

Diffusion Coefficients of Copper Chloride in Aqueous Solutions at 298.15 K and 310.15 K

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Mutual diffusion coefficients (interdiffusion coefficients) and molar conductivities have been measured for copper(II) chloride in water at 298.15 K and 310.15 K at concentrations between 0.005 mol·dm⁻³ and 0.05 mol·dm⁻³. The diffusion coefficients were measured using a conductometric cell. The experimental data are discussed on the basis of the Onsager–Fuoss model. The Nernst diffusion coefficients derived from diffusion (1.297×10^{-9} and 1.690×10^{-9}) m²·s⁻¹ and from conductance (1.282×10^{-9} and 1.663×10^{-9}) m²·s⁻¹ at two temperatures (298.15 K and 310.15 K, respectively) are in good agreement.

Introduction

The knowledge of electrolytes diffusion data is of great interest not only for fundamental purposes but also in order to be used in many technical fields as, for example, for corrosion studies. Our research group is especially interested in dental restoration research and therefore in obtaining data for ionic systems involved in the dental damage processes into the oral cavity,^{1–6} which are necessary but not available in the literature. The knowledge of these data is essential to adequately understand and solve some of the problems derived from the deterioration of the dental amalgams implanted, as a consequence of both the wear-and-tear and the mouth digestion processes.

Because up to now, data on differential mutual diffusion coefficients, D (interdiffusion coefficients), for Cu(II) salts appear not to be published,⁷ we have determined those related to CuCl₂ aqueous solutions in the concentration range from (0.005 to 0.05) mol·dm⁻³, which is the most probable one in the oral cavity. The experimental technique used was the conductometric one by using an open-ended capillary cell.^{8–24} The results thus obtained were analyzed with the help of the Onsager–Fuoss equations^{25–28} by considering that copper(II) species may be present either as under-hydrolyzed forms or as complexes.^{29,30} These studies are complemented by conductance measurements, having also in mind that they can contribute to the understanding of the diffusion of this electrolyte in solution.

Experimental Section

Reagents. Copper(II) chloride dehydrate (Riedel-de-Haen, Seelze, Germany, pro analysi >99 %) was used without further purification. The concentration of all aqueous CuCl₂ solutions was obtained by titration.

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 by using Millipore water ($\kappa = (0.7 \text{ to } 0.9) \times 10^{-4}$ S·m⁻¹). All solutions were freshly prepared just before each experiment.

Diffusion Measurements. An open-ended capillary cell, which has been used to obtain mutual diffusion coefficients for a wide variety of electrolytes,^{8,9} is described in great detail in previous papers.^{8–24} 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 c 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 thermostated 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 literature⁸ to solve Fick's second law of diffusion are applicable. Therefore, the so-called Δl effect⁸ 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 .

To measure the differential diffusion coefficient (D) at a given concentration (c), the bulk solution of concentration

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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 (SD)^b

c mol·dm ⁻³	$T = 298.15 \text{ K}$		$T = 310.15 \text{ K}$	
	D	SD	D	SD
	10 ⁻⁹ m ² ·s ⁻¹	10 ⁻⁹ m ² ·s ⁻¹	10 ⁻⁹ m ² ·s ⁻¹	10 ⁻⁹ m ² ·s ⁻¹
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 three experiments. ^b SD is the standard deviation of that mean.

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; 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

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.²² Cell constants were determined from measurements with KCl (reagent grade, recrystallized, and dried) using the procedure and data of Barthel et al.³¹ Measurements were taken at (25.00 ± 0.01) °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 micropipet Metrohm 765 dosimate. The conductance of the solution was measured after each addition and corresponds to the average of three ionic conductances, obtained through homemade software.

pH Measurements. pH measurements were carried out with a Radiometer pH meter PHM 240 with an Ingold U457-K7pH conjugated electrode; pH was measured in fresh solutions, and the electrode was calibrated immediately before each experimental set of solutions using IUPAC-recommended pH 2 and 4 buffers. From pH meter calibration a zero pH of 6.897 ± 0.030 and sensitivity higher than 98.7 % were obtained.

Visible Spectroscopy. Visible spectra of CuCl_2 solutions (0.005 to 0.1) mol·dm⁻³ were obtained using a spectrophotometer Jasco V-530; the spectra were obtained between (800 and 400) nm with a bandwidth of 0.5 nm.

Results and Discussion

Mutual diffusion coefficients (D) of CuCl_2 in aqueous solutions at 298.15 K and 310.15 K are shown in Table 1,

Table 2. Fitting Coefficients (a_0 – a_2) of the Polynomial Equation $[D/(\text{m}^2\cdot\text{s}^{-1}) = a_0 + a_1(c/\text{mol}\cdot\text{dm}^{-3}) + a_2(c/\text{mol}\cdot\text{dm}^{-3})^2]$ to the Mutual Diffusion Coefficients for Copper Chloride in Aqueous Solutions at 298.15 K and 310.15 K^a

T/K	$a_0\cdot 10^9$	$a_1\cdot 10^9$	$a_2\cdot 10^9$	R^2 ^b
298.15	1.297	-12.81	230.4	0.991
310.15	1.690	-6.58	55.62	0.999

^a These equations were fitted to experimental data, except for $c = 0.05 \text{ mol}\cdot\text{dm}^{-3}$ at 298.15 K (see Table 1). ^b See Experimental Section.

where D is the mean value of, at least, three independent measurements. The standard deviations of the means are shown in Table 1. Previous papers reporting data obtained with this conductometric cell support our view that the inaccuracy of our results should not be much larger than the imprecision. That is, we believe that our uncertainty is not much larger than (1 to 3) %. For the purposes of this study, it was not necessary to extend the limits in concentration beyond those indicated in Table 1.

The following polynomial in c was used to fit the data by a least-squares procedure:

$$D = a_0 + a_1c + a_2c^2 \quad (1)$$

where the coefficients a_0 , a_1 , and a_2 are adjustable parameters. Table 2 shows the coefficients a_0 to a_2 of eq 1. These may be used to calculate values of diffusion coefficients at specified concentrations within the range of the experimental data shown in Table 1. The goodness of the fit (obtained with a confidence interval of 98 %) can be assessed by the excellent correlation coefficients (R^2) and the low standard deviation (<1 %).

pH measurements were made on some of the copper chloride solutions to assist interpretation of these results. For 0.005 mol·dm⁻³ ≤ c ≤ 0.05 mol·dm⁻³ and $T = 298.15 \text{ K}$, the pH values were in the range 4.4 ≤ pH ≤ 5.4, respectively, due to hydrolysis. (The pH decreased when the concentration increased.) Visible spectra of CuCl_2 solutions show that, over the concentration range studied, no alteration in the absorption maximum was obtained and the Beer–Lambert law was obeyed. Therefore, we may conclude that there is no change in the main complex species present in CuCl_2 aqueous solutions under these conditions.

To understand the transport process of this electrolyte in aqueous solutions, as a first approach the experimental mutual diffusion coefficients at 298.15 K were compared with those estimated by using the Onsager–Fuoss equation suitable for dilute solutions [eq 2 (Table 3)]:

$$D = \bar{M} \left(\frac{|z_1| + |z_2|}{|z_1 z_2|} \right) \frac{RT}{c} \left(1 + c \frac{\partial \ln \gamma_\pm}{\partial c} \right) \quad (2)$$

where D is the mutual diffusion coefficient of the electrolyte in m²·s⁻¹; R is the gas constant in J·mol⁻¹·K⁻¹; T is the absolute temperature; z_1 and z_2 are the algebraic valences of a cation and of an anion, respectively; the last term in parentheses is the activity factor, with γ_\pm being the mean molar activity coefficient; c is the concentration in mol·m⁻³; and \bar{M} , in mol²·s·m⁻³·kg⁻¹, is given by

$$\bar{M} = \frac{1}{N_A^2 e_0^2} \left(\frac{\lambda_1^0 \lambda_2^0}{\nu_2 |z_2| \lambda_1^0 + \nu_1 |z_1| \lambda_2^0} \right) c + \overline{\Delta M'} + \overline{\Delta M''} \quad (3)$$

In eq 3, the first- and second-order electrophoretic terms

Table 3. Diffusion Coefficients of Copper Chloride Calculated from Onsager–Fuoss Theory (D_{OF}) at 298.15 K^{26,28}

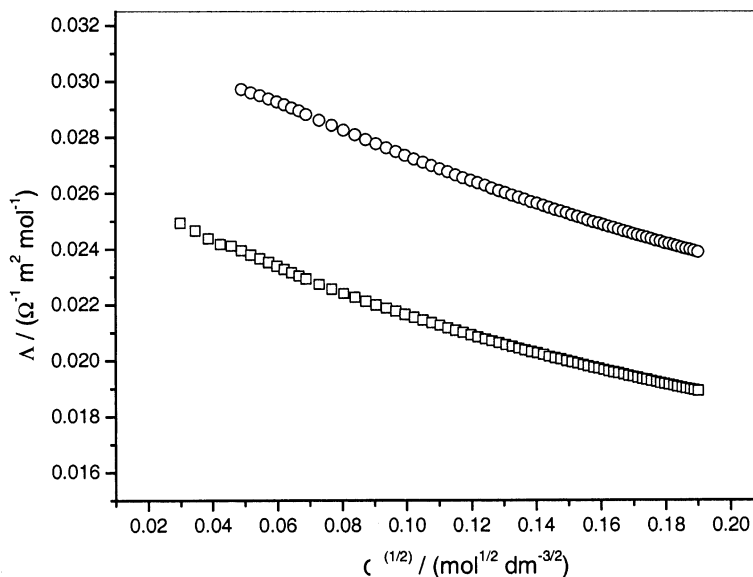
c (mol·dm ⁻³)	D'_{OF} (10 ⁻⁹ m ² ·s ⁻¹) ^a	$\Delta D/D'_{\text{OF}}$ % ^b	D''_{OF} (10 ⁻⁹ m ² ·s ⁻¹) ^c	$\Delta D/D''_{\text{OF}}$ % ^b	D'''_{OF} (10 ⁻⁹ m ² ·s ⁻¹) ^d	$\Delta D/D'''_{\text{OF}}$ % ^b
0.000	1.298	-0.08 ^e	1.298	-0.08 ^e	1.298	-0.08 ^e
0.005	1.202	+2.7	1.205	+2.4	1.205	+2.4
0.008	1.187	+1.8	1.190	+1.5	1.195	+1.1
0.010	1.180	+1.6	1.185	+1.2	1.190	+0.8
0.020	1.163	-3.0	1.164	-3.1	1.177	-4.2
0.030	1.158	-3.2	1.159	-3.3	1.175	-4.6
0.050	1.150	-2.6	1.153	-2.9	1.172	-4.6

^a $a = 2.5 \times 10^{-10}$ m obtained from the sum of the ionic radii (obtained from diffraction methods).³⁴ ^b $\Delta D/D'_{\text{OF}}$, $\Delta D/D''_{\text{OF}}$, and $\Delta D/D'''_{\text{OF}}$ represent the relative deviations between D (Table 1) and D'_{OF} , D''_{OF} , and D'''_{OF} values, respectively. ^c $a = 3.8 \times 10^{-10}$ m estimated using MM2.³⁵ ^d $a = 5.3 \times 10^{-10}$ m obtained from the sum of hydrated ionic radii (obtained from diffraction methods).³⁴ ^e Relative deviations between D extrapolated (Table 2) and the Nernst value (eq 6).

Table 4. Parameters Determined from Conductivity Data of CuCl₂ Solutions at 298.15 K and 310.15 K

T K	Λ_0 (10 ⁻⁴ m ² ·Ω ⁻¹ ·mol ⁻¹)	$\lambda_{\text{Cl}^-}^0$ (10 ⁻⁴ m ² ·Ω ⁻¹ ·mol ⁻¹)	$\lambda_{\text{Cu}^{2+}}^0$ (10 ⁻⁴ m ² ·Ω ⁻¹ ·mol ⁻¹)	D^0 (10 ⁻⁹ m ² ·s ⁻¹) ^a	D_{exp}^0 (10 ⁻⁹ m ² ·s ⁻¹) ^b
298.15	263.5 (0.4)	76.3	110.9	1.282	1.297
310.15	320.7 (0.2)	83.5	153.7	1.663	1.690

^a These values have been calculated with eq 6. ^b See Table 2.

**Figure 1.** Molar conductivity (Λ) versus square root of the molar copper(II) chloride concentration at different temperatures: □, 298.15 K; ○, 310.15 K.

are given by

$$\overline{\Delta M'} = -\frac{c}{N_A} \frac{(|z_2|\lambda_1^0 - |z_1|\lambda_2^0)^2}{(|z_1|\nu_1\lambda_2^0 + |z_2|\nu_2\lambda_1^0)^2} \frac{\nu_1\nu_2}{\nu_1 + \nu_2} \frac{k}{6\pi\eta_0(1+ka)} \quad (4)$$

$$\overline{\Delta M''} = \frac{(\nu_1|z_2|\lambda_1^0 + \nu_2|z_1|\lambda_2^0)^2}{(\nu_1|z_1|\lambda_2^0 + \nu_2|z_2|\lambda_1^0)^2} \frac{1}{(\nu_1 + \nu_2)^2} \frac{1}{N_A^2} \frac{k^4\phi(ka)}{48\pi^2\eta_0} \quad (5)$$

where η_0 is the viscosity of the water in N·s·m⁻²; N_A is the Avogadro's constant; e_0 is the proton charge in coulombs; ν_1 and ν_2 are the stoichiometric coefficients; λ_1^0 and λ_2^0 are the limiting molar conductivities of the cation and anion, respectively, in Ω⁻¹·m²·mol⁻¹; k is the “reciprocal average radius of ionic atmosphere” in m⁻¹ (see, for example, ref 32); a is the mean distance of closest approach of ions in m; $\phi(ka) = |e^{2ka}E_i(2ka)/(1+ka)|$ has been tabulated by Harned and Owen,³² and the other letters represent well-known quantities.³² In this equation, phenomena such as hydrolysis,^{29,30} complexation, and/or ion association³³ are

not taken into consideration. There is no direct method for measuring the ion size parameter a , “mean distance of closest approach” from the Debye–Hückel theory, but it may be estimated from the data of Marcus (Table 13 of ref 34) using two approximations. First, the a values were estimated as the sum of the ionic radii (R_{ion}) reported by Marcus.³⁴ The R_{ion} values were obtained as the difference between the mean internuclear distance of a monoatomic ion, or the central atoms of polyatomic ions, and the oxygen atom of a water molecule in its first hydration shells ($d_{\text{ion-water}}$), and the half of the mean intermolecular distance between two water molecules in liquid water (R_{water}). Briefly, $R_{\text{ion}} = d_{\text{ion-water}} - R_{\text{water}}$ and $a = R_{\text{cation}} + R_{\text{anion}}$. To account for the effect of the ion hydration shell on the a values, a second approximation considers the sum of the $d_{\text{ion-water}}$ values reported by Marcus.³⁴ In other words, in this approach the a values are determined as $a = d_{\text{cation-water}} + d_{\text{anion-water}}$.

When parameter a is estimated from molecular mechanic studies,³⁵ using the molecular mechanics force field MM+ to minimize the energy of a system of ionic CuCl₂ in a box

of 1103 water molecules (number chosen to create a similar CuCl_2 concentration to that of the experiments in the range of 0.05 M, see Appendix I in Supporting Information), we see that the calculated a value of 3.7×10^{-10} m is between those obtained by Marcus,³⁴ pointing to some compression of the respective hydration shells (Table 3).

Comparing the calculated diffusion coefficients of CuCl_2 , D_{OF} (Table 3), using the three values of the parameter a with the related experimental values at 298.15 K (Table 1), a reasonable agreement is observed between the experimental data and this model for $a = 3.8 \times 10^{-10}$ m (deviations ≤ 3 %). The deviation between the limiting D^0 value calculated by extrapolating experimental data to $c \rightarrow 0$ (Table 2) and the Nernst value (Table 3) is also acceptable (0.08 %). The decrease of the diffusion coefficient, when the concentration increases, may be interpreted on the basis of species resulting from the hydrolysis and complexation of this salt. From literature data, we may assume²⁹ that $\text{Cu}_2(\text{OH})_2^{2+}$, $\text{Cu}_3(\text{OH})_4^{2+}$, ..., $\text{Cu}_{n+1}(\text{OH})_{2n}^{2+}$ are dominant in those circumstances. The linear Beer–Lambert plot and absence of change in shape of the visible spectrum suggested these species must have very similar spectral signatures. The eventual formation of ion pairs, increasing with concentration, may also contribute to the decrease of $D_{(\text{CuCl}_2)}$ with concentration. In relation to the effect of temperature on diffusion, an increase in the experimental D values was found at all copper chloride concentrations. Also, the decrease of the diffusion coefficient was obtained when the concentration increases. However, given the absence of the values of parameters for estimations of D_{OF} , only the diffusion coefficient of copper chloride at infinitesimal concentration and the equivalent conductance of the copper ion were estimated.

From the following equation for analysis of the data, shown in Table 2, we estimated the diffusion coefficient of copper chloride at infinitesimal concentration as $D^0 = 1.690 \times 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$ at 310.15 K. To estimate $\lambda_{\text{Cu}^{2+}}^0$, we may assume that the above D^0 value coincides with the Nernst value²⁶ from

$$D^0 = \frac{RT}{F^2} \frac{|Z_{\text{Cu}^{2+}}| + |Z_{\text{Cl}^-}|}{|Z_{\text{Cu}^{2+}}Z_{\text{Cl}^-}|} \frac{\lambda_{\text{Cu}^{2+}}^0 \lambda_{\text{Cl}^-}^0}{\lambda_{\text{Cu}^{2+}}^0 |Z_{\text{Cl}^-}| + \lambda_{\text{Cl}^-}^0 |Z_{\text{Cu}^{2+}}|} \quad (6)$$

where $Z_{\text{Cu}^{2+}}$ and Z_{Cl^-} represent the algebraic valences of a cation and of an anion, respectively. $\lambda_{\text{Cl}^-}^0$ is the molar conductance of Cl^- at infinitesimal concentration, estimated by using a polynomial equation fitted to experimental data from ref 36 (that is, $\lambda_{\text{Cl}^-}^0 = 83.5 \times 10^{-4} \Omega^{-1} \cdot \text{m}^2 \cdot \text{mol}^{-1}$). Therefore, from eq 6 we have $\lambda_{\text{Cu}^{2+}}^0 = 158.6 \times 10^{-4} \Omega^{-1} \cdot \text{m}^2 \cdot \text{mol}^{-1}$ at 310.15 K.

Figure 1 (data shown in Appendix II in Supporting Information) shows the molar conductivity of CuCl_2 solutions (corrected for solvent conductance) at (298.15 and 310.15) K. The molar conductivity values at 298.15 K are in very close agreement with those reported in ref 37. The molar conductivity data shows a linear relationship at concentrations below $6.4 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ (at 298.15 K) and $12.1 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ (at 310.15 K) with the square root of concentration. Such a relationship will enable us to calculate the molar conductivity at infinitesimal concentration of the CuCl_2 solution (Λ_0) according to the Kohlrausch equation. Table 4 shows molar conductivity at infinitesimal concentration of the CuCl_2 solution (Λ_0), limiting molar conductivity for copper ion (λ_0^+) and limiting diffusion coefficient (D^0) at the two different temperatures. The limiting diffusion coefficients calculated from conductance and diffusion data are in close agreement.

Supporting Information Available:

Final configuration of the Cu^{2+} and Cl^- ions in a cubic box and data for molar conductances of aqueous copper(II) solutions at 298.15 K and 310.15 K. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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