

Ionic Association in CuSO_4 Aqueous Solutions up to 473 K.

Lucila Méndez De Leo,^{1,2} Hugo Bianchi^{1,2} and Roberto Fernández-Prini^{1,3*}

¹Unidad Act. Química, Comisión Nacional Energía Atómica, Buenos Aires, Argentina. *E-mail: rfprini@cnea.gov.ar

²Escuela de Ciencia y Tecnología, UNSAM, Argentina

³INQUIMAE Facultad Cs. Exactas y Naturales (UBA) Buenos Aires, Argentina

The formation of ion pairs is a well-known consequence of the strong electrostatic interactions between oppositely charged ions. In aqueous solutions bivalent sulfates form ion pairs that can be easily detected at room temperature, the extent of ion pair association is well described by the Bjerrum primitive model for ionic association. We have studied $\text{CuSO}_4(\text{aq})$ solutions between room temperature and 473 K using a spectrophotometric technique. The presence of ion pairs was observed to increase with temperature as expected. Also a change in the type of ion pairs was inferred from the temperature dependence of the values of the distance of closest approach of free ions. The Bjerrum primitive model can be used to represent ionic association in aqueous solutions at high temperature having liquid-like densities if a temperature dependent distance between cation and anion is accepted.

1. Introduction

Ionic association occurs in the majority of electrolyte solutions, a notable exception being aqueous solutions of electrolytes with ions of low charge at ambient conditions. Hence it is important to have information about the dependence of ion-pair formation in aqueous solutions as the temperature increases and, if possible, how the temperature dependence of ionic association can be described satisfactorily. We have studied $\text{CuSO}_4(\text{aq})$ solutions, an electrolyte which is well known [1,2] to be moderately associated at ambient temperature. In this case, as for other aqueous bivalent sulfates, ion pairs formation is due to the strong electrostatic interactions between oppositely charged ions. This study was made employing a spectrophotometric technique since the spectrum of aqueous $\text{Cu}(\text{II})$ is sensitive to ionic association; measurements were made up to 473 K.

2. Experimental Methods

The spectrophotometric technique adopted in this study required the design and construction of a high temperature-high pressure optical cell and the ancillary equipment necessary to prepare the solutions in the high p, T optical cell. Figure 1 is a sketch of the high p, T spectrophotometric cell employed in this work.

2.1. Experimental Apparatus

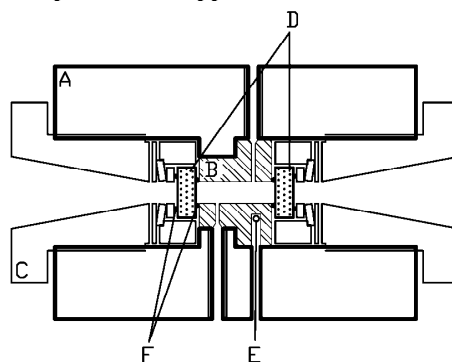


Fig. 1. Sketch of the high-temperature-pressure cell

The central part (B) is the actual optical cell, it was kept in place by a stainless steel container (A and C), the windows (D) were of sapphire. The cell material for this experiment was of titanium and the high pressure seals were made of gold (F). During the experiments the temperature, measured with a Pt resistance thermometer (E), was constant within ± 0.03 K. The optical path length of the cell was 2.120 ± 0.006 cm. Using optical fibres and a modular spectrophotometer the experimental setup depicted in Fig. 2 was employed.

2.2. Experimental Conditions

There were some important limitations in the range of concentrations that we could explore with our experimental procedure, as well as in the temperature range that could be covered in our

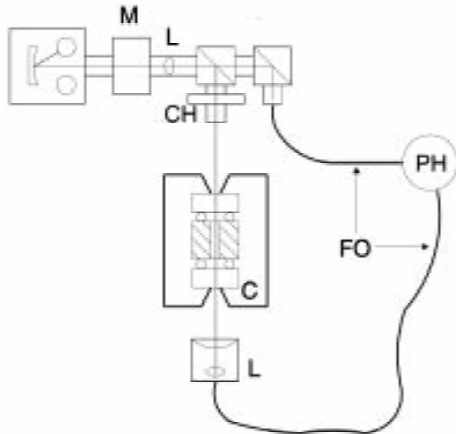
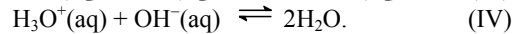
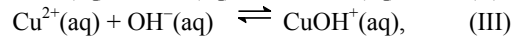
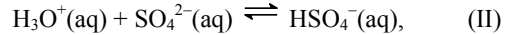
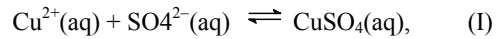


Fig. 2. Spectrophotometric setup. CH: Chopper, M: monochromator, L: Lenses, FO: Fiber optics, PH: Photomultiplier, C: optical cell.

study. Since $\text{Cu}^{2+}(\text{aq})$ can hydrolyze to some extent it was necessary to use slightly acid solutions adding either HClO_4 or trifluorosulfonic acid (triflic acid). On the other hand an excessive amount of HSO_4^- had to be avoided in order to maintain a reasonable concentration of sulfate ions in the solutions to enable the formation of sufficient the ion pairs to allow detection. These facts conditioned the *window* of accessible experimental conditions (concentrations and temperature); it was necessary that the ion pairing process was the dominant one in the solutions. Above 473 K these conditions could not be met, so that was the upper limit of our experiments.

The UV absorption band of Cu(II) is affected by the formation of the ion pair, this process produces an important increase of the molar absorptivity of the solutions [1]. The spectra were recorded in the range from 250 to 350 nm, at 300 nm and 473 K the molar absorptivity changed from less than 0.02 to $4.80 \text{ m}^2 \cdot \text{mol}^{-1}$ when the ratio of sulfate to Cu(II) increased from zero to unity. The following four equilibria took place in the solutions:



The hydrolysis of $\text{Cu}^{2+}(\text{aq})$ is the only of the four equilibria that introduces a new species,

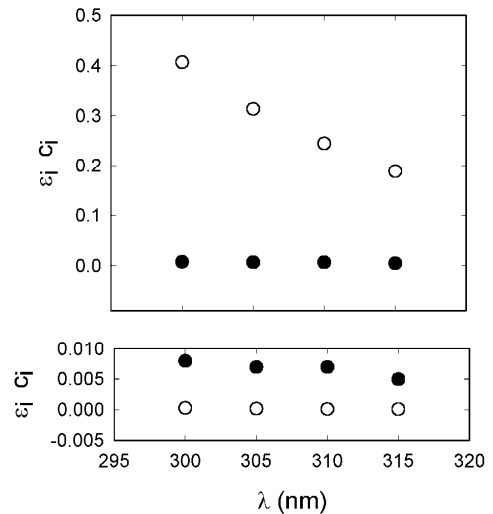


Fig. 3. A typical experiment at 423 K showing the contribution to optical absorption of different copper species. Solid circles correspond to $\text{Cu}^{2+}(\text{aq})$ ions, open circles in upper panel: CuSO_4 ion pair, lower panel: CuOH^+ . Note the different scale of the ordinates in the two graphs.

$\text{CuOH}^+(\text{aq})$, that contributes to the UV absorption of the solutions in the studied wavelength range. The equilibrium constant of process (III) has been determined as function of temperature by Ziemniak, *et al.* [3], we employed those results to evaluate the degree of hydrolysis of Cu(II) in our solutions. Figure 3 shows that in a typical experiment the contribution of the hydroxocopper ion to the absorption spectra was indeed negligible. Processing data like those illustrated in figure 3 we found that the molar absorptivity of CuOH^+ was 15 times smaller than that of the CuSO_4 ion pair, this fact plus the low concentration of CuOH^+ available meant that the contribution of the monohydroxocopper species to the spectra was never greater than 0.2 %.

3. Results and Discussion

3.1. Calculation of the Equilibrium Constants for Ion Pair Formation

The spectra of the solutions were used to obtain the equilibrium constant for ion pair formation K . Figure 4 shows the dependence of $\ln K$ with temperature. As expected ionic association increases significantly with temperature due to the appreciable concomitant decrease of the dielectric constant of water.

3.2. Model for Ionic Association.

In order to elucidate the nature of the ion pairing process at higher temperatures we have used the simple Bjerrum model [4] for ionic association. This is a primitive model that does not consider explicitly the molecular nature of the solvent. In spite of this limitation it has proved very successful to describe the behaviour of bivalent sulfate aqueous solutions under ambient conditions.

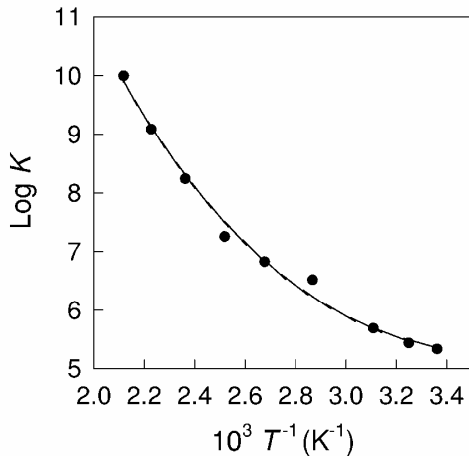


Fig. 4. Plot of $\text{Log } K$ vs $1/T$

Bjerrum's equation gives for K the following expression:

$$K = 4\pi\rho_1 N_A q^3 Q(b) \quad (1)$$

where ρ_1 is the solvent density, N_A Avogadro's number and $q = |z_+z_-|e^2/(4\pi\epsilon_0\epsilon kT)$ is twice the Bjerrum's length, ϵ_0 is the permittivity of vacuum,

ϵ the solvent's dielectric constant and $b = q/a$ where a is the distance of closest approach of cation and anion. Defining $x = q/r$ for oppositely charged ions separated by a distance r we have,

$$Q(b) = \int_2^b x^{-4} \exp x dx \quad (2)$$

Using these two equations to fit the experimental K values we calculated the value of a at each temperature. Table 1 reports the values of $\ln K$ and of the distances of closest approach at each temperature.

The results reported in table 1 indicate that the distance of closest approach of cation and anion, a , decreases strongly around 310 K. This is an important indication that two types of ion pairs exist in $\text{CuSO}_4(\text{aq})$ solutions, a phenomenon already postulated by Eigen [2] in his pioneering studies of ion pairing in bivalent sulfate aqueous solutions employing the ultrasonic absorption technique. He proposed that equilibrium (I) really is a two-step equilibrium that may be represented by the following chemical processes, where $\text{Cu}[\text{H}_2\text{O}]\text{SO}_4(\text{aq})$ denotes an ion pair separated by solvent molecules (SSIP) and $\text{CuSO}_4(\text{aq})$ denotes a contact ion pair (CIP), i.e.,

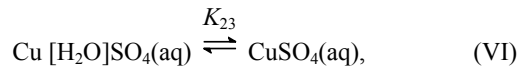
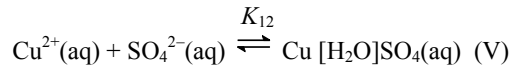


Table 1. Association constants and distance of closest approach of the ion pairs at different temperatures.

T/K	$10^{-2} \cdot K$	a/nm	K_{12}	K_{23}
297.51	20.8	0.45	205	---
307.82	23.0	0.44	218	---
321.75	29.7	0.41	239	(0.24)
348.83	62.5	0.35	290	1.2
373.51	92.6	0.34	367	1.5
397.03	142	0.34	460	2.1
423.37	380	0.31	625	5.1
449.05	885	0.30	879	9.1
472.18	2200	0.30	1262	16.5

The equilibrium constants of the two steps are related to the overall ion association constant by the relation: $K = K_{12}(1 + K_{23})$. We have assumed that the temperature dependence of K_{12} is adequately represented by Bjerrum's theory taking $a = 0.45$ nm, the distance of closest approach of SSIP at room temperature. The results obtained indicate that the relative population of contact ion pairs is dominant at higher temperatures. It should be noted that the value of the distance of closest approach appears to reach a value around 0.3 nm which is very close to that between Cu(II) and sulfate in solid CuSO_4 .

There is evidence that the SSIP and CIP exist in electrolyte solutions and their relative populations are determined by the reduced temperature T_{red} of the solutions, a quantity related to the interionic interactions in the solution. In aqueous solutions the CIP population increases when ions increase their charges and/or when the temperature increases, which implies a decrease in the reduced temperature that for electrolyte solutions (primitive model) is given by,

$$T_{red} = \frac{4\pi\epsilon_0\epsilon kTa}{z_+ |z_-| e^2} \quad (3)$$

Simulation studies have shown that SSIP and CIP exist in multiply charged electrolyte solutions [5] and that even for (1:1) salts dissolved in water both types of ion pairs are present when the temperature is sufficiently high [6]. The latter study also showed that the Bjerrum's model is unsatisfactory when the density of supercritical water is gas-like. This is not unexpected since the primitive model is bound to misrepresent that type of systems. However the possibility of employing a Bjerrum's model with a temperature dependent distance of closest approach $a(T)$ is an interesting practical alternative to account for the change of ionic association in aqueous solutions at high temperature at liquid like densities. This approach could be completed if a relation were found between the temperature dependence of a and the short range interaction of oppositely charged ions that is able to represent the repulsive effect for the approach of cation and anion due to solvent attached to the ions [7].

4. Conclusions.

Ionic association increases with temperature but its nature appears to remain essentially electrostatic. However the primitive Bjerrum model requires a temperature dependent distance of closest approach of oppositely charged ions to be able to describe the results. In this way the increasing population of CIP compared with SSIP may be accommodated.

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