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# Temperature Dependence of the Mutual Diffusion Coefficients in Aqueous Solutions of Alkali Metal Chlorides

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Measurements of mutual diffusion coefficients at infinite dilution in aqueous solutions of alkali-metal chlorides have been made with the Taylor dispersion technique. Data were obtained for the series $LiCl/H_2O$, $NaCl/H_2O$, $KCl/H_2O$, $RbCl/H_2O$, and $CsCl/H_2O$, at five temperatures between 298.15 and 318.15 K. A linear dependence with temperature was found. This technique is very convenient in comparison with other more time-consuming techniques.

**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 gives rise to several related diffusion coefficients. Examples of these coefficients are the mutual diffusion coefficient (MDC) for the salt taken as a single entity [1–20] and the ionic diffusion coefficients related to the electrolytic mobility and to Hittorf transport numbers [1, 21, 22]. Mutual diffusion of aqueous solutions of electrolytes is a property available for relatively few systems, due mainly to the large amount of effort involved in performing the experiments and to the lack of a suitable microscopic theory that could explain the basic features of the MDCs over wide ranges of concentration, temperatures, and pressures. Hence, mutual diffusion data for electrolyte solutions are scarce.

Most of the works related to diffusion in water solutions of electrolytes

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are concerned with the concentration dependence of the MDC or the development of a useful technique to do reliable measurements of MDCs in electrolyte systems. Hence, it is not surprising that there are many questions without a clear answer or validated by experimental verification. In particular, one important question that cannot be answered from the current literature is. How does the MDC depend on temperature? The only answer that one can obtain comes from the Nernst-Hartley equation, corrected to take into account the Onsager cross-coefficient [23]. But this equation must be used in conjunction with a lot of experimental ionic conductivity and electrochemical data and, hence, is not very illuminating.

Mutual diffusion coefficients of water solutions of alkali chlorides have been determined by several experimental methods. First, we can find measurements performed by observing the rate of diffusion through a porous plate [2–8]. These are usually variations of the diaphragm-cell technique developed a long time ago by Northrop and Anson [9]. A second method to measure MDCs is variations of the restricted diffusion conductance method developed by Harned and his colleges [10, 11–14]. Other techniques have also been used, such as the open-ended capillary method [15] and optical interferometric methods [16–19]. All these methods have several drawbacks, related mainly to the large amount of effort involved in performing the experiments. They are usually time-consuming and need a lot of systematic measurements over very long times. Clear examples can be given. Harned and his associates [10–13], who used a restricted diffusion cell and whose results remain the most exact and extensive in this field, reported that after 24–36 h of diffusion, the measurements were suitable for calculating the diffusion coefficients. They took readings every 2–4 h over several days. The same situation applies to the modified conductance cell of Kamakura [14], who estimated the diffusion coefficient making a lot of measurements, and at the end, a extrapolation process was needed to obtain reliable values. Probably, better measurement times were obtained by Hashitani and Tamamushi [6]. They used a diaphragm-cell method, and the experimental runs took less than 90 min, which is about 1/50th of the time in the conventional diaphragm method, however, other problems limit the use of this cell, such as adsorption effects, leakage, and calibration. Optical methods, although precise, involve a large amount of effort related to the interpretation of the photographic recors [18, 19]. Another problem with several of the above-mentioned methods is that there are no reliable working equations. Hence, it is difficult to estimate the errors that appear when an ideal instrument, for which the theory is usually developed, is implemented as a practical instrument. Notwithstanding the experimental difficulties, the reproducibility of some methods is quite good [10–13, 17–19].

The purpose of this paper is twofold. The first is to show that the Taylor dispersion technique [24, 25] can give reliable MDCs for electrolytic solutions. This technique is widely used for the measurement of mutual diffusion in organic mixtures [26–30], and as far as we know, no one has used this technique for electrolytes. This technique has several advantages; some of them are very attractive in comparison with the others mentioned above. For instance, in our experiments we can perform measurements every 30–45 min, and after approximately 10 measurements a final MDC value is obtained with the necessary statistical treatment. In addition, for this technique there is a full set of working equations and corrections for a working instrument [25]. This allows us to assess the accuracy of the measurements. The second purpose of this paper is to determine the temperature dependence of the MDCs at infinite dilution for aqueous solutions of alkali-metal chlorides (LiCl, NaCl, KCl, RbCl, and CsCl). Data were obtained at five temperatures.

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

## 2. INSTRUMENT DESIGN AND OPERATION

The Taylor dispersion technique [24, 25] is based on the dispersion of an injected binary-mixture pulse in a laminar flowing stream of the same mixture at slightly different composition, by the joint action of convection and molecular diffusion. Under proper 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 ideal equipment to measure MDCs with this method was revised by Alizadeh et al [25]. 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. 29.

Alizadeh et al. [25] derived expressions for the volume-fixed MDC in terms of the first ($\bar{t}$) and the second ($\sigma^2$) temporal moments of the distribution of the dispersed pulse for an ideal instrument. These expressions can be written as

$$D_{12}^{V} = \frac{(1+2\zeta)}{\zeta}\,\frac{a_0^2}{48\bar{t}_{\mathrm{id}}} \tag{1}$$

where

$$\zeta = \frac{2\sigma_{\mathrm{id}}^2 - \bar{t}_{\mathrm{id}}^2 + \left\{\bar{t}_{\mathrm{id}}^4 + 4\bar{t}_{\mathrm{id}}^2\sigma_{\mathrm{id}}^2\right\}^{1/2}}{\left\{8\bar{t}_{\mathrm{id}}^2 - 4\sigma_{\mathrm{id}}^2\right\}} + \delta\zeta \tag{2}$$

Here $a_0$ is the capillary radius, and $\delta\zeta$ is a correction due to the use of weaker conditions on the diffusion time. For details see Ref. 25.

In addition, Alizadeh et al. [25] 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

$$\bar{t} = \bar{t}_{\text{exp}} + \sum \delta \bar{t}_i \qquad \text{and} \qquad \sigma^2 = \sigma^2_{\text{exp}} + \sum \delta \sigma_i^2 \tag{3}$$

where $\bar{t}_{\text{exp}}$ and $\sigma^2_{\text{exp}}$ denote the experimentally determined moments, and $\delta\bar{t}_i$ and $\delta\sigma_i^2$ are corrections to be applied. For details see Refs. and 29.

The values of $\bar{t}_{\text{exp}}$ and $\sigma^2_{\text{exp}}$ were determined with a nonlinear fitting program of the digitized values corresponding to the analogycal signal of a differential refractometer. 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. The acquisition of data was performed with a data acquisition board (Lab Master DMA, Scientific Solutions, inc.) and a Printaform PC.

## 3. EXPERIMENTS

Alkali metal chlorides of 99.8% were supplied by Aldrich Chemical Co. Inc. (CsCl, RbCl, LiCl) and J. T. Baker Co. (NaCl, KCl). They were dried for 2 or 3 h before the preparation of solutions. Doubly distilled water was used. The aqueous mixtures used as injected $\delta$ peaks were prepared with an estimated error in the quoted mole fractions of less than $1 \times 10^{-5}$. Special care was taken to degas the aqueous mixtures in an ultrasonic cleaner without inducing concentration changes.

In the determination of MDCs as 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 determinations. Hence, we determined the values of $\bar{t}_{\text{exp}}$ and $\sigma^2_{\text{exp}}$, and after doing the mentioned corrections [25, 29] we obtained a mean precision better than 2.5%. Taking into account several uncertainties, related to the cross-sectional area and length of the diffusion tube, corrections, etc., the overall accuracy of the reported diffusion coefficients is estimated to be of 3.5%.

Our measurements were performed at almost-infinite dilution, namely, at a concentration between one and two orders of magnitude lower than previous reported work 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

$$C_{1r} = C_{1f} + \delta C_1 \tag{4}$$

where $C_{1f}$ is the flowing-stream composition (zero in our case), and $\delta C_1$ is a small correction described in Ref. 25.

## 4. RESULTS

Table I gives the results for several temperatures, all of them in the infinite dilution region. These results are also shown in Figs. 1 and 2.

Comparisons with experimental data coming from other sources [18, 19] cannot be done directly, since the MDC data were not obtained close enough to infinite dilution. At 298.15 K, data for infinite dilution have been compiled by Robinson and Stokes [31] and by Koryta and Dvorak [32]. The percentage deviations between our data and their data are −0.44, 2.61, −3.46, and 0.19 for LiCl, NaCl, RbCl, and CsCl, respectively. These authors also present compiled data for KCl at 298.15 and 303.15 K; the percentage deviations are −5.37 and −1.34, respectively.

As can be seen from Figs. 1 and 2, for all temperatures the values for the MDCs of the systems under study follow the sequence:

$$\text{CsCl} > \text{RbCl} > \text{KCl} > \text{NaCl} > \text{LiCl}$$

that is, the higher the molecular weight of the cation, the higher the MDC. Cation hydration numbers usually decrease with atomic number for alkali

**Table I.** Volume-Fixed Mutual Diffusion Coefficients for the Systems MCl–$H_2O$[a]

| | $D_{12}^{V} \times 10^{-9} (m^2 \cdot s^{-1})$ | | | | |
|---|---|---|---|---|---|
| $T$ (K) | LiCl[a] | NaCl[b] | KCl[c] | RbCl[d] | CsCl[e] |
| 298.15 | 1.36 | 1.65 | 1.89 | 1.98 | 2.05 |
| 303.15 | 1.54 | 1.79 | 2.20 | 2.26 | 2.55 |
| 308.15 | 1.70 | 2.04 | 2.48 | 2.53 | 2.84 |
| 313.15 | 1.94 | 2.34 | 2.72 | 2.81 | 3.18 |
| 318.15 | 2.16 | 2.58 | 2.89 | 3.12 | 3.45 |

[a] Concentration (mole fraction); $a = 1.52 \times 10^{-4}$; $b = 1.75 \times 10^{-4}$; $c = 0.88 \times 10^{-4}$; $d = 0.60 \times 10^{-4}$; $e = 1.29 \times 10^{-4}$.

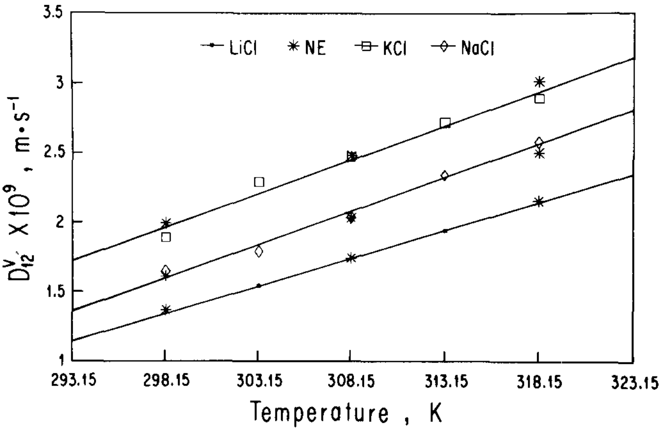

**Fig. 1.** Temperature dependence of the mutual diffusion coefficients of aqueous solutions of LiCl, KCl, and NaCl at infinite dilution, determined with the Taylor dispersion technique. The predictions of the Nernst equation (NE) for these systems are presented too.

chlorides. Cation decreased hydration should result in increased diffusion rates, since larger ions would have smaller hydrated radii [32]. This agrees well with our results. Moreover, we observe that the variation of the diffusion coefficient with temperature is linear. The data for each alkali metal were fitted by least-squares to a linear equation, and the correlation for

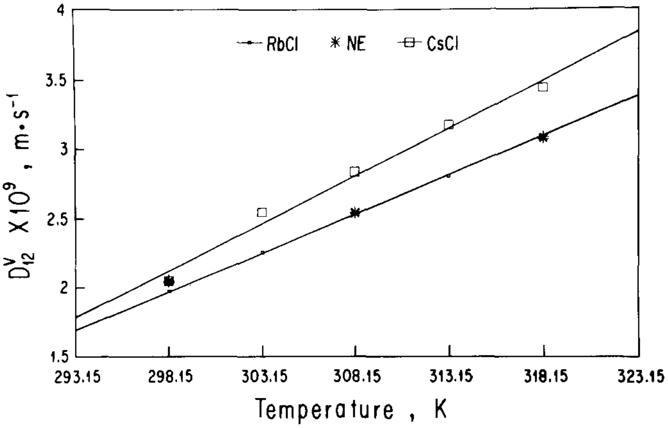

**Fig. 2.** Temperature dependence of the mutual diffusion coefficients of aqueous solutions of RbCl and CsCl at infinite dilution, determined with the Taylor dispersion technique. The predictions of the Nernst equation (NE) for these systems are presented too.

**Table II.** Parameters of the Linear Temperature Dependence of the Mutual Diffusion at Infinite Dilution[a]

| | $D_{12}^{V}(\mathrm{m}^2 \cdot \mathrm{s}^{-1}) = aT\,(\mathrm{K}) + b$ | | | |
|---|---|---|---|---|
| | $a$ | $s_a$ | $b$ | $s_b$ |
| LiCl | 0.040 | 0.002 | 0.345 | 0.065 |
| KCl | 0.050 | 0.003 | 0.669 | 0.109 |
| NaCl | 0.048 | 0.003 | 0.394 | 0.118 |
| RbCl | 0.056 | 0.001 | 0.561 | 0.026 |
| CsCl | 0.068 | 0.005 | 0.426 | 0.165 |

[a] The $s_i$ are the standard deviations for the slope and for the intercept.

each case was better than 0.99. The parameters for the linear regressions are presented in Table II.

In very dilute aqueous electrolyte solutions, the ions are so far apart that long-range Coulomb forces are the principal interaction and specific effects are negligible. Consequently, many ionic properties are additive, and on this basis one can derive the limiting expression for mutual diffusion at infinite dilution as given by the Nernst equation [1]. In addition to the experimental data, Figs. 1 and 2 present MDCs at infinite dilution calculated with the Nernst equation for the systems of interest here, at three temperatures. These calculations were done on the basis of the ionic conductivities at infinite dilution given in Ref. 32, for several temperatures. The comparison between MDCs calculated with the Nernst equation and our experimental data is quite good, except for the case of CsCl. The bad fitting for CsCl is because RbCl and CsCl have almost-identical ionic conductivities at infinite dilution [32]. We cannot explain the source of this discrepancy. The root mean square of the percentage deviations between our experimental results, and the numbers obtained from the Nernst equation is equal to 2.6, except for the case of CsCl. For this case, the root mean square of the percentage deviations is 9.9.

It is important to recall the limited reach of the Nernst equation to predict and to understand the behavior of the MDC at infinite dilution, since this equation needs of limiting ionic conductivities for the ions in solution. Nevertheless, theoretical developments to obtain these quantities are very limited [33].

The partial success of relating different electrolyte properties, with the aid of linear irreversible thermodynamics [23], has led to the erroneous perception that the problem of understanding the behavior of MDCs as a function of concentration or temperature, is solved. For the case of concentration dependence, there are several open questions related with crossovers in the MDC–concentration curves for periodic series and with the microscopic significance of the minimums and the maximums in these curves [19]. For the case of temperature dependence, as far as we know, this is the first work devoted to study the temperature dependence of MDC, although there are reported measurements for KCl at three different temperatures [12].

We hope that this paper will stimulate the measurement of MDCs in electrolyte systems by the Taylor dispersion technique.

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