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Chemical speciation in concentrated aqueous solutions of CuCl_2 using thin-film UV–visible spectroscopy combined with DFT calculations

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ABSTRACT

In this work, a thin-film UV–visible spectroscopic technique has been developed and combined with time-dependent density functional theory (TD-DFT) calculations for the study of the chemical speciation in concentrated aqueous solutions of $\text{Cu(II)} + \text{Cl}^-$. When the CuCl_2 concentration changed from $0.05 \text{ mol} \cdot \text{kg}^{-1}$ to $5 \text{ mol} \cdot \text{kg}^{-1}$, the UV peak shifted from $\sim 250 \text{ nm}$ to $\sim 262 \text{ nm}$. Similar shifts were recorded for CuCl_2 solutions containing up to $5 \text{ mol} \cdot \text{kg}^{-1}$ NaCl. Combination of the spectral data with our previous TD-DFT calculations provided a consistent model of the chemical speciation in the Cu(II)/Cl^- system up to high concentrations of both components. The results obtained indicate that many of the previous conclusions regarding these solutions, drawn from a variety of techniques are unreliable. Under the present conditions, the only species detected were inner-sphere complexes with one or two Cl^- ions bound to the aquated Cu(II) ion. For all the solutions, no remarkable peaks at $\sim 280 \text{ nm}$ or 380 nm , indicative of CuCl_3^- (aq) and CuCl_4^{2-} (aq) respectively, were observed.

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1. Introduction

The chemical speciation of copper(II) in chloride solutions continues to attract attention because of its relevance to various geochemical [1,2] and environmental [3] situations, and to the hydrometallurgical extraction of nickel and cobalt, where removal of copper impurities by resin adsorption from chloride-type electrolytes is known to be easier than from sulphate-types [4]. Realistic modelling of the behaviour of the Cu(II)/Cl system requires detailed knowledge of the number and nature of the species formed, particularly in concentrated solutions, which are of greatest practical interest. However, despite intensive investigation over many decades, employing a panoply of techniques such as X-ray diffraction (XRD) [5–7], X-ray absorption spectroscopy (XAS) [8], extended X-ray absorption fine structure spectroscopy (EXAFS) [9], Monte Carlo calculations [10–13], neutron diffraction [14,15] and ultraviolet–visible (UV–vis) spectroscopy [1,16–20], a consistent picture of the chemical speciation of the Cu(II)/Cl^- system has yet to emerge, especially at high concentrations.

Consider, for example, the various studies on the structure of aqueous solutions of CuCl_2 using X-ray techniques. Based on their XRD study, Bell et al. [5] reported that in $(3.18 \text{ and } 4.35) \text{ mol} \cdot \text{kg}^{-1}$ CuCl_2 (aq) solution, presumably at room temperature (RT), the Cu(II) ion has direct contact with an average of four Cl^- ions in equatorial and axial

positions. In contrast, Magini [7] found using XRD, again presumably at RT, only 1.2 Cl^- ions occupying equatorial positions in 2.952 mol/L (M) CuCl_2 . Employing XAS, D'Angelo et al. [8] claimed to detect axial Cu–Cl interactions in 0.1 M CuCl_2 (aq) at RT but an EXAFS study by Collings et al. [9] found no Cu–Cl complexation either in 0.1 M CuCl_2 or in 0.1 M $\text{CuCl}_2 + 2.0 \text{ M NaCl}$ solutions up to 75°C .

Other techniques show similar variations. Thus, Rode et al. [11,12] using Monte Carlo simulations found no direct Cu–Cl bonding in $1 \text{ mol} \cdot \text{kg}^{-1}$ CuCl_2 (aq), although they later reported [13] that in $0.5 \text{ mol} \cdot \text{kg}^{-1}$ $\text{CuCl}_2 + 5 \text{ mol} \cdot \text{kg}^{-1}$ NaCl, the 1:1 inner-sphere complex (contact ion pair) $[\text{CuCl}(\text{H}_2\text{O})_5]^+$ was the major species. Neutron diffraction experiments [14,15] also detected direct Cu–Cl contact in $4 \text{ mol} \cdot \text{kg}^{-1}$ CuCl_2 (aq) but with an average coordination number of $2.0 \pm 0.5 \text{ Cl}^-$ ions per Cu^{2+} .

Such discrepancies also occur in the thermodynamic data. For example, a recent comprehensive and critical review for IUPAC of stability constant data for the Cu(II)/Cl^- system [3] concluded that while CuCl^+ (aq) and, to a lesser extent, CuCl_2^0 (aq) were reasonably well characterised, the numerous independent reports of higher complexes at high Cl^- concentrations were in such poor agreement that no values were listed for them.

One of the difficulties in reconciling such contradictory findings is the great difference in the operational concentrations of the techniques employed. As is apparent from the above discussion, the major structural methods and most computer simulations are carried out at vastly higher (chromophore) concentrations than is customary for UV–visible spectroscopic studies (with chromophore concentrations typically $\leq 0.01 \text{ M}$). Such large differences inevitably create doubts about the

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interpretation of any observed discrepancies. It would therefore be very useful to develop a methodology that can deal with this difference.

To better understand the competition between Cl^- ions and solvent (H_2O) molecules for the coordination sites around Cu^{2+} in aqueous chloride solutions, a series of quantum mechanical calculations were carried out using time-dependent density functional theory (TD-DFT) in our previous papers [21–23]. Five main conclusions have been drawn from these studies.

- 1) The UV–visible (electronic) spectra of a hydrated Cu^{2+} ion (denoted as $[\text{Cu}(\text{H}_2\text{O})_n]^{2+}$ ($n \geq 4$)) with no Cl^- ion occupying any site in its first or second coordination sphere, and species with one or two Cl^- atoms present in the second coordination sphere of the hydrated Cu^{2+} ion (denoted here as $[\text{Cu}(\text{H}_2\text{O})_n\text{Cl}]^+$ ($n \geq 5$) and $[\text{Cu}(\text{H}_2\text{O})_n\text{Cl}_2]^0$ ($n \geq 6$) respectively), are degenerate and occur at about 150–180 nm [21,22].
- 2) The electronic spectra for a hydrated Cu^{2+} ion with only one Cl^- ion in its first coordination sphere ($[\text{CuCl}(\text{H}_2\text{O})_n]^+$ ($n \geq 4$)) and the species $[\text{CuCl}(\text{H}_2\text{O})_n\text{Cl}]^0$ ($n \geq 4$), with one Cl^- ion in the first coordination sphere and another in the second coordination sphere, are degenerate with $\lambda_{\text{max}} \approx 250$ nm [21,22].
- 3) The electronic spectra of a hydrated Cu^{2+} ion with two Cl^- ions in its first coordination sphere ($[\text{CuCl}_2(\text{H}_2\text{O})_n]^0$ ($n \geq 3$)) are also degenerate, with $\lambda_{\text{max}} \approx 275$ nm [21].
- 4) The electronic spectra of a hydrated Cu^{2+} ion with three Cl^- ions in its first coordination sphere ($[\text{CuCl}_3(\text{H}_2\text{O})_n]^-$ ($n = 3$ or 4)) are degenerate with λ_{max} at ~ 290 and ~ 380 nm [23].
- 5) The electronic spectrum for the species $[\text{CuCl}_4]^{2-}(\text{aq})$ with four Cl^- ions in the first coordination sphere of the Cu(II) has λ_{max} at ~ 280 and ~ 380 nm [23].

In short, the observed UV spectra in Cu(II)/ Cl^- solutions depend mainly on the number of Cl^- ion in the first coordination sphere of the Cu(II). Thus species with identical stoichiometries that differ only with respect to the location of their Cl^- ions in the first or second coordination shell, for instance $[\text{Cu}(\text{H}_2\text{O})_n\text{Cl}]^+$ and $[\text{CuCl}(\text{H}_2\text{O})_n]^+$, will have differing electronic spectra.

These TD-DFT calculations have been shown to account for the details of the UV–vis spectra reported by Brugger et al. [1] for aqueous solutions of $\sim 5 \times 10^{-4}$ mol·kg $^{-1}$ CuCl_2 + (0 to 18) mol·kg $^{-1}$ LiCl. Conversely, for present purposes, it is noted that if the UV–vis spectrum of a given $\text{CuCl}_2(\text{aq})$ solution can be accurately recorded, it can be used to deduce the local structure around the Cu(II), particularly with respect to the number of bound Cl^- ions and their location in the inner or outer sphere of the hydrated Cu(II) ion.

Many UV–vis measurements have been reported for $\text{CuCl}_2(\text{aq})$ solutions [1,3,17–20], using conventional cuvettes with optical pathlengths typically of 1 to 10 mm. Because of the rather high absorbances of the solutions, such measurements were usually limited to total Cu(II) concentrations $\lesssim 10^{-3}$ mol·kg $^{-1}$. To investigate the behaviour of more concentrated $\text{CuCl}_2(\text{aq})$ solutions, such as those of hydrometallurgical interest, and those commonly employed with techniques such as EXAFS and X-ray and neutron diffraction, an alternative approach has been developed.

An effective way to reduce solution absorbance at high concentrations is to drastically shorten the optical pathlength. This can be achieved by constructing a so-called “thin-film” (TF) cell. This approach has been widely adopted for qualitative and semi-quantitative measurements with UV [24,25] and fluorescence [26] spectroscopy, calorimetry [27], spectro-electrochemistry [28], and chromatography [29].

2. Experimental

2.1. Chemicals and solutions

Samples of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}(\text{s})$ and $\text{NaCl}(\text{s})$ (Sinopharm Chemical Reagent Co. Ltd, Shanghai, China) were prepared by twice re-crystallizing

their respective analytical reagents. Stock solutions of CuCl_2 were prepared by weight and the chloride content was determined gravimetrically by precipitation as $\text{AgCl}(\text{s})$. Less concentrated solutions were prepared by gravimetric dilution. A certain amount of $\text{NaCl}(\text{s})$ was added to the target CuCl_2 solutions and mixed well. Triple-distilled water was used for preparation of all solutions.

2.2. Thin-film UV–visible spectroscopy

For the present study, thin-film cells that could be fitted to a commercial UV–vis spectrometer (UV-2550, Shimadzu, Japan) were prepared as shown in Fig. 1. First, two quartz plates of suitable optical purity, thickness and size ($45 \times 13 \times 1.3$) mm were selected. A small drop of sample solution (~ 3 μL) was pipetted onto one of the plates and a second plate pressed against it and held in place with clamps at the two ends. This assemblage was then placed in the spectrometer and spectra were recorded in the usual manner. Of course, this approach does not permit background subtraction (which is normally unimportant at high chromophore concentrations) and, because of the uncertainty of the optical pathlength, provides only semi-quantitative information in its present state of development. Nevertheless, with the assignments provided by the TD-DFT calculations, the spectral information obtained is sufficient to identify the major species present.

3. Results and discussion

3.1. Speciation in aqueous solutions of CuCl_2

For comparison purposes, UV–vis spectra for a series of $\text{CuCl}_2(\text{aq})$ solutions were recorded at 298 K using both a conventional 1 mm cuvette and the TF cell. The results (Figs. 2 and 3) show that with the cuvette, satisfactory spectra (i.e., with, say, absorbances, $A \leq 4$) could only be obtained at CuCl_2 concentrations $\lesssim 0.1$ mol·kg $^{-1}$. In contrast, the TF technique could be used up to ~ 5 mol·kg $^{-1}$ $\text{CuCl}_2(\text{aq})$.

According to our previous TD-DFT calculations [21–23] the absorbance at < 225 nm (Figs. 2 and 3) will be mostly due to the aquated cation, $[\text{Cu}(\text{H}_2\text{O})_n]^{2+}$ ($n \geq 4$), and to the species $[\text{Cu}(\text{H}_2\text{O})_n\text{Cl}]^+$ ($n \geq 5$) and $[\text{Cu}(\text{H}_2\text{O})_n\text{Cl}_2]^0$ ($n \geq 6$). The band centred at ~ 250 nm can be attributed to two species: $[\text{CuCl}(\text{H}_2\text{O})_n]^+$ ($n \geq 4$) and $[\text{CuCl}(\text{H}_2\text{O})_n\text{Cl}]^0$ ($n \geq 4$). Note that in the latter, one Cl^- is bound directly to Cu^{2+} while the other is bound to a coordinated H_2O molecule, i.e., it forms an outer-sphere complex. These findings are consistent with UV–vis spectra in the literature [1] and are also qualitatively consistent with the diffraction data [8,14]. On the other hand they contradict the findings of the earlier simulations of Rode et al. [11,12] and the EXAFS results of Collings et al. [9], neither of whom detected any Cu–Cl complexation under similar conditions. Clearly, the combination of TF-UV–vis measurements with TD-DFT calculations is much more sensitive for detecting small concentrations of solution species in $\text{CuCl}_2(\text{aq})$ than EXAFS, diffraction techniques, and (at least some) computer simulations.

As seen in Fig. 3, the band centred at ~ 250 nm shifts to 261 nm when the CuCl_2 concentration increases from 0.5 to 5.0 mol·kg $^{-1}$. This can be attributed to overlap of the band at 250 nm, due to $[\text{CuCl}(\text{H}_2\text{O})_n]^+$ ($n \geq 4$) and $[\text{CuCl}(\text{H}_2\text{O})_n\text{Cl}]^0$ ($n \geq 4$), with that of $[\text{CuCl}_2(\text{H}_2\text{O})_n]^0$ 191

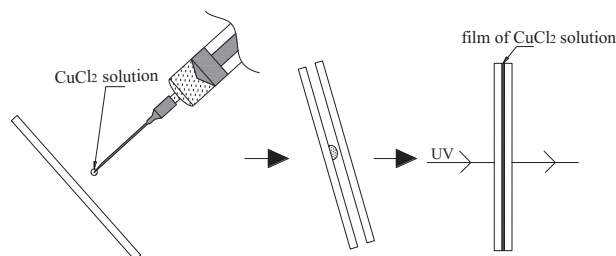


Fig. 1. Preparation of thin-film solutions for UV measurements.

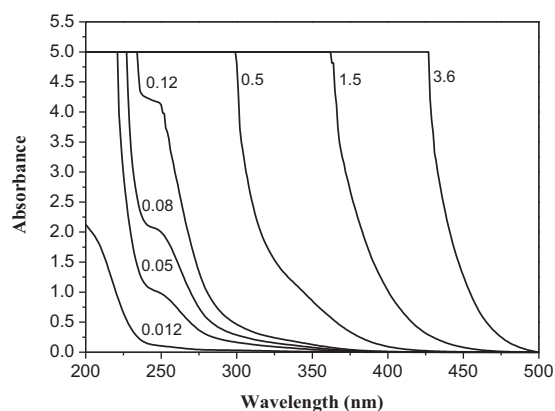


Fig. 2. UV-vis measurements on $\text{CuCl}_2(\text{aq})$ using a conventional cuvette with a 1 mm optical path length at 298 K. Numbers indicate concentrations in $\text{mol}\cdot\text{kg}^{-1}$.

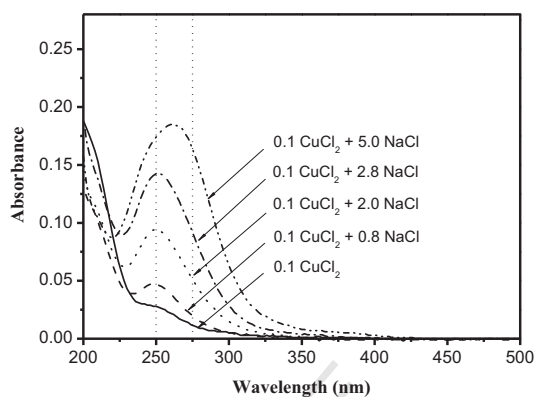


Fig. 4. UV measurements using the thin-film technique on $0.1 \text{ mol}\cdot\text{kg}^{-1} \text{CuCl}_2 + (0 \text{ to } 5) \text{ mol}\cdot\text{kg}^{-1} \text{NaCl}$ at 298 K. Numbers indicate concentrations in $\text{mol}\cdot\text{kg}^{-1}$.

($n \geq 3$) at 275 nm. With an increase of CuCl_2 concentration and a decrease of n (due to the lower water activity), the second Cl^- ion will enter the first coordination sphere of the $\text{Cu}(\text{II})$, forming $[\text{CuCl}_2(\text{H}_2\text{O})_n]^0$ ($n \geq 3$). No bands were observed at $\sim 380 \text{ nm}$, which are indicative [23] of the presence of $[\text{CuCl}_3(\text{H}_2\text{O})_n]^-$ and/or $[\text{CuCl}_4]^{2-}$, up to the solubility limit. In one of our previous papers on the properties of $\text{CuCl}_2(\text{aq})$ [30], we established a reaction model to qualitatively describe the properties of CuCl_2 -containing aqueous solutions, especially the abundance of various Cu-containing species. The model parameters were determined by the water activities of the $\text{CuCl}_2(\text{aq})$. That model predicted that the dominant species in (1 to 5) $\text{mol}\cdot\text{kg}^{-1} \text{CuCl}_2(\text{aq})$ should be $[\text{CuCl}(\text{H}_2\text{O})_n]^+$ and $[\text{CuCl}_2(\text{H}_2\text{O})_n]^0$, which is in good agreement with the present experimental work.

Based on this analysis, the main species existing in (0.5 to 5) $\text{mol}\cdot\text{kg}^{-1} \text{CuCl}_2(\text{aq})$ were found to be: $[\text{Cu}(\text{H}_2\text{O})_n]^{2+}$, $[\text{CuCl}(\text{H}_2\text{O})_n]^+$, $[\text{CuCl}_2(\text{H}_2\text{O})_n]^0$, and $[\text{CuCl}_3(\text{H}_2\text{O})_n]^-$, with an average of less than two Cl^- ions in the first coordination shell of Cu^{2+} . These results agree broadly with those of D'Angelo et al. [8] (see below) but contradict some previous investigations [5,11,12].

3.2. Speciation of aqueous solutions of $\text{CuCl}_2 + \text{NaCl}$

D'Angelo et al. [8] investigated the structure of solutions containing $0.1 \text{ mol}\cdot\text{kg}^{-1} \text{CuCl}_2 + (0.8 \text{ or } 2.8) \text{ mol}\cdot\text{kg}^{-1} \text{NaCl}$ by XAS at room temperature and reported, respectively, an average of 0.8 or 1.0 Cl^- ions bound to Cu^{2+} in both equatorial and axial positions, corresponding to a total average of 1.6 or 2.0 Cl^- ions directly coordinated to each Cu^{2+} ion. In order to provide a direct comparison with the results of D'Angelo et al., TF-UV-vis spectra were measured under identical

conditions. The results show (Fig. 4) that for the less concentrated 219 solution there is one band with $\lambda_{\text{max}} = 250 \text{ nm}$ and (unresolved) 220 bands centred below 225 nm. The former indicates the presence 221 of $[\text{CuCl}(\text{H}_2\text{O})_n]^+$ (with Cl^- in the first coordination sphere) and 222 $[\text{CuCl}(\text{H}_2\text{O})_n\text{Cl}]^+$ (with one Cl^- in the first coordination sphere and 223 another in the second sphere). The latter is attributable mostly to 224 $[\text{Cu}(\text{H}_2\text{O})_n]^{2+}$, $[\text{Cu}(\text{H}_2\text{O})_n\text{Cl}]^+$ and $[\text{Cu}(\text{H}_2\text{O})_n\text{Cl}_2]^0$, with no Cl^- in 225 the first coordination sphere. Furthermore, there is no evidence for 226 significant formation of $[\text{CuCl}_2(\text{H}_2\text{O})_n]^0$ (with two Cl^- in the first 227 coordination sphere), which has $\lambda_{\text{max}} = 275 \text{ nm}$. For the solution 228 containing $0.1 \text{ mol}\cdot\text{kg}^{-1} \text{CuCl}_2 + 2.8 \text{ mol}\cdot\text{kg}^{-1} \text{NaCl}$, the UV band 229 maximum shifts slightly (from $\lambda_{\text{max}} = 250 \text{ nm}$ to 252 nm) and the 230 absorbance below 225 nm, mostly due to $[\text{Cu}(\text{H}_2\text{O})_n]^{2+}$, $[\text{Cu}(\text{H}_2\text{O})_n\text{Cl}]^+$ 231 and $[\text{Cu}(\text{H}_2\text{O})_n\text{Cl}_2]^0$, decreases relative to the less-concentrated solu- 232 tion. This is consistent with a slight increase in the extent of Cu-Cl 233 association. 234

Collings et al. [9] measured solutions of $0.1 \text{ mol}\cdot\text{kg}^{-1} \text{CuCl}_2 + (0, 2 235 \text{ and } 5) \text{ mol}\cdot\text{kg}^{-1} \text{NaCl}$, by in situ EXAFS. They found no Cu-Cl 236 complexes at 0 and $2 \text{ mol}\cdot\text{kg}^{-1} \text{NaCl}$ but reported $[\text{CuCl}]^+$ to be the 237 dominant species at $5 \text{ mol}\cdot\text{kg}^{-1} \text{NaCl}$. The present TF-UV-vis spectra 238 (Fig. 4) detect, via the band at 250 nm , Cu-Cl association both at 239 (0 and $2) \text{ mol}\cdot\text{kg}^{-1} \text{NaCl}$. At $5 \text{ mol}\cdot\text{kg}^{-1} \text{NaCl}$, the band shifts from 240 250 nm to 260 nm indicating, as would be expected (Fig. 3), significant 241 formation of $[\text{CuCl}_2(\text{H}_2\text{O})_n]^0$ in addition to the 1:1 inner sphere species. 242

Rode's Monte Carlo simulation [10] of $0.5 \text{ mol}\cdot\text{kg}^{-1} \text{CuCl}_2 + 243 5 \text{ mol}\cdot\text{kg}^{-1} \text{NaCl}$ indicated that the only significant Cu(II) species 244 present was $[\text{CuCl}(\text{H}_2\text{O})_n]^+$. However, the TF-UV-vis spectrum for 245 this solution (Fig. 5) clearly shows a band at $\sim 264 \text{ nm}$ consistent 246 with the presence of both $[\text{CuCl}(\text{H}_2\text{O})_n]^+$ (and/or $[\text{CuCl}(\text{H}_2\text{O})_n\text{Cl}]^0$) 247 and $[\text{CuCl}_2(\text{H}_2\text{O})_n]^0$, in approximately equal amounts. Such direct 248

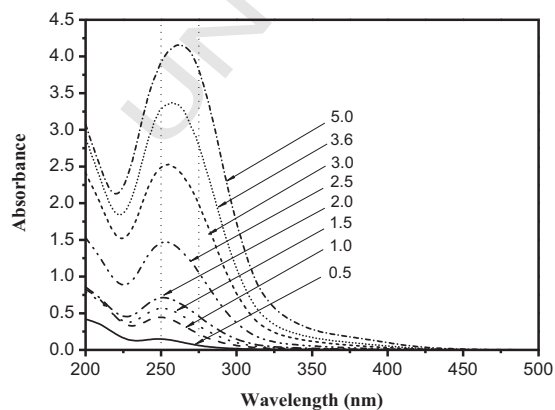


Fig. 3. UV-vis measurements on $\text{CuCl}_2(\text{aq})$ using the thin film technique at 298 K. Numbers indicate concentrations in $\text{mol}\cdot\text{kg}^{-1}$.

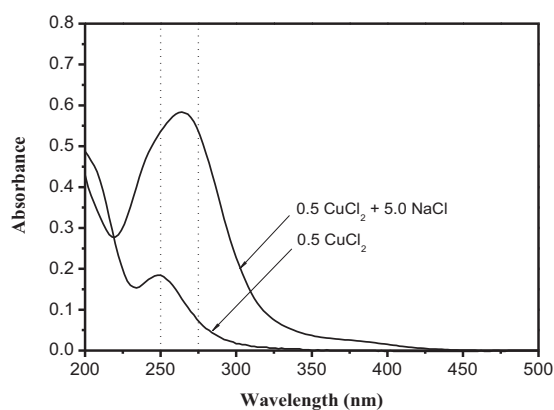


Fig. 5. UV measurements using the thin-film technique on $0.5 \text{ mol}\cdot\text{kg}^{-1} \text{CuCl}_2 + (0 \text{ and } 5) \text{ mol}\cdot\text{kg}^{-1} \text{NaCl}$ at 298 K. Numbers indicate concentrations in $\text{mol}\cdot\text{kg}^{-1}$.

249 comparisons would be impossible without the use of the present thin-
250 film UV–vis technique.

251 4. Conclusion

252 The present TF–UV–vis technique makes possible the recording of
253 electronic spectra for highly absorbing (highly concentrated) solutions.
254 The combination of such spectra with TD–DFT calculations [21–23] en-
255 ables realistic assignments of the spectral features to specific species
256 (or, sometimes, of groups of species).

257 This approach has shown unequivocally that in $\text{CuCl}_2(\text{aq})$ solutions
258 up to high concentrations, both without and with the addition of
259 NaCl, the only Cu(II)-containing species present were: $[\text{Cu}(\text{H}_2\text{O})_n]^{2+}$,
260 $[\text{Cu}(\text{H}_2\text{O})_n\text{Cl}]^+$, $[\text{Cu}(\text{H}_2\text{O})_n\text{Cl}_2]^0$, $[\text{CuCl}(\text{H}_2\text{O})_n]^+$, $[\text{CuCl}(\text{H}_2\text{O})_n\text{Cl}]^0$, and
261 $[\text{CuCl}_2(\text{H}_2\text{O})_n]^0$. No evidence was found under the present conditions
262 for the formation of $[\text{CuCl}_3(\text{H}_2\text{O})_n]^-$ or $[\text{CuCl}_4]^{2-}$, which have very dis-
263 tinctive electronic spectra [1,23], even though such species undoubtedly
264 form in solutions containing extremely high concentrations of Cl^- [1,3].

265 The present combination of TL–UV–vis with TD–DFT calculations
266 provides a powerful new tool for investigating chemical speciation of
267 highly concentrated (strongly absorbing) solutions. This allows for the
268 first time *direct* comparison of UV–vis data with structural techniques
269 such as XRD, XAS and EXAFS, and with computer simulations, all
270 of which generally need to employ concentrations well beyond that
271 usual in electronic spectroscopy. It should be noted that the present
272 TL–UV–vis + TD–DFT approach is readily applicable to many other
273 strongly absorbing solutions of both practical and theoretical interests,
274 including other transition-metal chloride systems.

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