one has the well-known $Cu_2(OAc)_4{\cdot}2H_2O$, containing the dimeric $Cu_2(OAc)_4$ group with four bridging acetate ions and the two water molecules as axial ligands.[2] Below 0.50 *M* H_2O, $Cu_2(OAc)_4{\cdot}2HOAc$[3,4] is stable, and a third solid forms at intermediate water concentrations. One is tempted to formulate the third solid by analogy to the other two as $Cu_2(OAc)_4{\cdot}H_2O{\cdot}HOAc$ as has been done in the recent literature,[5] in spite of the old analytical data of Sandved[3] corresponding to $Cu_2(OAc)_4{\cdot}2H_2O{\cdot}2HOAc$. This work establishes that Sandved's formulation is correct and provides thermodynamic values for all three solids based upon solubility data and potentiometric measurements with the Cu(Hg) and Hg–$Hg_2(OAc)_2$ electrodes in saturated solutions.

The Formulation of $Cu_2(OAc)_4{\cdot}2H_2O{\cdot}2HOAc$. For solutions saturated with $Cu_2(OAc)_4{\cdot}nH_2O{\cdot}mHOAc$ the Nernst equation takes the form

$$E = E° + (0.05916/4) \log (a_{H_2O})^n (a_{HOAc})^m$$

It was found that the variation of the potential with the water concentration in this region was not fitted by the value $n = 1$, so it was necessary to check the formula of the solid formed. A sample of 0.0709 mol of $Cu_2(OAc)_4{\cdot}2H_2O$ was stirred with 20.0 ml of glacial acetic acid in a volumetric flask suspended in a water bath at 25°. After equilibration including complete recrystallization of the solid, a sample of the supernatant was analyzed spectrophotometrically and found to be 0.53 *M* H_2O. The acetic acid used was 0.19 *M* in water, and the small increase observed can easily be due to incorporation of some of the acetic acid into the solid. If even one-fourth of the water present in the original solid were released upon recrystallization, the water concentration would be over 1.8 *M* in the supernatant. This simple experiment confirms that $n = 2$ as reported by Sandved.[3]

It is a little harder to determine the amount of acetic acid present in the solid formed, but it can be estimated indirectly by the increase in water concentration as the acetic acid is removed. Thus similar experiments with 1.0 ml of water present initially give $m = 2 \pm 0.4$.

Potentiometric Measurements on Saturated Solutions. As described in the Experimental Section, the best measurements with the Cu(Hg) and Hg–$Hg_2(OAc)_2$ electrodes were obtained with solutions saturated with either $Cu_2(OAc)_4{\cdot}2H_2O$ or $Cu_2(OAc)_4{\cdot}2H_2O{\cdot}2HOAc$. For the second of these solids the cell reaction is $2Cu(Hg) + 2Hg_2(OAc)_2 + 2H_2O + 2HOAc = 4Hg(l) + Cu_2(OAc)_4{\cdot}2H_2O{\cdot}2HOAc(s)$ and the Nernst equation takes the form

$$E = E° + (0.05916/4) \log (a_{H_2O})^2 (a_{HOAc})^2$$

To correct the observed potentials to $E°$ one needs the activities of water and acetic acid at each water concentration. These are readily calculated from the mole fractions using the formulas of Hansen, Miller, and Christian,[6] provided one assumes that the addition of copper acetate does not appreciably affect the activities. This is undoubtedly a poor assumption at high water concentrations where the solubility of copper acetate approaches 6.79%,[3] but it should be reasonable over the range from 0 to 19 *M* H_2O where the solubility is less than 1% by weight.

Table I shows the $E°$ values obtained in this way from the observed potentials over a range of water concentrations, with the value $E° = 0.2983 \pm 0.001$ V obtained by averaging the best values. This corresponds to $G° = -634.36$ kcal mol^{-1} for solid $Cu_2(OAc)_4{\cdot}2H_2O{\cdot}2HOAc$.

It is difficult to interpret the data at extremely high water concentrations, so the best data on solutions saturated with $Cu_2(OAc)_4{\cdot}2H_2O$ are at the driest point at 19.0 *M* H_2O. This solution gave $E = 0.2874$, $E° = 0.2917$ V, and $G° = -447.35$ kcal mol^{-1} for solid $Cu_2(OAc)_4{\cdot}2H_2O$.

From these two free energy values we can calculate $K =$

Table I. Observed Potentials for Cu(Hg) *vs.* $Hg-Hg_2(OAc)_2$ Electrodes in Solutions Saturated with $Cu_2(OAc)_4 \cdot 2H_2O \cdot 2HOAc$

$[H_2O]$, M	a_{H_2O}	a_{HOAc}	E, V	$E°$, V	X_{H_2O}
			Part A[a]		
0.508	0.0702	0.9728	0.2610	0.2955	0.02860
1.210	0.1445	0.9406	0.2676	0.2932	0.06613
1.550	0.1740	0.9266	0.2717	0.2952	0.08354
2.692	0.2533	0.8851	0.2716	0.2908[c]	0.1387
2.705	0.2541	0.8847	0.2763	0.2955	0.1393
7.132	0.4436	0.7572	0.2823	0.2963	0.3148
8.278	0.4802	0.7277	0.2842	0.2977	0.3525
			Av	0.2956 ± 0.003[a]	
			Part B[b]		
4.192	0.3307	0.8382	0.2814	0.2979	0.2043
6.749	0.4306	0.7672	0.2857	0.2972	0.3015
9.034	0.5028	0.7087	0.2857	0.2990	0.3761
14.20	0.6308	0.5911	0.2863	0.2990	0.5134
			Av	0.2983 ± 0.001[b]	

[a] Measurements in the cell with a capillary between the two electrodes. [b] Measurements in a cell without the capillary but with Hg recently removed from the copper electrode. [c] Value neglected in taking the average.

Table II. Thermodynamics of the Water–Acetic Acid System Expressed in the Power Series of Redlich and Kister[8]

Quantity	Ref	A_1	A_2	A_3	A_4	Units
$\bar{C}_p$	7, 10	0	0	0	0	cal mol^{-1} deg^{-1}
	9, *a*	3.594	1.501	2.810	0	cal mol^{-1} deg^{-1}
$\bar{H}$	7, 11	293.94	−435.92	0	−197.99	cal mol^{-1}
	9, *a*	292.06	−213.55	23.01	−247.17	cal mol^{-1}
$\log \gamma_{25}$	7	0.3337	0.0284	0.1081	0.0002	
	6, *a*	0.34764	0.02204	0.11981	0.01354	
$\log \gamma_{100}$	7	0.2904	0.0575	0.1081	0.0644	
	a	0.2862	0.0458	0.1020	0.0500	

[a] Calculated in this work from literature data as cited.

0.3571 for the equilibrium $Cu_2(OAc)_4 \cdot 2H_2O \cdot 2HOAc(s) = Cu_2(OAc)_4 \cdot 2H_2O(s) + 2HOAc(l)$. Thus the two solids should be in equilibrium at 25° when the activity of acetic acid is 0.5976, or at 13.89 M H_2O. This is not in satisfactory agreement with the equilibrium point found by Sandved[3] which corresponds to 14.97 M H_2O, and one of the $G°$ values must be shifted by 0.04 kcal mol^{-1}. We have decided to correct the free energy for $Cu_2(OAc)_4 \cdot 2H_2O \cdot 2HOAc$ to −634.40 kcal mol^{-1}, since this is equivalent to assigning a higher weight to the potentiometric results at the higher water concentrations ($E° = 0.2989$ V).

Potentiometry at 39°. In order to estimate the enthalpies of these two solids, voltage measurements were taken on a few solutions at 39°. To correct these measurements to $E°$ it is necessary to have activities for the water–acetic acid system at this temperature. Sabastiani and Lacquaniti[7] have given coefficients for the Redlich and Kister[8] equations which are supposedly valid at this temperature. Unfortunately their values differ from those of Hansen, Miller, and Christian[6] at 25° by as much as 4%, and it was necessary to revise all the coefficients reported as shown in Table II. The coefficients for $\log \gamma$ at 25° were selected to match the more complex equation used by Hansen, Miller, and Christian[6] as closely as possible (within 1%) and the enthalpy data of Payn and Perman[9] were used for the temperature dependence. Note that the coefficients agree quite well at 100°, close to the experimental temperatures of Sabastiani and Lacquaniti.[7] Thus most of the apparent discrepancy in the activity data appears to be a result of a poor choice of the thermal data used[10,11] by Sabastiani and Lacquaniti.[7]

Two solutions saturated with $Cu(OAc)_4 \cdot 2H_2O \cdot 2HOAc$ at 39° gave $E° = 0.2954 \pm 0.0005$ V, and thus $\Delta H° = n(23.061)(-E° + 298.15\, dE°/dT)$ for this cell reaction is −33.2 ± 2 kcal mol^{-1}. This gives −803.1 ± 2 kcal mol^{-1} for the enthalpy of this solid and the entropy value shown in Table III.

Similarly for one solution at 18.1 M H_2O saturated with $Cu_2(OAc)_4 \cdot 2H_2O$, $E° = 0.2910$ V, which gives $H° = -566.6$ kcal mol^{-1} for this solid. This is in good agreement with the value (−568.4) from ref 12, and the average (−567.5) is shown in Table III.

Solubilities of the Three Forms of Copper(II) Acetate at 25°. Sandved[3] has no experimental points around 0.53 M H_2O and so failed to find the correct equilibrium point between the two solids $Cu_2(OAc)_4 \cdot 2HOAc$ and $Cu_2(OAc)_4 \cdot 2H_2O \cdot 2HOAc$. To clarify this point and to check if possibly a fourth solid might be formed matching one of the formulas of Gerbault,[13] a detailed study of the solubility equilibria at 25° was undertaken. The solutions contain both monomeric and dimeric copper acetate,[5,14] but this equilibrium can be formulated[14] as

$$Cu_2(OAc)_4 + 4H_2O = 2Cu(OAc)_2 \cdot 2H_2O$$

and the value of the equilibrium constant is known.[5] Grasdalen and Svare[5] preferred to write the dimer in solution with the axial ligands explicitly shown, as in $Cu_2(OAc)_4 \cdot 2HOAc$. They were however wrong in the assertion that the dimer coordinates HOAc in preference to H_2O, and one major aim of this work was to provide quantitative data on the effect of the water concentration on the dimer in solution.

The copper concentrations were determined spectrophotometrically, and since the dimer absorbs much more strongly than the monomer,[5,14] it is convenient to express the results as the equilibrium concentration of dimer as in Figure 1. Note that all of Sandved's[3] points in this region of water concentrations cluster about one or another of our experimental curves, so that we must be dealing with the same set of solids. However the four points between 0.50 and 2.59 M H_2O for which Sandved[3] reported $Cu_2(OAc)_4 \cdot 2HOAc$ present are clearly on the curve for $Cu_2(OAc)_4 \cdot 2H_2O \cdot 2HOAc$.

The solubility equilibrium for this solid is

$$Cu_2(OAc)_4 \cdot 2H_2O \cdot 2HOAc(s) = Cu_2(OAc)_4 + 2H_2O + 2HOAc$$

and the dimer concentration, D, should be given by

$$\log D = \log K - 2 \log a_{H_2O} - 2 \log a_{HOAc} - \log \gamma_D$$

Thus D must increase as the activity of water approaches zero. The activities are known[6] and $\log D + 2 \log a_{H_2O} + 2 \log$

Table III. Thermodynamic Values for Copper(II) Acetate Species

Substance	Form	$H°$, kcal mol^{-1}	$G°$,[a] kcal mol^{-1}	$S°$, cal mol^{-1} deg^{-1}
$Cu_2(OAc)_4 \cdot 2H_2O$	Crystal	−567.5 ± 1	−447.35	118.5
$Cu_2(OAc)_4 \cdot 2H_2O \cdot 2HOAc$	Crystal	−803.1 ± 2	−634.40	184.0
$Cu_2(OAc)_4 \cdot 2HOAc$	Crystal	−663.3 ± 3	−517.93	150.8
$Cu_2(OAc)_4$	HOAc[b]	−423.4 ± 3	−329.12	93.9
$Cu_2(OAc)_2 \cdot 2H_2O$	HOAc[b]	−343.7 ± 2	−276.90	92.3

[a] Free energy values are reported to 0.01 in order to reproduce the observed equilibria; however, all the values have an uncertainty of the order of ±0.2 kcal mol^{-1} due mainly to uncertainties in the free energies of HOAc and $Hg_2(OAc)_2$. [b] Standard-state ideal solution of unit molality. For unit molarity at 25°, substract 0.03 from $G°$ and add 0.1 to $S°$ to allow for the density of acetic acid at 25°, 1.043 kg l^{-1}.

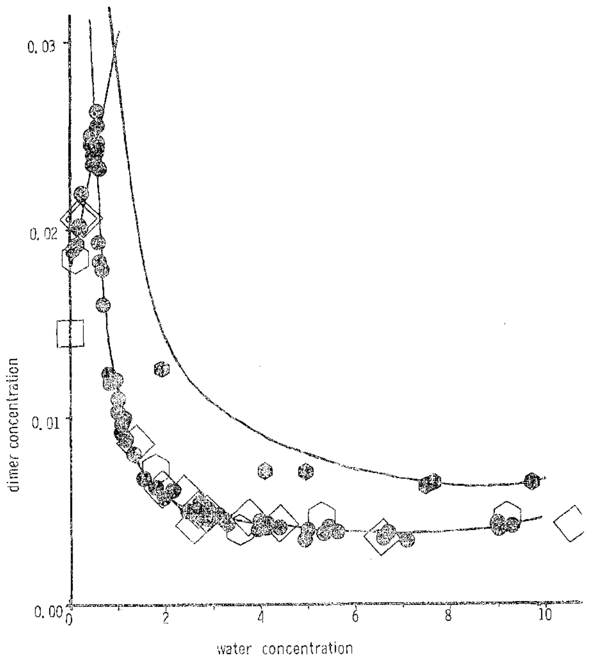

Figure 1. Solubilities of copper(II) acetate solids at 25° in acetic acid as a function of the water concentration. The solubilities are expressed as moles per liter present as the dimer $Cu_2(OAc)_4$. The small dark symbols represent our data, with the hexagons representing measurements with solid $Cu_2(OAc)_4 \cdot 2H_2O$ present. Literature values are represented by the open symbols: diamonds are for Sandved's values,[3] hexagons are for the values of Cheng and Howald,[14] and the single square for dry acetic acid is the 25.3° point of Davidson and Griswold.[4]

a_{HOAc} can be fitted as a power series in the water concentration. For the solutions saturated with this solid between 0.5 and 10 M H_2O this gives $K = 9.54 \times 10^{-5}$ and $\log \gamma_D = -0.2149M + 0.02672M^2 - 0.001339M^3$ where M is the molarity of water. This equilibrium constant corresponds to $G° = -329.15$ kcal mol^{-1} for the dimer dissolved in acetic acid. If molality is used in place of molarity at 25° in defining the standard state, one has $G° = -329.12$ kcal mol^{-1} for the dimer in acetic acid.

There is no *a priori* reason to expect the power series for $\log \gamma_D$ to extrapolate correctly to $M = 0$. The best value for the initial slope should be that which fits the solubility data for solid $Cu_2(OAc)_4 \cdot 2HOAc$, or 0.22 ± 0.05. Since 0.2149 is near the center of this range, it appears that the cubic expression is good over the entire range from 0 to 10 M H_2O. The three solid lines in Figure 1 are calculated dimer concentrations in equilibrium with the three solids using the activities of Hansen, *et al.*,[6] and the equation $\log \gamma_D = -0.2149M + 0.02672M^2 - 0.001339M^3$.

The first term in this equation is negative, showing that the presence of water in the solvent stabilizes the dimer in solution. This is true in spite of the fact that water shifts the monomer–dimer equilibrium toward the monomer. At 3.4 M H_2O, γ_D has dropped to 0.3354 and the activities are $a_{H_2O} = 0.2925$ and $a_{HOAc} = 0.8622$. At this point the activity of the species $Cu_2(OAc)_4 \cdot 2HOAc$ is $D(0.3354)(0.8622)^2 = 0.25D$, indicating that 25% of the dimer molecules have two acetic acid ligands, 25% have two water molecules, and 50% are half and half. This occurs where the water activity is only 0.34 of the activity of acetic acid, indicating that $\Delta G° = -0.64$ kcal mol^{-1} for replacing an acetic acid ligand by water using the pure liquids as the standard state in each case.

A very similar situation holds for the solids. The solubility data in Figure 1 indicate that $G° = -517.93$ kcal mol^{-1} for solid $Cu_2(OAc)_4 \cdot 2HOAc$. Therefore $\Delta G° = -2.45$ kcal mol^{-1} for the reaction

$$Cu_2(OAc)_4 \cdot 2HOAc(s) + 2H_2O(l) = Cu_2(OAc)_4 \cdot 2H_2O(s) + 2HOAc(l)$$

This is −1.2 kcal mol^{-1} for the displacement of one axial ligand. Thus the range $\Delta G° = -0.9 \pm 0.3$ kcal mol^{-1} includes the data on both solids and the dimer in solution.

Similarly we have $\Delta G° = -3.10$ kcal mol^{-1} and $K = 187.2$ for the reaction

$$Cu_2(OAc)_4 \cdot 2HOAc(s) + 2H_2O(l) = Cu_2(OAc)_4 \cdot 2H_2O \cdot 2HOAc(s)$$

and these two solids are in equilibrium when the activity of H_2O is $K^{-1/2} = 0.0731$. This corresponds to 0.532 M H_2O. There are 20 experimental points in Figure 1 clustered about the point where the lines for these two solids intersect. The average and standard deviation of the observed water concentrations for these 20 points are 0.504 and ±0.049. Thus the calculated value is well within one standard deviation of the average.

Further Estimates of Enthalpies. We are continuing this work with careful solubility determinations at other temperatures. So far we have five measurements of this invariant point at 16°, giving an average water concentration of 0.468 ± 0.05 M (moles per liter with the volume measured at 25°; this corresponds to a mole fraction of $X_{H_2O} = 0.0264$). At 16° this concentration gives $a_{H_2O} = 0.0673$ and $K = 220.8$. The temperature dependence of this equilibrium constant gives an estimate of $\Delta H° = -3.2$ kcal mol^{-1} for this reaction and $H° = -663.3 \pm 3$ kcal mol^{-1} for solid $Cu_2(OAc)_4 \cdot 2HOAc$.

The solubility equilibrium in dry acetic acid is

$$Cu_2(OAc)_4 \cdot 2HOAc(s) = Cu_2(OAc)_4 + 2HOAc$$

and the $G°$ values in Table III give an equilibrium value of 0.01803 M $Cu_2(OAc)_4$ in dry HOAc. As shown in Figure 1 this agrees well with the two driest points of Sandved[3] but is about 20% higher than the value of Davidson and Griswold.[4] It is not surprising that they are low, since they measured the temperature at which the last crystal dissolved on warming, and this system is rather slow in reaching equilibrium at 25° and below. The least-squares fit ($\log S$ *vs.* $1/T$) of all the data of Davidson and Griswold[4] gives $\Delta H = 9.5$ kcal mol^{-1} and brings the dimer concentration at 25° up to 0.015 M. The best determination of the temperature dependence appears to be to use our value at 25°, together with the data of Davidson and Griswold[4] above 40°, which gives $\Delta H° = 8.3$ kcal mol^{-1}. This value is used to obtain the value $H° = -423.4 \pm 3$ kcal mol^{-1} for the dimer dissolved in acetic acid.

The Monomer–Dimer Equilibrium. The experimental data from 2 to 11 M H_2O on the equilibrium

$$Cu_2(OAc)_4 + 4H_2O = 2Cu(OAc)_2 \cdot 2H_2O$$

are well represented by Grasdalen and Svare's[5] equations in K_d: $\log K_d = -4.85 + 3.7 \log M$ at 25° and $\log K_d = -4.35 + 3.1 \log M$ at 70°. K_d is defined directly in terms of the monomer and dimer concentrations, C_M and D, $K_d = C_M^2/D$. Using molality for these concentrations gives $\log K_d' = -4.87 + 3.7 \log M$ at 25° and no change in the equation for 70°. The medium effects on the activity coefficients of monomer, dimer, and water are all combined in the differences of 3.7 and 3.1 from 4.0. Equations of this form cannot be extrapolated to dry acetic acid. They do however give $\Delta H = +3.4$ kcal mol^{-1} at 2 M H_2O.

Changing to pure liquid water as the standard state will increase ΔH by 1.4 kcal mol^{-1}, since $\bar{H} - H° = 355$ cal mol^{-1} for water in 2 M H_2O ($X_{H_2O} = 0.10587$) according to the data summarized in Table II. We have made this change to be consistent with the solubility equilibria by calculating $K_d'/(a_{H_2O})^4$ and fitting this as a power series in the molarity of water. This gives $K° = 0.03105$, $2 \log \gamma_M - \log \gamma_D = -0.27525M + 0.019033M^2 - 0.0005918M^3$, and $\Delta H = 9.122 - 2.427M + 0.232M^2 - 0.0085M^3$. It is clear that adding water favors the monomer not only by appearing four times in the stoichiometry but also by decreasing ΔH.

Combining these equations with that for log γ_D from the solubility study gives log $\gamma_M = -0.2451M + 0.02288M^2 - 0.000965M^3$. Thus water stabilizes each monomer molecule about the same as it stabilizes the dimer. The same reason is presumably active in both cases: water is preferred over acetic acid in the axial ligand positions which we have consistently chosen not to include in the stoichiometry for the species in solution.

Experimental Section

Mercury–mercurous acetate electrodes were prepared by placing together triply distilled mercury, mercurous acetate (CP, Amend Drug and Chemical Co., Inc.), and acetic acid (glacial, reagent, Du Pont). In some cases mercurous acetate which had been stored with mercury and acetic acid was used, but this precaution was not necessary. A copper wire can be amalgamated by simply dipping it in the acetic acid solution above the mercury–mercurous acetate electrode. Strains in the copper wire disappear within a few days of the initial amalgamation. The best results were obtained by taking an old copper electrode, rinsing it with hydrochloric acid and distilled water, wiping it with soft paper, heating it over a flame in a hood to drive off the mercury present, and letting it stand overnight in air. Then the electrode was immersed in a solution above a mercury–mercurous acetate electrode stirred by bubbling nitrogen gas through the solution. The potential difference was measured with a voltmeter (John Fluke Mfg. Co., Inc., Model 881A) which could be read to microvolts except with quite dry acetic acid solutions. Readings were generally steady to millivolts after 10 or 20 min. The values given in the second section of Table I are averages of readings taken between 60 and 120 min after inserting the copper electrode. Readings almost as good were obtained with a copper electrode with a thicker amalgam coating in a cell with a capillary tube between the two electrode compartments as shown in the first section of Table I.

It is clear that most of the difficulties were due to the solubility of mercurous acetate in acetic acid. It reacts with copper as it reaches the copper electrode

$$2Cu + 2Hg_2(OAc)_2 = 4Hg + Cu_2(OAc)_4$$

and the obviously increasing copper acetate concentration is a problem except for saturated solutions. Also it appears that diffusion does not keep the outer layers of amalgam saturated with copper when the amalgam layer gets too thick. The cells were immersed in a thermostated water bath. The solutions from the cell were analyzed spectrophotometrically for water and copper acetate as described below after reproducible potential readings had been obtained on successive days. There were no systematic differences between the copper concentrations in solutions from the cell (saturated with mercurous acetate) and the bulk of the solubility measurements which were from solutions with excess solid in volumetric flasks suspended in the water bath.

In both cases a sample of solution was poured or pipetted into a clean dry test tube. Then a spectrophotometer cell equipped with a ball and socket closure and a quartz spacer allowing path lengths of 1, 3, or 10 mm was rinsed and filled decanting from the test tube. The water concentrations were calculated from the measured absorbance at 1425 nm in the near-infrared region as $4.2(a_{1425} - a_{1300})$. It was necessary to add the water concentration in the blank, determined by the same measurement *vs.* a cell with excess acetic anhydride. All the cells picked up measurable amounts of water from the air over long periods of time in spite of their ground-glass seals. This work suggests that a solution saturated with both $Cu_2(OAc)_4 \cdot 2HOAc$ and $Cu_2(OAc)_4 \cdot 2H_2O \cdot 2HOAc$ (0.53 M H_2O) would be just as satisfactory a long-term standard of water concentration as the cell with excess acetic anhydride.

Just before or after the near-infrared scan the visible spectrum was recorded usually with a 3-mm path length, and $a_{690} - a_{490}$ was calculated for a 10-mm path length. The dimer has a substantial extinction coefficient at 690 nm ($\epsilon_{690} - \epsilon_{490} = 370$) and is responsible for most of the observed blue-green color. The monomer absorbs in the same wavelength region, but much less strongly ($\epsilon_{690} - \epsilon_{490} = 35$). With these two values and $K_d = C_M{}^2/D$ from the equation of Grasdalen and Svare[5] (log $K_d = 4.85 - 3.7M$) it is a simple matter to solve a quadratic (by computer) for the concentrations of both monomer and dimer. The equation is not intended to be valid below 2 M H_2O, but for these drier saturated solutions the absorbance of the monomer is almost negligible, and the program still gives a good dimer concentration, D.

To get the mole fractions and activities of water and acetic acid from the observed molarity of H_2O, it is necessary to know the densities of the solutions. The best density data for acetic acid–water mixtures at 25° appear to be those of Waring, Steingiser, and Hyman[15] which can be represented quite accurately by the equation $V_{app} = 13.3155 + 5.1972X - 0.4653X^2$, giving the apparent molal volume of water as a function of the mole fraction of water. With this formula and the value 57.5592 for the molar volume of acetic acid, it is easy to calculate the density and molarity given X. The reverse calculation is required here, and the computer was programmed to get X by successive approximations from M and to print this together with activities for both water and acetic acid calculated from the coefficients of Table II or the equations of either of the literature references.[6,7] Listings of any of these programs are available on request.

Registry No. $Cu_2(OAc)_4 \cdot 2H_2O$, 15523-07-6; $Cu_2(OAc)_4 \cdot 2H_2O \cdot 2HOAc$, 53597-07-2; $Cu_2(OAc)_4 \cdot 2HOAc$, 36447-87-7; $Cu_2(OAc)_4$, 23686-23-9; $Cu(OAc)_2 \cdot 2H_2O$, 4465-79-6.

References and Notes

(1) Parts of this paper were presented at the Northwest Regional Meetings of the American Chemical Society at Pullman, Wash., June 14–15, 1973, and Cheney, Wash., June 13–14, 1974.
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