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Prediction of Individual Ionic Activity Coefficients for Some Aqueous Chloride Salt Solutions

Li Sun[1,2,3,*], *Jierong Liang*[4]

[1] Department of Chemical and Biochemical Engineering, Technical University of Denmark, 2800, Kgs. Lyngby, Denmark
[2] College of Mechanical and Electrical Engineering, Hohai University, Changzhou 213022, People's Republic of China
[3] School of Energy and Power Engineering, Wuhan University of Technology, Wuhan 430063, People's Republic of China
[4] Department of Energy Conversion and Storage, Technical University of Denmark, 2800 Kgs. Lyngby, Denmark
[*]E-mail: lsun@kt.dtu.dk; ORCID: 0000-0002-8448-1651

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Theoretical calculations of individual ionic activity coefficients (IIAC) for four chlorine salts in aqueous solutions are presented. The IIAC are predicted first by using Debye-Hückel theory with different ion radii, and the results show a significant deviation from experimental data. IIAC are also predicted by using Debye-Hückel theory plus the Born equation, and the results show that the Debye-Hückel theory plus Born equation can accurately predict the IIAC (for example, the average relative deviations between predicted values and experimental data for the activity coefficients of Na^+, Cl^- and NaCl are 0.6%, 1.7%, and 0.9%, respectively). In calculations, experimental liquid densities and relative static permittivity are used, and the ion-ion interaction and ion-water interaction contributions of the activity coefficients are analysed and discussed. The effects of ion size on electrostatic interaction calculations are further discussed.

Keywords: Individual Ionic Activity Coefficients; Aqueous Electrolyte Solution; Classical Solution Theory; Ion Radius

1. INTRODUCTION

In chemical engineering, hydrometallurgy, environmental biochemistry, and geochemistry, there is an abundance of aqueous electrolyte solutions [1]. When charged ions are present, the phase behaviour of the electrolyte solution deviates far from that of the nonelectrolyte system [1]. As a critical property of electrolyte solutions, the individual ionic activity coefficient (IIAC) has attracted considerable attention. IIAC is critical for describing the transport and thermodynamic phenomena of electrolyte systems [2]. IIAC is essential for the study and application of sodium–potassium pumps, membrane processes, and geological chemistry.

Despite some controversy over the experimental method, some experimental data for the IIAC have been published [3-5]. In addition to experimental studies, several modelling studies for IIAC have been presented. Fraenkel [6] applied Monte Carlo simulations for IIAC calculations for several inorganic salts in aqueous solutions. Liu and Eisenberg [7] developed the Poisson-Fermi model, which can accurately predict the IIAC.

There are certainly some modelling studies that exist that are based on the classical solution theory (e.g., the Debye-Hückel theory [8]). Fraenkel [6] extended the Debye-Hückel theory for the case of ions of unequal size. Liu and Li [9] also presented a generalized Debye-Hückel theory for electrolyte solutions. Valiskó et al. [10] divided the contributions of excess chemical potential into ion-ion interaction parts and ion-water interaction parts. The ion-ion interaction part can be computed from the Debye-Hückel theory [8], and the ion-water interaction part can be computed from the Born equation [11]. Shilov and Lyashchenko [12] extended the Debye-Hückel theory, and they also presented ion−ion interaction contributions and ion−water interaction contributions for the excess chemical potential.

All these models state that they give good agreement between the predicted and experimental IIAC for electrolytes in aqueous solutions. However, the importance of the original Debye-Hückel theory seems to be downplayed, and prediction of the IIAC using the original Debye-Hückel theory should be investigated further.

This work investigates the IIAC using the original Debye-Hückel theory. This manuscript is divided into three parts: Section 2 presents the details for the physical model; Section 3 presents the prediction results for the IIAC, as well as the discussion; Section 4 presents the conclusions.

2. METHOD

2.1 Basic Equations

The excess chemical potential is derived from the excess Helmholtz energy function by molar differentiation at constant temperature and volume [1]:

$$\mu_i{}^{EX} = \left[\frac{\partial A^{EX}}{\partial n_i}\right]_{T,V,n_j} \tag{1}$$

The rational activity coefficient of ion *i* is related to the excess chemical potential:

$$\mu_i{}^{EX} = RT \ln \gamma_i^* \tag{2}$$

The molality activity coefficient of ion *i*, γ_i^m, is related to the rational activity coefficient:

$$ln\gamma_i^m = \ln(x_w\gamma_i^*) = \ln \gamma_i^* - \ln[1 + 0.001M_w \sum m_k] \tag{3}$$

The mole fraction of water x_w is calculated from:

$$x_w = \frac{nw}{nw + \sum nion_k} = \frac{1000/M_w}{1000/M_w + \sum m_k} \tag{4}$$

where nw is the mole number of the solvent (water), $nion_k$ is the mole number of ion k, M_w is the molecular weight of water, m_k is the molality of ion k, and the sum is over all ions present.

A strong electrolyte, it dissociates into νC cations and νA anions with ionic charges Z_C and Z_A. The Greek letter ν is the sum of the stoichiometric coefficients (ν = νC + νA).

The mean molal activity coefficient is defined as follows:

$$\gamma_{\pm}^{m} = ((\gamma_{C}^{m})^{\nu C}(\gamma_{A}^{m})^{\nu A})^{1/\nu} \tag{5}$$

2.2 The Debye-Hückel Theory

The Debye-Hückel theory [8] represents the most important progress for the study of modern electrolyte solution theory. It is a typical primitive model, which is based on the physical interaction between ions. In the Debye-Hückel theory, the system's free energy is only the sum of the Coulomb attraction between positive and negative ions without considering short-range interactions.

The excess Helmholtz energy from the long-range interaction between positive and negative ions can be expressed by the following equation:

$$A^{DH} = -\frac{k_B T V}{4\pi N_A \sum_i n_i Z_i^2} \sum_i n_i Z_i^2 \chi_i \tag{6}$$

Here, the function χ_i is given by:

$$\chi_i = \frac{1}{d_i^3}\left[\ln(1+\kappa d_i) - \kappa d_i + \frac{1}{2}(\kappa d_i)^2\right] \tag{7}$$

where d_i is the hard-sphere diameter of the ion, and κ is the inverse Debye screening length:

$$\kappa = \left(\frac{e^2 N_A^2}{\varepsilon_r \varepsilon_0 R T V} \sum_{ions} n_i Z_i^2\right)^{1/2} \tag{8}$$

Here, e is the electronic charge, N_A is the Avogadro constant, n_i is the number of moles of ion i, V is the total volume, ε_0 is the permittivity in vacuum, and ε_r is the relative static permittivity of the solvent.

Some extended versions of the Debye-Hückel theory have been presented for high molality applications. Hückel [13] tried to extend the Debye-Hückel theory to high molality ranges by considering the concentration dependency of the relative static permittivity. Shilov and Lyashchenko [12] pointed out that the original Debye-Hückel theory can be extended to a wide molality range by considering the concentration dependency of the relative static permittivity.

2.3 Born Equation

When ions are dissolved in a solvent, the charged ions polarize the surrounding solvent molecules. While the original Debye-Hückel theory addresses the ion-ion interaction, Born [11] proposed an equation for the interaction between an ion and surrounding solvent. The Born equation [11] can be used for estimating the electrostatic component of the Gibbs free energy for the solvation of an ion.

Born expressed the electrostatic contribution to the excess Helmholtz energy from the ion-water interaction as follows [11]:

$$A^{Born} = \frac{N_A e^2}{8\pi\varepsilon_0}\sum_i \frac{n_i Z_i^2}{r_{Born,i}}\left(\frac{1}{\varepsilon_r} - 1\right) \tag{9}$$

Note that $r_{Born,i}$ is the Born radius of the ion, not the crystallographic radius of the ion. The Born equation can be extended to high molality by using the concentration dependency of the relative static permittivity [12].

3. RESULTS AND DISCUSSION

In this work, we present two approaches to predict the IIAC for four salts (sodium chloride: NaCl, potassium chloride: KCl, calcium chloride: $CaCl_2$, magnesium chloride: $MgCl_2$) in aqueous solutions. The first approach uses the original Debye-Hückel theory alone. The second approach uses a combination of the original Debye-Hückel theory and the Born equation.

In Debye-Hückel calculations, crystallographic ion radii should be used; some models use Pauling radii; and some models use Marcus radii. In our work, we use both Pauling radii and Marcus radii. Valiskó [10] determined the Born radii for some ions by fitting the hydration free energy of ions; in this work, we used these published Born radii in calculations of the Born equation. All the crystallographic radii and Born radii are listed in Table 1.

Table 1. Crystallographic radii and Born radii of ions.

Ion	r_p [a] [Å] [14]	r [b] [Å] [15]	r_{Born} [c] [Å] [10]
Na^+	0.95	1.18	1.62
K^+	1.33	1.39	1.95
Ca^{2+}	0.99	1.21	1.71
Mg^{2+}	0.65	1.05	1.42
Cl^-	1.81	1.60	2.26

a. Pauling radius; b. Marcus radius; c. Born radius.

Table 2. Parameters for the correlation of the static permittivity of solvent for aqueous electrolyte solutions.

Salt	A [mol^{-1}]	B [$mol^{-3/2}$]	m_{max} [mol/kg water]
NaCl	-14.06	3.39	4.0
KCl	-12.04	2.32	4.0
$CaCl_2$	-28.85	11.62	3.0
$MgCl_2$	-23.03	1.10	3.0

In these predictions, experimental liquid density and relative static permittivity are used. The liquid density of the aqueous solutions is correlated as a function of the temperature and concentration [16], and the correlation equation and the parameters for a specific electrolyte can be found in the original paper [16]. Some scholars gave the correlations for the relative static permittivity as a function of molarity (mol/L solution); here, we give a correlation equation related to molality (mol/kg water):

$$\varepsilon_r(m) = 78.45 - Am + Bm^{3/2} \quad (10)$$

The adjustable parameters A and B are obtained by fitting the experimental relative static permittivity (shown in Table 2), and all the experimental data are taken from the CRC Handbook [17] and Electrolyte Database [18].

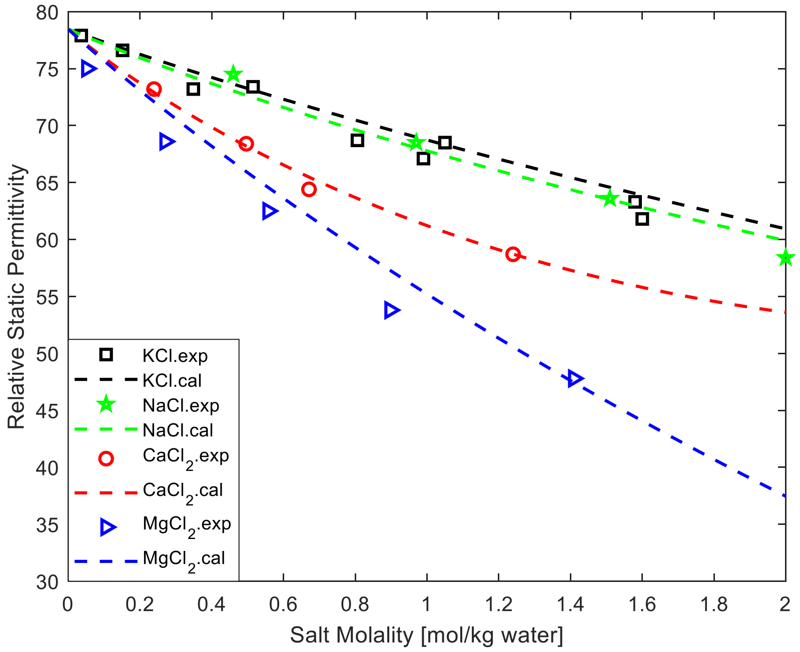


Figure 1. Relative static permittivity of aqueous electrolyte solutions at 298.15 K.

Figure 1 shows the performance of Eq. (10); it can be observed that Eq. (10) with the fitted parameters can give good agreement between the predicted and experimental values. The relative static permittivity of the aqueous electrolyte solution is concentration-dependent, and a constant value for the relative static permittivity cannot be used in electrostatic interaction calculations.

3.1 Prediction using the Debye-Hückel Theory

Some models [6, 19, 20] use the adjustable ion radius in the calculation of the electrostatic interaction to account for the ion-water interaction contributions. In the first part of our prediction work, we only use the original Debye-Hückel theory. Three kinds of radii are used: Pauling radii, Marcus radii, and fitted radii (as obtained by fitting the experimental IIAC). Table 3 lists the fitted radii and the average relative deviations (ARD) between the predicted values and experimental activity coefficients.

Table 3. Prediction of the IIAC by using the Debye-Hückel theory with different ion radii.

Salt		Pauling	Marcus	Fitted	
		ARD [%]	ARD [%]	radius	ARD [%]
NaCl	Cation	21.0	15.6	6.40	7.1
	Anion	11.1	9.1	3.57	5.9
	Salt	16.3	12.2	-	6.3
KCl	Cation	9.9	3.9	2.81	3.8
	Anion	14.9	13.2	5.33	2.6
	Salt	12.4	8.5	-	3.0
$CaCl_2$	Cation	32.3	23.5	3.67	13.4
	Anion	33.5	29.1	5.62	14.9
	Salt	56.8	47.9	-	30.1
$MgCl_2$	Cation	77.9	72.6	6.62	53.5
	Anion	39.2	32.9	6.19	18.6
	Salt	85.1	75.9	-	41.9

From Table 3, it can be observed that the results predicted by using crystallographic radii (Pauling radii and Marcus radii) are bad, and that the fitted values for the ion radii give reasonably good results. The results for the Marcus radii are, overall, slightly better than those for the Pauling radii because the values for the Marcus radii are different from those for the Pauling radii, i.e., for cations, the values for the Marcus radii are larger than those for the Pauling radii; for Cl^-, the values of Marcus radii are smaller than those for the Pauling radii.

The fitted values for the ion radii are significantly larger than those for the crystallographic ion radii. Using the fitted ion radii instead of the crystallographic ion radii weakens the ion-ion interactions, which amounts to a disguised increase in the ion-water interactions. This increase is also easy to determine from the mathematical formulas. The ion-water interactions are not included in the original Debye-Hückel theory. Thus, the original Debye-Hückel theory cannot be used to describe the phase phenomena for aqueous electrolyte solutions individually. The original Debye-Hückel theory can only weaken the ion-ion interactions by adjusting the ion radius.

For all three radius sets, the ARDs for the 1:1 electrolyte systems are smaller. This can be explained mathematically (Eq. (5)); another reason may be that there may be more significant physical interactions in aqueous solutions of $CaCl_2$ and $MgCl_2$.

3.2 Prediction using the Debye-Hückel Theory plus Born Equation

The ion-ion interaction and ion-water interaction are equally critical in aqueous electrolyte solutions[21]; in other words, the ion-water interactions cannot be ignored in predictions of the IIAC.

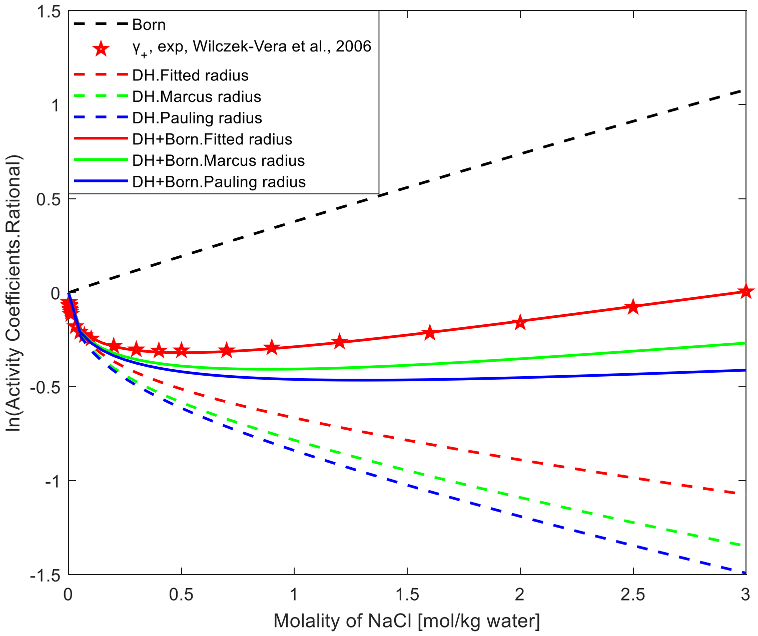
Valiskó et al. [10] and Shilov and Lyashchenko [12] used the Born equation to compute the ion-water interactions.

In this section, we apply the Debye-Hückel theory plus Born equation to predict the IIAC. Table 4 and Figures 2-5 show the prediction results.

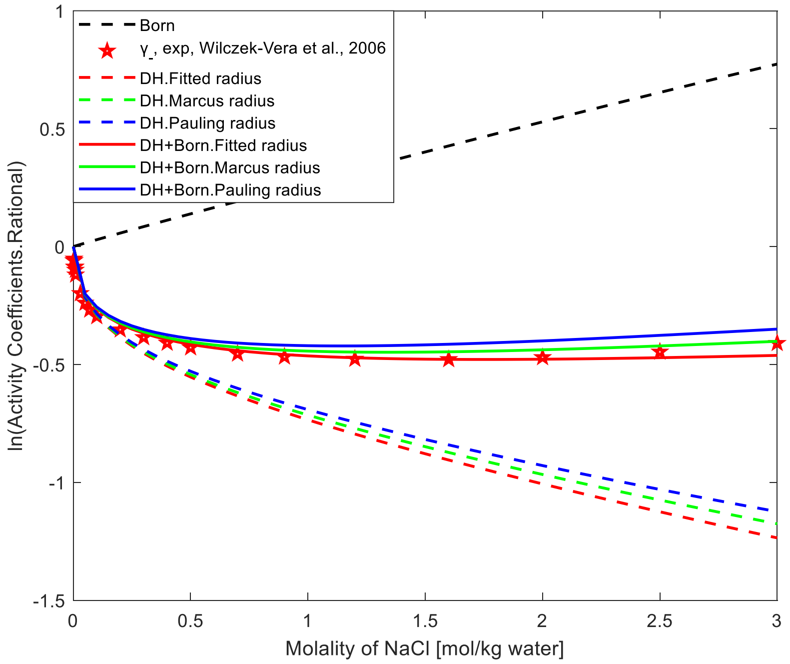
Table 4. Prediction of IIAC using the Debye-Hückel theory plus Born equation with different ion radii.

Salt		Pauling	Marcus	Fitted	
		RAD [%]	RAD [%]	radius	RAD [%]
NaCl	Cation	8.6	6.1	1.81	0.6
	Anion	3.5	2.1	1.36	1.7
	Salt	3.7	2.9	-	0.9
KCl	Cation	7.7	7.9	0.83	0.5
	Anion	3.0	4.2	2.08	2.9
	Salt	3.6	3.0	-	1.7
$CaCl_2$	Cation	18.3	12.2	1.50	5.2
	Anion	5.3	2.3	1.48	2.3
	Salt	26.1	18.4	-	7.4
$MgCl_2$	Cation	69.0	41.6	1.13	29.6
	Anion	2.2	3.6	1.49	1.2
	Salt	53.4	16.3	-	11.3

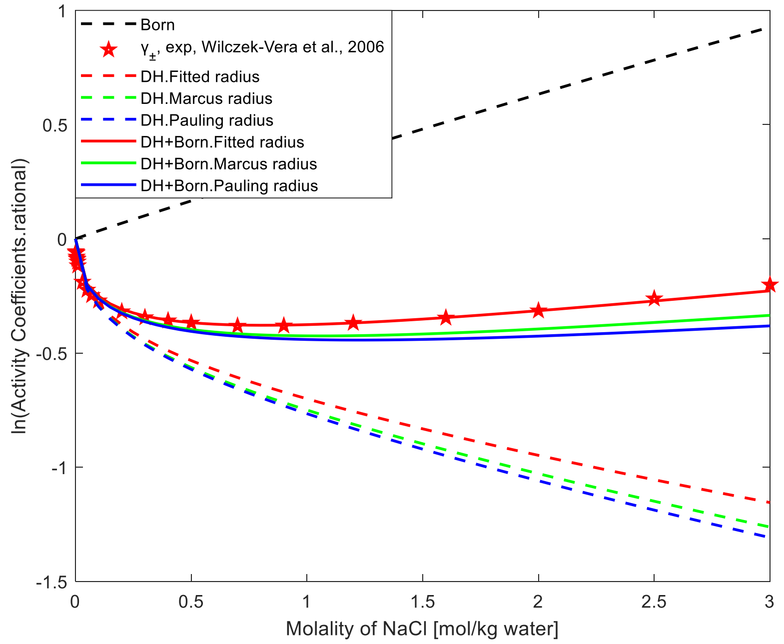
From Table 4, it can be observed that the Debye-Hückel theory plus Born equation gives good agreement between the predicted and experimental values for the IIAC. Compared with the predictions using Debye-Hückel theory alone, the combination of Debye-Hückel theory and Born equation performance is significantly better. Unlike the first calculation part, it is hard to say whether using Marcus or Pauling radii leads to better performance. The fitted values for the ion radii present satisfactory results, especially for the 1:1 electrolyte systems. The fitted values for the ion radii are different from the crystallographic radii. That is, by adjusting the values for the ion radii, the calculations increase or decrease the contribution from ion-ion interactions.



(a) cation



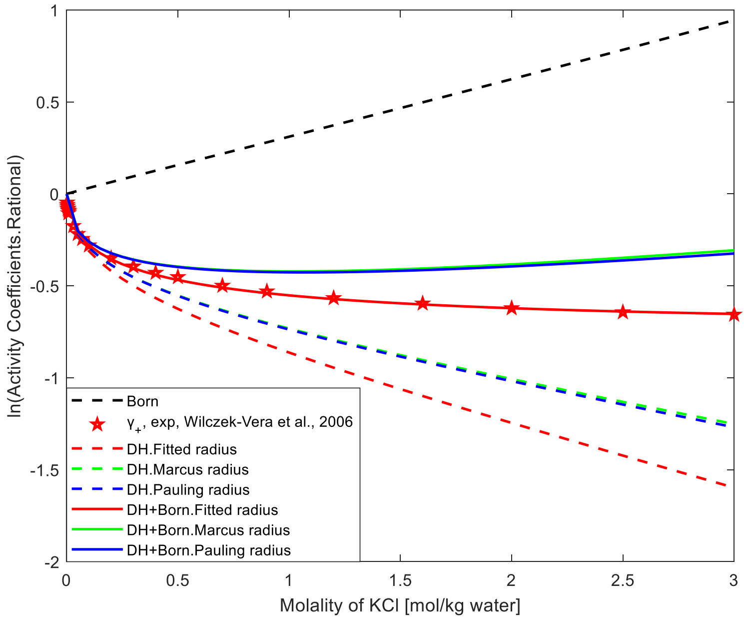
(b) anion



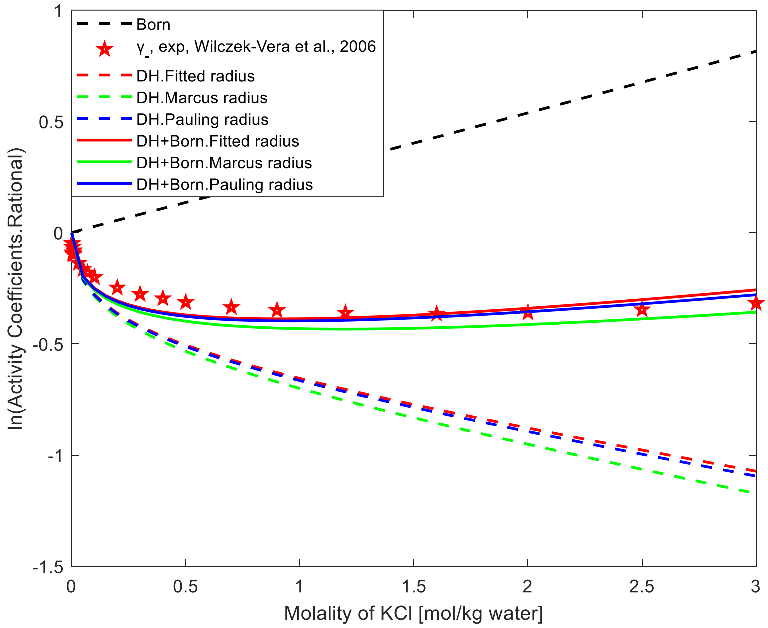
(c) salt

Figure 2. Contributions of the activity coefficients for ions and salt in aqueous NaCl solution.

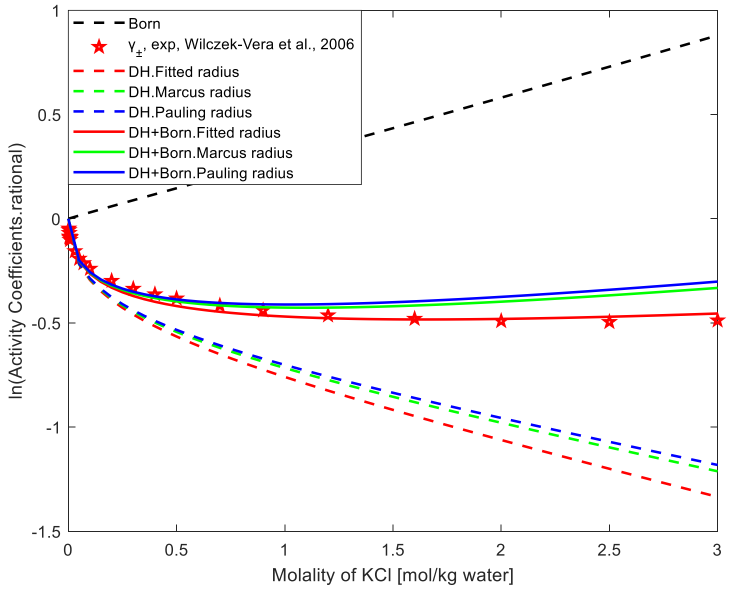
From Figure 2, it can be clearly seen that the Debye-Hückel theory plus Born equation predicts the IIAC for NaCl in aqueous solutions very well. The ion-ion interaction contributions (using the Debye-Hückel theory) contribute to the negative part, and the contributions increase with increasing NaCl molality. The ion-water interaction contributions (using the Born equation) contribute to the positive part, and the contributions increase with increasing NaCl molality. It can be said that the activity coefficient is a balance of ion-ion interaction contributions and ion-water interaction contributions. It can also be seen from Figure 2 that the fitted ion radii give the best performance, and that the Marcus radii perform slightly better than the Pauling radii. From the cation results, we can see that using the Pauling radius and Marcus radius for Na^+ overestimates the ion-ion interactions. The fitted value for the Na^+ radius is larger than that of the Pauling radius and Marcus radius, so as to weaken the ion-ion interactions. From the anion results, we can see that using the Pauling radius and Marcus radius for Cl^- underestimates the ion-ion interactions, and the fitted value for the Cl^- radius is smaller than that for the Pauling radius and Marcus radius, which strengthens the ion-ion interactions.



(a) cation



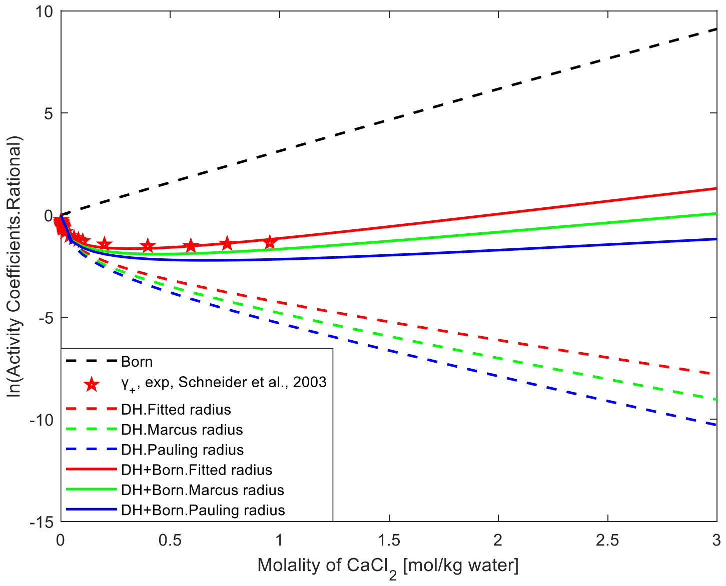
(b) anion



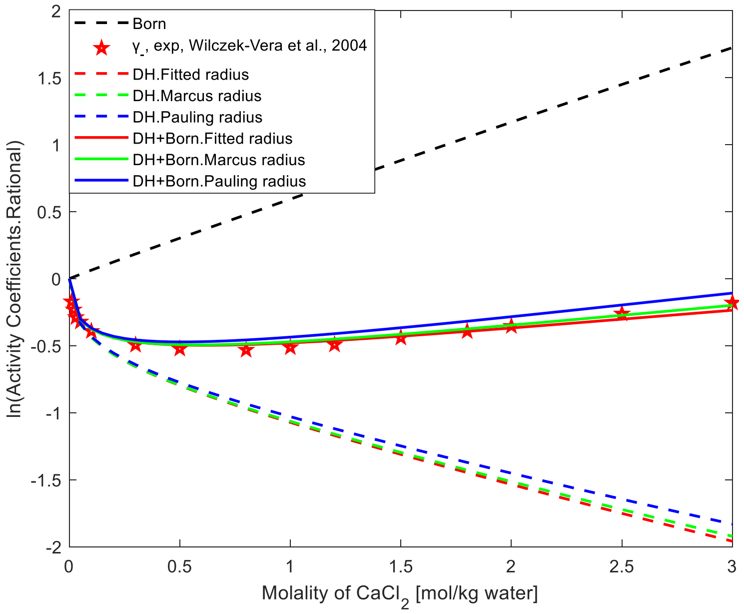
(c) salt

Figure 3. Contributions of the activity coefficients for ions and salt in aqueous KCl solution.

Figure 3 shows the results obtained for KCl. Combined with the fitted values for the ion radii, it can be observed that by using the Pauling radius and Marcus radius for K^+, one underestimates the ion-ion interactions, and the fitted value for the K^+ radius is smaller than the Pauling radius and Marcus radius, which strengthens the ion-ion interactions. From the anion results, we can see that by using the Pauling radius and Marcus for Cl^-, one slightly overestimates the ion-ion interactions. The fitted value for the Cl^- radius is slightly larger than the Pauling radius and Marcus radius, so as to weaken the ion-ion interactions. The values for the K^+ radius from Pauling and Marcus are very close, so the performances of the ion-ion interactions for K^+ are similar when using either the Pauling radius or Marcus radius. It also needs to be noted that the fitted values for the Cl^- radius are different in different electrolyte systems.



(a) cation



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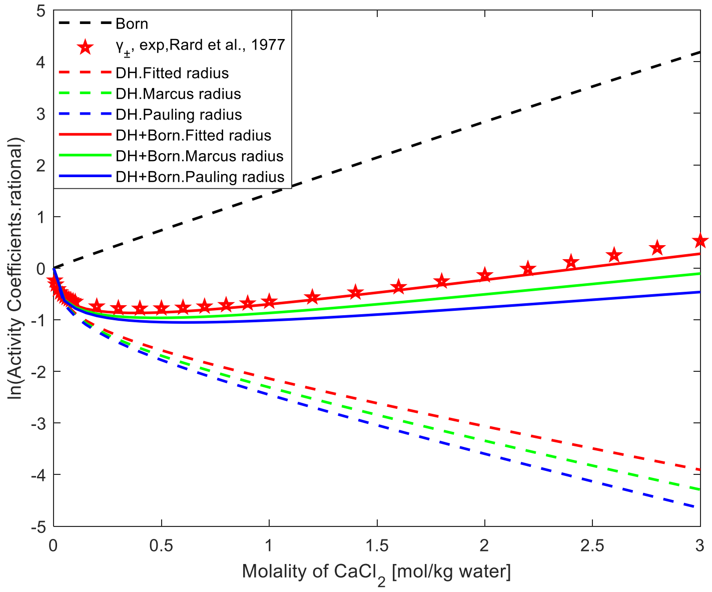


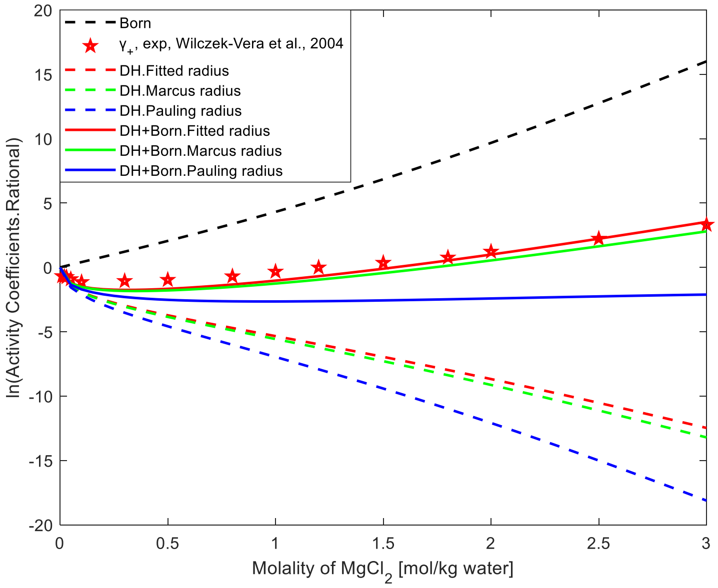
(c) salt

Figure 4. Contributions of the activity coefficients for ions and salt in aqueous $CaCl_2$ solution.

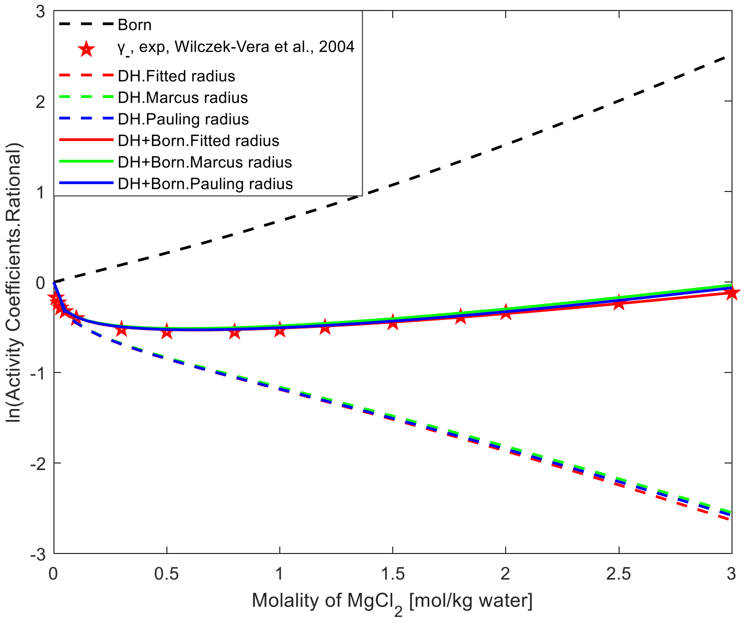
The results obtained for $CaCl_2$ using the fitted radii seem to be not as satisfactory as those obtained for 1:1 electrolytes. Using the Pauling radius and Marcus radius for Ca^{2+} to overestimate the ion-ion interactions, the fitted value for the Ca^{2+} radius is larger than the Pauling radius and Marcus radius, so as to weaken the ion-ion interactions. The performance of all three radius sets for the anions are similar, so the performance differences in terms of the mean ionic activity coefficients between the three radius sets follow those for Ca^{2+}.

By using the Marcus radius for Mg^{2+}, one obtains a similar performance to that obtained using the fitted radius of Mg^{2+} because the fitted value is close to the Marcus value. The Pauling radius for Mg^{2+} overestimates the ion-ion interactions because the Pauling radius of Mg^{2+} is smaller than the

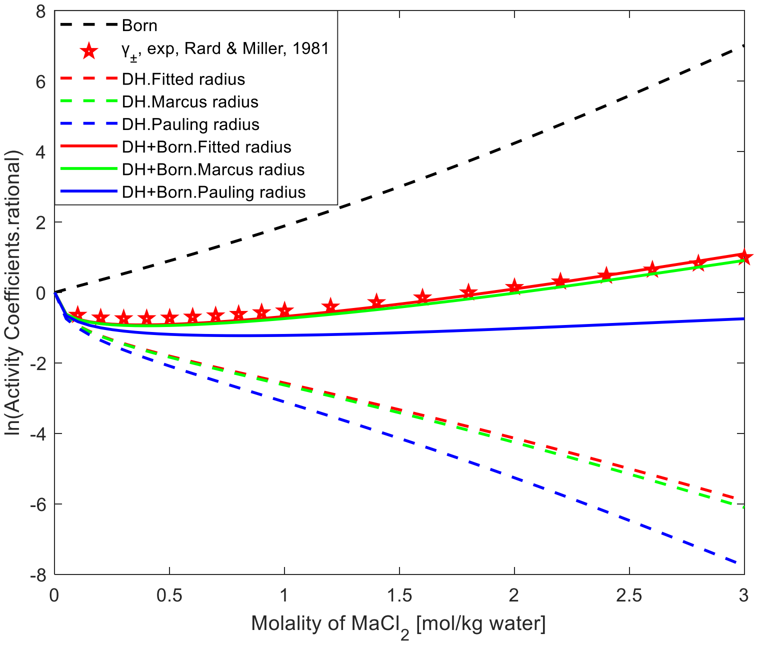
Marcus radius and fitted value. Similar to the anion results for $CaCl_2$, the results for $MgCl_2$ show that the performance of all three radius sets of anions is similar. Therefore, the performance differences in terms of the mean ionic activity coefficients between the three radius sets follow those found for the IIAC of Mg^{2+}.



(a) cation



(b) anion



(c) salt

Figure 5. Contributions of the activity coefficients for ions and salt in aqueous $MgCl_2$ solution.

Overall, the combination of the Debye-Hückel theory plus the Born equation with the Pauling radii and Marcus radii can give reasonably good performance for the IIAC of electrolytes in aqueous solutions. By adjusting the ion radius values, the combination of Debye-Hückel theory and the Born equation predicts the IIAC accurately. From the above, it can be concluded that the activity coefficient for the ions and electrolytes in aqueous solutions is a balance between the ion-ion interactions and the ion-water interactions.

For a better theoretical understanding, a review of other models based on classical theory is needed. The Debye-Hückel theory treats ions as point charges with a minimum separation distance [22]. Moreover, the ion-water interactions are not included in the original Debye-Hückel theory.

In the Debye-Hückel-SiS [6] model, the calculated ion size is used in place of the crystallographic ion size. In Debye-Hückel-SiS [6], the relative static permittivity of pure solvent is used, and ion solvation is neglected. In Valiskó et al.'s model [10] and Shilov and Lyashchenko's model [12], the activity coefficient is calculated from the ion-ion interaction and ion-water interaction parts. Valiskó et al. [10] and Shilov and Lyashchenko [12] used the crystallographic radius, experimental liquid density and relative static permittivity. All of these models only consider electrostatic interactions and neglect physical interactions. Using the crystallographic radii of ions cannot give accurate results. Adjusting the values of ion radii is the usual approach for improving the prediction performance.

4. CONCLUSIONS

A theoretical calculation of the IIAC in aqueous solutions using Debye-Hückel theory and a combination of Debye-Hückel theory and the Born equation is presented. IIAC are predicted by using the different ion radii of the ions. The original Debye-Hückel theory alone cannot give good performance. A combination of Debye-Hückel theory and the Born equation leads to good performance for determining the IIAC, especially using the fitted values for the ion radii. It can be concluded that ion-ion interactions and ion-water interactions are equally significant for aqueous electrolyte solutions. The ion radius is a critical parameter in the prediction of the IIAC. Different ion radii give different ion-ion interactions. Moreover, to improve the prediction performance for complex systems, the physical interactions in aqueous electrolyte solutions should be investigated further.

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