

Solvation of Copper(II) Sulfate in Binary Water/*N,N*-Dimethylformamide Mixtures: From the Solution to the Gas Phase

Nikos G. Tsierkezos,[†] Jana Roithová,^{‡,§} Detlef Schröder,^{*,†} Ioanna E. Molinou,[§] and Helmut Schwarz^{||}

Institute of Organic Chemistry and Biochemistry, Flemingovo nám. 2, 16610 Prague 6, Czech Republic, Department of Organic Chemistry, Charles University in Prague, Hlavova 8, 12843 Prague 2, Czech Republic, Laboratory of Physical Chemistry, Department of Chemistry, National and Kapodistrian University of Athens, P.O. Box 64004, 157 10 Zografou, Greece, and Institut für Chemie, Technische Universität Berlin, Strasse des 17. Juni 135, 10623 Berlin, Germany

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The solvation of copper(II) sulfate in binary mixtures of water and *N,N*-dimethylformamide (DMF) is studied by a combined approach using electrochemical studies in solution and a mass spectrometric assay of the solvated ions formed from these solutions upon electrospray ionization (ESI). In the condensed phase, the limiting transference numbers (t_{\pm}°) and the apparent ion association constants (K_A 's) of CuSO_4 have been determined in water/DMF solutions at 20 °C. The t_{+}° values decrease with increasing DMF content, demonstrating a gradual solvation of Cu^{2+} by DMF molecules. The association constants indicate that aggregation becomes more pronounced as the DMF content increases. In order to achieve complementary insight, the intrinsic interactions among the ions and solvent molecules are investigated in gas-phase experiments of the CuSO_4 /water/DMF system using ESI mass spectrometry. Under the conditions used, the dications $[\text{Cu}(\text{DMF})_n]^{2+}$ ($n = 3-6$), $[\text{Cu}_2(\text{DMF})_n\text{SO}_4]^{2+}$ ($n = 2-7$), and $[\text{Cu}_3(\text{DMF})_n(\text{SO}_4)_2]^{2+}$ ($n = 2-7$), and the monocations $[\text{Cu}(\text{OH})(\text{DMF})_n]^{+}$, $[\text{Cu}(\text{DMF})_n(\text{HSO}_4)]^{+}$ (both, $n = 1-3$), and $[\text{Cu}(\text{DMF})_n]^{+}$ ($n = 1, 2$), are formed as the leading copper-containing cations. Likewise, polynuclear copper clusters observed in the anion ESI spectra support partial aggregation occurring in solution. The gas-phase studies clearly support the conclusions that (i) DMF is a highly preferred ligand for Cu^{II} in comparison to water and that (ii) DMF supports ion association for which the mass spectrometric data suggest the formation of polynuclear copper clusters.

Introduction

Accurate data about the interactions of electrolytes in mixed solvents find applications in many industrial processes, as they provide a wide choice of solutions with engineerable properties. Interactions involving symmetrical 1:1 electrolytes in mixed solvents have received quite a bit of attention, whereas fewer reports on 2:2 electrolytes in mixed-solvent systems appeared. The investigation of ionic interactions usually is performed via the determination of thermodynamic properties of the bulk, such as the partial molar volume, the solvation enthalpy, the isentropic compressibility, the free energy of transfer, and transport properties, such as conductivity, viscosity, and transference numbers.¹ It is important to realize, however, that these methods probe macroscopic quantities of the bulk solution. Information about the microscopic interactions existing in solution can be obtained with several spectroscopic methods,²⁻⁷ but the achievable molecular insight still remains limited. In part, this is due to the fluxional behavior in solution (e.g., ref 3), but it is also a result of the indirect nature of most measured quantities, which require extensive modeling and assumptions in the deduction of the underlying molecular circumstances.⁸ Hence, complementary information about the microsolvation of ions in the

gas phase might add helpful information for a molecular understanding of solvation phenomena.⁹⁻¹¹

In general, the behavior of ions in an electrolyte solution depends on the physicochemical properties of the solvent.¹² Specifically, the extent of ion association and ion solvation is related not only to the size and charge of the involved ions, but also to properties of the solvent such as the dipole moment of the separate solvent molecules or the dielectric constant and the viscosity, where the latter two reflect the sum of the dipoles in the bulk. Some of the advantages which motivate the use of mixed solvents derive from the possibility to gradually change physicochemical properties of a bulk solvent by a change in composition.¹³ The determination of thermodynamic, electrochemical, or transport properties allows conclusions about the interactions between the components of the solution, but cannot provide insight into the electrolyte solution at a molecular level. Such a general qualitative picture of the situation of a solution of an electrolyte, i.e., the types of solvated ions being present and the extent to which they are formed, can be obtained via electrospray ionization mass spectrometry (ESI-MS),^{14,15} and the correlations between ESI mass spectra and the situation in solution have been reviewed recently.¹⁶ While several exceptions are known, the ESI data often correlate well with the situation in solution, although quantitative analysis might be cumbersome. For the binary solvent mixtures described in this work, some semiquantitative considerations appear justified, however.

N,N-Dimethylformamide (DMF) is a versatile solvent with wide use, and is fully miscible with water. The behavior of

* To whom correspondence should be addressed. E-mail: Detlef.Schroeder@uochb.cas.cz.

[†] Institute of Organic Chemistry and Biochemistry.

[‡] Charles University in Prague.

[§] University of Athens.

^{||} Technische Universität Berlin.

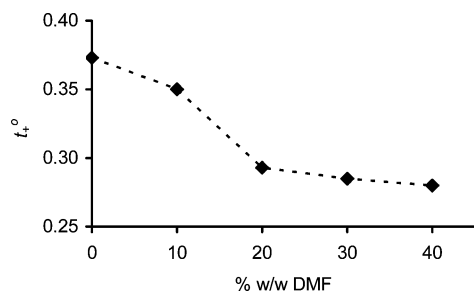


Figure 1. Limiting transference numbers of Cu^{2+} (t_{+}^0) for CuSO_4 as a function of DMF content in water/DMF mixtures at 20 °C. Due to limited solubility of CuSO_4 , the evaluation of transference numbers was impossible for mixtures with more than 40% w/w DMF.

electrolytes in pure DMF and its binary mixtures has been addressed frequently due to many applications of DMF as a solvent. The majority of the literature data available deals with symmetrical 1:1 electrolytes in pure DMF^{17–19} and its binary mixtures with water,^{20–22} acetone,²³ acetonitrile,²⁴ and methanol,²⁵ whereas 2:2 electrolytes have not been addressed so far. Here, we report a combined study of copper(II) sulfate in water/DMF mixtures in bulk solution as well as in the gas phase, which may form a starting point for searching direct correlations between solution-phase chemistry and the molecular species detected in the gas phase using electrospray ionization in combination with tandem mass spectrometry.¹⁶

Experimental Section

The transference numbers of Cu^{2+} and SO_4^{2-} ions were determined in the concentration range 0.0050–0.0250 mol L⁻¹ in water/DMF mixtures using a concentration cell with transference similar to that described by Braun and Weingärtner.²⁶ The voltage of the cell was measured with a Xenon PH129 potentiometer against a CuSO_4 reference solution with 0.0025 mol L⁻¹. Prior to use, the copper-rod electrodes were cleaned with dilute nitric acid, distilled water, and acetone; the maximal bias potential did not exceed 0.1 mV. The glass cell was immersed in a thermostat (± 0.01 °C); the uncertainty of the voltage measurements was ± 0.1 mV. The relative uncertainty of the calculated transference numbers in the water/DMF mixtures is $\pm 0.2\%$, and the absolute error is conservatively estimated as $\pm 5\%$: note that the absolute errors are of remote importance for the binary solvent mixtures investigated here.

The conductivity measurements were carried out with a digital bridge-type conductivity meter (Metrohm 712) in a dipping-type conductivity cell with platinum black electrodes. The cell constant (0.814 ± 0.001 cm⁻¹) was determined by calibration with aqueous solutions of potassium chloride in the concentration range from 0.0010 to 0.1000 mol L⁻¹ at 20 °C. The specific conductivities of the electrolyte in water/DMF mixtures have been measured in the concentration range 0.0001–0.0010 mol L⁻¹ at 20 °C. All measurements were corrected with the specific conductivity of each solvent mixture. Within the range of the measurements (2–20 mS cm⁻¹), the uncertainty of the relative specific conductivities is $\pm(0.1–0.5)\%$; the absolute error is conservatively estimated as $\pm 5\%$. The dielectric constants and viscosities of the solvent mixtures are adopted from the literature.²⁷

The ESI-MS experiments were performed with a VG BIO-Q instrument which consists of an ESI source followed by a mass spectrometer of QHQ configuration (Q = quadrupole, H = hexapole).²⁸ For each ion of interest, the instrument parameters were optimized for maximum ion abundances by changing from soft to increasingly harsher ionization conditions, as described

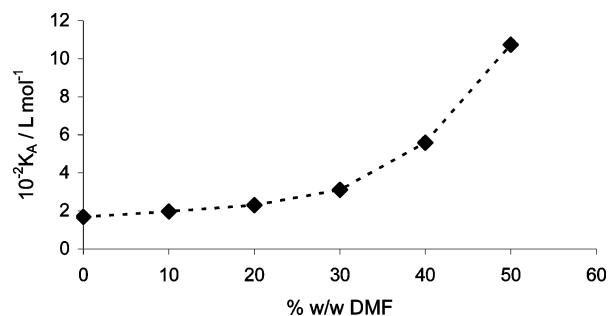


Figure 2. Apparent association constants (K_A 's) of CuSO_4 as a function of DMF content in water/DMF mixtures at 20 °C.

previously.^{29–31} In the present experiments, millimolar solutions of CuSO_4 in distilled water or water/DMF mixtures were introduced via a syringe pump (flow rate 5 $\mu\text{L}/\text{min}$) to the fused-silica capillary of the ESI source. Nitrogen was used as nebulizing and drying gas at a source temperature of 110 °C; in some experiments, methanol was used as a cosolvent improving the spray conditions.³² In the ESI mass spectra, the copper-containing ions (as well as copper clusters) are readily identified by their characteristic isotope envelopes.³³ For CID, the ions of interest were mass-selected using Q1, interacted with xenon in the hexapole collision cell at various collision energies ($E_{\text{Lab}} = 0$ to 20 eV) at a collision-gas pressure of ca. 3×10^{-4} mbar, while scanning Q2 to monitor the ionic fragments.

All CuSO_4 solutions were prepared by weight (± 0.0001 g) from a stock solution; molar concentrations were obtained from molalities and densities with an accuracy of ± 0.0001 mol L⁻¹. *N,N*-Dimethylformamide (Fluka, 99.8%) was distilled and stored over 4 Å molecular sieve.³⁴ The water was doubly distilled with a specific conductivity below 0.40 $\mu\text{S cm}^{-1}$ at 20 °C. Anhydrous copper(II) sulfate (Fluka 99.5%) was dried before use at 110 °C for 24 h.

Results and Discussion

The present work describes the interactions between ions and among ions and solvent molecules in solutions of copper(II) sulfate in water/DMF mixtures. To this end, bulk properties of the solutions, such as transference numbers and specific conductivities, have been measured at 20 °C, and the ion-association constants of CuSO_4 have been evaluated. These investigations of the macroscopic properties in the condensed phase are complemented by a gas-phase study employing ESI-MS which probes the microsolvation of the ions evolving from solution in the presence of water and DMF. One motivation of this work is thus to evaluate whether the results of microscopic and macroscopic solvation could at all correlate with each other or if the gap between these regimes is too large.^{9,16,35,36}

Transference Numbers and Conductivities in Solution. The limiting transference numbers for CuSO_4 have been determined from measurements of the voltages of a $\text{Cu}|\text{CuSO}_4(c_{\text{ref}})|\text{CuSO}_4(c_i)|\text{Cu}$ concentration cell, where c_{ref} represents the concentration of the reference solution against which all other solutions with the concentrations c_i were measured ($c_i > c_{\text{ref}}$); see Supporting Information for further details.

The decrease of t_{+}^0 with the increase of DMF content (Figure 1) can be attributed to the gradual replacement of the water molecules of the Cu(II) solvation sheath by DMF molecules, leading to an increase of the size of the solvated ions and consequently to their reduced mobility. For pure water, the somewhat divergent literature values of $t_{+}^0 = 0.320$ (25 °C) by Sinha and Bhat³⁷ and $t_{+}^0 = 0.401$ (25 °C) by Pikal and Miller,³⁸ both determined using the Hittorf method, and $t_{+}^0 =$

TABLE 1: Limiting Molar Conductivities (Λ_0 , in S·cm² mol⁻¹), Limiting Ion Conductivities ($\lambda_{+}^0, \lambda_{-}^0$, in S·cm² mol⁻¹),^a and Association Constants (K_A , in L mol⁻¹) of CuSO₄ in Water/DMF Mixtures at 20 °C

% DMF	Λ_0	λ_{+}^0	λ_{-}^0	K_A
0	249.0	92.9	156.1	169
10	185.1	64.8	120.3	197
20	111.6	32.7	78.9	230
30	80.2	22.9	57.3	311
40	67.4	18.9	48.5	558
50 ^b	46.5	13.0	33.5	1074

^a Calculated as: $\lambda_{\pm}^0 = \Lambda_0 \cdot t_{\pm}^0$. ^b For 50% w/w DMF, the t_{\pm} values were assumed to be equal to those for 40% w/w, see Table 1.

0.403 (25 °C) as determined by Fritz and Fuget³⁹ by the moving boundary method are in reasonable agreement with our experimental value of 0.373 (20 °C);⁴⁰ for a compilation of the various literature values of CuSO₄ solutions in pure water, see Supporting Information.

The limiting molar conductivities (Λ_0 's) and the thermodynamic ion-association constants (K_A 's) for the equilibrium $\text{Cu}^{2+} + \text{SO}_4^{2-} \rightleftharpoons \text{CuSO}_4$ were evaluated according to Pethybridge and Taba⁴¹ using the method of successive approximations (Table 1). With respect to the equilibrium constant K_A , it is important to note that its value is determined from measurements of macroscopic quantities such as conductivity of the solution. At a molecular level, changes of the apparent K_A cannot distinguish between ion recombination (i.e., $\text{Cu}^{2+} + \text{SO}_4^{2-} \rightarrow \text{CuSO}_4$) or the formation of polynuclear clusters (e.g., $2\text{Cu}^{2+} + \text{SO}_4^{2-} \rightarrow [\text{Cu}_2\text{SO}_4]^{2+}$).⁴² In this context, it is mentioned that the commonly used activity coefficients may allow a perfect description of the condensed-phase behavior but do not represent any intrinsic molecular properties.

The nonzero value of K_A in pure water suggests a significant amount of association of CuSO₄ even in dilute aqueous solutions (Figure 2).⁴³ The association constants increase with the gradual increase of the DMF content, which may be regarded as an indication that the short range interactions become stronger, thereby supporting ion association. The increase of the association constants follows the decrease of the dielectric constant of the solvent media from $\epsilon = 79.9$ (25 °C) for pure water to $\epsilon = 36.7$ (25 °C) in pure DMF; note, however, that dielectric constant and ion association do not strictly correlate with each other.¹

One of the reasons affecting the progressive decrease of Λ_0 as the DMF content increases is the rising viscosity of the solvent which imposes mechanical restrictions to the movement of the ions. The viscosity of the mixed solvent changes from 1.002 mPa s in pure water to 2.827 mPa s in 50 w/w % DMF.²⁷ Further, the increasing size of the solvation sheath of the Cu(II) ions upon coordination of DMF lowers their mobility and consequently causes an alleviation in Λ_0 . In comparison, the differential solvation of the sulfate anion is much less pronounced, which can be attributed to the fact that SO_4^{2-} is most likely only solvated by hydrogen bonds with water in these water-rich solvent mixtures,^{44–46} whereas the aprotic DMF solvent cannot efficiently assist anion solvation.⁴⁷ Another factor which contributes to the decrease of Λ_0 is the amplification of ion association and, consequently, the conversion of the conductive “free” ions (carriers of the electric charge) to nonconductive neutral ion pairs.⁴⁸ As noted above, formation of polynuclear clusters would have the same effect on the macroscopically measured quantity. Complementary information about the nature of the aggregates being present in solution therefore is thus desirable for achieving a deeper understanding of ion solvation at a molecular level.

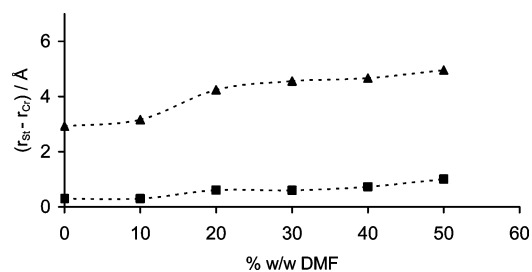


Figure 3. Differences between the Stokes radius and the crystallographic radius ($r_{st} - r_{cr}$) for Cu^{2+} (\blacktriangle) and SO_4^{2-} (\blacksquare) as a function of DMF content in water/DMF mixtures at 20 °C.

The conductivity data (Table 1) can further be used for the calculation of the Stokes' ionic radii (r_{st}) for Cu^{2+} and SO_4^{2-} ions, which represent the radii of the spheres which are hydrodynamically equivalent to the solvated ions.⁴⁹ The differences between Stokes' ionic radii and crystallographic radii, $r_{cr}(\text{Cu}^{2+}) = 0.73 \text{ \AA}$ and $r_{cr}(\text{SO}_4^{2-}) = 1.49 \text{ \AA}$,⁵⁰ are shown in Figure 3.

The Stokes' radius of the Cu^{2+} dication always exceeds the crystallographic radius, and the difference tends to increase with the content of DMF, whereas the trend for SO_4^{2-} is marginal. These results indicate strong solvation of the Cu^{2+} dication by DMF, whereas the differential solvation of the SO_4^{2-} dianion is negligible. It is important to point out that the absence of a notable effect for SO_4^{2-} does not at all imply that the dianion is only weakly solvated (see above); in fact, without solvation, the bare sulfate dianion is not stable and undergoes spontaneous electron detachment.⁵¹ The results confirm the above conclusion that the DMF molecules progressively replace water in the first solvation sheath of Cu^{2+} leading to the increase of the size of the solvation sphere and thus to the decrease of the mobility of the Cu^{2+} ion.

Electrospray Ionization Mass Spectra. Investigations of aqueous copper(II) sulfate using ESI-MS have already been reported by Stone and Vukomanovic,⁵² who observed the formation of dications of the general type $[\text{Cu}(\text{H}_2\text{O})_n]^{2+}$ (with $n = 4-14$) along with $[\text{Cu}(\text{OH})(\text{H}_2\text{O})_m]^+$ monocations which can be described as the products of a formal rebound of hydroxide ions with $[\text{Cu}(\text{H}_2\text{O})_n]^{2+}$. Our experiments fully reproduce these patterns and qualitatively also agree with the predictions for aqueous Cu(II) solutions.⁴³ In pure water, the amount of polynuclear clusters is very low for the dilute CuSO₄ solutions investigated here, whereas increased formation of such species is observed in the presence of DMF. Specifically, the solvated cations formed upon ESI of CuSO₄ dissolved in water/DMF mixtures with 10–50% w/w DMF, respectively, are of the same type in all cases: the dications $[\text{Cu}(\text{DMF})_n]^{2+}$ ($n = 3-6$), $[\text{Cu}_2(\text{DMF})_n\text{SO}_4]^{2+}$, and $[\text{Cu}_3(\text{DMF})_n(\text{SO}_4)_2]^{2+}$ (both $n = 2-7$), the monocations $[\text{Cu}(\text{OH})(\text{DMF})_n]^+$ and $[\text{Cu}(\text{DMF})_n(\text{HSO}_4)]^+$ (both $n = 1-3$), as well as $[\text{Cu}(\text{DMF})_n]^+$ (with $n = 1, 2$), of which the latter are due to a reduction from Cu(II) to Cu(I) upon harsher ionization conditions.^{28,53} In addition to the copper-containing ions, the ESI spectra show intense signals due to protonated DMF clusters of the type $(\text{DMF})_n\text{H}^+$ ($n = 1-3$). The absence of signals corresponding to complexes which mostly contain water, even in a mixture with only 10% w/w DMF, demonstrates that gaseous copper(II) ions have a high preference for coordination with DMF compared to water (see below).⁵⁴ However, at 10% w/w DMF additional weak signals of complexes which contain both DMF and water are observed, such as $[\text{Cu}(\text{DMF})_5(\text{H}_2\text{O})]^{2+}$ and $[\text{Cu}(\text{DMF})_4(\text{H}_2\text{O})_2]^{2+}$, which disappear when the content of DMF increases. This implies that DMF progressively replaces the water molecules in the solvation

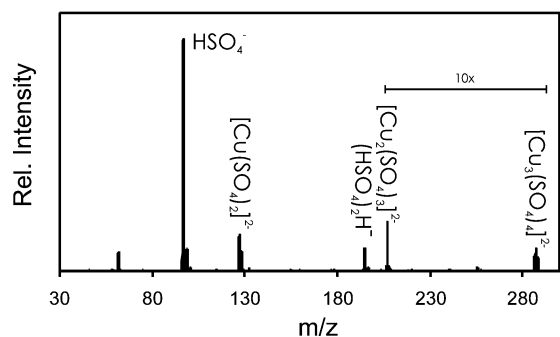


Figure 4. ESI spectrum of an aqueous CuSO_4 solution with 10% w/w DMF in the negative-ion mode at $U_c = 20$ V.

sheath of Cu^{2+} , as concluded from the condensed-phase results (Figures 1 and 3).

The pattern of the Cu(II) complexes formed upon ESI is sensitive to the cone voltage (U_c) which is the difference in potential between the capillary exit and the skimmer in the source region.^{28–32,54} At low voltages ($U_c = 0–10$ V), ionization is gentle, and therefore, multiply ligated ions (as well as multiply charged species)⁵⁵ prevail, whereas at high voltages ($U_c \geq 20$ V) the observed ions result from the collisional fragmentation of the larger complexes. At about $U_c = 30$ V, electron transfer from the DMF to Cu(II) takes place yielding solvated Cu(I) which finally dissociates to give bare Cu(I) at $U_c > 50$ V. Failure to observe peaks corresponding to the smallest dications $[\text{Cu}(\text{DMF})_2]^{2+}$ and $[\text{Cu}(\text{DMF})]^{2+}$ in the ESI mass spectra is not too surprising.⁵⁶ Probably, these ions are completely destroyed via charge separation in the cone region. However, a distinct signal corresponding to $[\text{Cu}(\text{DMF})_2]^{2+}$ is observed upon CID of the larger dication $[\text{Cu}(\text{DMF})_3]^{2+}$ (see below).

Whereas solvation of the SO_4^{2-} dianion by water is well documented in the literature,^{44–46} the ESI spectra of the $\text{CuSO}_4/\text{water}/\text{DMF}$ solutions in the negative ion mode do not reveal any SO_4^{2-} species solvated by DMF molecules. This observation agrees well with the conclusions derived from consideration of the Stokes ionic radii (see above). Further, the observation of the dianions $[\text{Cu}_n(\text{SO}_4)_{n+1}]^{2-}$ ($n = 1–3$) in 10% and 50% w/w DMF directly demonstrates the formation of polynuclear cluster ions. Hence, the mass spectrometric data agree well with the above conclusion that ion association is significant in solutions containing larger percentages of DMF, and the ESI spectra provide direct evidence for the formation of ion pairs both in the positive and the negative ionization mode. As an example, the ESI spectrum of CuSO_4 in 10% w/w DMF in the negative ion mode at $U_c = 20$ V is given in Figure 4, which shows a considerable amount of polynuclear copper ions formed via association.

In addition, the fragmentations of the solvated Cu^{2+} dications formed upon ESI have been investigated by means of collision-induced dissociation (CID) using xenon as a collision gas. The CID spectra of the mass-selected dications $[\text{Cu}(\text{DMF})_n]^{2+}$ ($n = 4–6$) show eliminations of neutral ligands, according to reaction 1, until the formation of the dication $[\text{Cu}(\text{DMF})_3]^{2+}$.



For the complexes with $n = 5$ and 6, the loss of one and two DMF ligands already occurs at a collision energy of $E_{\text{CM}} \approx 0$ eV, confirming that the bond energies of the fifth and sixth DMF ligands are of the magnitude of thermal energy.^{36,57} Similar phenomena have been observed for DMF-solvated Ni(II) dications,²⁹ but they are more pronounced in this case because

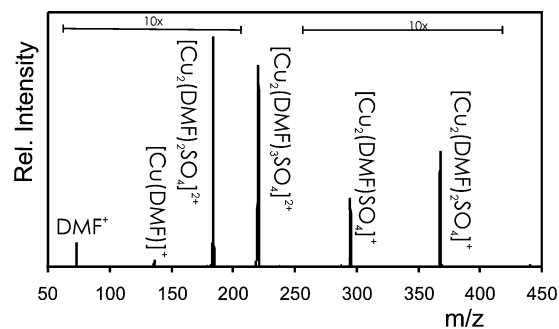
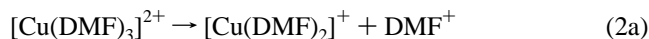
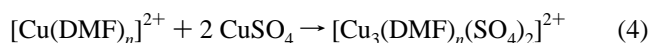


Figure 5. CID spectrum of mass-selected $[\text{Cu}_2(\text{DMF})_3\text{SO}_4]^{2+}$ at a collision energy of 4.6 eV.

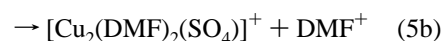
the fifth and sixth DMF are further away from the metal atom and hence more weakly bound than the other four DMF ligands due to the Jahn–Teller effect operative in Cu^{2+} ($4s^03d^9$).⁵⁸ With the triligated dication $[\text{Cu}(\text{DMF})_3]^{2+}$, the thermochemical boarder of stability for the multiply charged species in the gas phase is reached⁵⁹ in that the difference between the ionization energies of Cu^+ (20.29 eV) and DMF (9.13 eV) enables electron transfer from the ligand to Cu^{2+} (reaction 2a) to compete with the loss of the neutral ligand (reaction 2b).^{15,60}



The tendency of Cu(II) to form polynuclear clusters via the formal reactions 3 and 4 is revealed by the observation of the dications $[\text{Cu}_2(\text{DMF})_n(\text{SO}_4)]^{2+}$ and $[\text{Cu}_3(\text{DMF})_n(\text{SO}_4)_2]^{2+}$ (both $n = 2–7$). The abundances of the polynuclear complexes rise as the concentrations of either CuSO_4 or DMF increase, which parallels the above suggested amplification of ion association in DMF-rich solvent mixtures and also demonstrates that the ESI data for gaseous ions show a direct correlation with the composition of the liquid phase.



The formation of the polynuclear dications follows the same pattern as the formation of the polynuclear dianions $[\text{Cu}_n(\text{SO}_4)_{n+1}]^{2-}$ reported above with the difference that the charged cluster cations retain solvent molecules in this case. Upon CID of the mass-selected complexes $[\text{Cu}_2(\text{DMF})_n(\text{SO}_4)]^{2+}$ ($n = 3–7$), elimination of DMF is observed as the only important dissociation process. However, at the stage of $n = 3$, competition between the elimination of neutral DMF (reaction 5a) and electron transfer from DMF to Cu(II) (reaction 5b) to yield $[\text{Cu}(\text{II})\text{Cu}(\text{I})(\text{DMF})_2(\text{SO}_4)]^+$ is observed.



The CID spectrum of the mass-selected dication $[\text{Cu}_2(\text{DMF})_3(\text{SO}_4)]^{2+}$ ($m/z = 220.5$) is shown in Figure 5 as an example. Interestingly, cluster degradation to the mononuclear species $[\text{Cu}(\text{DMF})]^+$ can hardly compete with loss of (neutral or ionized) DMF, pointing to the stability of the binuclear copper sulfate clusters. Qualitatively similar results are obtained upon CID of the trinuclear clusters $[\text{Cu}_3(\text{DMF})_n(\text{SO}_4)_2]^{2+}$ ($n = 2–5$, not shown).

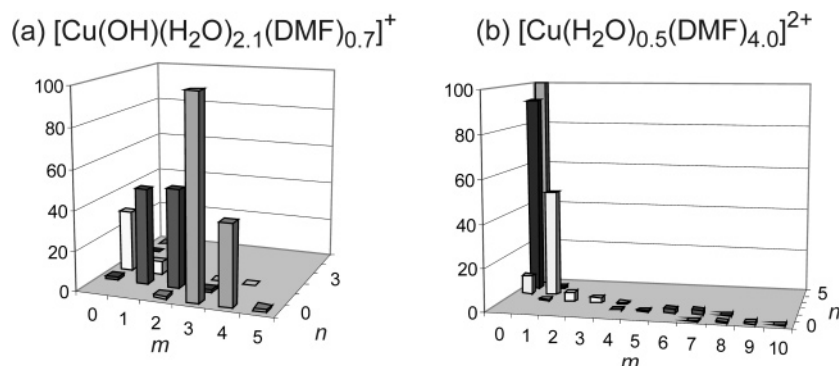
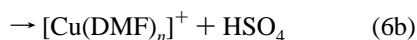
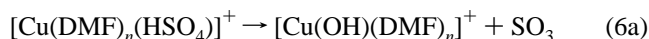
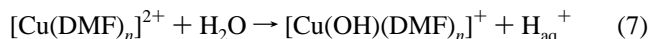


Figure 6. Relative intensity patterns of the mixed water/DMF complexes for (a) the monocations $[\text{Cu}(\text{OH})(\text{H}_2\text{O})_m(\text{DMF})_n]^+$ and (b) the dications $[\text{Cu}(\text{H}_2\text{O})_m(\text{DMF})_n]^{2+}$ upon ESI of an aqueous solution of copper(II) sulfate with a substoichiometric amount of DMF at soft ionization conditions. The average ion compositions are given on top of the diagrams. Both histograms are normalized to the most intense complex of both series set to 100; under the ionization conditions chosen, the ratio of the most intense signals $[\text{Cu}(\text{OH})(\text{H}_2\text{O})_3]^+$ and $[\text{Cu}(\text{DMF})_3]^{2+}$ is ca. 1:2.

Upon CID of the monocations $[\text{Cu}(\text{DMF})_n(\text{HSO}_4)]^+$ ($n = 1-3$), the elimination of neutral DMF is the main dissociation process. At large collision energies, also elimination of SO_3 (reaction 6a) to afford $[\text{Cu}(\text{OH})(\text{DMF})_n]^+$ ($n = 1, 2$) as well as homolysis of the $\text{Cu}-\text{SO}_4\text{H}$ bond (reaction 6b) to yield the reduced complexes $[\text{Cu}(\text{DMF})_n]^+$ ($n = 1, 2$) are observed.



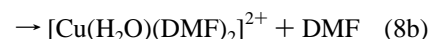
The major source of the $[\text{Cu}(\text{OH})(\text{DMF})_n]^+$ monocations ($n = 1-3$) observed in the ESI mass spectra is, however, solvolysis of Cu^{2+} dications in the protic solvent (reaction 7), as already described for Cu(II) dissolved in pure water.⁵²



Finally, the ESI mass spectra of an aqueous millimolar solution of copper(II) sulfate with a substoichiometric amount of DMF (molar ratio $\text{CuSO}_4:\text{DMF}$ 5:1) were recorded in order to investigate the preference for DMF binding. In addition to the DMF-containing ions described above, DMF-free mono- and dications, such as $[\text{Cu}(\text{OH})(\text{H}_2\text{O})_m]^+$ and $[\text{Cu}(\text{H}_2\text{O})_m]^{2+}$, were observed as already found by Stone and Vukomanovic.⁵² Of interest are the relative intensities of the mixed ions, containing both water and DMF ligands, for both the mono- and dicationic species, i.e., $[\text{Cu}(\text{OH})(\text{H}_2\text{O})_m(\text{DMF})_n]^+$ and $[\text{Cu}(\text{H}_2\text{O})_m(\text{DMF})_n]^{2+}$, respectively.

From the intensity histograms of the mixed water/DMF complexes (Figure 6), obtained under identical, soft ionization conditions, several conclusions can be drawn. (i) The average coordination number decreases with increasing DMF incorporation, e.g., the pure DMF clusters $[\text{Cu}(\text{DMF})_n]^{2+}$ are most intense for $n = 4$ and 5, whereas the pure water clusters $[\text{Cu}(\text{H}_2\text{O})_m]^{2+}$ have values of $m = 7-10$. In other words, at similar ionization conditions for ion formation, one DMF ligand can replace several water molecules, which is consistent with the better donor properties of DMF compared to H_2O . (ii) The average coordination number is larger for the dicationic species than for the monocations, as expected from the larger charge density to be compensated by solvation. (iii) The copper dication bears a much larger tendency for binding with DMF than the monocationic species, as revealed by the larger values of n for the solvated dications in Figure 6b in comparison to Figure 6a. Although the shape of the histograms very much depends on the concentration of DMF as well as variations of the ionization conditions, the two latter aspects can be analyzed in a semi-

quantitative manner by consideration of the averaged composition of the ions as derived from the histograms obtained under identical conditions, i.e., $[\text{Cu}(\text{OH})(\text{H}_2\text{O})_{2.1}(\text{DMF})_{0.7}]^+$ for the monocations and $[\text{Cu}(\text{H}_2\text{O})_{0.5}(\text{DMF})_{4.0}]^{2+}$ for the dications. As expected from earlier work,^{15,61} the average coordination number of copper is significantly lower for the monocations (3.8)⁶² than for the dicationic species (4.5). Furthermore, the preference for dication coordination with DMF amounts to ca. $(4.0/0.5)/(0.7/2.1) = 24$ in comparison to the monocation. With additional consideration of the ca. 2×10^{-4} molar concentration of DMF in the dilute solution used in this particular experiment and the stoichiometry of the dicationic complexes observed, DMF binding to Cu(II) is about 7 orders of magnitude favored compared to that of water. In order to further back up this conclusion, the mixed complex $[\text{Cu}(\text{H}_2\text{O})(\text{DMF})_3]^{2+}$ was mass-selected and subjected to CID. The almost exclusive fragmentation pathway of this dication corresponds to the loss of neutral water (reaction 8a), and only at elevated collision energies can loss of neutral DMF compete to some extent (ratio between reactions 8a and 8b about 50 : 1 at a collision energy of 3 eV).



A similar analysis of the ion abundances of the dicationic dicopper clusters $[\text{Cu}_2(\text{H}_2\text{O})_m(\text{DMF})_n(\text{SO}_4)]^{2+}$ observed upon ESI of aqueous copper(II) sulfate with a substoichiometric amount of DMF under soft ionization conditions shows that more than 90% of the clusters contain at least one DMF molecule, with the clusters $[\text{Cu}_2(\text{H}_2\text{O})_3(\text{DMF})(\text{SO}_4)]^{2+}$, $[\text{Cu}_2(\text{H}_2\text{O})_2(\text{DMF})_2(\text{SO}_4)]^{2+}$, $[\text{Cu}_2(\text{H}_2\text{O})(\text{DMF})_3(\text{SO}_4)]^{2+}$, and $[\text{Cu}_2(\text{DMF})_4(\text{SO}_4)]^{2+}$ as the most abundant species under these conditions. Further, the abundances of the clusters notably increase upon addition of DMF. For example, dinuclear and larger clusters are almost absent upon ESI of a millimolar CuSO_4 solution in pure water (less than 0.1% of the total ion current), whereas the fraction of cluster ions increases to about 2% if 1 equiv of DMF is added. Both findings lend further support to the above conclusion that DMF essentially supports clustering of copper to dinuclear species which is best explained by the sulfate counterion as well as DMF acting as bridging ligands in the dinuclear clusters.⁶³ Only recently, tetramethylethylenediamine (TMEDA) was found to exert a similar effect in that it specifically supports the formation of anion-bridged, binuclear copper(II) clusters.⁶⁴ For more detailed quantitative studies of this phenomenon, the system $\text{CuSO}_4/\text{DMF}/\text{H}_2\text{O}$ is not ideal, however, due to the rather large difference in binding constants

(see above) such that the range of concentrations in which notable changes occur in the ESI mass spectra is very narrow. Presently, we are searching for more suitable systems for the quantification of this effect.⁶⁵

In return to the outset, let us finally attempt to phenomenologically extrapolate the results obtained in the gas-phase study to the situation existing in the bulk. Gradual addition of DMF to a solution of CuSO₄ in water first leads to the formation of [Cu(H₂O)_m(DMF)_n]²⁺ species ($m > n$). Increasing the amount of DMF results in a replacement of all water ligands in the coordination sphere of copper and thus the formation of larger [Cu(DMF)_n]²⁺ complexes with a more effectively shielded charge. In contrast, the sulfate counterions rest in an aqueous environment and become increasingly destabilized as the DMF content rises further. To some extent, the system can escape from this unfavorable situation by the formation of anion-bridged metal clusters at larger DMF fractions in the solvent mixture, until solid CuSO₄ begins to precipitate from the water/DMF mixture.⁶⁶ Precipitation is hence proposed to essentially occur as an anion-triggered process because SO₄²⁻ appears to be most destabilized with increasing DMF content. In this context, we note that for CuSO₄ dissolved in pure water dielectric spectroscopy could provide no evidence for the formation of metal clusters,⁷ which is consistent with the low amount of clusters found in the ESI spectra of CuSO₄ solutions in pure water.⁶⁷ In contrast, the ESI mass spectra reveal that addition of DMF promotes the clustering of CuSO₄ already at stoichiometric concentrations, such that the clustering is, in part, an effect occurring at a molecular level, rather than being associated with changes of the bulk properties of the solvent. With respect to the ESI measurements, it is to be recognized, however, that the transfer of ions from solution into the gas phase is associated with considerable changes of conditions, concentrations in particular, and the ESI mass spectra may thus not directly reflect the situation in the bulk.^{16,68} Specifically, in the course of the droplet formation in the ESI process, the vast majority of the solvent evaporates prior to the release of ions into the gas phase, such that the actual concentrations differ between the bulk solution which is admitted to the source and the droplets which evaporate the ions. Moreover, ESI can be associated with significant discrimination effects in the charging process, and ionization efficiencies can thus be different for different samples. However, according to the arguments outlined in the review by Di Marco and Bombi,¹⁶ in the above analysis of the series of singly and doubly charged copper complexes with either water or DMF as ligands, being sprayed from a solvent primarily consisting of water under identical conditions, these effects are assumed to be of minor importance.⁵⁴ The experimental observation that the patterns of the solvated copper clusters do not change upon tenfold dilution of the sample solutions with pure water (except decrease of clustering), and the outlined parallels between the ESI spectra and the condensed-phase measurements lend further support to this assumption.

Conclusions

The solvation of CuSO₄ in binary water/DMF mixtures has been investigated in a combined approach based on electrochemical measurements of bulk solutions on the one hand and mass spectrometric studies employing electrospray ionization (ESI) on the other. Both the solution studies and the gas-phase experiments clearly demonstrate that, as expected, DMF molecules progressively replace water molecules bound to copper. This leads to a larger size of the Cu²⁺ solvation sheath and, consequently, a lowered mobility of the cations in solution. The

sulfate counterions are hardly affected by the change of solvent composition which is attributed to their preferential coordination to water via hydrogen bonds. With increasing DMF content, ion association becomes more important and leads to the formation of polynuclear copper clusters, such as [Cu_n(SO₄)_{n+1}]²⁻ and [Cu₂(DMF)_mSO₄]²⁺, respectively, which are directly detected in the ESI mass spectra. Further, the ESI experiments reveal that the affinity of Cu(II) for ligation of DMF in comparison to water is notably larger for the dicationic clusters compared to the monocations. Despite many open questions about the correlations between the condensed phase studies and the gas-phase experiments, e.g., the increase of concentration in the evaporating droplets formed in ESI, several linkages between these two regimes observed in this work appear promising and will be pursued in future studies on ion solvation in systems less sensitive than CuSO₄/DMF/H₂O.

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Supporting Information Available: Compilation of literature data for aqueous CuSO₄ solutions, tables of the experimental measured transference numbers, some thermochemical properties of water/DMF mixtures, and the measured conductivities of the CuSO₄ solutions. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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