



Diffusion coefficients and electrical conductivities for calcium chloride aqueous solutions at 298.15 K and 310.15 K

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ABSTRACT

Experimental values for mutual diffusion coefficients (interdiffusion coefficients) for CaCl_2 aqueous solutions at 298.15 K and 310.15 K, not available in the literature, were experimentally determined between $0.005 \text{ mol dm}^{-3}$ and 0.1 mol dm^{-3} . The measurements were performed by using a conductimetric open-ended capillary cell. Values at infinitesimal concentration, D^0 , were also obtained. These data were analysed using the Onsager–Fuoss and Gordon models. In addition, molar conductance data were measured at 310.15 K for CaCl_2 aqueous solutions at the same concentration range and the value at infinitesimal concentration determined. Afterwards, it was split into the ionic limiting values. By replacing them into the Nernst equation, diffusion coefficients at infinitesimal concentration were derived ($1.335 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ and $1.659 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$) at both temperatures (298.15 K and 310.15 K, respectively). They agree well with the extrapolated experimental ones ($1.312 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ and $1.613 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$).

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1. Introduction

The interest in the transport properties of calcium chloride in solution arises from the broad applications that this salt still has nowadays.

Calcium ions take part in different engineering processes. Likewise, they play an important role in the health sciences because they are present in many tissues (bones, teeth) and in physiological processes (muscle functions). A calcium deficiency is accompanied by adverse effects, being osteoporosis the most common bone metabolic disorder and is aging dependent. Different commercial preparations, usually containing calcium salts have been used as nutritional supplements in therapies to minimize osteoporosis. The development of new and more effective treatments concerning osteoporosis, as well as to optimize the existing ones, needs knowledge about the transport process of these ions in aqueous solutions.

Diffusion coefficients are one of the transport parameters which give substantial information about this phenomenon in solution. No data on mutual diffusion coefficients of calcium salts at physiological temperature (37°C) are published in the literature. In the present paper, experimental data in the concentration range from $0.005 \text{ mol dm}^{-3}$ to 0.1 mol dm^{-3} at 298.15 K and 310.15 K, are reported. To obtain these, an open-ended conductimetric capillary cell, which has been proved to give precise and accurate results [1–5], was used. The results obtained are analysed using both the Onsager–Fuoss [6] and Gordon [7] models to elucidate if either the ion pairs that this calcium salt originates in aqueous solutions, or the viscosity of the solution, affect their diffusion in the solvent.

Transport data analysis involves the use of the structural a parameter (the mean distance of closest approach between the ions). As it is well known, a direct method to measure this is not available. Hence, it must be estimated from some experimental thermodynamic and transport properties (activity coefficients, conductances, etc) or from theoretical simulation computations. In this paper, molecular mechanic calculi were performed and meaningful numerical values for this a parameter were obtained.

Conductance measurements give complementary information about the transport of calcium chloride in solution. In fact, Nernst empirical equation [8] associates both parameters, diffusion and conductance, at infinitesimal concentration. Because no conductivity values for calcium chloride at 37°C are available in literature,

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they were measured and the limiting values estimated to be used in the Nernst analysis.

2. Experimental

2.1. Reagents and solutions

Calcium chloride (Sigma–Aldrich, *pro analysi* >99.9%) was used as supplied, without further purification. Potassium chloride (Sigma–Aldrich, reagent grade) was recrystallized and afterwards dried in vacuo at 150 °C. Millipore quality water $\{\kappa = (0.7–0.9) \times 10^{-4} \text{ S m}^{-1}\}$ was used as solvent.

All the solutions were freshly prepared before each experiment (concentration uncertainty less than $\pm 0.1\%$). For diffusion studies, they were prepared by volume and de-aerated during 30 min, approximately, before use. For conductimetric measurements, the solute adding method was used.

2.2. Diffusion measurements

Mutual diffusion coefficients were obtained from the conductimetric method developed by Lobo and co-workers [2,3]. This method, profusely described in previous publications by this group [4,5,9,10], has given accurate results for a wide variety of electrolytes [1].

The measurements were carried out by using an automatic equipment. The resistance ratio value, $w = R_t/R_b$ (R_t and R_b being the electrical resistances of the upper and lower capillary tubes in the open-ended conductimetric capillary cell) was obtained using a Solartron digital voltmeter (DVM) 7061 with 6 1/2 digits. This calculates the w value from the voltage readings, V' and V'' measured between either the top or bottom Pt-electrodes, respectively, and a central grounded Pt-electrode in the conductance cell (after a 250 mV sinusoidal signal at 4 kHz is applied to both the upper and the lower electrodes).

For a given bulk solution at concentration c , the top and the bottom solutions were prepared at concentrations 0.75 c and 1.25 c , respectively and these solutions diffuse into the bulk solution once the equipment is started. The resistance ratio values were recorded at constant intervals (beginning 1000 min after starting the experiment) to calculate the quantity $\tau = 10^4/(1+w)$. The value at infinite time, $\tau_\infty = 10^4/(1+w_\infty)$, was determined by filling the top and bottom capillaries of the cell with bulk solution.

The mutual diffusion coefficient values were calculated by firstly using a linear least-squares procedure and, afterwards, an iterative process involving 20 terms of a Fick's second law expansion series, considering the present boundary conditions. The theory developed for this capillary cell has been described elsewhere [2].

In all measurements, the temperature was controlled with an uncertainty of ± 0.01 °C in water thermostat baths.

2.3. Conductance measurements

A Wayne-Kerr, model 4265 Automatic LCR meter at 1 kHz, was used to measure the electrical resistances of the solutions. A Shedlovsky-type cell was used. Its constant ($0.1181 \pm 0.0002 \text{ cm}^{-1}$) was determined from conductivity measurements of KCl by using the procedure and data of Barthel et al. [11].

In a typical experiment, 20 mL of water was placed into the conductivity cell and its electrical resistance measured. Then, aliquots of the calcium chloride solution (0.25 mol dm^{-3}) were consecutively added, in a stepwise manner, with the help of a Metrohm 765 Dosimate micropipette. After each addition, the electrical resistance of the solution was measured and its conductance calculated

Table 1

Experimental values for the diffusion coefficient, D^a , of CaCl_2 in aqueous solutions at various concentrations, c , and different temperatures and the standard deviations of the means, S.D.^b

$c/\text{mol dm}^{-3}$	298.15 K		310.15 K	
	$D/10^{-9} \text{ m}^2 \text{ s}^{-1}$	S.D./ $10^{-9} \text{ m}^2 \text{ s}^{-1}$	$D/10^{-9} \text{ m}^2 \text{ s}^{-1}$	S.D./ $10^{-9} \text{ m}^2 \text{ s}^{-1}$
0.005	1.260	0.020	1.601	0.017
0.008	1.237	0.019	1.600	0.013
0.010	1.215	0.022	1.590	0.011
0.05	1.115	0.012	1.530	0.017
0.10	1.110	0.008	1.440	0.001

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

^b S.D. is the standard deviation of that mean.

using a home-made software. The values presented correspond to the average of, at least, three values obtained.

2.4. Computational studies

The molecular mechanics simulations involved in this study were performed on a 3.2 MHz Pentium 4 workstation with HyperChem v7.5. The MM+ molecular mechanics force field was used with a Polak-Ribiere algorithm. The convergence limit of it was of 0.1 kcal/Å mol. The Density Functional Theory (DFT) determinations were made by using the base set Large (6–31G**).

3. Results and discussion

In Table 1, mean values of the mutual diffusion coefficients, D , for CaCl_2 aqueous solutions at 298.15 K and 310.15 K are shown together with standard deviations of the mean. These D values were obtained from, at least, three independent runs. As it has been shown in previous papers by our group, the uncertainty of these values is not larger than 1–3%.

These D values were fitted, by using a least-squares procedure (with a confidence interval of 98%), to the polynomial

$$D = a_0 + a_1 c + a_2 c^2 \quad (1)$$

the coefficients a_0 , a_1 and a_2 being adjustable parameters. The values for these coefficients, in the concentration range studied, are given in Table 2 together with the relevant standard deviations. This equation can be used for interpolating purposes in the concentration range studied.

The experimental mutual diffusion coefficient values obtained at 298.15 K, were compared with those estimated from the Onsager–Fuoss equation [6] (Table 3)

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

where D_{OF} is the mutual diffusion coefficient of the electrolyte, in $\text{m}^2 \text{ s}^{-1}$; R is the gas constant, in $\text{J mol}^{-1} \text{ K}^{-1}$; T , the absolute temperature; z_1 and z_2 are the algebraic valences of cation and anion, respectively; and the last term in parenthesis is the activity factor, with y_{\pm} being the mean molar activity coefficient; c , the concen-

Table 2

Fitting coefficients (a_0 – a_2) of the polynomial equation $[D/(\text{m}^2 \text{ s}^{-1}) = a_0 + a_1 (c/\text{mol dm}^{-3}) + a_2 (c/\text{mol dm}^{-3})^2]$ to the mutual differential diffusion coefficients for CaCl_2 in aqueous solutions at 298.15 K and 310.15 K, in the concentration range from 0.005 mol dm^{-3} to 0.10 mol dm^{-3}

T/K	$a_0 \times 10^9$	$a_1 \times 10^9$	$a_2 \times 10^9$	R^2
298.15	1.273 ± 0.010	-4.79 ± 0.67	31.7 ± 6.4	0.971
310.15	1.608 ± 0.003	-1.47 ± 0.20	-2.2 ± 1.9	0.997

Table 3
Diffusion coefficients for CaCl₂ calculated from Onsager–Fuoss (D_{OF}) and Gordon (D_G) models at 298.15 K

c/(mol dm ⁻³)	D _{OF} ^a /(10 ⁻⁹ m ² s ⁻¹) ^a	(ΔD/D _{OF})/% ^b	D _{OF} ^c /(10 ⁻⁹ m ² s ⁻¹) ^c	(ΔD/D _{OF})/% ^b	D _{OF} ^d /(10 ⁻⁹ m ² s ⁻¹) ^d	(ΔD/D _{OF})/% ^b	D _G ^e /10 ⁻⁹ m ² s ⁻¹ ^e	(ΔD/D _G)/% ^b	D _A ^f /10 ⁻⁹ m ² s ⁻¹ ^f	(ΔD/D _A)/% ^b
0.000	1.335	+1.7 ^g	1.335	+1.7 ^g	1.335	+1.7 ^g	1.335	+1.7 ^g	1.335	+1.7 ^g
0.005	1.234	+2.1	1.239	+2.2	1.233	+1.7	1.232	+2.3	1.231	+2.3
0.008	1.218	+1.6	1.228	+1.5	1.219	+0.7	1.231	+0.5	1.230	+0.6
0.010	1.210	+0.4	1.222	+0.2	1.213	-0.6	1.206	+0.7	1.204	+0.9
0.050	1.168	-4.5	1.204	-6.1	1.182	-7.4	1.148	-2.9	1.140	-2.2
0.100	1.172	-5.3	1.220	-6.2	1.184	-9.0	1.135	-2.2	1.118	-0.7

^a D_{OF}^a represents the diffusion coefficient of CaCl₂ calculated from the Onsager–Fuoss model, using $a = 2.8 \times 10^{-10}$ m, obtained from the sum of the ionic radii (from diffraction methods).
^b ΔD/D_{OF}^a, ΔD/D_G^e and ΔD/D_A^f represent the relative deviations between D (Table 1) and D_{OF}^a, D_G^e, D_A^f values, respectively.

^c D_{OF}^c represents the diffusion coefficient of CaCl₂ calculated from the Onsager–Fuoss model with $a = 5.6 \times 10^{-10}$ m, obtained from the sum of hydrated ionic radii (from diffraction methods).
^d D_{OF}^d represents the diffusion coefficient of CaCl₂ calculated from the Onsager–Fuoss model with $a = 4.0 \times 10^{-10}$ m, estimated by using MM⁺ and activity coefficients.

^e D_G^e represents the diffusion coefficient of CaCl₂ calculated from Gordon model, by using $a = 2.8 \times 10^{-10}$ m.

^f D_A^f represents the diffusion coefficient of CaCl₂ calculated from Agar model using $a = 2.8 \times 10^{-10}$ m and $h = 4$ [8].

^g Relative deviations between the value of D extrapolated without that for $c = 0.1$ M (that is, $D = 1.312 \times 10^{-10}$ m in Table 2) and the Nernst value (equation (8)).

Table 4

Values obtained for the ionic distance in CaCl₂ from computational studies (A: distance Cl⁻ (1)–Ca²⁺; B: distance Ca²⁺–Cl⁻ (2))

Method	A/10 ⁻¹⁰ m	B/10 ⁻¹⁰ m	Mean value a/10 ⁻¹⁰ m
Ab Initio (DFT) (in vacuo)	3.27	3.27	3.27
Molecular Mechanics MM+ (in vacuo)	3.70	3.75	3.72
Molecular Mechanics MM+ (in water)	4.14	3.94	4.05

tration in mol m⁻³, and \bar{M} , in mol² s m⁻³ kg⁻¹, is given by

$$\bar{M} = \frac{1}{N_A^2 e_0^2} \left(\frac{\lambda_1^0 \lambda_2^0}{v_2 |z_2| \lambda_1^0 + v_1 |z_1| \lambda_2^0} \right) c + \overline{\Delta M'} + \overline{\Delta M''} \quad (3)$$

being $\overline{\Delta M'}$ and $\overline{\Delta M''}$ the first and second-order electrophoretic terms, respectively, which are given by

$$\overline{\Delta M'} = -\frac{c}{N_A} \frac{(|z_2| \lambda_1^0 - |z_1| \lambda_2^0)^2}{(|z_1| v_1 \lambda_2^0 + |z_2| v_2 \lambda_1^0)^2} \left(\frac{v_1 v_2}{v_1 + v_2} \right) \left(\frac{\kappa}{6 \pi \eta_0 (1 + \kappa a)} \right) \quad (4)$$

and

$$\overline{\Delta M''} = \frac{1}{N_A^2} \frac{(v_1 |z_2| \lambda_1^0 + v_2 |z_1| \lambda_2^0)^2}{(v_1 |z_1| \lambda_2^0 + v_2 |z_2| \lambda_1^0)^2} \frac{1}{(v_1 + v_2)^2} \left(\frac{\kappa^4 \phi(\kappa a)}{48 \pi^2 \eta_0} \right) \quad (5)$$

In these equations, η_0 is the water viscosity, in N s m⁻²; N_A , the Avogadro's constant; e_0 , the proton charge, in coulombs; v_1 and v_2 are the stoichiometric coefficients; λ_1^0 and λ_2^0 , the limiting molar conductivities of cation and anion, respectively, in m² mol⁻¹ Ω⁻¹; κ is the reciprocal average radius of the ionic atmosphere, in m⁻¹; a , the mean distance of closest approach of ions, in m; $\phi(\kappa a) = |e^{2\kappa a} \text{Ei}(2\kappa a)/(1 + \kappa a)|$ has been tabulated by Harned and Owen [12] and the other symbols represent well-known quantities. Complexation and/or ion association phenomena [13,14] as well as hydrolysis [15,16] are not taken into consideration in these equations.

The use of equation (2) demands that a parameter values (the mean distance of closest approach of ions) be available. Because there is no any direct method for measuring this value, it must be estimated [17]. Three different estimations were done:

- Two of them came from Marcus data (Table XIII in [18]) by using two approximations.
 - By considering it as the sum of the ionic radii ($a = R_{\text{cation}} + R_{\text{anion}}$). In this case, the R_{ion} values were obtained as the difference between the mean internuclear distance from a monoatomic ion (or the central atoms of polyatomic ions) to the oxygen atom of a water molecule in its first hydration shell ($d_{\text{ion-water}}$), and the half of the mean intermolecular distance between two water molecules in liquid water (R_{water}), i.e., $R_{\text{ion}} = d_{\text{ion-water}} - R_{\text{water}}$. A mean value of 2.8×10^{-10} m was thus found.
 - It was assumed as the sum of the hydrated ionic radii ($a = R_{\text{cation-water}} + R_{\text{anion-water}}$). This way, the effect of the ion hydration shell on the a -values is taken into account ($R_{\text{ion-water}} = d_{\text{ion-water}}$). A mean value of 5.6×10^{-10} m was obtained.
- The third estimation was done from computational studies performed on the CaCl₂ system. The values calculated are shown in Table 4.

As it can be seen, from the Density Functional Theory the values obtained for A (distance between the left Cl⁻ (1) ion and the central

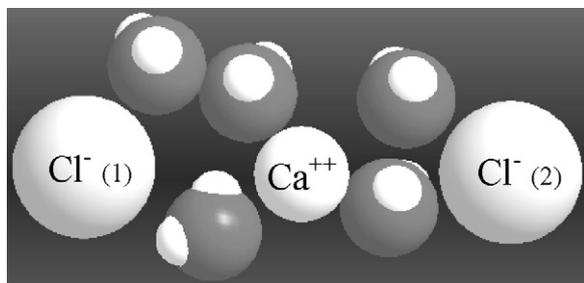


Fig. 1. Schematic representation of CaCl_2 in water from the MM+ simulation.

Ca^{2+} ion) and B (distance between the central Ca^{2+} ion and the right Cl^- (2) ion) are equal, whereas differences appear between both geometrical distances from the Molecular Mechanic Force Field model (MM+). Nevertheless, the results reached from both methods, DFT and MM+ (by using a Polak-Ribiere algorithm and a final RMS gradient of $0.1 \text{ kcal}/(\text{\AA mol})$), are quite similar. The calculated values are always in the range of the empirical ones.

When the calculation is performed in water (from the MM+ method, by considering a 256 water molecules square box, of 18.701 \AA wide, which creates a CaCl_2 concentration similar to that of the experiments in the range of 0.01 M) greater differences appear to each geometrical A and B distances. In all cases, the final mean value, which is identified with the a parameter ($(3.3\text{--}4.1) \times 10^{-10} \text{ m}$), is in between those obtained from Marcus data, which points out to some compression effect of the ionic hydration shells. As a conclusion, despite the variations obtained for A and B change in each calculation, they make possible to sustain that some water molecules are placed between the Ca^{2+} and the Cl^- ions, as it is illustrated in Fig. 1. In this case, the values shown in Table 4 (4.14 \AA and 3.94 \AA , for A and B , respectively) were found by considering an average number of 2–3 water molecules between Cl^- (1) and Ca^{2+} and of 1–2 water molecules between Ca^{2+} and Cl^- (2) (which, we think, is the most accurate and realistic picture for this system).

Calculation with large amounts of water molecules (>1000) does not affect significantly these A and B values. Less water (which is equivalent to more concentrated solutions) results in a reduction of the average A and B distances, less than 5%.

On the base of the above a results, empirical values for the diffusion coefficient, D_{OF} , were calculated. They are collected in Table 3. As it can be observed in that Table, at 298.15 K , the results predicted by the Onsager–Fuoss model, by using any of the three values found for the parameter a , show differences in between -0.6% and 2.2% , with respect to the experimental ones (see Table 1), when $c \leq 0.01 \text{ mol dm}^{-3}$. A reasonable agreement is also observed between our experimental data and those obtained by others authors ($<3\%$) [1].

Considering that those deviations are approximately of the same order than the experimental uncertainty (within $\pm 1\text{--}3\%$ for this type of studies), and that phenomena like association and hydrolysis are not considered by the Onsager–Fuoss model, it can be

interpreted, from this agreement of results, that at concentrations below 0.01 mol dm^{-3} the predominant species responsible for the behaviour of D are calcium and chloride ions.

The decrease of the diffusion coefficient, when the concentration increases, may be attributed to the non-ideality thermodynamic behaviour which is regulated by the factor $(1 + \partial \ln \gamma / \partial \ln c)$ (equation (2)) [6]. We may assume that other species, like associated pairs, are present in solution in lower proportions, but they do not influence significantly the behaviour of the diffusion of this system.

At higher concentrations ($c > 0.01 \text{ mol dm}^{-3}$), greater differences are observed between the results predicted by the Onsager–Fuoss model and our experimental values (deviations between -4.5% and -9%). This is understandable if we take into account that changes for parameters such as viscosity, dielectric constant and hydration, with the solution concentration, are not taken into account by the Onsager–Fuoss model either. In this context, the consideration of the viscosity effect on the diffusion of this electrolyte through the Gordon equation [7]

$$D_G = D_{\text{OF}} \left(\frac{\eta_0}{\eta} \right) \quad (6)$$

D_G and η being the diffusion coefficient and solution viscosity, respectively, gets to results at higher concentrations much closer to our experimental data (deviations $<3\%$) by using, for instance, $a = 2.8 \times 10^{-10} \text{ m}$. Therefore, it can be concluded that, at higher concentrations, the behaviour of this electrolyte depends strongly on the viscosity change in the solution.

The effect of the hydration on the diffusion has also been taken into account using Agar's model [8]

$$D_A = D_G \left[1 + 0.036 m \left(\frac{D_{\text{H}_2\text{O}}}{D^0} - h \right) \right] \quad (7)$$

in which $h = 4$ [8]. The results obtained are summarized in the last two columns in Table 3. As it can be observed, at low and moderate concentrations ($c \leq 0.01 \text{ mol dm}^{-3}$) the differences observed with respect to the experimental values (ca 2%) are of the same order than those found from the other models here used. Nevertheless, in the range of higher concentrations, the results are much closer the experimental data, which indicates that the hydration factor seems to have a significant role on the diffusion of this salt when the solution concentration increases.

Due to the absence of literature values for the parameters necessary to estimate D_{OF} at temperatures different from 298.15 K , it was not possible to make a similar analysis at 310.15 K , which would permit to infer the temperature effect on diffusion for this system. Related to this, the only information possible to derive from our data is an increase of the diffusion coefficient D when the temperature increases, together with a decrease of this parameter when the concentration increases, at a given temperature. Consequently, diffusion coefficient values for calcium chloride at infinitesimal concentration were obtained at both temperatures (the best values were obtained by using the more dilute solutions studied, $c \leq 0.05 \text{ mol dm}^{-3}$). These values are collected in Table 5.

Table 5

Infinitesimal concentration values for conductivity and diffusion coefficient of CaCl_2 aqueous solutions at 298.15 K and 310.15 K

T/K	$\Lambda^0/(10^{-4} \text{ m}^2 \Omega^{-1} \text{ mol}^{-1})$	$\lambda_{\text{Cl}^-}^0/(10^{-4} \text{ m}^2 \Omega^{-1} \text{ mol}^{-1})$	$\lambda_{\text{Ca}^{2+}}^0/(10^{-4} \text{ m}^2 \Omega^{-1} \text{ mol}^{-1})$	$D^0/(10^{-9} \text{ m}^2 \text{ s}^{-1})^a$	$D^0_{\text{exp}}/(10^{-9} \text{ m}^2 \text{ s}^{-1})^b$
298.15	271.70 ^c	76.35 ^c	119.00 ^c	1.335	1.312 ± 0.010
310.15	325.49 ± 0.36	92.38 ^d	140.73	1.659	1.613 ± 0.012

^a These values have been calculated with equation (8).

^b Obtained by extrapolating data at $c \leq 0.05 \text{ mol dm}^{-3}$.

^c From Ref. [8].

^d Value obtained from data in Ref. [19].

The above diffusion limiting values can be compared with those calculated by replacing limiting conductances into the Nernst equation [8]:

$$D^0 = \frac{RT}{F^2} \left(\frac{|z_{\text{Ca}^{2+}}| + |z_{\text{Cl}^-}|}{|(z_{\text{Ca}^{2+}})(z_{\text{Cl}^-})|} \right) \left(\frac{(\lambda_{\text{Ca}^{2+}}^0)(\lambda_{\text{Cl}^-}^0)}{(\lambda_{\text{Ca}^{2+}}^0)|z_{\text{Cl}^-}| + (\lambda_{\text{Cl}^-}^0)|z_{\text{Ca}^{2+}}|} \right) \quad (8)$$

z_i and λ_i^0 being, respectively, the algebraic valence and the molar conductance at infinitesimal concentration of the i ion.

Limiting molar conductivity values at 298.15 K for CaCl_2 aqueous solutions are found in the literature [8]. Nevertheless, at 310.15 K no data have been reported for this electrolyte and, hence, we obtained them. The molar conductivity values performed are shown in Appendix A. At this temperature (310.15 K) these data exhibit a linear relationship, with the concentration square root, up to $7.3 \times 10^{-3} \text{ mol dm}^{-3}$. Such a relationship enables to calculate the molar conductivity at infinitesimal concentration for the CaCl_2 , Λ_0 , according to the Kohlrausch equation. This value was split into both ionic contributions by estimating the value for $\lambda_{\text{Cl}^-}^0 = 92.38 \times 10^{-4} \Omega^{-1} \text{ m}^2 \text{ mol}^{-1}$ from the data in ref [19]. All these molar conductivity values, at both temperatures (298.15 K and 310.15 K), are shown in Table 5.

Another way to obtain this limiting value at 310.15 K is from the Walden product (or Walden rule): $\Lambda^0(T) \eta(T) = \text{cte}$, being $\eta(T)$ the viscosity of the pure solvent at temperature T . Recently, Apelblat has extensively illustrated, by using different electrolytic solutions [20], the usefulness of this empirical relationship, which considers the changes of the solvent viscosity are the responsible of the changes in the conductivity of the ions. From it, a value of $350.12 \times 10^{-4} \text{ m}^2 \text{ mol}^{-1} \Omega^{-1}$ was estimated by using 0.8903 (cP) and 0.6909 (cP) for the viscosity of pure water at 298.15 K and 310.15 K, respectively [21]. The value thus found appreciably differs (more than 7%) with respect to the experimental one.

By inserting both limiting molar ionic conductivities into equation (8), limiting diffusion coefficients, D^0 , are estimated at both temperatures. They are also shown in Table 5. As it can be ascertained, the values thus derived agree quite well (with differences <3%) with those calculated by extrapolating our experimental data (given in the last column). As a consequence of that, it can be inferred that the diffusion data here reported are acceptable within the experimental error (<3%). In the same way, the limiting molar conductivity value calculated for the calcium ion at 310.15 K ($140.73 \times 10^{-4} \Omega^{-1} \text{ m}^2 \text{ mol}^{-1}$) can also be acceptable within a confidence of 97%.

4. Conclusions

The experimental values for CaCl_2 diffusion coefficients fit a second-order polynomial function in both the concentration ($0.005\text{--}0.1 \text{ mol dm}^{-3}$) and temperature (298.15 K and 310.15 K) ranges studied. Consequently, accurate values at infinitesimal concentration, D^0 , were obtained.

Because these D results adjust properly the Onsager–Fuoss model up to 0.01 mol dm^{-3} , it is possible to suggest that, in this concentration range, the calcium and chloride ions are the predominant species responsible for the transport and the ionic association and the hydrolysis effect can be neglected. At higher concentration, the behaviour of this electrolyte strongly depends on both the viscosity changes of the solution and on the hydration of the ions.

Limiting values, D^0 , calculated from the Nernst equation agree well with the extrapolated experimental ones and, consequently, the $\lambda_{\text{Ca}^{2+}}^0$ value estimated for 310.15 K can be considered adequate.

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Appendix A. Experimental molar conductances for CaCl_2 aqueous solutions at 310.15 K

$c/(10^{-3} \text{ mol dm}^{-3})$	$\Lambda/(10^{-4} \Omega^{-1} \text{ m}^2 \text{ mol}^{-1})$
0.6234	297.70
1.244	286.47
1.861	278.19
2.475	271.14
3.086	264.32
3.695	258.64
4.300	253.54
4.902	248.57
5.501	244.04
6.098	239.76
6.691	235.72
7.282	230.69

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