

# Mutual diffusion coefficients of concentrated 1:1 electrolyte from the modified mean spherical approximation

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## Abstract

Mutual diffusion coefficients of concentrated 1:1 electrolyte solutions are investigated using a modified mean spherical approximation (MSA), in which the effective cationic diameter is a function of total ionic strength. We apply this improved MSA to calculate the equilibrium pair correlation function, and the Smoluchowski equation is used for the dynamics. We compare the calculated mutual diffusion coefficients of 18 uni-valence electrolyte solutions for molar concentrations up to 4.0 mol/L known experimental data. Good agreement between theoretical results and the experimental mutual diffusion coefficients are found for all the cases studied.

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## 1. Introduction

Aqueous electrolyte solutions are involved in many industrial processes, such as extractive distillation, solution crystallization, ion exchange, membrane separation, wastewater treatment, absorption refrigeration, etc. They also appear in every-day life as detergents, dyes and carriers in drug delivery systems as well. The knowledge of their properties, especially the transport properties are vital not only for the design and optimization of various chemical and environmental engineering processes but also for the understanding of charged particle solutions. Due to the strong interactions of long-ranged Coulomb forces and the solvation of ions, electrolyte solutions exhibit appreciable deviations from ideal solution behavior, particularly at high concentration [1–3]. Consequently, the description of their transport properties is a significant theoretical challenge.

After decades of research, there has been great progress in the theoretical investigation on the electrolyte solution. A variety of approaches, including hydrodynamic theory, kinetic theory, and statistical mechanics, have been applied to the problem of predicting liquid mass-transport properties [4]. Statistical mechanics becomes one of the most promising approaches

to study electrolyte solutions after the mathematic difficulties involved were overcome by Debye and Hückel [5] by introducing the concept of “ionic atmosphere” to compute the thermodynamic properties of this system in very dilute solution.

Onsager and Fuoss [6] developed a limiting law for the variation of the diffusion coefficients and the conductivity with concentration, which is essentially an extension of Debye–Hückel ion atmosphere model. In 1957, Onsager [7] made an attempt to extend the validity of the law to higher concentrations using more accurate equilibrium pair distribution functions. These theories provide a quantitative representation of the relation and electrophoretic effects. But due to the limitations of the Debye–Hückel theory, the models are generally valid only at very dilute condition [8,9]. A major improvement over the classical theories is obtained by some research groups through formulating a linear response theory in which Onsager continuity equations are combined either with the mean spherical approximation (MSA) [10,11] or the hypernetted chain equations (HNC) [12,13]. The theory has been applied to the self-diffusion [14], acoustophoresis [15] and conductance [16] for non-associating electrolytes. The satisfactory agreement between theoretical results and experimental values shows some limited success for these approaches.

Unfortunately, less attention has been paid to the theoretical description of mutual diffusion until Bernard et al. [17] cast a new light on the research in this field. However, the validation

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of the approach is limited below 1.0 mol/L. Furthermore, in these studies a unique hard sphere diameter is taken for a given electrolyte over the whole concentration range. In fact, previous findings have shown a diameter variation with concentration, particularly for cations [1,18]. At the same time, Dufreche et al. [19] took into account the influence of association for 2–2 electrolyte with a chemical model. But the theory is less conclusive. The problem results from the fact that there are many unknown parameters, such as the ion size and the mobility of the pair of ions.

More recently, Dufreche [20] modified Bernard's method to high concentration range up to 4.0 mol/L for four alkali chlorides solutions. Although impressive agreements have been obtained, this approach is not ideal in that the cationic diameter is fixed and tried arbitrarily. To date, no theory is available for the prediction of mutual diffusion in more concentrated electrolyte solutions [8,19].

In this work, we extend the method proposed by Dufreche [20] to higher concentration through introducing an effective cationic diameter, which is a function of total ionic strength. The mutual diffusion coefficients of 13 alkali halides and five other uni-valence electrolyte solutions are reproduced over wide concentration ranges (0–4.0 mol/L). Only two parameters,  $\sigma_0$  and  $\lambda_0$ , are used to represent the effective cationic diameter for a given electrolyte, where  $\sigma_0$  denotes the hydration diameter of the cation at infinite dilution and  $\lambda_0$  represents the variation in hydration effect with the concentration.

## 2. Previous theory

In an electrolyte solution containing only two kinds of ions, the dominant forces that determine the deviations from the ideal behavior of transport processes are assumed to be the relaxation and electrophoretic forces [3,21,22]. The former tends to restore the local electroneutrality perturbed by an external force, while the later, mediated by the solvent, tends to equalize the drift velocities of particles submitted to an external force. In the case of mutual diffusion, the condition of zero current flow requires that both ions move with the same velocity. Thus, the ion atmosphere of a given ion is displaced as a whole and develops no asymmetry. As a result, the electrostatic relaxation effect can be neglected, even in concentrated solution. However, the electrophoretic effect must be taken into account in binary system.

Dufreche [20] calculated the mutual diffusion coefficient of the electrolyte solution by combining the Smoluchowski equation for the thermodynamic and the MSA for equilibrium pair correlation function. The main expressions are outlined below. You can find the detailed derivation in the relevant reference if you are interested. The mutual diffusion coefficient is

$$D_m^S = \frac{Q_{11}D_{21}^* + Q_{22}D_{12}^*}{Q_{11} + Q_{22}} \quad (1)$$

with

$$Q_{ij} = \frac{z_j e^2 \rho_i}{k_B T \epsilon_0 \epsilon_r} \left( z_i D_i^0 + k_B T \sum_{k=1}^2 z_k \Omega_{ik} \right) \quad (2)$$

$$D_{ij}^* = D_i^0 \frac{\partial \beta P}{\partial \rho_i} + k_B T \sum_{k=1}^2 \Omega_{ik} \frac{\partial \beta P}{\partial \rho_k} \quad (3)$$

$$\Omega_{ij} = \frac{2}{3\eta} \rho_j \int_0^\infty r h_{ih}(r) dr \quad (4)$$

where  $\rho_i$  and  $z_i$  are the number density and the ionic charge of the  $i$ th ion, respectively,  $e$  the electronic charge,  $\epsilon_0$  the permittivity of vacuum,  $\epsilon_r$  the relative permittivity of pure water (taken as 78.36 at 298 K),  $k_B$  the Boltzmann constant,  $T$  is the absolute temperature and  $P$  denotes the pressure of electrolyte solution.  $h_{ij}(r)$  is the total correlation function,  $\eta$  the pure solvent viscosity, and  $D_i^0$  is the limiting ionic diffusion coefficient, which is calculated from the corresponding limiting ionic conductivity  $\lambda_i^0$  via Nernst-Einstein relation [3]

$$D_i^0 = \frac{RT}{|z_i| F^2} \lambda_i^0 \quad (5)$$

where  $R$  is the gas constant and  $F$  is the Faraday constant.

Eqs. (1)–(4) give the relationship of mutual diffusion coefficient with the compressibility and electrophoretic correlation, which will be dealt with in the following section.

Because in the MSA theory, Ornstein-Zernike (OZ) equation can be solved analytically, it is widely used to describe the primitive model of electrolyte solution, in which solute ions of an electrolyte solution are modeled as electrically charged hard spheres with different diameters, while the solvent is treated as a continuous dielectric medium. The basic assumption of the primitive model of the MSA for electrolyte solution is

$$g_{ij}(r) = 0, \quad r < \sigma_{ij}, \quad C_{ij}(r) = \frac{-z_i z_j e^2}{\epsilon_r k_B T r}, \quad r > \sigma_{ij} \quad (6)$$

where  $\sigma_{ij} = (\sigma_i + \sigma_j)/2$ .  $\sigma_i$  is the ion diameter of the  $i$ th ion.

Based on Eq. (6), Blum [23] solved the Ornstein-Zernike equation and expressed the MSA shielding parameter  $\Gamma$  as

$$\Gamma^2 = \pi L_B \sum_i \rho_i \left( \frac{z_i - (\pi/2\Delta) \sigma_i^2 P_n}{1 + \Gamma \sigma_i} \right)^2 \quad (7)$$

where

$$L_B = \frac{e^2}{4\pi \epsilon_0 \epsilon_r k_B T} \quad (8)$$

$$P_n = \frac{1}{\Omega} \sum_k \frac{\rho_k z_k \sigma_k}{1 + \Gamma \sigma_k} \quad (9)$$

$$\Omega = 1 + \frac{\pi}{2\Delta} \sum_k \frac{\rho_k \sigma_k^3}{1 + \Gamma \sigma_k} \quad (10)$$

$$\Delta = 1 - \frac{\pi}{6} \sum_k \rho_k \sigma_k^3 \quad (11)$$

The summations in Eq. (7) are carried out over all positive and negative ions,  $\Gamma$  can be solved by a simple iterative procedure

with the initial value of  $K/2$  or  $K/6$ , where

$$K = \left( \sum_k \rho_k^2 z_k \right)^{1/2} \quad (12)$$

Previous studies [24,25] have suggested that it may be possible to set  $P_n=0$  when the ion diameters are not too different from each other or when the Bjerrum length  $L_B$  is large as in molten salt systems. In these cases, the compressibility of electrolyte solutions reduces to the sum of contributions from hard-sphere and long-range electrostatic interactions. The former contribution can be derived from the Boublik–Mansoori–Carnahan–Starling–Leland (BMCSL) equation of state for the hard-sphere mixture.

$$\begin{aligned} \left( \frac{\partial \beta P}{\partial \rho_i} \right)^{\text{HS}} &= \frac{1}{\Delta} + \frac{3\sigma_i X_2 + 3\sigma_i^2 X_1 + \sigma_i^3 X_0}{\Delta^2} \\ &+ \frac{\sigma_i^2 X_2^2 (9 - 3X_3) + \sigma_i^2 X_2 (6X_1 - X_2^2)}{\Delta^3} \\ &+ \frac{\sigma_i^3 X_2^3 (9 - 3X_3)}{\Delta^4} \end{aligned} \quad (13)$$

The latter contribution is given by

$$\left( \frac{\partial \beta P}{\partial \rho_i} \right)^{\text{C}} = - \frac{L_B \Gamma^2 Z_i^2}{2(1 + \Gamma \sigma_i)^2 (\Gamma + \sum_k \rho_k (\pi L_B Z_k^2 \sigma_k) / (1 + \Gamma \sigma_k)^3)} \quad (14)$$

where

$$X_i = \frac{\pi}{6} \sum_k \rho_k \sigma_k^i \quad (15)$$

As for electrophoretic corrections, the contribution can be expressed as the sum of three terms

$$\Omega_{ij} = \Omega_{ij}^{\text{HS}} + \Omega_{ij}^{\text{C}} + \Omega_{ij}^{(2)} \quad (16)$$

The first term  $\Omega_{ij}^{\text{HS}}$  is the hard sphere electrophoretic contribution calculated by the integration of total correlation function deduced from PY theory with an average diameter.

$$\Omega_{ij}^{\text{HS}} = - \frac{((\sigma_i + \sigma_j)/2)^2}{3\eta} \rho_j \frac{(1 - \tilde{X}_3)/(5 + \tilde{X}_3^2)/10}{1 + 2\tilde{X}_3} \quad (17)$$

where

$$\tilde{X}_3 = \frac{\pi}{6} \sum_k \rho_k \sigma_k^3 \quad (18)$$

$$\sigma_{\text{HS}}^3 = \frac{3X_1 X_2 / (X_0 + X_3)}{4X_0} \quad (19)$$

The second term  $\Omega_{ij}^{\text{C}}$  is the electrostatic contribution in first order expansion of the Bjerrum's length.

$$\Omega_{ij}^{\text{C}} = - \frac{1}{3\eta} \frac{Z_i Z_j L_B \rho_j}{(1 + \Gamma \sigma_i)(1 + \Gamma \sigma_j) (\Gamma + \sum_k \rho_k (\pi L_B Z_k^2 \sigma_k) / (1 + \Gamma \sigma_k)^2)} \quad (20)$$

The last term  $\Omega_{ij}^{(2)}$  is the second order expansion, that is

$$\Omega_{ij}^{(2)} = - \frac{(Z_i Z_j L_B \rho_j)^2}{3\eta(1 + \Gamma \sigma_i)^2(1 + \Gamma \sigma_j)^2} e^{2\kappa_D \sigma_{ij}} E(2\kappa_D \sigma_{ij}) \quad (21)$$

with

$$E(x) = \int_x^\infty \frac{e^{-u}}{u} du \quad (22)$$

$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2} \quad (23)$$

It should be mentioned that the method to get the mutual diffusion coefficient in aqueous electrolyte solution is established in the solvent-fixed frame of reference while the experiment is performed at fixed volume. As a result, a conversion must be performed between these two reference frames. A feasible choice is to convert the concentration  $m$  in molality into the corresponding concentration  $c$  in molarity using the following equation [1]

$$c = \frac{md}{1000 + mM} \quad (24)$$

where  $M$  is the molecular weight of the solute.

Another choice is to convert the calculated mutual diffusion coefficient from solvent fixed reference frame into the volume fixed ones.

$$D_m^{\text{V}} = \phi D_m^{\text{S}} \quad (25)$$

where  $\phi$  is the volume fraction of the solvent.

$$\phi = 1 - cV_{\pm} \quad (26)$$

where  $V_{\pm}$  is the mean solute partial molal volume of the electrolyte calculated from (26).

$$V_{\pm} = \frac{M - d'}{d - cd'} \quad (27)$$

where  $d' = \partial d / \partial c$ . The density of the electrolyte solution  $d$  in Eqs. (24) and (27) can be expressed by the equation of Novotny and Sohnel [27].

$$d = d_w + Ac + Bc^{3/2} \quad (28)$$

for a given electrolyte,  $A$  and  $B$  are constants. The density of water is  $d_w = 999.65 \text{ kg m}^{-3}$  and  $c$  is the concentration of electrolyte solution in mol/L.

Actually, the two conversion approaches are equivalent and you may take anyone at your convenience.

### 3. Modified theory

Although the ions are treated as hard spheres in primitive MSA, in fact, the cationic diameter used is not the diameter of a bare ion but the diameter of a hydrated one. The hydration of anions is weak and can therefore be neglected; however, the hydration of cations is strong and the hydration layer must be taken into account. Because the thickness of the hydration layer decreases as the ion strength increases, the diameter of cations in the MSA should decrease with increasing ionic strength. If

we assume that the hydration of the cation is proportional to the electrostatic potential  $\psi$  in the solution, and  $\lambda$  is twice the thickness of the hydration layer of a cation, then

$$\frac{\lambda}{\lambda_0} = \frac{\psi(a)}{\psi_0(a)} \quad (29)$$

where  $\lambda_0$  is twice the thickness of the hydration layer of the cation at infinite dilution. The electrostatic potential in the solution can be calculated by the Debye–Hückel theory using the ion atmosphere approach.

The diameter of the hydrated cation in solution is

$$\sigma_+ = \sigma_{P+} + \lambda = \sigma_{P+} + \frac{\lambda_0}{1 + Ka} \quad (30)$$

where  $\sigma_{P+}$  is Pauling diameter of cation. If we take  $a$ , the distance between cation centers, as approximately equal to unity, and  $I^{1/2}$  is substituted for  $K$ , Eq. (30) becomes

$$\sigma_+ = \sigma_{P+} + \frac{\lambda_0}{1 + I^{1/2}} \quad (31)$$

Assuming  $\sigma_0 = \sigma_{P+} + \lambda_0$ , then

$$\sigma_+ = \sigma_0 - \frac{\lambda_0 I^{1/2}}{1 + I^{1/2}} \quad (32)$$

where  $\sigma_0$  is the hydration diameter of the cation at infinite dilution, and  $I$  is the total ionic strength of electrolyte MA in the electrolyte solution.

$$I_{MA} = \frac{1}{2}(m_M Z_M^2 + m_A Z_A^2) \quad (33)$$

where  $m_M$  and  $m_A$  are the total molalities of ions M and A in the solution, respectively.

#### 4. Results and discussion

In the calculation, the anion diameters are kept constant and their values are listed in Table 1. The diameters of the

Table 1

Ion diameters and diffusion coefficients at infinite dilution for some anions

Anions	$\sigma_P (\times 10^{-10} \text{ m})$	$\sigma (\times 10^{-10} \text{ m})$	$D_i^0 (\times 10^{-9} \text{ m}^2 \text{ s}^{-1})$
$\text{NO}_3^-$		2.30	1.7203
$\text{F}^-$	2.62	2.62	1.4753
$\text{Cl}^-$	3.62	3.62	2.0345
$\text{Br}^-$	3.90	3.90	2.0798
I	4.32	4.32	2.0451

halide anions are equal to the Pauling diameters; the others are regressed because there are no specific diameter values for these ions in literature. This treatment is based on a previous finding showing that the cation size increases more than the anion size due to the effect of hydration [26,28]. The effective diameters of cations are calculated using Eq. (32). For a single electrolyte, the two parameters can be regressed from the experimental mutual diffusion coefficient data.

Alkali metal halides solutions are the simplest of all aqueous electrolyte systems. Most of them are completely dissociated in dilute solution producing strong electrolyte solutions that have been widely employed to test theories of ionic solution [3,29,30]. We first investigate the mutual diffusion coefficients of 13 alkali metal halides in aqueous solution. The present treatment is applied to the case of alkali halides MA solutions, in which M and A represent cation and anion, respectively. M is either Li, Na, K, Rb or Cs and A is either F, Cl, Br or I. For a given cation M, the data concerning the salts MA have been fitted at the same time with a common value for the parameter  $\sigma_0$ . We also investigate some other uni-valence electrolyte solution including HCl, HBr,  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{NO}_3$  and  $\text{NaNO}_3$ . The fitted parameters of the effective diameter of cations, the maximum concentration, and the average relative deviation (ARD) for each salt are listed in Table 2. The experimental mutual diffusion coefficients of KF and NaF solution is measured by Lu and Leait [31] using a Taylor dispersion tube and those of RbCl and CsCl in aqueous solution is measured by Lyons

Table 2

Parameters of the cations from fit of mutual diffusion coefficients and the average relative deviations of the calculated values from the experimental data

Salts	$\sigma_P (\times 10^{-10} \text{ m})$	$\sigma_0 (\times 10^{-10} \text{ m})$	$\lambda_0 (\times 10^{-11} \text{ m})$	$c_m (\text{mol/L})$	ARD (%)
LiCl	1.20	4.35	9.89	4.0	0.75
LiBr	1.20	4.35	-1.69	3.5	1.10
LiI	1.20	4.35	-4.41	1.0	0.90
NaF	1.90	3.05	3.57	1.0	1.24
NaCl	1.90	3.05	3.07	4.0	0.69
NaBr	1.90	3.05	0.44	2.5	1.92
NaI	1.90	3.05	-5.41	3.0	2.10
$\text{NaNO}_3$	1.90	3.05	19.31	4.0	1.49
KF	2.66	2.95	-2.20	4.0	1.37
KCl	2.66	2.95	2.38	4.0	0.83
KBr	2.66	2.95	0.18	4.0	1.01
KI	2.66	2.95	1.01	3.5	2.08
RbCl	2.96	2.94	-1.96	3.0	0.29
CsCl	3.38	2.78	-3.57	3.0	0.28
HCl		4.56	4.73	4.0	1.57
HBr		4.56	16.09	1.0	0.67
$\text{NH}_4\text{Cl}$		3.86	18.09	4.0	0.22
$\text{NH}_4\text{NO}_3$		3.86	24.98	4.0	0.77

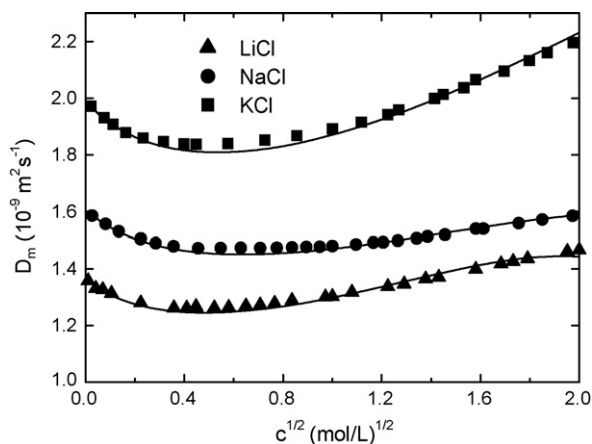


Fig. 1. The mutual diffusion coefficients of lithium, sodium and potassium chlorides in aqueous solutions at 298 K. Lines represent the results from MSA, scatter symbols refer to experimental values.

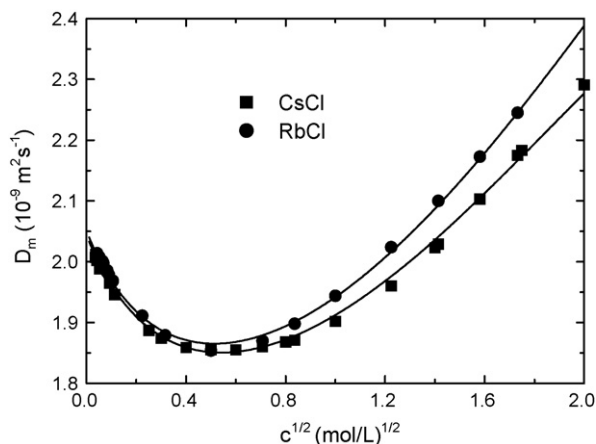


Fig. 2. The mutual diffusion coefficients of rubidium and cesium chlorides in aqueous solutions at 298 K. Symbols have the same meaning as in Fig. 1.

and Riley [32] and Jalota and Paterson [33]. If not expressly states, all the experimental data is taken from Lobo [34,35]. ARD denotes the average relative deviation of the calculated mutual diffusion coefficients from the experimental data; i.e.,  $ARD (100\%) = (100/N) \sum_{k=1}^N \left| \frac{D_{m,k}^{cal} - D_{m,k}^{exp}}{D_{m,k}^{exp}} \right|$ , where  $N$  is the number of experimental data points.

It is clear from results in Table 2 that our fits to experimental data using only two parameters are very good up to very high concentration. The major reason lies in that we take into account the variation of the hydration effect with concentration by introducing an effective cationic diameter, as shown in Eq. (32), while the previous theory neglect the fact that the hydration of cation is strong and the thickness of the hydration layer decreases as the ion strength increases. Table 2 also shows that the fit yield unique parameter  $\sigma_0$  for a specific cation, namely, same value is taken for different salts involving common cation. On the other hand, the values of  $\sigma_0$  for different cations share the sequence of  $Rb < Cs < Na < K < Li$  due to a corresponding increase in the degree of cation hydration with a decrease in atomic number. The effective cationic diameter is larger than its Pauling diameter with the exception of Rb and Cs. It may be explained by the effect of short-range forces between ions which is caused not only by the overlap of hydration spheres but also by an additional short-range Coulomb attraction due to the high polarizability of the rubidium, cesium and halide ions [26,36].

Comparisons of the calculated and experimental mutual diffusion coefficients for 13 alkali metal halides are shown in Figs. 1–4. Clearly the agreement between calculated values and experimental data is good up to the molarity of 4 mol/L. The mutual diffusion coefficients of alkali halide solutions decrease with concentration at low concentrations and increase steadily at higher concentration with the exception of NaF.

In dilute concentrations, electrolyte solutions are often modeled as consisting of highly solvated “free” ions. The concentration dependence of mutual diffusion coefficients is governed by long-range Coulombic forces as predicted from the Debye–Hückel theory, i.e., they decrease monotonically with the increase of concentration. With increasing concentration, the

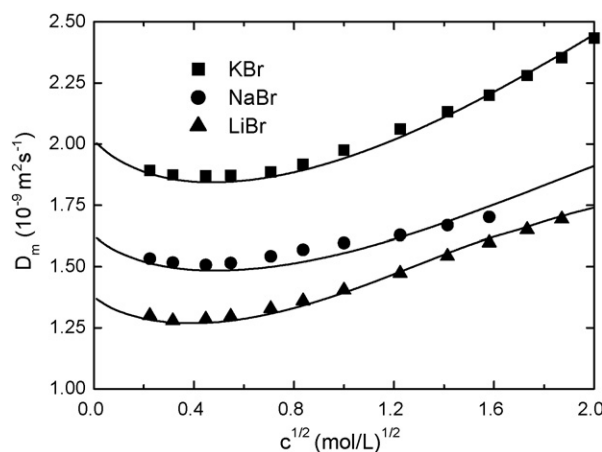


Fig. 3. The mutual diffusion coefficients of lithium, sodium and potassium bromides in aqueous solutions at 298 K. Symbols have the same meaning as in Fig. 1.

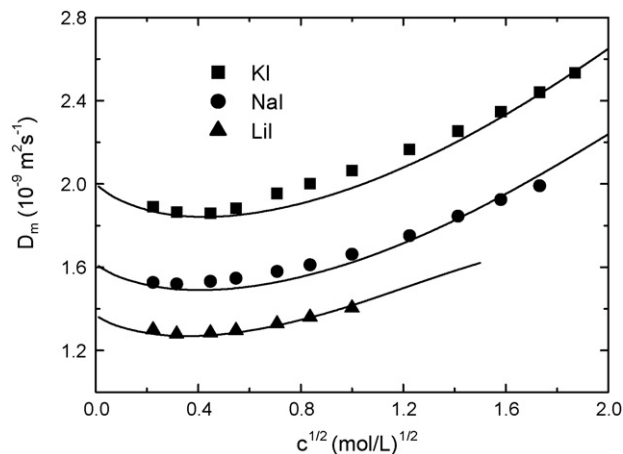


Fig. 4. The mutual diffusion coefficients of lithium, sodium and potassium iodides in aqueous solutions at 298 K. Symbols have the same meaning as in Fig. 1.



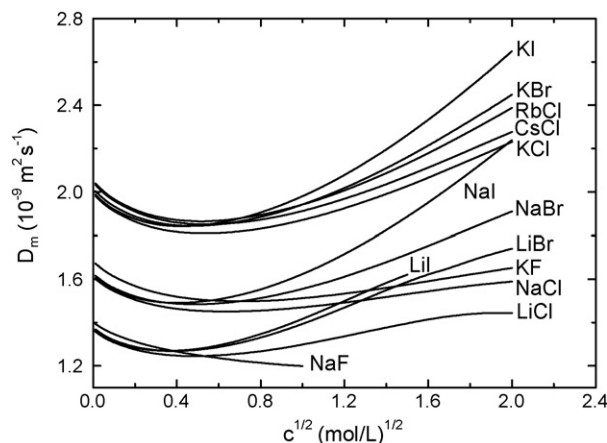


Fig. 5. The mutual diffusion coefficients of alkali metal halides in aqueous solutions at 298 K.

ions being to directly interact and ionic association may occur. The competition between the effect of activity coefficients and hydrodynamic interactions determines the trend of the curve of the mutual diffusion coefficient as a function of square root concentration.

Fig. 5 shows the collection of mutual diffusion coefficients of alkali halide solutions studied. It reveals a curious result that aqueous alkali halides can be classified into three main groups depending on their diffusion coefficients in dilute solutions, known as the Nernst limiting diffusion coefficient, which is given by

$$D_m^0 = \frac{RT}{F^2} \frac{|z_1| + |z_2|}{|z_1 z_2|} \frac{\lambda_1^0 \lambda_2^0}{\lambda_1^0 + \lambda_2^0} \quad (34)$$

We can see that in this region differences in the  $D_m$  values are governed primarily by differences in the limiting ionic equivalent conductivities. At 298 K, the limiting ionic equivalent conductivities of  $K^+$ ,  $Rb^+$ ,  $Cs^+$ ,  $Cl^-$ ,  $Br^-$ , and  $I^-$  ions are: 7.35, 7.78, 7.73, 7.64, 7.81 and 7.68  $mS\ m^2\ mol^{-1}$ , respectively, which are nearly identical. Subsequently, it is not surprising that  $D_m$  values for dilute KCl, KBr, KI, RbCl and CsCl solutions are in the same group. By coincidence, however, the limiting ionic equivalent conductances of  $Na^+$  and  $F^-$  ions are similar, i.e., 5.01 and 5.54  $mS\ m^2\ mol^{-1}$ , respectively. Hence KF, NaCl, NaBr and NaI form a second group of salts with similar diffusion coefficients in dilute solution. Similarly, NaF, LiCl, LiBr and LiI form the third group, as can be clearly seen from Fig. 5.

The mutual diffusion coefficients in dilute electrolyte solutions obey a limiting law proposed by Onsager and Fuoss [6]. When the concentration increases, the simple pattern of diffusion coefficients clearly breaks down. The concentrated electrolyte solutions show strongly non-ideal behavior. For example, the diffusion coefficients of LiBr, NaI, KCl, KBr, RbCl and CsCl increase rapidly with concentration increase, producing a number of crossovers. While the mutual diffusion coefficients of LiCl, NaCl and KF show a sluggish increase with the concentration increase. For a given cation M, the larger the anion diameter, the higher the values of mutual diffusion coefficients of the salts MA. For example, the mutual diffusion coefficients of the potas-

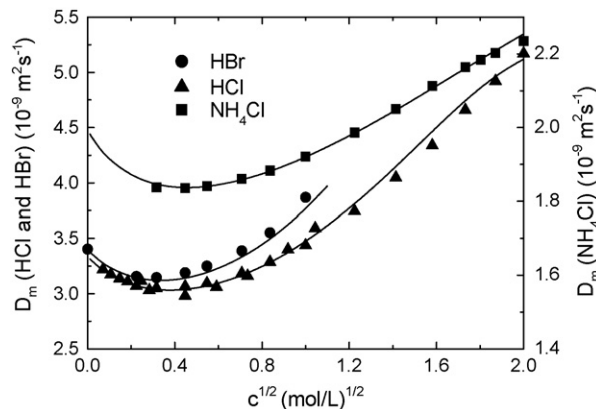


Fig. 6. The mutual diffusion coefficients of hydrochloric acid, hydrobromic acid and ammonium chloride in aqueous solutions at 298 K. Symbols have the same meaning as in Fig. 1.

sium halides fall in the series  $KI > KBr > KCl > KF$ , in coincide with the size order of the anion diameter. For a given anion A, the mutual diffusion coefficients of the salts MA increase with increasing cationic radius, with the exception of the rubidium. Let's take Cl as an example, the sequence of mutual diffusion coefficient is  $RbCl > CsCl > NaCl > KCl > LiCl$ . Although no theory can explain the anomaly, we think that it is partially due to the association between ions. The conductivity measurements in dilute solutions have shown that both caesium and rubidium chlorides are significantly associated while other alkali metals are not. It should be pointed out that the concentration dependence of mutual diffusion coefficients for fluorides solution differs obviously from those of other halides. The good interpretation for this phenomenon is likely the rather strong hydration of aqueous F ions.

We now turn to the case of other uni-valence electrolyte solutions including HCl, HBr,  $NH_4Cl$ ,  $NH_4NO_3$  and  $NaNO_3$ . It can be seen from Table 2 that the parameters of  $\lambda_0$  for these five electrolytes are larger than those of alkali halides. The result is likely due to either the association between cation and anion in concentrated solution or the complexity of ions. In our calculation, the ammonium and nitrate are regard as a hard sphere with a regressed diameter, although the actual nitrate ion possesses a planar geometry and the real ammonium ion is tetrahedral.

In Fig. 6, we compared the calculated mutual diffusion coefficients with the experimental data for aqueous HCl, HBr and  $NH_4Cl$  solutions at 298 K. It shows that at both low and high electrolyte concentration, excellent agreements is obtained. The curves of mutual diffusion coefficients versus square root of concentration for HCl, HBr and  $NH_4Cl$  solutions take the same trend as for alkali metal halides solution, i.e., they decrease firstly with the increasing concentration and then increase after reaching a minima. From Fig. 6, we can also find that the mutual diffusion coefficients of HCl and HBr vary more pronounced than that of  $NH_4Cl$ .

Fig. 7 illustrates the mutual diffusion coefficients of  $NH_4NO_3$  and  $NaNO_3$  solutions as a function of the square roots of the molar concentration. It is found that the mutual diffusion coefficients of  $NaNO_3$  and  $NH_4NO_3$  monotonically decrease with the

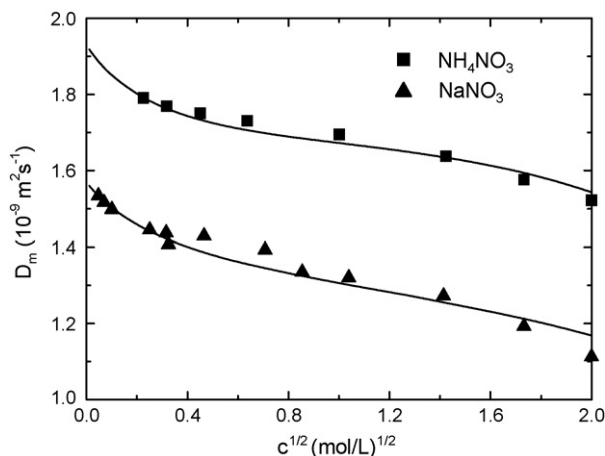


Fig. 7. The mutual diffusion coefficients of sodium and ammonium nitrates in aqueous solutions at 298 K. Symbols have the same meaning as in Fig. 1.

increased concentration. This tendency contrasts sharply with the concentration dependence of mutual diffusion coefficients for alkali halides aqueous solution, which decrease firstly and then increase with concentration increase. The main reason for this phenomenon is primary due to association in nitrates solution. Rard and Miller [37] have pointed out that the electrolytes whose  $D_m$  decrease regularly with the increasing concentration are all associated. Evidence from a variety of techniques, including conductance data and spectral data support the existence of ion-pair formation in the nitrate salts, especially at high concentrations [38]. In fact, the variation of mutual diffusion coefficients with concentration is largely due to the change of free energy gradient. Interionic effects, hydration, viscosity, and association are complicating factors at higher concentrations. All these factors lead to a very large value of parameter  $\lambda_0$  for the nitrates, as seen from Table 2. Consequently, only a semi-qualitative prediction can be made for the shape of the mutual diffusion coefficients curve as a function of the concentration in various electrolyte solutions.

## 5. Conclusions

In this work, the primitive MSA is used to calculate the mutual diffusion coefficients of electrolytes aqueous solutions by introducing an expression for the effective cationic diameter. In contrast to other approaches, this method can be applied to higher concentration up to 4.0 mol/L with only two parameters for a given electrolyte. Moreover, the same values of  $\sigma_0$  are taken for a specific cation in different electrolyte solutions. Extensive comparisons of the theoretical results with the experimental mutual diffusion coefficient data show that the proposed model is able to accurately reproduces the mutual diffusion coefficients of 13 alkali halides electrolytes and 5 other uni-valence electrolyte solutions over wide concentration ranges (0–4.0 mol/L).

Just as what have been mentioned above, association play a very important role in the mutual diffusion process, especially in concentrated solution and for 2:2 electrolyte solution. In

our method, parameter  $\lambda_0$  can partially includes this association effect.

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