

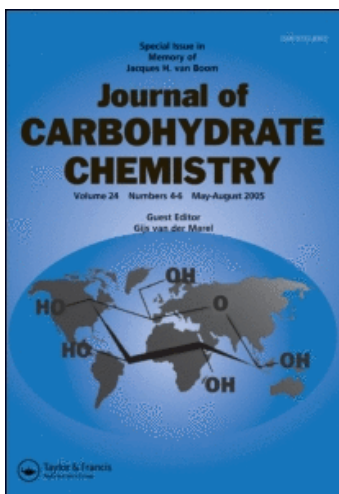
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Interactions of Copper (II) Chloride with -Cyclodextrin in Aqueous Solutions

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Interactions of Copper (II) Chloride with β -Cyclodextrin in Aqueous Solutions

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The interaction between copper (II) chloride and the carbohydrate β -cyclodextrin (β -CD) has been studied in aqueous solutions (298.15 K and 310.15 K) using measurements of

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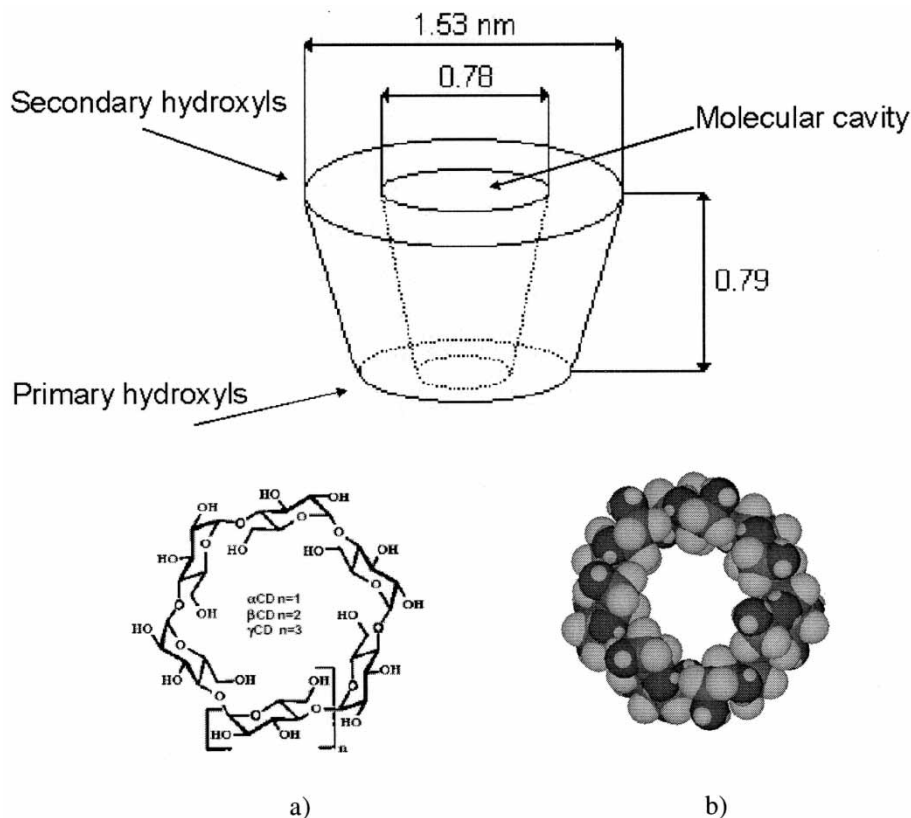
diffusion coefficients and electrical conductivity. Significant effects on the electrical conductivity were observed in the presence of the β -CD, suggesting interactions between this carbohydrate and copper chloride. Support for this came from diffusion coefficient measurements. These studies have been complemented by molecular mechanics calculations.

Keywords Diffusion, Electrolytes, Transport properties, Cyclodextrins, Carbohydrates, Mots Clé, Diffusion, Électrolytes, Propriétés de transport, Cyclodextrins, Hydrates de carbone

INTRODUCTION

The characterization of diffusion and electrical conductivity in electrolyte solutions is important both for fundamental reasons, helping us to understand the nature of the structure of aqueous electrolytes, and for practical application in fields such as corrosion. 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.^[1–6] Bearing in mind the fact that oral restorations involve various dental metallic alloys, we are particularly interested in those involving metal ions such as copper (II). However, the properties and behavior 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 carbohydrates. We are particularly interested in data on the diffusion and conductance of copper (II) chloride with β -cyclodextrin (β -CD) in aqueous solutions at different temperatures. This results from the importance of cyclodextrins in aqueous solutions in applied research due to their wide range of applications (e.g., those related to pharmaceutical chemistry).^[7] The most common pharmaceutical application of cyclodextrins is to enhance the solubility, stability, and bioavailability of drug molecules.

β -Cyclodextrin is a cyclic oligosaccharide comprised of seven glucose units.^[8–10] Each of the chiral glucose units is in the rigid 4C_1 -chair conformation, giving the macrocycle the shape of a truncated cone. The cone is formed by the carbon skeletons of the glucose units and the glycosidic oxygen atoms joining them. The primary hydroxyl groups of the glucose units are located at the narrow rim of the cone and the secondary hydroxyls at the wider rim. A schematic side view is shown in Scheme 1. The primary hydroxyl groups on the narrow side of the cone can rotate to partially block the cavity. In contrast, the secondary hydroxyl groups are attached by relatively rigid chains and as consequence cannot rotate. The primary and secondary hydroxyls on the outside of the



Scheme 1: a) General formula of the cyclodextrin molecules and b) 3D view of β -CD.

cyclodextrins make them water-soluble, while the cavity is nonpolar. Because of the relative nonpolar character of the cavity in comparison to the polar exterior, cyclodextrins can form inclusion complexes with a wide variety of guest molecules, predominantly due to hydrophobic interactions.^[11,12] The possibility of forming hydrophobic interactions represents only one of the requirements of formation of inclusion complexes. Another is that the guest molecule must be able to fit inside the cavity of cyclodextrin.^[13,14] However, it should be emphasized that not only hydrophobic interactions will lead to an association between a guest molecules and CD. Nonpolar solutes such as inorganic nonassociated salts can also be involved in these complexes.^[15–17]

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

RESULTS AND DISCUSSION

Conductance Measurements and Molecular Mechanics Studies (MM2)

Figure 1 shows the effect of temperature and β -cyclodextrin on the molar conductivity of aqueous solutions of CuCl_2 . It can be noted that temperature has a significant effect on the molar conductivity, in particular at the lowest $[\text{CuCl}_2]/[\beta\text{-CD}]$ ratios. At 298.15 K the presence of β -CD on solution leads to a decrease in the molar conductivity of CuCl_2 , while the opposite effect is found when temperature increases to 310.15 K. Before proceeding with the discussion of such behavior, a quantitative analysis of the effect of temperature and β -CD will be made.

Figure 2 shows the variation of the molar conductivity of CuCl_2 in the presence and absence of β -CD at different temperatures. When the concentration ratio $[\beta\text{-CD}]/[\text{CuCl}_2]$ increases, the difference of molar conductivities

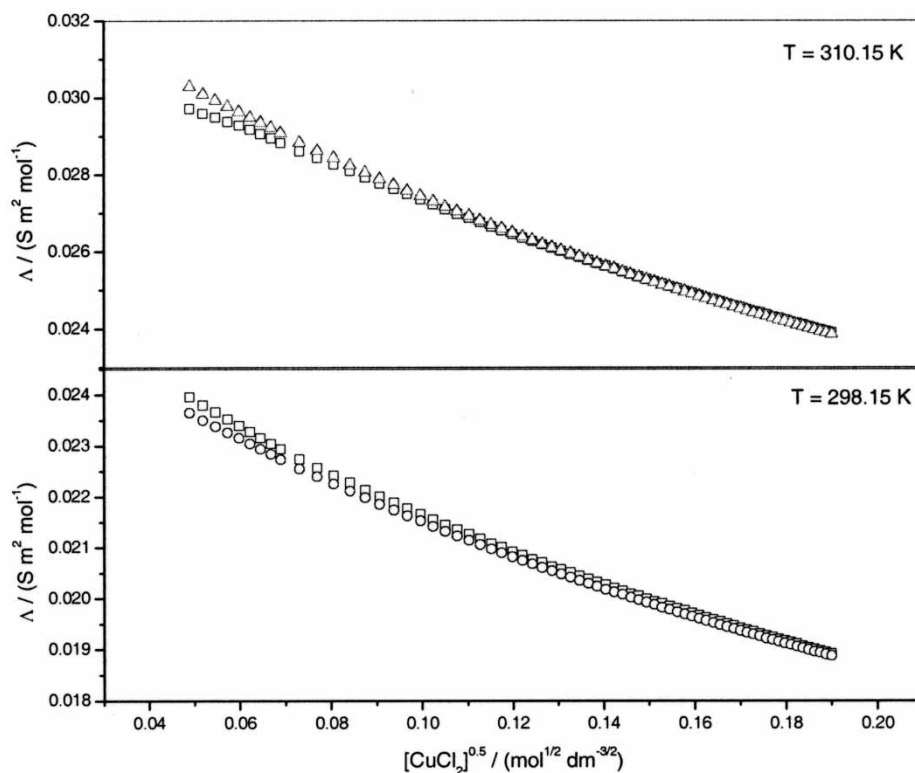


Figure 1: Effect of β -CD on the molar conductivity of CuCl_2 aqueous solutions at 298.15 K and 310.15 K. (\square) (β -CD) = 0; (\circ) (β -CD) = 1.025 mM; (Δ) (β -CD) = 1.042 mM.

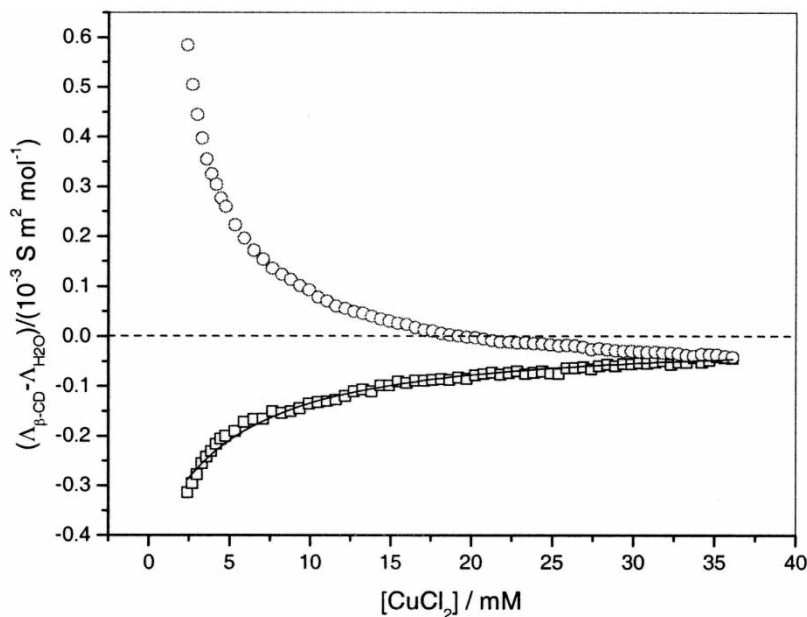


Figure 2: Variation of the molar conductivity of CuCl_2 in the presence ($\Lambda_{\beta\text{-CD}}$) and absence ($\Lambda_{\text{H}_2\text{O}}$) of $\beta\text{-CD}$ at (\square) 298.15 K and (\circ) 310.15 K. Solid line represents the difference of the molar conductivities predicted by Eq. 1, assuming 1:1 ($\text{Cu(II)}:\beta\text{-CD}$) association (see text for further details).

with and without $\beta\text{-CD}$, $\Delta\Lambda = \Lambda_{\beta\text{-CD}} - \Lambda_{\text{H}_2\text{O}}$, also increases, clearly suggesting that complexation between the salt or dissociated ions and cyclodextrin is occurring.

Assuming that there is a 1:1 ($\text{Cu(II)}:\beta\text{-CD}$) association, and using the experimental conductivity data described here, the association constant for the formation of a 1:1 complex can be calculated using the following equation;^[18,19]

$$\Delta\Lambda = \frac{\Delta\lambda}{2Kc_{\text{Cu}}} [K(c_{\text{Cu}} + c_{\text{CD}}) + 1 - (K(c_{\text{Cu}} + c_{\text{CD}}) + 1)^2 - 4K^2c_{\text{Cu}}c_{\text{CD}}]^{1/2} \quad (1)$$

where $\Delta\lambda$ is the difference of ionic conductivity of the complexed and non-complexed Cu^{2+} ions, c_{Cu} and c_{CD} are the concentrations of CuCl_2 and $\beta\text{-CD}$ (constant in the present case and equal to 1.025 mM), respectively, and K is the association constant. The value of K was obtained by nonlinear least-squares regression using a *wgnuplot* software. The best fitting (sum of squares of residuals = 0.00351 and reduced chi square = 5.24×10^{-5} ; see Fig. 2) was obtained for the following values: $\Delta\lambda = 1.77(\pm 0.03) \times 10^{-3} \text{ S m}^2 \text{ mol}^{-1}$ and $K = 307(\pm 15) \text{ mol}^{-1} \text{ dm}^3$. Comparing this association constant, obtained at acid aqueous solutions – pH around 5.5, with that calculated for $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}/\beta\text{-CD}$ at pH > 11, $K = 5.01 \times 10^{19}$, it is possible to

conclude that the pH has a great influence on K . Under very basic conditions, strong ionic interactions occur between the Cu (II) and the cyclodextrin, while at neutral pH such ionic interactions are much weaker even if they cannot be neglected. The very small value of K is in agreement with results of MM2 calculations, where the presence of β -CD in aqueous solutions contributes to an increase of the free energy of mixture when compared with that obtained without β -CD.

When temperature increases, an “anomalous” behavior on CuCl_2 molar conductivity is observed. In the presence of an excess of β -CD, the mobility of CuCl_2 increases. Although no definite explanation of this behavior has been obtained, we believe that one possibility is that since the interaction (association) between CuCl_2 and β -CD is not very strong, there is a relative decrease in the β -CD/ Cu^{2+} interactions on increasing temperature; that is, the thermal motion makes the stabilization of the associated β -CD/ Cu^{2+} structures more difficult.

Molecular mechanic studies are a valuable tool to interpret atom or ion dynamic processes, such as solvation changes, and to analyze cation and anion energetics in different conformations. Among the various MM methods, MM2 developed by Burkert and Allinger^[20] is frequently taken as the reference in the area.

We have used this method to investigate the relative potential energy of several possible β -CD and CuCl_2 systems to evaluate the favorability of Cu^{2+} inclusion inside β -CD. The relevant systems involving CuCl_2 and β -CD are presented in Figure 2 for (a) β -CD alone in water; (b) β -CD in the presence of CuCl_2 with the Cu^{2+} ion in the internal cavity; (c) β -CD in the presence of CuCl_2 with the Cl^- ion in the internal cavity; (d) β -CD in the presence of CuCl_2 with no ions in the internal cavity; and (e) CuCl_2 alone in water.

The relative energies of the several β -CD/ CuCl_2 systems, presented in Figure 3, show that the β -CD does not have a large effect on the coordination of the ions. This is not surprising due to the nonionic nature of the internal β -CD cavity. However, despite those low values for ion coordination, the system has a clearly favorable tendency to incorporate Cu^{2+} in the internal cavity, rather than Cl^- , or for the cavity to remain unassociated. This supports the observed β -CD/ Cu^{2+} interactions revealed by the diffusion and conductivity experiments.

Measurements of Diffusion Coefficients

Tables 1 and 2 show the experimental diffusion coefficients with copper chloride solutions from 5×10^{-3} to $5 \times 10^{-2} \text{ mol dm}^{-3}$ at 298.15 K and 310.15 K, both alone and in the presence of β -CD. These results are the average of 3 experiments performed on consecutive days. Good reproducibility

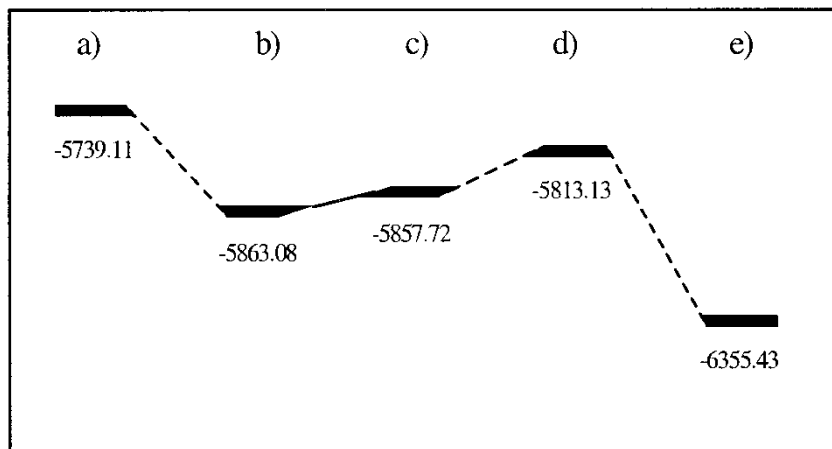


Figure 3: Energy, in kcal/mol, as determined by molecular mechanics of several systems involving CuCl_2 and β -CD in a box of 2,236 water molecules: a) β -CD alone in water; b) β -CD in the presence of CuCl_2 with the Cu^{2+} ion in the internal cavity; c) β -CD in the presence of CuCl_2 with the Cl^- ion in the internal cavity; d) β -CD in the presence of CuCl_2 with no ions in the internal cavity; e) CuCl_2 alone in water.

was observed, as seen by the small standard deviations of the mean, $S_{D_{\text{av}}}$. Previous papers^[21–25] reporting data obtained with our conductivity cell have shown that the inaccuracy of our results should be close to the imprecision, therefore giving an experimental uncertainty of 1% to 3%.

The decrease of the diffusion coefficients, when the concentration increases, may be interpreted on the basis of species resulting from the hydrolysis and complexation of this salt. The eventual formation of ion pairs, increasing with concentration, may also contribute to the decrease of $D(\text{CuCl}_2)$ with concentration.^[26]

Table 1: Diffusion coefficients, D ,^a of CuCl_2 in aqueous solutions at various concentrations, c , and different temperatures and the standard deviations of the means, S_D .

$c/\text{mol} \cdot \text{dm}^{-3}$	$T = 298.15 \text{ K}$		$T = 310.15 \text{ K}$	
	$D/10^{-9}$ $\text{m}^2 \cdot \text{s}^{-1a}$	$S_D/10^{-9}$ $\text{m}^2 \cdot \text{s}^{-1b}$	$D/10^{-9}$ $\text{m}^2 \cdot \text{s}^{-1a}$	$S_D/10^{-9}$ $\text{m}^2 \cdot \text{s}^{-1b}$
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 2: Diffusion coefficients, D ,^a of CuCl_2 in aqueous solutions of β -cyclodextrin (0.001 M) at various concentrations, c , and different temperatures and the standard deviations of the means, \mathbf{s}_D .

$c/\text{mol} \cdot \text{dm}^{-3}$	$T = 298.15 \text{ K}$			$T = 310.15 \text{ K}$		
	$D/10^{-9} \text{ m}^2 \cdot \text{s}^{-1\text{a}}$	$\mathbf{s}_D/10^{-9} \text{ m}^2 \text{ s}^{-1\text{b}}$	$\Delta D/D/\% \text{c}$	$D/10^{-9} \text{ m}^2 \text{ s}^{-1\text{a}}$	$\mathbf{s}_D/10^{-9} \text{ m}^2 \cdot \text{s}^{-1\text{b}}$	$\Delta D/D/\% \text{c}$
0.005	1.231	0.002	-0.3	1.615	0.001	-2.7
0.01	1.200	0.002	+0.08	1.679	0.002	+3.0
0.03	1.120	0.001	-0.09	1.520	0.001	-1.6
0.05	1.119	0.003	-0.09	1.477	0.002	-1.5

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

^b \mathbf{s}_D is the standard deviation of that mean.

^c $\Delta D/D$ Represents the relative deviations between the diffusion coefficients of CuCl_2 at the specified concentration in 0.001 M β -cyclodextrin, D , and that of the CuCl_2 in water, D (see Table 1).

The diffusion behavior of copper chloride in aqueous solutions at 298.15 K and 310.15 K is unaffected by the presence of β -CD molecules. From the present experimental conditions (i.e., $[\text{CuCl}_2]/[\beta\text{-CD}]$ 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. The interpretation of the behavior of diffusion of those systems can be made on the basis of the Onsager-Fuoss model,^[27] suggesting that D 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). Thus, two different effects can control the diffusion process: the ionic mobility and the gradient of the free energy. These effects can contribute to the diffusion coefficients in the opposite way and, consequently, from the final balance no alteration of diffusion coefficients is found. In fact, at 298.15 K and 310.15 K this situation is verified. Based on these measurements, in conjunction with the conductance measurements and molecular mechanics studies, this leads us to conclude that over the concentration range studied (Table 2), the diffusion of CuCl_2 in aqueous solutions at 298.15 K does not appear to be affected by the presence of 1 : 1 complexes ($\text{Cu(II)}:\beta\text{-CD}$). This possibly results from the fact that these interactions can be responsible for two opposing effects: (a) decreasing of the mobility of CuCl_2 (see Fig. 2) and (b) increasing the gradient of the free energy with concentration (see Fig. 3). However, at 310.15 K, the association between $\beta\text{-CD}$ and CuCl_2 is reduced, leading to an increase of the mobility of CuCl_2 (as supported by conductance measurements) and probably to a decrease in the gradient of the free energy with concentration. These considerations should be taken into account when studying the corrosion of dental alloys having copper.

CONCLUSIONS

We have measured diffusion coefficients and electrical conductivity and carried out molecular mechanics analysis for copper (II) chloride in aqueous solutions of $\beta\text{-CD}$ at 298.15 K and 310.15 K to obtain structural information on these systems.

The diffusion coefficients of copper (II) chloride in free solutions and in mixtures with the carbohydrate decrease with an increase of the initial concentration of copper chloride. The effect of $\beta\text{-CD}$ on the copper (II) chloride is confirmed by analysis of the dependence of these transport properties on concentration as well as by molecular mechanics calculations.

EXPERIMENTAL

Reagents

Copper (II) chloride dehydrate (Riedel-de-Haen, Seelze, Germany, *pro analysi* > 99%) was used without further purification. The concentration of

all aqueous $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (for the sake of simplicity this will be described as CuCl_2) solutions was obtained by titration. β -cyclodextrin (β -CD) was purchased from Sigma, and had a water content of 13.1% as verified from thermal analysis.

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 $\{\kappa = (0.7 \text{ to } 0.9) \times 10^{-4} \text{ S m}^{-1}\}$. Solutions were freshly prepared just before each experiment.

Diffusion Measurements

The open-ended capillary cell employed, which has previously been used to obtain mutual diffusion coefficients for a wide variety of electrolytes,^[28,29] has been described in great detail in previous papers.^[21–25] 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 $0.75c$ and $1.25c$, respectively, are surrounded with a solution of concentration c . This ambient solution is contained in a glass tank ($200 \times 140 \times 60$ 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^[28] to solve Fick's second law of diffusion are applicable. Therefore, the so-called Δl effect^[28] 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 1,000 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.^[28]

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. Cell constants were determined from measurements with KCl (reagent grade, recrystallized, and dried) using the procedure and data of Barthel et al.^[30] Measurements were taken at $25.00 \pm 0.01^\circ\text{C}$ in a Grant thermostat bath. Solutions were always used within 12 h of preparation. In a typical experiment, 100 mL of water was placed in the conductivity cell; then, aliquots of the copper (II) chloride solution 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.

The molar conductivity (Λ) was calculated using

$$\Lambda = (\kappa - \kappa_0) / (c \times 1000) \quad (2)$$

where κ and κ_0 are specific conductances of solution and water, respectively, and c is the surfactant concentration.

Molecular Mechanics Studies (MM2)

We use the molecular mechanics MM2 method developed by Burkert and Allinger^[20] to investigate the dynamic process of distribution of ions both around and inside the β -CD. The molecular mechanic studies were performed with HyperChem v6.03 software from Hypercube Inc., 2000, USA, using a Polak-Ribiere conjugated gradient algorithm for energy minimization in water, with a final gradient of $0.05 \text{ kcal}/\text{\AA} \text{ mol}$.

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