

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
CORNELL UNIVERSITY, ITHACA, NEW YORKSolvation of Copper(II) Ion in Acetone-Water and Ethanol-Water Solutions¹

BY NEWTON J. FRIEDMAN AND ROBERT A. PLANE

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Spectrophotometric measurements have been made of solutions containing Cu^{+2} in acetone-water or ethanol-water mixtures. Although evidence is found for association of Cu^{+2} with NO_3^- , no evidence is found for ClO_4^- association. As water concentration is decreased, extinction coefficients in the visible region increase markedly. The increase is interpreted as being due to the successive replacement of two H_2O molecules of the Cu^{+2} hydration sphere by two acetone or alcohol molecules. For the first replacement by acetone the equilibrium constant is 3.7. The corresponding value for ethanol is 1.8. For the second replacement the equilibrium constant values are 3.1×10^{-3} for acetone and 3.9×10^{-2} for alcohol, respectively. Whereas the small deviation of the first constants from the statistical expectation (6) can be accounted for in terms of ligand field strengths, the very small values of the second constants cannot. It seems probable that these constants are depressed by a general solvent effect.

In an attempt to understand better the state of solvation of metal ions in mixed solvents, the present spectrophotometric study was undertaken. Similar studies had been made previously, in which gradual spectral intensity changes were interpreted as indicating a statistical replacement of all H_2O molecules coordinated to dissolved cations.² In a related study, the importance of low mole fractions of water in mixed solvents was emphasized.³ An important difference between the present investigation and the earlier work in ethanol-water mixtures was the extension of measurements to as low mole fractions of H_2O as solubility permitted. This extension revealed behavior quite distinct from that found earlier.

For the present study Cu^{+2} was chosen because its absorption spectrum allows measurements to be made conveniently. Furthermore, the spectrum has been interpreted⁴ to show that the ion in aqueous solution exists as the distorted octahedron $\text{Cu}(\text{H}_2\text{O})_6^{+2}$. Therefore, the spectrum should be sensitive to changes in the degree of distortion, and this sensitivity could give indication of the geometry of substituted species. Also, the geometry of the ion might have important consequences in determining the tendency for stepwise replacement of solvent molecules. Acetone and alcohol were chosen as ligands because their miscibility with water permits a wide range of variation of concentration. Alcohol has the added advantage of having an ultraviolet band. This band allowed additional measurements to be made which served to check those involving the ligand field bands of Cu^{+2} .

In a previous study the behavior of Cu^{+2} and $\text{Cu}(\text{ethylenediamine})_2^{+2}$ as studied in ethanol-water mixtures.² This work was criticized on the basis that at the lower dielectric constant considerable ion pairing might occur between the copper and the anions used (nitrate or chloride).⁵ To meet this objection, both

nitrate and perchlorate ions were used in preliminary experiments of the present investigation. The results were found to be essentially identical for mole fraction H_2O greater than *ca.* 0.5. For solutions with less H_2O , the nitrate solutions showed slightly larger differences in extinction as H_2O was decreased. Thus, for the balance of the work, ClO_4^- was used as the only anion, and the effect of changing its concentration was studied.

Experimental

Absorption spectra were measured in matched 1-cm. or 10-cm. silica cells with a Beckman Model DU spectrophotometer, thermostated at 27°. In a few cases, measurements were made with a Cary Model 14 spectrophotometer. In general, the spectra were run *vs.* a blank which was identical with the solution studied except that the copper salt was omitted. To minimize changes of solution composition due to exposure to the atmosphere, absorption cells were fitted with ground glass stoppers, and solutions were prepared and stored in flasks of minimum volume. The water content of stock solutions was determined either by the Karl Fischer method or by that of Smith and Bryant⁶ prior to addition of the cupric salt (which was found to interfere with the determination). Solutions of increased water content were prepared by addition of water, or water-solvent mixtures, to the stock solution.

Copper(II) perchlorate dihydrate was prepared by adding C.P. copper(II) hydroxide to a 20% excess of strong (*ca.* 6 M) HClO_4 . The mixture was heated at 80° for 2 hr., filtered, and twice recrystallized from water. The final product was washed with sufficient cold water to half dissolve it. This precaution was necessary in order to eliminate traces of HClO_4 which adhere to the crystals. The washed crystals were dried in a vacuum oven at 110° for 3 hr. and stored over $\text{Mg}(\text{ClO}_4)_2$. Copper analysis, by electrodeposition, showed the salt to contain 2.0 ± 0.1 moles of H_2O per mole of copper.

Anhydrous NaClO_4 was prepared by heating the recrystallized salt for 24 hr. at 120°. All other chemicals were reagent grade, used without further purification.

All solutions were slightly acidic (*ca.* pH 5); even so, solutions containing less than about 50 mole % water slowly became turbid. Filtering served to remove the turbidity.

As is noted below, the data obtained were interpreted in terms of two consecutive, solvent exchange equilibria. The equilib-

(1) Presented at the 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., September, 1962.

(2) J. Bjerrum and C. K. Jørgenson, *Acta Chem. Scand.*, **7**, 951 (1953); C. K. Jørgenson, *ibid.*, **8**, 175 (1954).

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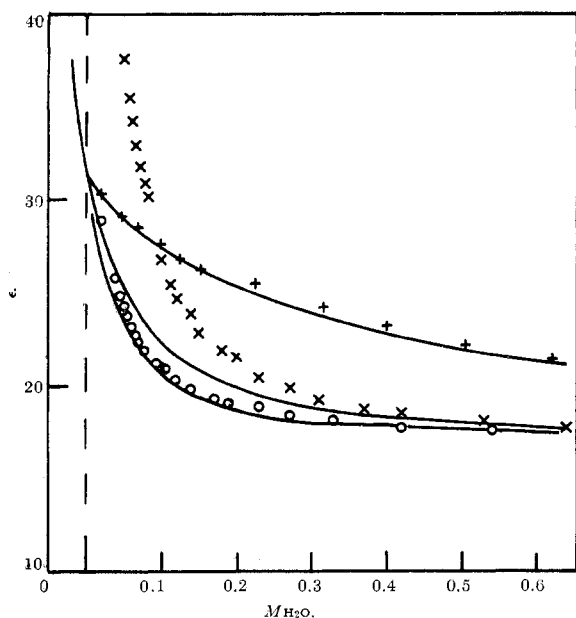


Fig. 1.—Extinction coefficients at 8200 Å. for cupric ion in acetone solutions as a function of H₂O concentration: data points plotted *vs.* total H₂O; solid curves are for same data plotted *vs.* free H₂O assuming Cu(H₂O)₄(acetone)₂⁺²; circles refer to $2.5 \times 10^{-3} M$ Cu(ClO₄)₂; × to $1.8 \times 10^{-2} M$ Cu(ClO₄)₂; + to $1.8 \times 10^{-3} M$ Cu(ClO₄)₂ + 1.0 M NaClO₄.

rium constants for these equilibria, K_1 and K_2 , were evaluated as follows. For a solution containing two absorbing species in equilibrium, the relationship between the apparent extinction coefficient ϵ (*i.e.*, optical density per formal concentration of metal ion) and those of the two individual species, ϵ_0 and ϵ_1 , can be expressed as

$$\frac{1}{\epsilon - \epsilon_0} = \frac{1}{\epsilon_1 - \epsilon_0} + \frac{[\text{H}_2\text{O}]}{K_1(\epsilon_1 - \epsilon_0)[\text{A}]}$$

where [H₂O] and [A] are the actual concentrations of free solvents. Thus, a plot was made of $1/(\epsilon - \epsilon_0)$ *vs.* [H₂O]/[A], for points of moderate to low concentration of either ethanol or acetone. The resulting curve was a straight line with intercept of $1/(\epsilon_1 - \epsilon_0)$ and slope of $1/K_1(\epsilon_1 - \epsilon_0)$. Because the second equilibrium was ignored, these values represented only first approximations. Data obtained at low H₂O concentration were treated in an analogous way and approximations to K_2 values were obtained. These then were used to correct K_1 values and *vice versa* until consistent values were obtained. In the course of the calculations, it was found that the data were sensitive to changes of K values of about $\pm 5\%$. This precision also was reflected in the assigned values for ϵ_1 .

Results

The visible absorption spectrum of the Cu⁺² ion in aqueous solution was found to have a broad asymmetric absorption band with a nearly flat plateau extending from 7950 to 8350 Å. As the solvent was changed by addition of either acetone or ethanol, no appreciable shift occurred; however, the extinction coefficients increased gradually, by as much as a factor of 2. It was found that the spectra were independent of pH in the region studied, pH 2–5. In this pH range and through the entire range of solvent concentrations, no indication of hydrolyzed species was noted.

Data were obtained and analyzed for acetone–water solutions at wave lengths of 7000, 7200, 8200, 9000,

and 9500 Å. and for alcohol–water solutions at 2300, 2500, 2700, 7000, 8200, and 9500 Å. For deciding the changes of species responsible for the spectral changes, the data obtained at very low water and high acetone are most informative. Typical data, at 8200 Å., are plotted in Fig. 1. The figure shows data points, for three different solutions, plotted *vs.* total molarity of H₂O. It is to be noted that at very low H₂O concentration the extrapolated extinction coefficients differ for the three solutions; *i.e.*, they do not appear to obey Beer's law. If, however, the data are plotted differently, this problem disappears. For the second plot, rather than using total H₂O concentration as the abscissa, the total H₂O minus four times the Cu⁺² concentration is used. This shifts the points to the left on the plot to positions given by the three solid curves. It is now seen that all three solutions give the same extinction coefficient at zero free H₂O. Thus it appears that at the point marked zero on the abscissa, all three solutions contain a species with four H₂O molecules/Cu⁺². As H₂O is removed from the solution, as was possible in one case, the extinction coefficient rises; as H₂O is added the extinction coefficient falls. The latter fall is noted to be of slightly different form for the solutions of Cu⁺² = $2.5 \times 10^{-3} M$ and Cu⁺² = $1.8 \times 10^{-2} M$. There is a similar, though larger, discrepancy for the solution with added 1 M NaClO₄. It seems probable that the cause for these differences is due to the effect of added salt concentration. Although it would be possible to postulate a specific ClO₄⁻–Cu⁺² interaction, the effect is small and cannot be separated from a general salt effect on the activity of the H₂O. Thus, ClO₄⁻ could merely lower the activity of the H₂O (the latter being of lower concentration than the ClO₄⁻ in the one solution) so that the more concentrated solutions behave as though they have somewhat less H₂O.

In the extended region of nearly pure acetone to pure water as solvent, the spectral changes which occur accompany the conversion of the ion Cu(H₂O)₄(acetone)₂⁺² to the completely hydrated ion. The latter has been fairly convincingly formulated⁴ as the distorted octahedral Cu(H₂O)₆⁺². Thus, the simplest explanation of the observed spectral changes involves the replacement, on going from pure H₂O to nearly pure acetone, of two H₂O molecules in Cu(H₂O)₆⁺² by two acetone molecules. In the interpretation of all the remaining spectra, such a scheme is used and two equilibria are proposed

$$K_1 = \frac{[\text{Cu}(\text{H}_2\text{O})_5(\text{acetone})^{+2}][\text{H}_2\text{O}]}{[\text{Cu}(\text{H}_2\text{O})_6^{+2}][\text{acetone}]}$$

$$K_2 = \frac{[\text{Cu}(\text{H}_2\text{O})_4(\text{acetone})_2^{+2}][\text{H}_2\text{O}]}{[\text{Cu}(\text{H}_2\text{O})_5(\text{acetone})^{+2}][\text{acetone}]}$$

That the form of the data is consistent with this interpretation can be seen from Fig. 2. Here, formal extinction coefficients for 8200 Å. are plotted *vs.* the mole % acetone for the entire range. The solid curve is calculated assuming that only two solvent exchange equilibria are involved. For the calculation of the

equilibrium constants no corrections are made for activity coefficient changes. If activities of acetone and H_2O are used instead of concentrations, the fit to the data is slightly poorer; thus there is apparently a cancellation due to the unknown activity coefficients of the copper-containing species. The actual values of the equilibrium constants are affected by about a factor of 2 as will be discussed below. Values calculated for K_1 and K_2 (using concentrations exclusively) for various solutions and various wave lengths are given in Table I. Included in the table are some duplicate experi-

TABLE I
EVALUATION OF ϵ_1 , K_1 , AND K_2 FOR Cu^{+2} -ACETONE

[Cu ⁺²], mM	λ , Å.	ϵ_0	ϵ_1	ϵ_2	K_1	K_2
18	7200	7.8	11.6	...	3.7	...
18	8200	11.6	17.0	...	3.7	...
18	9000	10.0	15.7	...	3.8	...
18	8200	...	16.5	32.0	...	4.0×10^{-3}
18	8200	...	16.4	32.0	...	4.3×10^{-3}
2.5	7000	...	10.0	19.8	...	3.2×10^{-3}
2.5	8200	...	16.0	32.0	...	3.1×10^{-3}
2.5	9500	...	12.9	23.5	...	3.0×10^{-3}
2.5	8200	...	16.0	32.0	...	3.0×10^{-3}
1.8 ^a	8200	...	17.0	31.0	...	2.1×10^{-2}

^a Contained 1 M NaClO₄.

ments which were measured and calculated independently in order to check precision. The table lists extinction coefficients: ϵ_0 refers to the completely aqueous ion; ϵ_2 , to the ion with four molecules of H_2O and presumably two acetone molecules; ϵ_1 , to the intermediate species having five waters and one acetone. Although ϵ_0 and ϵ_2 would be measured directly, ϵ_1 was treated as a parameter and evaluated along with the equilibrium constants. It is seen that the values obtained for it at 8200 Å. are essentially independent of whether it is evaluated at low acetone or at low H_2O . The only apparent discrepancy in the table occurs for the solution with added NaClO₄. As was noted, the added salt has the effect of apparently increasing K_2 . The same trend is noted in comparing values of K_2 for different concentrations of $Cu(ClO_4)_2$. Data obtained for alcohol-water mixtures are qualitatively very similar for the acetone solutions. Again the data are fitted by use of the two consecutive solvation equilibria. The fit can be judged from Fig. 3, which gives data points and calculated curves. Included in the figure are data for 8200 and for 2300 Å. using in both cases the same equilibrium constants ($K_1 = 1.9$, $K_2 = 3.7 \times 10^{-2}$). It is found that use of alcohol and H_2O activities, in place of their concentrations, slightly improves the fit. However, for consistency with the acetone results, concentrations have been used throughout.

Data for various concentrations and various wave lengths are given in Table II. It is seen that values of equilibrium constants are not dependent on wave length or on solute concentration. Perhaps the difference, in the latter regard, between these solutions

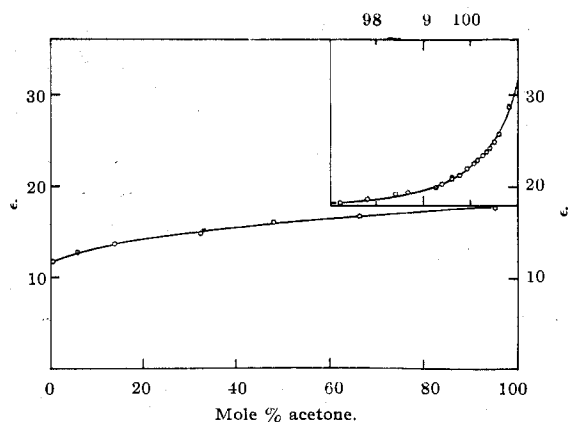


Fig. 2.—Extinction coefficients at 8200 Å. for cupric ion in acetone-water mixtures.

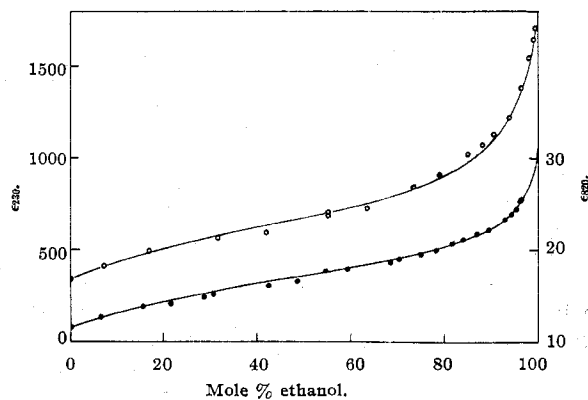


Fig. 3.—Extinction coefficients at 2300 Å. (upper curve and left hand scale) and at 8200 Å. (lower curve and right hand scale) for cupric ion in ethanol-water mixtures.

and the acetone solutions which showed a slight dependence of K_2 on salt concentration is due to the different magnitudes of K_2 . Thus, for alcohol solutions, K_2 becomes important at much higher H_2O concentrations where changes of salt concentration less drastically effect the H_2O activity.

TABLE II
EVALUATION OF ϵ_1 , K_1 , AND K_2 FOR Cu^{+2} -ETHANOL

[Cu ⁺²], mM	λ , Å.	ϵ_0	ϵ_1	ϵ_2	K_1	K_2
24	7000	6.3	9.8	...	2.1	...
24	8200	11.6	20.0	...	1.9	...
24	9500	8.7	16.0	...	1.6	...
0.51	2300	340	890	1776	1.7	0.037
.51	2500	52	195	1538	1.9	.040
.40	2300	...	945	1776038
.40	2500	...	205	1538036
.40	2700	...	7)	900030
1.53	7000	...	10.2	16.8036
1.53	8200	...	20.9	31.0042
1.53	9500	...	16.3	22.0042
3.1	7000	...	10.2	16.5043
3.1	8200	...	19.5	31.0036
3.1	9500	...	15.8	22.0043
16	7000	...	10.3	16.5036
16	8200	...	19.6	31.0040
16	9500	...	15.6	22.0042
38	7000	...	10.2	16.0042
38	8200	...	19.9	31.0036
38	9500	...	15.9	22.0038

Conclusions

The values found for the replacement of one molecule of H_2O coordinated to Cu^{+2} by acetone (3.7) or by alcohol (1.8) are not unexpected. If it is assumed that the aquo ion is octahedral with but slight distortion, a statistical value of 6 for the equilibrium constant applies since there are six ways of replacing H_2O and but one of replacing acetone or alcohol. That the measured values do not differ much from the statistical expectation is consistent with the lack of significant spectral shifts, indicating that ligand field strengths of H_2O , acetone, and alcohol are about equal. Co^{+2} and Ni^{+2} have sharper absorption bands than does Cu^{+2} and their spectra show that the ligand field strengths for the three ligands, although nearly equal, decrease slightly: $\text{H}_2\text{O} > \text{acetone} > \text{alcohol}$. Consequently, the K_1 values show the trend expected purely on the basis of ligand field stabilization. All other factors, such as differences of inter-ligand interactions and differences of solvation outside the primary solvation shell, apparently are either small or tend to cancel.

The values found for the replacement of a second molecule of H_2O coordinated to Cu^{+2} by acetone (3.1×10^{-3}) and by alcohol (3.9×10^{-2}) are smaller than expected. If the second replacement occurs *cis* to the first, the statistical constant would be 2; if *trans*, 0.5. Space-filling molecular models show that a *cis* product cannot be dismissed on steric grounds. However, Jahn-Teller distortion for the copper ion

could favor a *trans* product. In any case, the observed K_2 values are low even for the *trans* case. Two causes for the low values can be imagined. One would involve a specific interaction within the complex species, *e.g.*, *trans* effect, if the product is indeed *trans*; the other would be a general solvent effect operating from without, *e.g.*, a difference of solvation of product and reactants by the solvent in question. It is difficult to decide the relative importance of these two explanations, but what evidence there is would indicate that the second is of major importance. It would seem that a *trans* effect, or other specific interaction, should be most pronounced for the two more different ligands, *i.e.*, should depress K_2 more for alcohol than for acetone, whose ligand field strength is intermediate between H_2O and ethanol. This is contrary to fact. On the other hand, the solvent effect should cause the greater difference for the case of changing the solvent from mainly water to mainly acetone as opposed to a change from water to the more water-like alcohol. Whatever the cause, the abnormal depression of K_2 by both solvents is completely consistent with the failure to replace more than two of the first sphere solvent molecules by either acetone or ethanol.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF PITTSBURGH, PITTSBURGH 13, PENNSYLVANIA

Polarography of the Rare Earth Elements and Other Inorganic Substances in Acetone as Solvent

BY J. F. COETZEE¹ AND WEI-SAN SIAO²

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Cations, particularly the solvated proton and metal ions of high charge type, generally are reduced at less negative potentials in acetone than in water. The half-wave potentials (*vs.* the aqueous saturated calomel electrode) obtained at the dropping mercury electrode in 0.1 *M* tetraethylammonium perchlorate as supporting electrolyte were (in volts, with an asterisk denoting a reversible or near-reversible electro-reaction): oxygen, -0.92 and -1.4 ; sodium, -1.92 ; potassium, -1.97^* ; rubidium, -1.97^* ; magnesium, -1.75 ; cadmium, -0.18^* ; silver, more positive than the anodic discharge potential of mercury ($+0.68$ v.); copper(II) \rightarrow copper(I), $+0.53^*$; copper(I) \rightarrow copper amalgam, $+0.31^*$; samarium, europium, and ytterbium, a first wave (III \rightarrow II) at -1.13^* , -0.03 , and -0.71^* , respectively, and a second (2-electron) wave at -1.70 , -1.79 , and -1.71 , respectively. All other rare earth elements gave only one (3-electron) wave near -1.4 v., with some irregularities, shown to be caused by solvolysis effects. It is likely that the second (2-electron) wave of samarium, europium, and ytterbium, as well as the single (3-electron) wave of the remaining rare earth elements, is caused by hydrogen evolution, rather than by amalgam formation. It is shown that the overpotential of hydrogen on mercury is approximately 0.8 v. smaller in acetone than in water. Iodide ion gives two anodic waves at the dropping mercury electrode, corresponding to successive formation of HgI_3^- and HgI_2 , with half-wave potentials equal to -0.37^* and $+0.20^*$ v.

Introduction

Acetone has been neglected as a solvent for electrochemical studies. Very few systematic quantitative investigations have been carried out in essentially

anhydrous acetone, and these have been limited mainly to the conductometry of salts, particularly those of

(1) Address all correspondence to this author.

(2) From the M.S. thesis of Wei-San Siao, University of Pittsburgh, 1961.