

Mutual Diffusion Coefficients of Alkaline-Earth and Third-Family Metal Chlorides in Aqueous Solutions

R. Castillo^{1,2} and C. Garza¹

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Measurements of mutual diffusion coefficients of several metal chlorides in aqueous solutions close to infinite dilution have been made with the Taylor dispersion technique. Data were obtained for alkaline-earth metal chlorides, $\text{BeCl}_2/\text{H}_2\text{O}$, $\text{MgCl}_2/\text{H}_2\text{O}$, $\text{CaCl}_2/\text{H}_2\text{O}$, $\text{SrCl}_2/\text{H}_2\text{O}$, and $\text{BaCl}_2/\text{H}_2\text{O}$, and for third-family metal chlorides, $\text{AlCl}_3/\text{H}_2\text{O}$, and $\text{GaCl}_3/\text{H}_2\text{O}$. All the measurements were obtained at five temperatures between 298.15 and 318.15 K. A linear dependence between the mutual diffusion coefficient and temperature was found. In the range of temperatures studied here, the values of the mutual diffusion coefficients follow a sequence: $\text{BaCl}_2 > \text{SrCl}_2 > \text{CaCl}_2 > \text{MgCl}_2 > \text{BeCl}_2$ for alkaline-earth metal chlorides and $\text{GaCl}_3 > \text{AlCl}_3$ for third-family metal chlorides. That is, the higher the atomic weight of the cation, the higher the mutual diffusion coefficient. A comparison of mutual diffusion coefficients of alkaline, alkaline-earth, and third-family metal chlorides is presented.

KEY WORDS: aqueous solutions; diffusion coefficients; electrolytes; Taylor dispersion.

1. INTRODUCTION

When an electrolyte is dissolved in water, it does not diffuse as a single molecule. Instead, the anions and the cations move correlated through the solution. This phenomenon gives rise to several related diffusion coefficients [1]. Examples of these coefficients are the mutual diffusion coefficient (MDC) for the salt taken as a single entity and the ionic diffusion coefficients for the resulting ions in solution [1, 2]. The MDC measures the rate at which the concentration fluctuations (gradients) in a solution approach their equilibrium values. Therefore, the decay of these gradients to obtain the equalization of the concentration throughout the binary mixture takes place

¹ Instituto de Física, Universidad Nacional Autónoma de México, P.O. Box 20-364, D.F. 01000, México.

² To whom correspondence should be addressed.

by direct change of the composition of every small portion of the fluid. The thermodynamic theory of interdiffusion [1, 3] has provided unequivocal statements concerning the minimum number of independent coefficients required to describe the mass transport in an isothermal electrolyte fluid.

Most of the published work studying the MDC of electrolytes in aqueous solutions is concerned with its dependence on concentration or the development of useful techniques to do reliable measurements in electrolyte systems. Hence, it is not surprising that there are still many questions without a clear answer or validation by experimental verification. In particular, one question that has not been answered by the current literature is, How does the MDC depend on temperature? An answer can be obtained using the Nernst–Hartley equation, corrected to take into account the Onsager cross-coefficient [4]. However, this equation must be used in conjunction with extensive ionic-conductivity and electrochemical experimental data, hence, this is not very illuminating. Quite recently, our group became interested in this problem and presented the temperature dependence of the MDC for alkali–metal chlorides in aqueous solution very close to infinite dilution [5]. The purpose of the present paper is to show the temperature dependence of the MDC for alkaline–earth metal chlorides and for two third-family (IIIB) metal chlorides in water solutions, all of them very close to infinite dilution. Our measurements were done following the Taylor dispersion technique.

MDCs for alkali–metal chlorides in water solutions have been determined by several experimental methods, some of them quite accurate [6]. The concentration dependence of MDC at 298.15 K as a function of the square root of the molarity can be found in Refs. 7 and 8. Of course, theory is quite far from explaining those data. Temperature dependence of MDC for alkali chlorides was presented by us [5]. We found that the variation of MDC with temperature is linear and the values for these diffusion coefficients followed the sequence $\text{CsCl} > \text{RbCl} > \text{KCl} > \text{NaCl} > \text{LiCl}$, for all temperatures. That is, the higher the atomic weight of the cation, the higher the MDC.

MDCs for alkaline–earth metal chlorides in water solution have been determined by several experimental methods, addressed mainly to studying their concentration dependence at 298.15 K. The most accurate experimental results come from Miller and his colleagues for MgCl_2 [9], CaCl_2 [10], SrCl_2 [8], and BaCl_2 [11]. In all of these cases, they used the free-diffusion Rayleigh interferometry method. Previously, there were other measurements by Harned and Polestra [12, 13] for SrCl_2 , BaCl_2 , and CaCl_2 , using the conductometric method, and by Hashitani and Tamamushi [14] for BaCl_2 and CaCl_2 , using the diaphragm-cell method. In the same way as in the case of alkaline–metal chlorides, theory is quite

far from explaining the experimental results. As far as we know, there are no measurements for determining the temperature dependence of the MDC for alkaline-earth metal chlorides.

For the case of third-family metal chlorides, experimental data are very scarce. For AlCl_3 , there are some measurements for self-diffusion in water solution using the NMR pulsed-field-gradient method [15]. Intra-diffusion coefficients for gallium have been measured in aqueous solutions of gallium perchlorate using the diaphragm-cell method [16]. As far as we know, there are no MDC measurements in aqueous solution for other metal chlorides of this family (IIIB).

For a single electrolyte in a neutral solvent, there is only one independent mutual diffusion coefficient (D_1) [1, 3]. This coefficient at infinite (D_1^∞) dilution can be related to other quantities, in particular, to ionic mobility which has been studied extensively. There are three pictures trying to explain what determines the mobility of an ion in a liquid, all of them at infinite dilution. In the first one, the solvent molecules near the ion are thought to be rigidly bound to the charged particle, creating a particle much larger than the bare ion. This larger particle moves like a Brownian particle, hence reducing its original ion mobility. This picture is referred as the "solventberg" model. The second picture is known as the "continuum dielectric friction" model. In this model, the ion is treated as an impenetrable sphere with a symmetric charge distribution, while the surrounding solvent is regarded as an incompressible fluid having uniform viscosity and dielectric constant. The method for obtaining the mobility is based on an extension of Stokes' law so as to incorporate the so-called "dielectric friction." The most complete analysis using this picture is due to Hubbard and Onsager [17, 18]. The third picture is based on the "molecular" model developed by Wolynes [19, 20], where the solventberg model and the dielectric friction model can be found as limiting cases. Evans et al. [21] have shown how the continuum dielectric friction model and the molecular model predict finite mobilities as the ionic size decreases, thus, they can successfully account for some of the observed features of the conductivity data. However, they are far from explaining the experimental data. Therefore, it appears that none of the theoretical descriptions of ion mobility is entirely satisfactory.

Altenberg, Zhong, Friedman, and co-workers [23–25] have developed a theory of transport in electrolyte solutions that is capable of giving diffusion coefficients up to the molar range for solvent-averaged models. It has been formulated at the Smoluchowsky level. Those authors have been able to calculate the self-diffusion and distinct diffusion coefficients of the ions or, what is equivalent, the self and distinct parts of the relevant Onsager phenomenological coefficients. This theory has been tested using several specific models for aqueous solutions, with success in some cases [25].

Molecular dynamics simulation studies to obtain ion mobility in aqueous solutions have appeared in the literature, devoted mainly to study alkaline ions [22, 26–28]. Quite recently, Lee and Rasaiah [29] have presented the most valuable molecular dynamics simulation study to understand the ionic mobility of Li^+ , Na^+ , K^+ , Rb^+ , and Cs^+ in an electric field and in its absence. They reported diffusion coefficients from their molecular dynamics study calculated from the mean square displacement and from velocity autocorrelation functions. They found that the water molecules in the first solvation shell around the small Li^+ ion are stuck to the ion and move with it as an entity for about 190 ps. While the water molecules around the Na^+ ion remain for 35 ps, and those around large cations stay for 8–11 ps before significant exchange with the surroundings occurs. The picture emerging from this study is that of a solvated cation whose mobility is determined by its size, as well as the static and dynamic properties of its solvation sheath and the surrounding water.

This paper is organized as follows. In Section 2 we describe the instrument design, and in Section 3 some specific experimental details are presented. Our results and a discussion are presented in Section 4.

2. EXPERIMENTAL PROCEDURE

2.1. Instrument Design and Operation

The Taylor dispersion technique is based on the dispersion, by the joint action of convection and molecular diffusion, of an injected binary-mixture pulse in a laminar flowing stream of the same mixture at slightly different composition. Under adequate conditions, the pulse concentration profile will eventually become normal, and the center of gravity of the profile will move with the mean velocity of the laminar flow. The theory for the development of an ideal equipment to measure MDCs using this method was revised by Alizadeh et al. [30] Furthermore, they presented detailed criteria for the design of a practical instrument for measuring MDCs. In the present paper, we followed that work in order to design a measuring instrument, and the details of our instrument were presented in Ref. 31.

Alizadeh et al. derived expressions for the volume-fixed MDC for an ideal instrument, in terms of the first (\bar{t}) and second (σ^2) temporal moments of the distribution of the dispersed pulse. These expressions can be written as

$$D_1^v = \frac{(1 + 2\zeta)}{\zeta} \frac{a_0^2}{48\bar{t}_{id}} \quad (1)$$

where

$$\zeta = \frac{2\sigma_{\text{id}}^2 - \bar{t}_{\text{id}}^2 + \{\bar{t}_{\text{id}}^4 + 4\bar{t}_{\text{id}}^2\sigma_{\text{id}}^2\}^{1/2}}{\{8\bar{t}_{\text{id}} - 4\sigma_{\text{id}}^2\}} + \delta\zeta \quad (2)$$

Here a_0 is the capillary radius, and $\delta\zeta$ is a correction due to the use of a weaker condition on the diffusion time. For details see Refs. 30 and 31.

In addition, Alizadeh et al. [30] derived a set of corrections for this ideal instrument in order to include the deviations of a practical instrument. They found that the ideal moments have to be corrected according to

$$\bar{t} = \bar{t}_{\text{exp}} + \sum \delta\bar{t}_i \quad (3)$$

and

$$\sigma^2 = \sigma_{\text{exp}}^2 + \sum \delta\sigma_i^2 \quad (4)$$

where \bar{t}_{exp} and σ_{exp}^2 denote the experimentally determined moments, and the $\delta\bar{t}_i$ and the $\delta\sigma_i^2$ are the corrections to be applied. For details see Refs. 30 and 31.

The values of \bar{t}_{exp} and σ_{exp}^2 were determined with a nonlinear fitting program of the digitized values corresponding to the analogical signal of a differential refractometer (Waters 402). This instrument was used to determine the temporal shape of the injected pulse, in the region where it has a linear response to the concentration difference between the cells. Data acquisition was carried out using a data acquisition board (PC-LabCard, Advantech, Co.) and a Printaform PC.

2.2. Experiments

Metal chlorides were supplied by Johnson Mathey Company (USA)—BeCl₂, 99.5%; and GaCl₃, 99.999%—and by J. T. Baker (USA and Mexico)—MgCl₂ · 6H₂O, 99.5%; CaCl₂, 99.7%; SrCl₂ · 6H₂O, 99.8%; BaCl₂ · 2H₂O, 99%; and AlCl₃ · 6H₂O, 99.99%. They were dried for 2 or 3 h before the preparation of solutions. Doubly distilled water was used throughout. The aqueous mixtures used for the injected δ peaks were prepared with an estimated error in the quoted mole fractions of less than 1×10^{-5} . Special care was taken to degas the aqueous mixtures in an ultrasonic bath without inducing concentration changes. The solutions of GaCl₃ used were very dilute and prepared in cold water to avoid decomposition of the salt.

In the determination of the MDCs described above, we followed the common practice of employing the reproducibility of the results of a series of experiments, under nominally identical experimental conditions, as a measure of the precision of the observations. Hence, we determined the values of \bar{t}_{exp} and σ_{exp}^2 , and after considering the mentioned corrections, we obtained a mean precision better than 1.5%. Taking into account several uncertainties related to the cross-section area and the length of the diffusion tube, etc., the overall accuracy of the reported diffusion coefficients is estimated to be of 2.5%.

Our measurements were performed at almost-infinite dilution, namely, at a concentration between one and two orders of magnitude lower than previous work reported in the literature. Hence, following the principle of the Taylor dispersion technique, we had pure water flowing through the capillary tubing and injected the salt mixture pulse at a specified, but very dilute, concentration. The diffusion coefficient obtained corresponds to the salt molar concentration given by

$$C_{1r} = C_{1f} + \delta C_1 \quad (5)$$

where C_{1f} is the flowing-stream composition (zero in our case), and δC_1 is a small correction described in Refs. 30 and 31.

3. RESULTS AND DISCUSSION

In Table I, we present the results of our measurements for several temperatures all of them close to infinite dilution, and the reference concentrations for all the measurements. Our MDCs were not determined at infinite dilution, but at a concentration lower than the most diluted of the

Table I. Volume-Fixed Mutual Diffusion Coefficients Close to Infinite Dilution^a

| T (K) | $10^9 D_1$ ($\text{m}^2 \cdot \text{s}^{-1}$) | | | | | | |
|---------|--|--|---|--|--|--|--|
| | BeCl ₂ (8.12 $\times 10^{-6}$) | MgCl ₂ (8.94 $\times 10^{-6}$) | CaCl ₂ (9.6 $\times 10^{-6}$) | SrCl ₂ (5.97 $\times 10^{-6}$) | BaCl ₂ (6.33 $\times 10^{-6}$) | AlCl ₃ (6.52 $\times 10^{-6}$) | GaCl ₃ (82.4 $\times 10^{-6}$) |
| 298.15 | 1.10 | 1.15 | 1.22 | 1.21 | 1.29 | 1.02 | 1.25 |
| 303.15 | 1.23 | 1.31 | 1.38 | 1.38 | 1.44 | 1.16 | 1.50 |
| 308.15 | 1.39 | 1.46 | 1.55 | 1.56 | 1.65 | 1.33 | 1.77 |
| 313.15 | 1.52 | 1.65 | 1.74 | 1.71 | 1.81 | 1.50 | 2.06 |
| 318.15 | 1.71 | 1.83 | 1.93 | 1.87 | 1.96 | 1.70 | 2.50 |

^a Concentration (mole fraction) is given under the substance, in parentheses.

solutions used by Miller and his associates, who have the most accurate data. Therefore, it is difficult to test the accuracy of our experiments against theirs. To obtain a rough estimate of our accuracy, we extended the results of Miller and colleagues by numerical fitting for the systems that we have in common, at the only temperature they worked on, 298.15 K. The percentage deviations of our data from their extended data are the following: 1.7% for $MgCl_2$, 0.8% for $CaCl_2$, 3.2% for, $SrCl_2$, and 0% for $BaCl_2$. Considering that we are making comparisons with extended data in a region where the MDC has a rapid variation with the concentration and, therefore, the numerical fitting could be not good enough, we can say that our results are in good agreement with those of Miller and his associates.

Figure 1 shows the MDC vs temperature for alkaline-earth and third-family metal chlorides. Here, for comparison we included the MDC for alkaline metal chlorides [5]. A linear relation between the MDC and the temperature can be observed in the range of temperatures studied here.

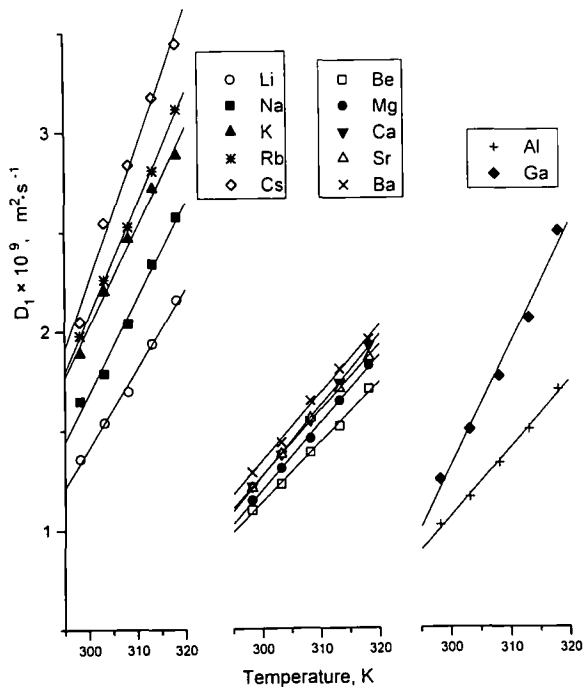


Fig. 1. Temperature dependence of the mutual diffusion coefficients for aqueous solutions of alkaline, alkaline-earth, and third-family metal chlorides close to infinite dilution.

Table II. Parameters of the Linear Temperature Dependence for the Mutual Diffusion Coefficient of Metal Chlorides in Water Close to Infinite Dilution^a

| | $10^9 D_1$ ($\text{m}^2 \cdot \text{s}^{-1}$) | |
|-------------------|---|----------|
| | <i>A</i> | <i>B</i> |
| LiCl | -10.59 | 0.040 |
| NaCl | -12.77 | 0.048 |
| KCl | -13.10 | 0.050 |
| RbCl | -14.90 | 0.057 |
| CsCl | -18.32 | 0.067 |
| BeCl ₂ | -7.92 | 0.030 |
| MgCl ₂ | -8.10 | 0.034 |
| CaCl ₂ | -9.41 | 0.036 |
| SrCl ₂ | -8.62 | 0.033 |
| BaCl ₂ | -8.91 | 0.034 |
| AlCl ₃ | -9.13 | 0.034 |
| GaCl ₃ | -17.04 | 0.061 |

^a Alkaline chlorides from data in Ref. 5. $10^9 D_1 = A + BT$, where T is in K.

Table II presents the parameters of the best linear fit for those linear relations. Also, in Fig. 1, we can see some interesting features: the MDCs for the alkaline-earth metal chlorides present the least variation with temperature of the three-family metal chlorides presented there, and their values are quite similar. The slopes for all the lines presented in Fig. 1 are very close, although for the case of alkali metals, their slopes increase progressively as the molecular weight of the cation increases (from 0.040 to 0.069). For alkaline-earth metals the slopes are quite constant (~ 0.034). For the case of third-family metal chlorides, the line of AlCl₃ presents a slope very similar to that of alkaline metal chlorides and GaCl₃ presents a very large slope close to that of CsCl or RbCl.

In the range of temperatures studied here, the values of the MDC in a particular family follow a sequence CsCl > RbCl > KCl > NaCl > LiCl for alkaline metal chlorides, BaCl₂ > SrCl₂ > CaCl₂ > MgCl₂ > BeCl₂ for alkaline-earth metal chlorides, and GaCl₃ > AlCl₃ for third-family metal chlorides. That is, the higher the atomic weight of the cation, the higher the MDC.

Figure 2 presents the MDC vs temperature for two periods in the periodic table. Here, for the case of NaCl, MgCl₂, and AlCl₃, the

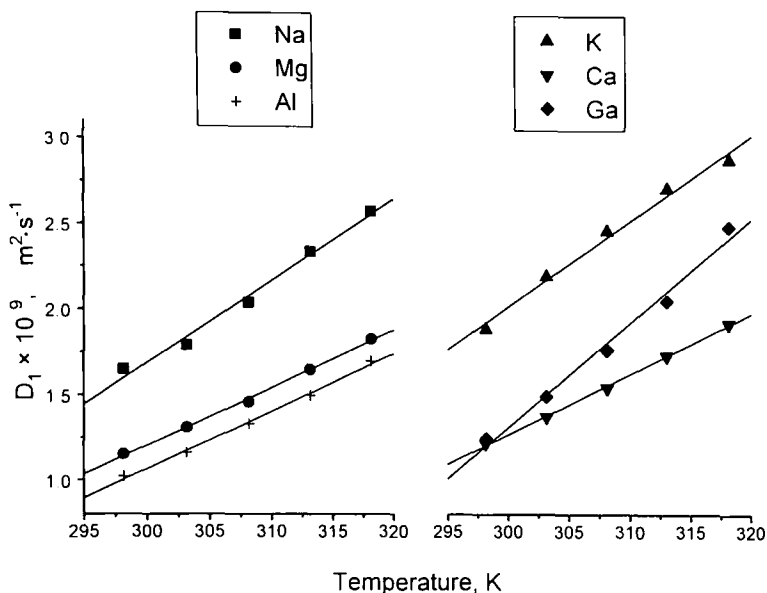


Fig. 2. Temperature dependence of the mutual diffusion coefficient for aqueous solutions of metal chlorides for two periods in the periodic table.

temperature dependence is quite similar and the MDCs decrease as we go to the right in the periodic table, i.e., in the direction of increasing the charge of the cations. This decreasing of the MDC as we go to the right in the periodic table could be explained by a solvation shell as it is invoked in the "solventberg" model, since, on one hand, the larger the charge of the ion, the larger the solvation shell and, on the other, going to the right in the periodic table, ions have a smaller size. Thus, polarization of water molecules seems to be more effective. On the contrary, for the case of KCl, CaCl₂, and GaCl₃, the MDCs for CaCl₂ are smaller than those for GaCl₃. Therefore, the sequence in the periodic table is not followed, even when the qualitative arguments of the "solventberg" are more favorable for this case.

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