

Interactions of copper (II) chloride with sucrose, glucose, and fructose in aqueous solutions

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Abstract

The interaction between copper (II) chloride and the carbohydrates sucrose, glucose, and fructose has been studied in aqueous solutions at 298.15 and 310.15 K, using measurements of diffusion coefficients and electrical conductivity. Significant effects on the electrical conductivity were observed in the presence of these carbohydrates, suggesting interactions between them and copper chloride. Support for this came from diffusion coefficient measurements. These studies have been complemented by molecular mechanics calculations.

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1. Introduction

The characterization of the diffusion and conductance in electrolyte solutions is important for fundamental reasons, helping us to understand the nature of the structure of aqueous electrolytes, and for practical application in fields such as corrosion [1–6]. We have been particularly interested in data on these properties for chemical systems occurring in the oral cavity, to understand and resolve corrosion problems related to dental restorations in systems where such data are not currently available. Bearing in mind the fact that oral restorations involve various dental metallic alloys, we have been studying interactions with various metal ions, and turn our attention now to systems involving copper. The properties and behaviour of such chemical systems in the oral cavity are poorly known, even though this is a prerequisite to obtain adequate understanding and resolve these wear and corrosion problems. This has provided the impetus for the present study of the diffusion

and conductance of copper (II) chloride, in aqueous solutions in the presence of some carbohydrates. The behaviour of this electrolyte in presence of β -cyclodextrin has been reported [7].

In this paper we present the results of studies of the interaction between copper (II) chloride and the carbohydrates sucrose, glucose, and fructose, using electrical conductivity and measurements of diffusion coefficients by an open-ended conductimetric capillary cell. For a better understanding of the structure of the chemical species formed and the main biochemical mechanisms involved, we have complemented these studies using molecular mechanics calculations.

2. Experimental

2.1. Reagents

The solutes used in this study were copper (II) chloride dihydrate (Riedel-de-Haen, Seelze, Germany, *pro analysi* >99%), sucrose (Sigma, *pro analysi* >99%), D(–)-fructose (Riedel-de-Haën, Chem. pure) and D(+)-glucose (Sigma, >97%). These were used without further purification.

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The solutions for the diffusion measurements were prepared in calibrated volumetric flasks using bi-distilled water. The solutions were freshly prepared and de-aerated for about 30 min before each set of runs.

Solutions used in conductance measurements were prepared with Millipore-Q water $\{\kappa = (0.7\text{--}0.9) \times 10^{-4} \text{ S m}^{-1}\}$. Solutions were freshly prepared just before each experiment.

2.2. Diffusion measurements

The open-ended capillary cell employed, which has previously been used to obtain mutual diffusion coefficients for a wide variety of electrolytes [8,9], has been described in great detail in previous papers [10–15]. Basically, this consists of two vertical capillaries, each closed at one end by a platinum electrode, and positioned one above the other with the open ends separated by a distance of about 14 mm. The upper and lower tubes, initially filled with solutions of concentrations 0.75 and 1.25 c , respectively, are surrounded with a solution of concentration c . This ambient solution is contained in a glass tank (200 × 140 × 60) mm immersed in a thermostat bath at 25 °C. Perspex sheets divide the tank internally and a glass stirrer creates a slow lateral flow of ambient solution across the open ends of the capillaries. Experimental conditions are such that the concentration at each of the open ends is equal to the ambient solution value c , that is, the physical length of the capillary tube coincides with the diffusion path. This means that the required boundary conditions described in the literature [8] to solve Fick's second law of diffusion are applicable. Therefore, the so-called Δl effect [8] is reduced to negligible proportions. In our manually operated apparatus, diffusion is followed by measuring the ratio $w = R_t/R_b$ of resistances R_t and R_b of the upper and lower tubes by an alternating current transformer bridge. In our automatic apparatus, w is measured by a Solartron digital voltmeter (DVM) 7061 with 6 1/2 digits. A power source (Bradley Electronic Model 232) supplies a 30 V sinusoidal signal at 4 kHz (stable to within 0.1 mV) to a potential divider that applies a 250 mV signal to the platinum electrodes in the top and bottom capillaries. By measuring the voltages V' and V'' from top and bottom electrodes to a central electrode at ground potential in a fraction of a second, the DVM calculates w .

In order to measure the differential diffusion coefficient D at a given concentration c , the bulk solution of concentration c is prepared by mixing 1 L of "top" solution with 1 L of "bottom" solution, measured accurately. The glass tank and the two capillaries are filled with c solution, immersed in the thermostat, and allowed to come to thermal equilibrium. The resistance ratio $w = w_\infty$ measured under these conditions (with solutions in both capillaries at concentration c) accurately gives the quantity $\tau_\infty = 10^4/(1 + w_\infty)$.

The capillaries are filled with the "top" and "bottom" solutions, which are then allowed to diffuse into the "bulk"

solution. Resistance ratio readings are taken at various recorded times, beginning 1000 min after the start of the experiment, to determine the quantity $\tau = 10^4/(1 + w)$ as τ approaches τ_∞ . The diffusion coefficient is evaluated using a linear least-squares procedure to fit the data and, finally, an iterative process is applied using 20 terms of the expansion series of Fick's second law for the present boundary conditions. The theory developed for the cell has been described previously [8].

2.3. Conductance measurements

Solution electrical resistances were measured with a Wayne-Kerr model 4265 Automatic LCR meter at 1 kHz. A Shedlovsky-type conductance cell, with a cell constant of around 0.8465 cm^{-1} , was used [12]. Cell constants were determined from measurements with KCl (reagent grade, re-crystallized, and dried) using the procedure and data of Barthel et al. [16]. Measurements were taken at $(25.00 \pm 0.01) \text{ }^\circ\text{C}$ in a Grant thermostat bath. Solutions were always used within 12 h of preparation.

In a typical experiment, a 100 mL of water, or carbohydrate solution, was placed in the conductivity cell; then, aliquots of the copper (II) chloride solution (the solvent used is the same carbohydrate solution placed in the conductivity cell, to maintain a constant carbohydrate concentration throughout the experiment) were added in a stepwise manner using a Metrohm 765 *Dosimate* micropipette. The conductance of the solution was measured after each addition and corresponds to the average of three ionic conductances, obtained using homemade software.

2.4. Molecular mechanics studies (MM2)

Molecular mechanics studies are a valuable tool to interpret atom or ion dynamics of solute/solvent interactions in molecular systems involving hundreds of molecules or ions [17]. The calculations presented in this study were performed using the MM+ molecular mechanics force field, with a Polak-Ribiere algorithm having a convergence limit of 0.05 kcal/A.mol, performed on a 3.2 MHz Pentium 4 workstation with HyperChem v6.

The molecular mechanics studies here presented were based on the evaluation of the individual contributions of the specific carbohydrate, Cu^{2+} and one or two chloride ions in a cage of 2160 water molecules, corresponding to a cube of a side of $4.04 \times 10^{-9} \text{ m}$. The final overall energy of the MM+ minimized set was then compared for the various systems.

3. Results and discussion

3.1. Conductance measurements

Fig. 1 shows the effect of three different sugars (sucrose, glucose, and fructose) on the molar conductivity of aqueous solutions of CuCl_2 at 298.15 K. In the presence of

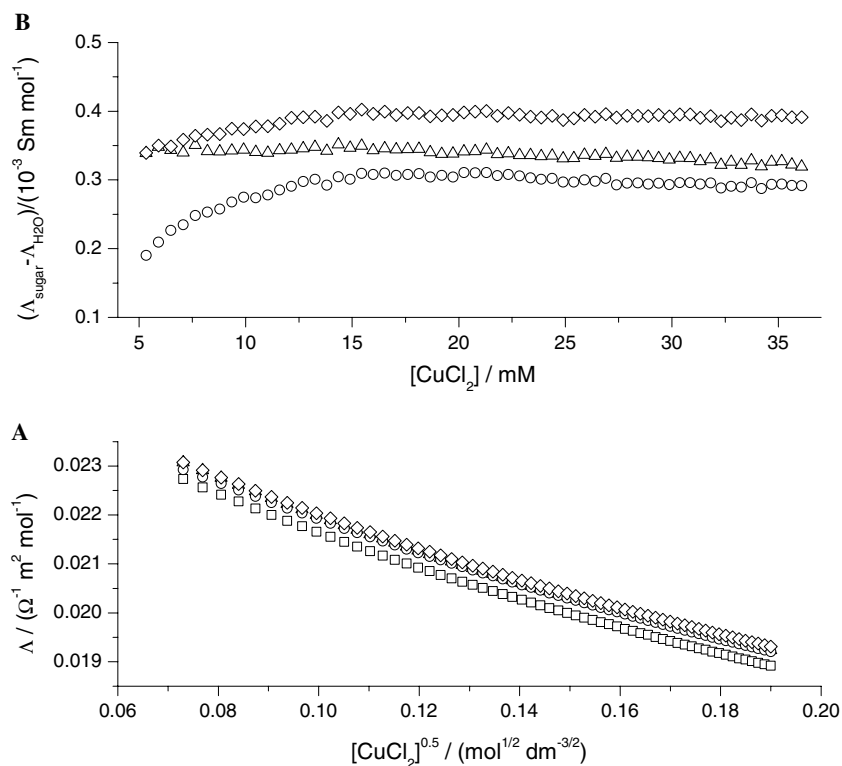


Fig. 1. (A) Effect of sugars, (□) [sugar] = 0, (○) [sucrose] = 1.037 mM, (Δ) [glucose] = 1.104 mM, and (◇) [fructose] = 1.082 mM, on the molar conductivity of CuCl_2 aqueous solutions at 298.15 K; (B) Variation of the molar conductivity of CuCl_2 in the presence (Λ_{sugar}) and absence ($\Lambda_{\text{H}_2\text{O}}$) of sugars as a function of CuCl_2 concentration.

sugars a slight positive deviation of the CuCl_2 molar conductivities is found, with reference to the aqueous CuCl_2 solution. The contribution of sucrose, glucose, and fructose to the increase in the CuCl_2 molar conductivity is almost independent of copper (II) chloride concentration ($5 \text{ mM} < [\text{CuCl}_2] < 35 \text{ mM}$) (Fig. 1B).

The increase of CuCl_2 molar conductivity and, therefore, of the ionic mobility, can be explained by a decrease in the overall hydration of ionic species in the presence of carbohydrates, which may be due to the competition for hydration between carbohydrates and CuCl_2 , by changes in the structure of water, and its effects on diffusion processes. We will also consider the alternative explanation in terms of association of copper (II) ions by the sugars, and show this is less important.

It has been reported that sucrose can stabilise proteins to thermal denaturation without directly binding to them by changing the degree of hydration [18,19]. Support for the importance of such decreases in hydration also comes from calculations of the effect of sucrose on the potential of mean force between sodium and chloride ions in aqueous solutions [20], which show that addition of sucrose decreases the number of water molecules in the first hydration sphere of the ions. However, with sodium, the waters of the first hydration sphere are relatively weakly bound, while there is good evidence from neutron diffraction and other techniques [21], that with copper (II) perchlorate the cation is more tightly bound in its primary hydration

sphere to four water molecules, with two other ones at slightly larger distance, as expected from the presence of Jahn-Teller distortion with this metal ion [22] while with CuCl_2 at relatively high concentration (4.32 M), there is evidence for some inner sphere coordination of Cl^- by Cu^{2+} . It is probable that with copper (II) chloride in the presence of the sugars, various types of interactions occur, depending on the circumstances. Furthermore, we should consider that as a consequence of dehydration, possibly in the second hydration sphere, an appreciable fraction of the transport of CuCl_2 may occur as a result of larger aggregates, since these species may have a higher mobility than the dissociated part of the electrolyte. This phenomenon can be explained if we consider hydration water loss from both copper and chloride ions, which will lead to less resistance to motion through the liquid and, consequently, a larger mobility and hence an increased conductivity. It is also known that fructose has a high affinity for water [23]. These destructuring effects on water are the result of steric constraints imposed by the carbohydrate molecule and of the ability of a carbohydrate to form stable H bonds with water, respectively [24]. From our molar conductivity experimental results we may conclude that the effect of different carbohydrates on the CuCl_2 mobility follows the order sucrose < glucose < fructose, with changes in the CuCl_2 molar conductivity of 0.30%, 0.37%, and 0.40%, respectively, taking water as reference. These results are in close agreement with those found for carbohydrate-NaCl

systems, where it has been shown that the salting constants for NaCl-sucrose, NaCl-glucose, and NaCl-fructose are $0.116 \text{ kg mol}^{-1}$, $0.088 \text{ kg mol}^{-1}$, and $0.005 \text{ kg mol}^{-1}$, respectively [25–27]. Such results clearly support the idea that carbohydrates have a *salting-out* effect.

A further point of interest is the decrease of difference of CuCl_2 molar conductivity with and without carbohydrate as a function of copper (II) chloride concentration when $[\text{CuCl}_2]/[\text{carbohydrate}]$ decreases and approaches 5 (Fig. 1B). This is most marked for the sucrose-containing system. In fact, when $[\text{CuCl}_2]/[\text{carbohydrate}]$ becomes lower, other factors such as steric hindrance to the ion movement, and alteration in the solution viscosity may be important [28]. Evidence for this was reported by Stokes and Stokes [29] in their study of the conductance of KCl in aqueous sucrose solutions; they found that the limiting equivalent conductance of KCl drops by 18.6% (to $121.87 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$) and 37.1% (to $94.26 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$) in 10% and 20% sucrose solutions, respectively. Similar results were found by measuring diffusion coefficients of NaCl and KCl 0.1 mol dm^{-3} in solutions of sucrose (Table 1) showing that in the presence of large concentration of sucrose the competition with hydration water molecules does not play the major role.

It can be noted that the influence of the different carbohydrates on the CuCl_2 molar conductivity is less accentuated when the temperature increases from 298.15 K to 310.15 K (Fig. 2). It is possible to conclude that: (a) the differences between CuCl_2 molar conductivities with and without carbohydrates are only slightly positive, and (b) we cannot imply any selective effect of sucrose, glucose or fructose on the CuCl_2 molar conductivity. These results can be justified by an increase of the mobility of CuCl_2 , which is not accompanied by any increase in the hydrated radii of carbohydrates. This is in agreement with self-diffusion studies carried out with certain carbohydrate solutions, where no significant variations of size and shape of hydrated sugar are observed in the temperature range 20–60 °C [30]. However, an increase of temperature will lead to a decrease in the viscosity of sugar-electrolyte solutions [31] as well as to an increase of diffusion coefficients (see next section). These two opposite effects can contribute to the observed very small effect of sugars on the CuCl_2 mobility.

3.2. Measurements of diffusion coefficients

Tables 2 and 3 show the experimental diffusion coefficients of copper chloride solutions (5×10^{-3} to

Table 1
Diffusion coefficients of NaCl 0.1 mol dm^{-3} , D_{NaCl} , and KCl 0.1 mol dm^{-3} , D_{KCl} in aqueous sucrose solutions, at 298.15 K

[sucrose] / (mol dm^{-3})	D_{NaCl} / ($10^{-9} \text{ m}^2 \text{ s}^{-1}$)	D_{KCl} / ($10^{-9} \text{ m}^2 \text{ s}^{-1}$)
0	1.490	$1.845 (\pm 0.006)^a$
0.1	1.492	1.771^a
0.5	1.075	1.682^a

^a See ref. 28

$5 \times 10^{-2} \text{ mol dm}^{-3}$) at 298.15 K and 310.15 K, alone and in the presence of sucrose, fructose, and glucose. These results are the average of 3 experiments performed on consecutive days. Good reproducibility was observed, as seen by the small standard deviations of the mean, S_{Dav} . Previous papers [10–15] reporting data obtained with our conductivity cell have shown that the error limits of our results should be close to the imprecision, therefore giving an experimental uncertainty 1–3%.

The decrease of the diffusion coefficients, when the concentration increases, may be interpreted on the basis of formation of new species resulting either from association of this salt, as suggested by neutron scattering [19], or hydrolysis. The possible formation of ion pairs, increasing with concentration, may also contribute to the decrease of $D_{(\text{CuCl}_2)}$ with concentration [32].

The diffusion behaviour of copper chloride in aqueous solutions at 298.15 and 310.15 K is unaffected by the presence of these carbohydrate molecules. Under the present experimental conditions, i.e., $[\text{CuCl}_2]/[\text{carbohydrate}]$ ratio values ≥ 5 and dilute solutions, the motion of the solvent and the change of parameters such as viscosity, dielectric constant and degree of hydration with concentration can be neglected. With a concentration gradient in a solution of only CuCl_2 , exactly the same as that in a solution of CuCl_2 but now with identical concentrations of sucrose, glucose, and fructose, we observe that the diffusion coefficient D is the same, in those solutions, though the electrical conductivity is higher in the latter case. Assuming that D [33] is a product of both kinetic (molar mobility coefficient of a diffusing substance, U_m) and thermodynamic factors ($c\partial\mu/\partial c$, where μ represents the chemical potential), we suggest that the thermodynamic factor decreases, and the kinetic factor increases, when we pass from a solution of pure CuCl_2 to a mixed solution having both CuCl_2 and carbohydrates. Thus, two different effects can control the diffusion process: the ionic mobility and the gradient of the chemical potential. These effects compensate each other by contributing in opposite directions to the diffusion coefficients, such that there is no net change in diffusion coefficients. This is confirmed by the results at 298.15 and 310.15 K. Based on these measurements, in conjunction with the conductance measurements, we conclude that, over the concentration range studied (Table 3), the diffusion of CuCl_2 in aqueous solutions at 298.15 K does not appear to be affected by any association or by aggregate formation between Cu(II) and sucrose, fructose, and glucose. Possibly, if such interactions exist within this region, the lack of effect on diffusion arises from two opposing effects: (i) increasing of the mobility of CuCl_2 (see Fig. 2); (ii) decreasing the gradient of the chemical potential with concentration. At 310.15 K, close to physiological temperatures, this association is reduced, leading to a less accentuated increase of the mobility of CuCl_2 (as supported by conductance measurements) and probably to a less accentuated decrease in the gradient of the chemical potential with concentration. These considerations should be taken

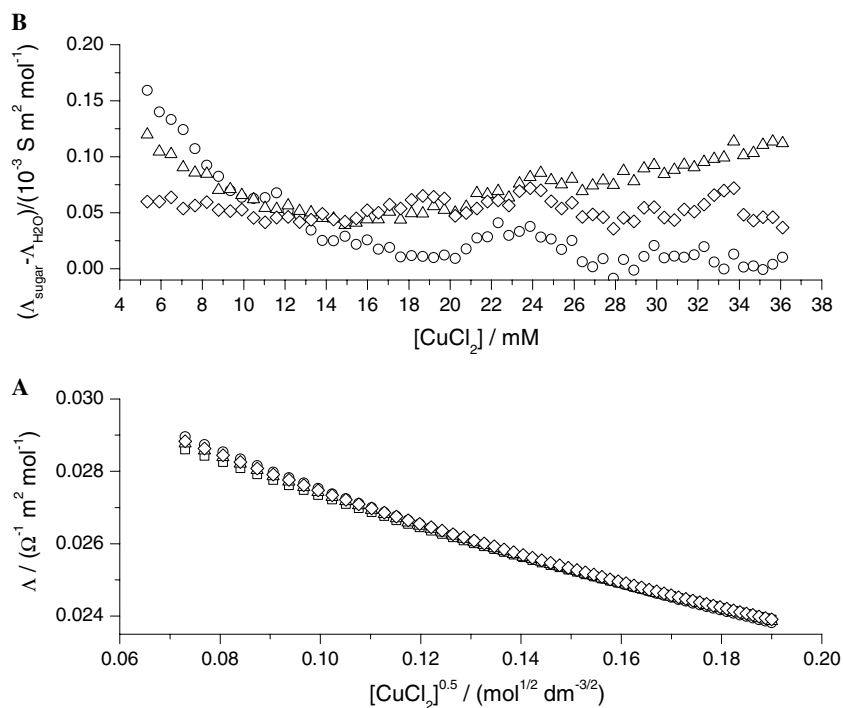


Fig. 2. (A) Effect of sugars, (□) [sugar] = 0, (○) [sucrose] = 1.093 mM, (Δ) [glucose] = 1.004 mM, and (◇) [fructose] = 1.077 mM, on the molar conductivity of CuCl₂ aqueous solutions at 298.15 K; (B) Variation of the molar conductivity of CuCl₂ in the presence (Λ_{sugar}) and absence (Λ_{H₂O}) of sugars as a function of CuCl₂ concentration.

Table 2

Diffusion coefficients, D^a , of CuCl₂ in aqueous solutions at different concentrations, c , and different temperatures, T , and the standard deviations of the means, S_D [32]

$c/\text{mol}\cdot\text{dm}^{-3}$	$T = 298.15 \text{ K}$		$T = 310.15 \text{ K}$	
	$D/10^{-9} \text{ m}^2 \text{ s}^{-1} \text{ }^a$	$S_D/10^{-9} \text{ m}^2 \text{ s}^{-1} \text{ }^b$	$D/10^{-9} \text{ m}^2 \text{ s}^{-1} \text{ }^a$	$S_D/10^{-9} \text{ m}^2 \text{ s}^{-1} \text{ }^b$
0.005	1.235	0.001	1.660	0.010
0.008	1.208	0.001	1.640	0.011
0.01	1.199	0.001	1.630	0.010
0.02	1.128	0.002	1.580	0.010
0.03	1.121	0.001	1.544	0.010
0.05	1.120	0.017	1.500	0.011

^a D is the mean diffusion coefficient for 3 experiments.

^b S_D is the standard deviation of that mean.

Table 3

Diffusion coefficients, D^a , of CuCl₂ in aqueous solutions of sucrose, glucose, and fructose (0.001 M) at different concentrations, c , and different temperatures, T , and the standard deviations of the means, S_D

Carbohydrate	$c/\text{mol}\cdot\text{dm}^{-3}$	$T = 298.15 \text{ K}$			$T = 310.15 \text{ K}$		
		$D/10^{-9} \text{ m}^2 \text{ s}^{-1} \text{ }^a$	$S_D/10^{-9} \text{ m}^2 \text{ s}^{-1} \text{ }^b$	$\Delta D/D/\% \text{ }^c$	$D/10^{-9} \text{ m}^2 \text{ s}^{-1} \text{ }^a$	$S_D/10^{-9} \text{ m}^2 \text{ s}^{-1} \text{ }^b$	$\Delta D/D/\% \text{ }^c$
Sucrose	0.005	1.245	0.002	-0.8	1.679	0.001	+1.1
	0.010	1.216	0.002	+1.4	1.668	0.002	+2.3
Fructose	0.005	1.236	0.001	-1.4	1.669	0.002	+0.5
	0.010	1.218	0.001	+1.6	1.647	0.001	+1.0
Glucose	0.005	1.263	0.001	+2.3	1.672	0.001	+0.7
	0.010	1.203	0.001	+0.3	1.637	0.002	+0.4

^a D is the mean diffusion coefficient for 3 experiments.

^b S_D is the standard deviation of that mean.

^c $\Delta D/D$ represent the relative deviations between the diffusion coefficients of CuCl₂ at the specified concentration in 0.001 M sucrose, fructose, and glucose, respectively, D , and that of the CuCl₂ in water, D (Table 1).

Table 4
Relative carbohydrate evaluation of available hydroxyl groups to hydrogen bond formation with water

Carbohydrate	Fructose	Glucose	Sucrose
Molecular Volume (A ³) (Hyperchem v6.0 after MM+ geometry optimization)	487.25	506.74	880.02
Number of Hydroxyl groups	5	5	8
Ratio: (number of hydroxyl groups/molecular volume)	0.0103	0.0099	0.0091 (8.7% less)

into account when studying the corrosion of dental alloys containing copper.

3.3. Molecular mechanics studies

Molecular mechanics calculations were used to obtain further information on the contribution of the various species to the observed behaviour. The main result is that the overall energetics of these aqueous systems are largely dominated by the water, while the carbohydrate, Cu²⁺, and Cl⁻ ions make a small contribution to the overall energy of the molecular set. Also, this small contribution is almost exclusively due to carbohydrate/water interactions, with the effect of Cu²⁺ and Cl⁻ ions being residual.

Although the sugar/water interactions are weak, the simulations indicate small but significant effect of the structure of the carbohydrate. The fructose and glucose appear to slightly destabilise the structure while sucrose slightly stabilises the structure relative to pure water. It should be noted that difficulties exist due to the limited number of molecules involved in the simulation, problems of standard states and the fact one is looking at small differences in large energy terms, qualitatively the results suggest a destructuring effect of fructose and glucose, in agreement with the molar conductivity measurements, and that this is greater than that of sucrose.

Although more quantitative simulations should include effects on the structure of water aggregates, as shown by Lee et al. [24], such calculations are very time consuming, and not appropriate for the present study. However, qualitative interpretation of the relative effects of fructose, glucose and sucrose comes from study of the number of hydrogen bonds formed between the carbohydrate and water expressed as the ratio of hydroxyl groups to the molar volume (Table 4). A calculation of this ratio shows that sucrose presents the smallest value, which lends support to the explanation of the effect of the three carbohydrate molecules on the conductance behaviour of copper (II) chloride in water.

4. Conclusions

We have measured diffusion coefficients and electrical conductivity for copper (II) chloride with sucrose, glucose and fructose in aqueous solutions and have complemented these studies with molecular mechanics calculations. The

results indicate that the presence of these carbohydrates affects the mobility of the CuCl₂ and its thermodynamic behaviour. This behaviour can be explained by the destructuring effects of fructose, sucrose, and glucose on the water structure.

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