The Non-Monotonic Concentration Dependence of the Mean Activity Coefficient of Electrolytes is a Result of a Balance Between Solvation and Ion-Ion Correlations

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(Dated: September 11, 2014)

Abstract

We propose a simple model to explain the non-monotonic concentration dependence of the mean activity coefficient of simple electrolytes without using any adjustable parameters. The Primitive Model of electrolytes is used to describe the interaction between ions computed by the Adaptive Grand Canonical Monte Carlo method. For the dielectric constant of the electrolyte, we use experimental concentration dependent values. This is included through a solvation term in our treatment to describe the interaction between ions and water that changes as the dielectric constant changes with concentration. This term is computed by a Born-treatment fitted to experimental hydration energies. Our results for LiCl, NaCl, KCl, CsCl, NaBr, NaI, $MgCl_2$, $CaCl_2$, $SrCl_2$, and $BaCl_2$ demonstrate that the principal reason of the non-monotonic behavior of the activity coefficient is a balance between the solvation and ion-ion correlation terms. This conclusion differs from previous studies that assumed that it is the balance of hard sphere repulsion and electrostatic attraction that produces the non-monotonic behavior. Our results indicate that the earlier assumption that solvation can be taken into account by a larger, 'solvated' ionic radius should be reconsidered. To explain second order effects (such as dependence on ionic size), we conclude that explicit water models are needed.

PACS numbers: 02.70.-c, 02.70.Uu, 05.10.Ln

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I. INTRODUCTION

It is well known that the mean activity coefficient, $\gamma_\pm$, of many electrolytes shows a non-monotonic behavior as a function of concentration: (1) increasing the concentration from zero (the infinite dilution limit) $\gamma_\pm$ decreases from 1 with a slope obeying the Debye-Hückel (DH) limiting law[1], (2) reaches a minimum at a large concentration, then (3) increases again (often above unity) as the concentration approaches saturation. The explanation of this behavior has been a topic of several attempts starting from various empirical modifications[2–7] of the DH theory, through more developed statistical mechanical theories[8–19], to computer simulations[5,6,21]. It is also the topic of this letter.

The activity coefficient describes the deviation from ideality through the excess chemical potential

$$\gamma_i = \exp\left(\mu_i^{\mathrm{ex}}/kT\right), \tag{1}$$

with

$$\mu_i = \mu_i^0 + kT \ln c_i + \mu_i^{\mathrm{ex}}, \tag{2}$$

where μ_i is the chemical potential of species i, c_i is the concentration of species i, μ_i^0 is a reference chemical potential independent of the concentration, μ_i^{ex} is the excess chemical potential characterizing the effect of interaction between particles, k is Boltzmann's constant, and T is the temperature. The reference point is chosen in such a way that $\mu_i^{\mathrm{ex}} \to 0$ when $c_i \to 0$ for every i. The mean activity coefficient of a simple electrolyte with a stoichiometry $\mathrm{C}_{\nu_+}\mathrm{A}_{\nu_-} \rightleftarrows \nu_+\mathrm{C}^{z_+} + \nu_-\mathrm{A}^{z_-}$ is defined as

$$\gamma_\pm = \sqrt[\nu_+ + \nu_-]{\gamma_+^{\nu_+}\gamma_-^{\nu_-}}, \tag{3}$$

where C and A refer to cations and anions, ν_+ and ν_- refer to their respective stoichiometric coefficients, and z_+ and z_- refer to their respective valences. In this study, we restrict ourselves to pure electrolytes, where only one concentration is present as an independent variable (the other is bound by electroneutrality). We will express our results as a function of the salt concentration denoted by c, where $c = c_+/\nu_+ = c_-/\nu_-$.

It has been believed for a long time that the primary reason of the failure of the DH theory is that it treats the ions as point charges[2–4]. Therefore, modifications of the DH theory involved an adjustable size parameter (usually denoted by a) characterizing the excluded volume of ions. When modern statistical mechanical theories became available, the Primitive

Model (PM) of electrolytes became the subject of extensive study because it includes finite ion size in a natural way using a well-defined molecular model: ions are modeled as charged hard spheres (HS), while the solvent is modeled as a dielectric continuum with a dielectric constant ϵ. The corresponding interparticle potential is

$$u_{ij}^{\mathrm{PM}}(r) = \begin{cases} \infty & \text{for } r < \dfrac{R_i + R_j}{2} \\ \dfrac{z_i z_j e^2}{4\pi\epsilon_0 \epsilon r} & \text{for } r \geq \dfrac{R_i + R_j}{2}, \end{cases} \tag{4}$$

where R_i is the radius of ionic species i, e is the electronic charge, ϵ_0 is the permittivity of vacuum, and r is the distance between ions.

Extensions of the DH theory[5–7], as well as MSA[11–19] and simulation[5,6] studies of the PM showed that agreement with experiments can be achieved only if an ionic radius larger than the Pauling radius[20] is used. The large radius was interpreted as the 'solvated' radius of the ion and thus as representing solvation effects beyond those described by the interaction with a continuum dielectric. The optimal ion size was obtained by fitting to experimental $\gamma_{\pm}(\mathrm{c})$. In most cases, the Pauling radius was used for the anions and R_+ was fitted. In some cases R_+ was constant[5,11,12,16–18]; in other cases R_+ was concentration-dependent[5,13–15,19].

The reason that an increased ion size can reproduce the increase in $\gamma_{\pm}(c)$ at high concentrations is that larger 'solvated' radius produces larger excluded volume interactions among the ions, and, thus, a larger HS component in the chemical potential, which can compensate for the attractive electrostatic term and even overcompensate at large concentrations. Therefore, it was believed that the reason of the non-monotonic behavior is a balance between the repulsive volume exclusion and the attractive electrostatic terms.

With solvation represented in an empirical 'solvated' ionic radius the contribution of ion-water (IW) interaction to the excess chemical potential was rarely discussed in implicit solvent based electrolyte models. Here, the dielectric constant carries the information about the ability of water to screen the ion. If the dielectric constant does not change with concentration, the IW interaction is unchanged and solvation does not contribute to μ_i^{ex}. This was assumed in several studies[5,11,13,19], where the dielectric constant was kept fixed at that of pure water.

The dielectric constant, however, decreases with increasing concentration, a well known experimental fact[22]. This decrease is mainly due to dielectric saturation[23]. Increasing electric field produced by the ions orients the water molecules in the solution thus decreasing their ability to adjust their orientation in the solvation shell of an ion. Consequently, the screening ability of the solvent (expressed by its dielectric constant) decreases as the concentration of ions increases.

If the dielectric constant is concentration dependent, the IW interaction cannot be ignored. One must compute the change in the direct interaction with water as the dielectric environment changes with concentration.

The concentration dependence of the dielectric constant has been considered by many workers. In several studies, it was an adjustable parameter[12,14,15]. In these calculations, both the ionic radius and the dielectric constant were adjusted to reproduce experimental $\gamma_{\pm}$.

The dielectric constant of an electrolyte, however, is a measurable thermodynamic quantity rather than an adjustable parameter. Fawcett and Tikanen[16–18] proposed using an experimental concentration dependent dielectric constant expressed in the form

$$\epsilon(c) = \epsilon_{\mathrm{w}} - \delta_{\mathrm{S}} c + b_{\mathrm{S}} c^{3/2}, \tag{5}$$

where $\epsilon_{\mathrm{w}} = 78.46$ is the dielectric constant of the infinitely dilute solution (pure water). The coefficients δ_{S} and b_{S} are tabulated in Table I for the electrolytes studied in this work. Fawcett and Tikanen[16–18] used the MSA similar to that of Simonin *et al.*[14,15]. The IW interaction, however, was not included in these calculations[14–18]. The concentration dependence of the dielectric constant was taken into account by differentiating the free energy with respect to concentration thus obtaining a contribution involving $\partial\epsilon/\partial c$. Again, the ionic radii were adjusted to fit the results to experimental $\gamma_{\pm}$.

In the works cited so far[5–7,11–19], a wide variety of fitting procedures were used to bring calculations into agreement with experiments. This sometimes resulted in exotic values of the fitted parameters such as an ionic radius smaller than the crystallographic value or dielectric constant at infinite dilution smaller than that of water.

Instead of using fittable parameters, we propose a model where all the parameters have an experimental origin. It is not our goal to reproduce experimental data for $\gamma_{\pm}(c)$ accurately. Our primary intention in this letter is to understand the physics behind the non-monotonic behavior of the activity coefficient. We use experimental parameters so we can see how well the PM deals with experimental data without adjustable parameters. The second goal of our study then is to explore the domain of applicability of the PM in describing activity coefficients.

II. MODEL AND METHODS

In our approach, the excess chemical potential splits into two terms

$$\mu_i^{\mathrm{ex}} = \mu_i^{\mathrm{II}} + \mu_i^{\mathrm{IW}}, \tag{6}$$

where II refers to ion-ion interactions. For the ionic radii, the Pauling radii were used (Table II), while for the dielectric constant the experimental value was used for a given concentration (see Eq. 5 with the data of Table I). The II term is determined from the Adaptive Grand Canonical Monte Carlo (A-GCMC) simulation method using the PM of electrolytes (Eq. 4). For details of the A-GCMC method, we refer the reader to the original papers[24,25]. In short, it is an iterative procedure that allows the computation of the chemical potentials that correspond to prescribed concentrations. In the Grand Canonical ensemble, the number of ions fluctuate due to ion insertion/deletion steps. The chemical potentials (which are independent variables of the ensemble) are adjusted during the iteration process to obtain the desired concentrations during iteration. A cubic simulation cell was used with periodic boundary condition and the minimum image convention.

We assume that the IW term contains the interaction of an inserted ion only with the surrounding water represented as a continuum dielectrics. This corresponds to an electrolyte at infinite dilution. The free energy change at infinite dilution can be interpreted as the excess chemical potential, an intensive quantity. The information that the electrolyte is, in fact, not infinitely diluted and ions are present at large concentration is included only in the concentration dependent dielectric constant.

We estimate the ϵ-dependence of the IW term using the treatment of Born[26] for solvation, which is probably the simplest way to compute an ion's energy in a dielectric environment. The Born term is the electrostatic energy required to bring a charged spherical ion from vacuum ($\epsilon = 1$) to the solution ($\epsilon = \epsilon(c)$). This term estimates only the electrostatic energy of this ion insertion, the change in entropy is not included. The Born expression usually overestimates the experimental Gibbs free energy of solvation, ΔG_i^{s}. Therefore, following Nonner *et al.*[27], we use the Born equation for the mere purpose to estimate the ϵ-dependence of the solvation free energy.

As a first step, we approximate the experimental Gibbs free energy of solvation, ΔG_i^{s}, (tabulated in Table II, taken from Fawcett[4]) with the Born expression:

$$\Delta G_i^{\mathrm{s}}[\epsilon(c)] = \frac{z_i^2 e^2}{8\pi\epsilon_0 R_i^{\mathrm{B}}} \left(\frac{1}{\epsilon(c)} - 1 \right). \tag{7}$$

The output of this equation is the Born radius, R_i^{B}, that does not have to be the same as the Pauling radius, R_i. As a matter of fact, it is usually larger than the Pauling radius and, in an approximative way, it includes all the contributions that are beyond the crude Born-model.

The reference state of μ_i^{ex} is the infinitely dilute electrolyte. Therefore, in the second step, we express the free energy required to bring the ion from the infinitely dilute electrolyte (ϵ_{w}) to a concentrated electrolyte ($\epsilon(c)$) and identify this free energy difference with the solvation (IW) term of the excess chemical potential:

$$\mu_i^{\mathrm{IW}}(c) = \Delta G_i^{\mathrm{s}}(c) - \Delta G_i^{\mathrm{s}}(c \to 0) = \Delta G_i^{\mathrm{s}}[\epsilon(c)] - \Delta G_i^{\mathrm{s}}[\epsilon_{\mathrm{w}}] = \frac{z_i^2 e^2}{8\pi\epsilon_0 R_i^{\mathrm{B}}} \left(\frac{1}{\epsilon(c)} - \frac{1}{\epsilon_{\mathrm{w}}} \right). \tag{8}$$

Expressing the Born radius R_i^{B} from Eq. 7 and substituting it into Eq. 8, we obtain

$$\mu_i^{\mathrm{IW}}[\epsilon(c)] = \Delta G_i^{\mathrm{s}} \frac{\epsilon(c) - \epsilon_{\mathrm{w}}}{\epsilon(c)\ (\epsilon_{\mathrm{w}} - 1)}, \tag{9}$$

which scales the experimental ΔG_i^{s} in inverse proportion to the dielectric coefficient. This way, we constructed a model that does not contain any adjustable parameter.

Note that the II and IW terms are coupled only by the dielectric constant and computed with independent methods. The IW term is computed as if only water were present and the effect of ions appears only via the concentration dependence of $\epsilon(c)$. The II term is simulated on the basis of the PM, where the effect of water appears only in the dielectric constant.

The need for a treatment of solvation when the dielectric constant is changed was also considered by Abbas *et al.*[5] and Inchekel *et al.*[28] We will discuss these studies later in comparison with our results.

We have also calculated the II term with the MSA using the formulae given by Nonner *et al.*[29]. Our primary method, however, is computer simulation because it reproduces the II term exactly within certain statistical accuracy. Our results then show how accurately the model can reproduce experimental results. Using an approximate theory we introduce another kind of error into our calculations: the error within which the theory can reproduce results for a given model compared to simulation data. Separation of these two kinds of errors is possible if we know the accuracy of the applied theory from comparison to simulations.

III. RESULTS AND DISCUSSION

Figure 1 presents experimental activity coefficients[30] for NaCl (Fig. 1a) and $CaCl_2$ (Fig. 1b) together with the predictions of our model. The II interaction in the model is solved by both A-GCMC simulation and MSA theory, and the II and IW contributions to the activity coefficient are presented for either treatment. The non-monotonic dependence on concentration seen in the activity coefficient is predicted by the model. The increase of the model activity coefficient at high concentration is the consequence of the increase of the IW term (Eq. 9) – the II term (which includes electrostatic and excluded volume interactions) is monotonic and increasingly negative. The variations of both the II and IW terms involve the substantial variation of dielectric constant with salt concentration.

The sum of the two large terms with opposite signs is quite close to the experimental data. Because the sum of these two terms of large absolute values is sensitive to errors in the two terms and because our model does not contain any adjustable parameters, we are satisfied with the results. Any of the two terms could be adjusted by changing R_i and/or R_i^{B}, but our goal is not to obtain perfect agreement with experimental results using an admittedly imperfect theory.

Our attention in this paper is rather to understanding principles and to the physical implications of our results. Our results imply that it is not the balance of the HS and electrostatic terms what causes the non-monotonic behavior of $\gamma_{\pm}$, but rather the balance of the II and IW terms. More properly, because the II term contains the HS and the electrostatic terms, it is the balance of three terms: HS exclusion, electrostatic attraction, and solvation (IW). Only two of these terms are formally separated in our formalism (the II and IW terms), although the HS and electrostatic terms are formally separated in the MSA treatment.

This behavior was also found by Inchekel *et al.*[28] (see Fig. 1 of their paper). They used an extension to the Cubic Plus Association equation of state. They had several free energy terms with many adjustable parameters, but they found that the two dominant terms are those corresponding to our II and IW terms, although computed differently. They used a simplified MSA for the II term, while they interpreted the Born term (Eq. 7) as a Gibbs free energy and obtained the chemical potential by differentiation. The factor $\partial\epsilon/\partial c$, therefore, appeared in their equations similarly to those of Simonin *et al.*[14,15].

Abbas *et al.*[5] used practically the same formalism that we used (Eq. 8), and their results are in accordance with ours. To obtain the II term, they applied canonical MC simulations with Widom's particle insertion method[31] modified by Svensson and Woodward[32]. They had, however, different ways of choosing the model parameters. (1) They used the same radius for both ions and this radius was an adjustable parameter. (2) They used the same radius in the Born-term and in the calculations for the II term. Because of this, they overestimated the IW term. Therefore, when they used a fitted 'solvated' radius 0.199 Å for KI (fitted without the Born term), they concluded that "the Born model gives unrealistically high activity coefficients" in agreement with Cruz and Renon[33]. When they fitted the radius with the Born term included, they also obtained large radii that were necessary to make the Born term small enough (2.2 Å for LiBr and 1.775 Å for KI).

In this paper we suggest that the Pauling radii[20] should be used in the II term, while the IW term should be fitted to experimental solvation data, which results in a Born radius larger than the Pauling radius. Pair correlation functions given by molecular dynamics (MD) simulations using explicit water indicate[34] that the cations and anions approach each other and can be in contact without any water molecules between them. Using a 'solvated' radius for the ions, therefore, seems unphysical. Solvation should be taken into account through the different screening properties of the solvent as the dielectric constant is changed with electrolyte concentration. We emphasize that the IW term *must* be computed when a concentration dependent dielectric constant is used. It is a non-vanishing term and it is necessary to make the model consistent.

The agreement between simulation and MSA results is qualitative at best. The two kinds of error described previously have similar magnitudes as seen in Fig. 1. The error within which the model can reproduce experiments is the difference of experimental points (filled black circles) and the II+IW curve optained with A-GCMC (solid blue line with open triangles). The error within which MSA can reproduce simulations for the PM is the difference between II curves obtained with MSA (red dotted line) and A-GCMC (solid red line with open squares). These differences have similar magnitudes in our calculations. With using MSA, therefore, we introduce an error that sometimes improves results (NaCl), while in other cases worsen results ($CaCl_2$) accidentally. In the absence of simulation data it would be hard to separate the effects of the two kinds of errors when we intend to elucidate the disagreement of our results with experiments. The advantage of MSA, nevertheless, is that it is easy to compute.

Having described the basic mechanism behind the non-monotonic concentration dependence of the activity coefficient, we now show our results for various sequences of electrolytes where only one kind of ion is changed. We have performed calculations for the series (1) LiCl, NaCl, KCl, and CsCl; (2) NaCl, NaBr, and NaI; and (3) $MgCl_2$, $CaCl_2$, $SrCl_2$, and $BaCl_2$. The shape of the II and IW curves as well as their sum is quite similar to those shown for NaCl and $CaCl_2$ (Fig. 1), therefore, we discuss the effect of ionic species on mean activity coefficient considering the results for the fixed salt concentration of 1 M. Results for this concentration will characterize the agreement with experimental data for the whole concentration range: if $\gamma_\pm$ is under/overestimated for $c = 1$M, then it is under/overestimated for other concentrations too (Fig. 1).

Figure 2 shows the excess chemical potential and its II and IW components determined from A-GCMC in comparison to experiments. The net excess potentials are close to the experimental values for all tested salts. Our model, however, does not reproduce the slope of the $\ln(\gamma_\pm)$ versus ionic radius curves properly. The experimental slopes have opposite signs for cations and anions (filled black symbols in Fig. 2). Our model gives positive slope in every case.

The asymmetrical nature of this behavior might arise from the asymmetric nature of water molecules. Calculations with explicit water are needed to get a clue. MD simulations using classical force fields is one possibility although consideration of quantum effects might be necessary. Such simulations are very difficult technically: the chemical potential is computed by a thermodynamic integration process[35]. The simulations of Zhang *et al.*[36] provided larger mean activity coefficients for NaCl than for KCl in agreement with experiments but in disagreement with our results. This behavior seems to be closely connected to the molecular nature of water, and in this respect, it is beyond the capabilities of the PM. We would probably need a better theory for solvation (that distinguishes between anions and cations) in order to reproduce this behavior in our model[37].

We have proposed a simple treatment for the activity coefficient of electrolytes based on computer simulations of the PM to compute the interaction between ions and a Born-treatment of solvation to compute the interation between ions and water. We demonstrated that without using any adjustable parameter, the non-monotonic behavior of the mean activity coefficient can be explained by the balance of these two basic physical interactions.

Proper agreement with experiments can be achieved if we use the Pauling radius[20] in the PM to simulate the II interactions, while we use the usually larger Born radius (obtained from fit to experimental solvation data) in the calculation of the IW term. Note that using the Shannon-Prewitt ionic radii[38] instead of the Pauling radii does not change our results. The reason is that the Pauling radius for cations is a little bit larger than the Shannon-Prewitt radius, while the reverse is true for the anions (at least, for the ions considered in this paper). The net result is that the mean activity coefficient does not depend on this choice. Our results imply the the idea of using a 'solvated' ion radius in computation of the II term to take solvation into account should be reconsidered.

Acknowledgment

The authors acknowledge the support of the Hungarian National Research Fund (OTKA K75132). We are grateful for the valuable discussions with Wolfgang Nonner, Dirk Gillespie, István Szalai, and Bob Eisenberg.

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Salt	δ_S	b_S
NaCl[18]	16.2	3.1
KCl[18]	14.7	3.0
CsCl[18]	13.1	2.9
NaBr[16]	20.0	5.0
NaI[16]	21.0	5.0

TABLE I: Coefficients of series expansion of $\epsilon(c)$ (Eq. 5) for salts used in the calculations. For LiCl, the expression $\epsilon(c) = \epsilon_w - 15.5c + 1.96c^2 - 0.306c^{5/2}$ was used[18]. For 2:1 electrolytes ($MgCl_2$, $CaCl_2$, $SrCl_2$, and $BaCl_2$), the values $\delta_S = 34$ and $b_S = 10$ were used (W. R. Fawcett, personal communication).

Ion	z_i	R_i/Å	R_i^B/Å	ΔG_i^s/kJmol^{-1}
Li^+	1	0.6	1.3	-529
Na^+	1	0.95	1.62	-424
K^+	1	1.33	1.95	-352
Cs^+	1	1.69	2.24	-306
Mg^{2+}	2	0.65	1.42	-1931
Ca^{2+}	2	0.99	1.71	-1608
Sr^{2+}	2	1.13	1.85	-1479
Ba^{2+}	2	1.35	2.03	-1352
Cl^-	-1	1.81	2.26	-304
Br^-	-1	1.95	2.47	-278
I^-	-1	2.16	2.82	-243

TABLE II: Experimental parameters of the ions used in the calculations. R_i denotes Pauling radius. The Born radius, R_i^B, was obtained by fitting Eq. 7 to the experimental hydration free energy ΔG_i^s. We used the data for ΔG_i^s found in the book of Fawcett[4]. Values from other sources provided similar results.

Captions of figures

Figure 1 The mean activity coefficient of NaCl (a) and $CaCl_2$ (b) as a function of $\sqrt{c}$ as obtained from simulations and MSA compared with experiments[30].

Figure 2 The mean activity coefficient (computed from A-GCMC) of different electrolytes at concentration $c = 1$ M. Left panel: the monovalent cation is changed with Cl^- kept fixed (alkali metal chlorides); middle panel: the monovalent anion is changed with Na^+ kept fixed (sodium halides); right panel: the divalent cation is changed with Cl^- kept fixed (alkaline earth metal chlorides). The results are plotted as functions of the Pauling radii of the ion which is changed in the given sequence.

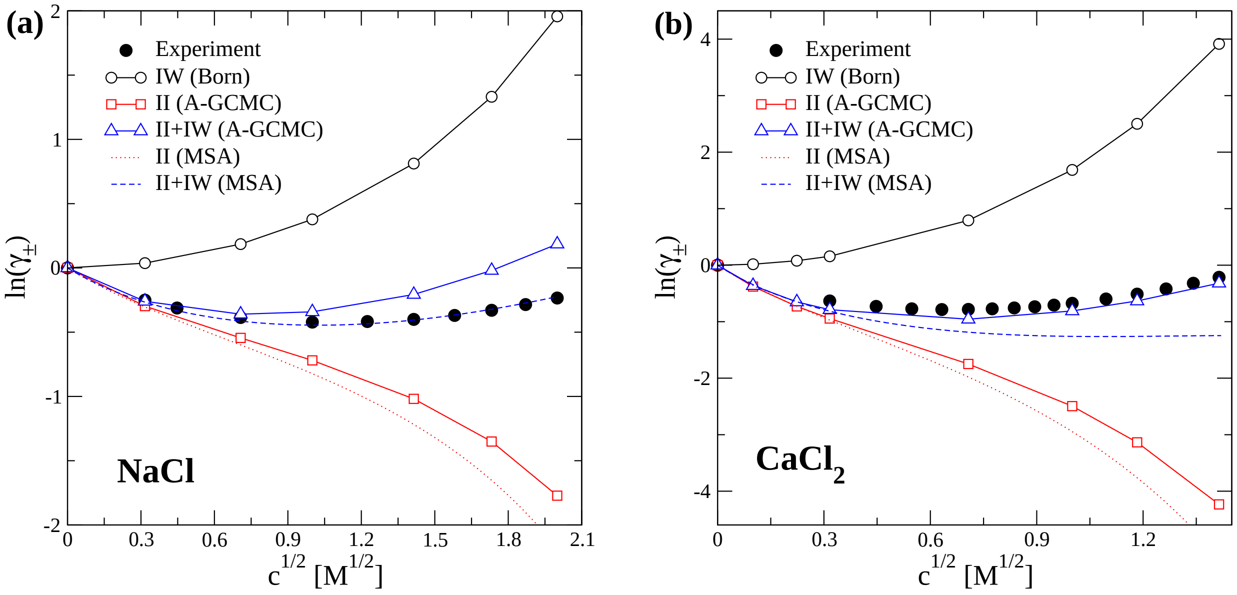

FIG. 1: Vincze *et al.* *J. Chem. Phys.*

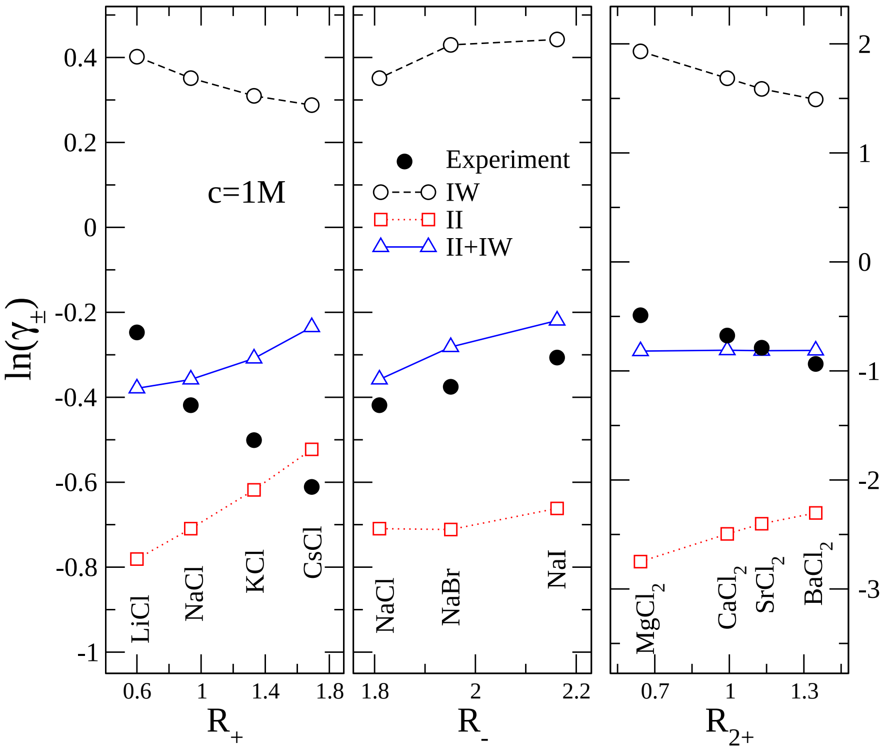

FIG. 2: Vincze *et al.* *J. Chem. Phys.*