Single-Ion Activity: Experiment versus Theory

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ABSTRACT: The almost century-old dispute over the validity of the experimentally derived activity of a single ion, a_i, is still unsettled; current interest in this issue is nourished by recent progress in electrochemical cell measurements using ion-specific electrodes (ISEs) and advanced liquid junctions. Ionic solution theories usually give expressions for a_i values of the positive and negative ions, that is, the respective a_+ and a_-, and combine these expressions to compute the mean ionic activity, $a_{\pm}$, that is indisputably a thermodynamically valid property readily derivable from experiment. Adjusting ion-size parameters optimizes theory's fit with experiment for $a_{\pm}$ through "optimizing" a_+ and a_-. Here I show that theoretical a_i values thus obtained from the smaller-ion shell treatment of strong electrolyte solutions [Fraenkel, *Mol. Phys.* **2010**, *108*, 1435] agree with a_i values estimated from experiment; however, theoretical a_i values derived from the primitive model, the basis of most modern ionic theories, do not agree with experiment.

Computation of Single-Ion Activity Coefficients

$$\log \gamma_+ = -z_+^2 \frac{\mathcal{A}}{\mathcal{B}} \times \frac{\kappa}{1+\kappa a} \left\{ 1 - \frac{2\exp[\kappa(a-b_+)]-\kappa(a-b_+)-2}{1+\kappa b_+} \right\}$$

$$\log \gamma_- = -z_-^2 \frac{\mathcal{A}}{\mathcal{B}} \times \frac{\kappa}{1+\kappa a} \left\{ 1 + \frac{2\exp[\kappa(b_--a)]-2\kappa(b_--a)-2}{1+\kappa b_-} \right\}$$

1. INTRODUCTION

Even though from a straightforward thermodynamic standpoint only the mean ionic activity, $a_{\pm}$, has a clear, undisputable physical meaning, there has been literature yearning for almost a century to "measure" single-ion activities (a_i values) because of their great importance in many fields of science and technology; perhaps the most known example is the concept of pH built on the "conventional" activity of the proton (hydronium ion, H_3O^+, or simply H^+), a_{H+}, that, according to the common literature,[1] cannot be measured in experiment. The perceived lack of a clear physical meaning of the activity coefficient of H^+, γ_{H+} ($= a_{H+}/m_{H+}$; m, concentration) in molal terms, has never deterred serious scientists (let alone many outside the scientific community) from applying this very useful concept, or the more popular term pH that equals (in molal terms) $-\log(m_{H+}\gamma_{H+})$, as if it were a real physical factor. The same rule as applied to γ_{H+} should, in principle, be applied to all other single-ion γ (i.e., γ_i) values, that is, γ_+ and γ_- values, but the debate over the conceptual validity of γ_i is nonetheless legitimate. The current report compares γ_i values derived from theory with those estimated from experiment.

The electrochemical derivation of a_i values, using ion-specific electrodes (ISEs), has been reported by a number of groups, especially in the past two decades. Here I shall focus on two specific studies published in recent years. In one study, involving aqueous sodium halides, Zhuo et al.[2] measured γ_+ and γ_- independently, at different electrolyte concentrations, by an improved technique involving a double junction, an assumed null junction potential and an improved ISE calibration; the geometric average of γ_+ and γ_-, $\gamma_{\pm}$ (the mean molal ionic activity coefficient), was calculated and shown to be in fair agreement with experimental $\gamma_{\pm}$. In another study, Wilczek-Vera et al.[3] reported results for various 1−1, 2−1, and 1−2 aqueous electrolytes, including some alkali metal halides and alkaline earth metal halides, for which only γ_- was measured. Both research groups were criticized by Malatesta,[4] who

strongly and passionately argued against the notion that a_i values could be obtained from experiment, in principle, and that what is claimed to be measured has any physical meaning. Malatesta's main point of argument was that it is simply impossible to evaluate the liquid junction potential (LJP) because this potential and the single-ion potential are interdependent. As a result, concluded Malatesta, reported a_i (and γ_i) values are conventional, not physical, quantities; that is, they depend on the particular convention used in their derivation process. Different conventions would yield different a_i (and γ_i) values. Researchers measuring single-ion activities, such as Wilczek-Vera and coworkers,[5] have argued back that the LJP can be estimated (e.g., by Henderson's equation or a modified expression) or can be set about constant and therefore eliminated in the equation used to estimate a γ_i from a known other γ_i. The Debye−Hückel (DH) limiting law, or another expression for γ_i at very high dilution, can be used to estimate the γ_i of the lowest concentration of the experiment.

Despite the intensive effort to estimate single-ion activities from electrochemical measurements, the obtained a_i values of many experimental attempts have been incoherent, inconsistent, or inconclusive, perhaps owing to difficulties to reach the required experimental accuracy or due to calculation inaccuracies relating to the models and methods used. This has shed doubt on the real meaning of a_i, in general, thereby playing into the hands of the skeptics, but in recent literature, a_i data have been emerging, which seem more consistent and solid compared with those previously reported; yet, such data should be carefully selected and distinguished from those that are less reliable. The literature's experimental a_i values used in the present Article are believed through close inspection but without scientific proof to be of reasonable quality. As

experimental research becomes more mature, it is hoped that data of even better quality will become available and that more electrolytes of the various families will be included in single-ion activity studies.

In 1960, Friedman proposed[6] the primitive model (PM) as a more advanced and physically more sound model of strong electrolytes that should replace the older models based on the DH concept of a chosen ion interacting electrostatically with its ionic atmosphere. Emanating from the McMillan−Mayer formalism and Mayer's ionic theory, the PM considers ions as charged hard spheres immersed in a continuum that is characterized by a constant bulk permittivity. Ion-size parameters (ISPs) are simply the sums of radii of the hard spheres; therefore, ion-size additivity is an inherent property of the PM.[6] The PM has been the basis of most modern electrolyte theories of the past half century, among them the hypernetted chain (HNC) advanced integral equation,[7] the popular mean spherical approximation (MSA) theory,[8] and the more recent dressed ion theory (DIT).[9] The PM and theories based on it combine the electrostatic interactions in the ionic solution with the nonelectrostatic interactions arising from dispersive forces, such as London-type forces between electron clouds of adjacent ions; the latter interactions are called "hard sphere" or "core" interactions. The PM thus assumes that the initial decrease in $\gamma_\pm$ as concentration increases, starting from zero (where $\gamma_\pm \equiv 1$), is due to electrostatic attraction between ions with opposite electric signs, whereas the $\gamma_\pm$ behavior at higher concentration, going through a minimum then increasing, is governed by the (repulsive) core effect that at high ionic concentration overcomes the electrostatic attraction effect. The validity of the PM, that is, its fit with experiment, can be examined directly, for example, through Monte Carlo (MC) simulations. There is obviously no need to examine theories based on the PM if this model is found to be inadequate as representative of real ionic solutions. However, if the PM *is* valid, then theories based on it may be very accurate, such as the HNC equation that replicates PM-derived excess thermodynamic functions almost precisely, or less accurate, such as the simplified theory of MSA. Until very recently, the PM has been simulated with arbitrary ISP values, for example, 400 pm (4 Å), and using the simple case of equal-size ions, called the restricted primitive model (RPM). In a few cases, the unrestricted primitive model (UPM), that is, the PM with ions of unequal size, has been employed in the simulation but again with arbitrary ISPs. Results have been reported for the osmotic coefficient (ϕ) or $\gamma_\pm$,[10−12] and theories have been judged for accuracy only based on their ability to generate the PM's prediction when using the same (arbitrary) ISPs.

In what seems to be a long-overdue effort in the field of electrolyte theories, Abbas et al.[13] using an MC method, have recently simulated the PM systematically for many real electrolytes by adjusting ISPs until best fits (with experimental ϕ and $\gamma_\pm$ as functions of concentration) have been achieved. One consequence of this study is a list of recommended sizes for many ions, positive and negative. Here, referring to the study of Abbas et al., I shall restrict myself to the analysis in which (1) the model is UPM, (2) only the cation size is adjusted (the anion size is fixed as Pauling's diameter), and (3) the excess function computed is $y_\pm$ (mean molar ionic activity coefficient). However, I shall examine not the best-fit $y_\pm$ of Abbas et al.[13] but the optimized single-ion activity coefficients y_+ and y_- that produce the best-fit $y_\pm$. I shall hereinafter call the study of Abbas et al., within the above restrictions, MC−UPM.

The smaller-ion shell (SiS) treatment of strong electrolyte solutions[14−16] is an extension of the DH theory for the case of ions of unequal size. It will be referred to here as DH−SiS. The theory accounts only for the electrostatic interaction between a chosen ion and its ionic atmosphere and does so by the use of the linearized Poisson−Boltzmann equation. It attributes the change in $\gamma_\pm$ at higher electrolyte concentration to the combined electrostatic effect arising from the two shells of the smaller ion, that around the smaller ion as chosen ion, and that around the larger ion as chosen ion. The shell around the small ion produces a repulsion effect, whereas the one around the large ion causes an "extra attraction" effect.[14,15] Therefore, as the electrolyte concentration increases, the disparity between the DH−SiS derived γ_+ and γ_- expands. For the case in which the cation is the smaller ion (e.g., in NaCl), γ_+ first decreases, then passes a minimum and rises at higher concentration, whereas γ_- declines monotonically without passing a minimum.

In view of the intrinsic difference in approach between the PM and the SiS model, it is justified to ask which model is right and which is wrong. Because PM-derived γ_i (or y_i) values follow a single trend of decreasing, passing a minimum, then increasing, it may be expected that the most notable γ_i (y_i) difference between MC−UPM and DH−SiS, when the negative ion is larger, would be the different behavior of γ_- (y_-). [Note that the γ versus $I(m)$ and y versus $I(M)$ functions, with I being the ionic strength, practically differ from each other only at high electrolyte concentration, above ∼2 m (or M). In the current text, which deals with lower concentrations (less than ∼1.5 m or M), I shall generally assume that these functions are about the same.] In metal halides, the above question may then reduce to whether experimentally derived γ_{X-} (with X being, say, Cl or Br) fits the MC−UPM prediction or the DH−SiS one. However, through the correlation of γ_+ and γ_- with $\gamma_\pm$, the "right model" should be right also for γ_+, thus further contrasting itself from the "wrong model".

Before proceeding further, I should mention the very recent publication[17] of Sakaida and Kakiuchi, in which γ_{H+} and γ_{Cl-}, measured independently in aqueous HCl solutions at 25 °C using the standard Harned electrochemical cell but with a special ionic liquid salt bridge, have been shown to agree fairly well with the DH−SiS prediction of those activity coefficients.[15] In the present Article, I seek to extend the γ_i comparison between DH−SiS and experiment beyond ref 17. However, I also compare DH−SiS and experiment with MC−UPM.

2. METHODS

All activity coefficients of this work are at 25 °C. y_+ and y_- values at various concentrations, as derived from the MC−UPM simulations, were taken from the supporting information of ref 13. (But note the switchover in notation there between y and γ.) γ_+ and γ_- values of the SiS treatment (DH−SiS) were computed from the equations[14]

$$\log \gamma_+ = -z_+^2 \frac{\mathcal{A}}{\mathcal{B}} \frac{\kappa}{1+\kappa a}$$
$$\left\{ 1 - \frac{2 \exp[\kappa(a-b_+)] - \kappa(a-b_+) - 2}{1+\kappa b_+} \right\}$$

(1)

and

$$\log \gamma_- = -z_-^2 \frac{\mathcal{A}}{\mathcal{B}} \frac{\kappa}{1 + \kappa a}$$
$$\left\{ 1 + \frac{2 \exp[\kappa(b_- - a)] - 2\kappa(b_- - a) - 2}{1 + \kappa b_-} \right\} \quad (2)$$

where κ is the reciprocal Debye screening length; z_+ is the valence of the cation and z_- is that of the anion; $\mathcal{A}$ and $\mathcal{B}$ are the familiar constants in the DH extended equation (see Appendix A) for $\log \gamma_\pm$; and b_+, b_-, and a, the ISPs, are, respectively, the cation–cation, anion–anion, and cation–anion closest internuclear distances in the ionic solution, for which we apply the condition $b_+ \leq a \leq b_-$. The Appendices at the end of the main text describe $\mathcal{A}$, $\mathcal{B}$, and κ in more detail (Appendix A) to facilitate the use of eqs 1 and 2, including applying these equations to calculate γ_i values at different temperatures, between 0 and 100 °C, as exemplified in detail for aqueous NaCl (Appendix B).

The fit between theory (SiS) and experiment has been done as previously described.[14,15] The exact values of the universal constants, the fundamental charge, Boltzmann factor, and Avogadro's number, used for the calculation of $\mathcal{A}$ and $\mathcal{B}$ ($= \kappa/I^{1/2}$), see Appendix A, are as in refs 14–16 and so are the values of the density and permittivity of water at 25 °C. $\gamma_\pm$ is, of course, calculated from the relation

$$\log \gamma_\pm = \frac{\nu_+ \log \gamma_+ + \nu_- \log \gamma_-}{\nu} \quad (3)$$

where ν_+ and ν_- are, respectively, the numbers of cations and anions in the electrolyte molecular formula, and $\nu_+ + \nu_- = \nu$. Substituting eqs 1 and 2 into eq 3 obviously gives eq 1 of refs 15 and 16. $y_\pm$ is likewise calculated from the analogue of eq 3 for molar activity coefficients. The conversion of $\gamma_\pm$ to $y_\pm$ for best fit of the DH–SiS with experiment in molar terms was done following previously described methods.[13,15]

3. RESULTS

Figures 1 and 2 present single-ion activity coefficients of common 1−1 halides as a function of concentration, and Figures 3 and 4 depict those of typical 2−1 halides. Figure 5 shows the behavior of K_2SO_4, a 1−2 electrolyte. In all cases, literature data [of Zhuo et al.[2] ("Zhuo") or Wilczek-Vera et al.[3] ("Vera")] are shown as the corresponding symbols, and lines (and also broken lines in Figure 2) represent the DH–SiS prediction. In Figures 1, 3, and 4, broken lines are the MC−UPM predictions. The ISPs used in each case in DH–SiS and MC−UPM are listed in Table 1. In DH–SiS, b values are equal or close to the crystallographic diameters; for the halides, a is larger than the arithmetic average of the b values, and this may be attributed to elongation of the anion by the approaching small cation due to ionic polarization.[14,15] The divalent cations appear somewhat larger than expected based on their crystallographic sizes, perhaps due to a certain extent of strong hydration.[14] However, on the molar scale, the best-fit ISP of Ca^{2+} is identical to its crystallographic diameter (Table 1). In MC−UPM, the cation size is consistently far greater than expected, and this has been explained by Abbas et al. as reflecting extensive ion hydration.[13] As a result, also a is larger than the sum of the crystallographic radii of the cation and anion; the a values of MC−UPM are about parallel to those of
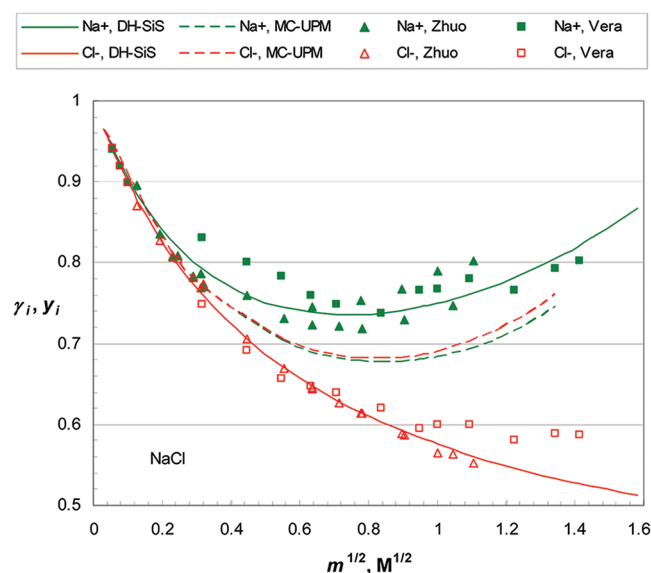

Figure 1. Single-ion activity coefficients of Na^+ and Cl^- in aqueous NaCl solution at 25 °C and their dependence on electrolyte concentration. Experimental data (symbols) and DH−SiS calculated curves (solid lines) are on the molal scale (γ_i vs $m^{1/2}$); MC−UPM computed curves (broken lines) are on the molar scale (y_i vs $M^{1/2}$). "Zhuo" stands for Zhuo et al.[2] and "Vera" stands for Wilczek-Vera et al.[3]
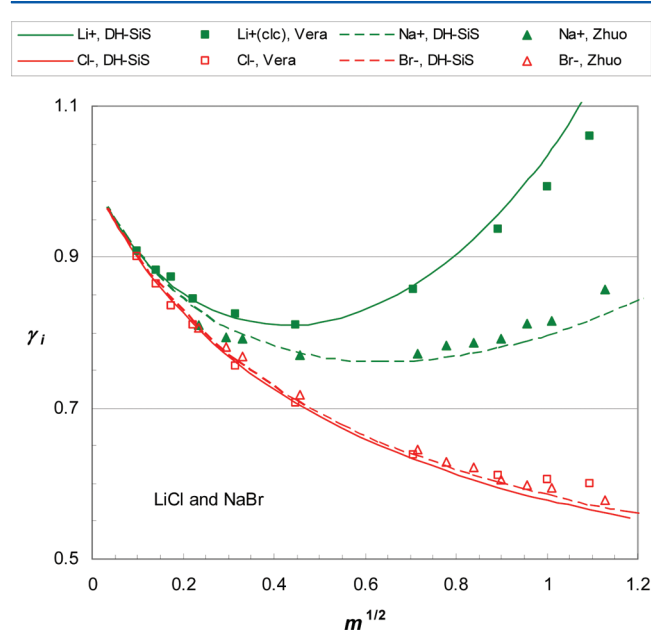

Figure 2. Single-ion activity coefficients of Li^+ and Cl^- in aqueous LiCl solution and of Na^+ and Br^- in aqueous NaBr solution, all at 25 °C, and their dependence on electrolyte concentration. The LiCl experimental data (square symbols) are of Wilczek-Vera et al.;[3] the NaBr experimental data (triangle symbols) are of Zhuo et al.[2] Theoretical lines (full for LiCl, broken for NaBr) are those of DH−SiS.

DH−SiS for the 1−1 electrolytes but much larger than those of DH−SiS for the 2−1 electrolytes (Table 1).

It is important to note that the DH−SiS fit quality for the $\gamma_\pm$ versus $I^{1/2}$ function is excellent up to at least ∼1 m concentration,[14] whereas the parallel fit quality of MC−UPM (as $y_\pm$ versus $I^{1/2}$), also extending to ∼1 m (M), is considerably worse.[18] Therefore, the term "best fit" has different meaning
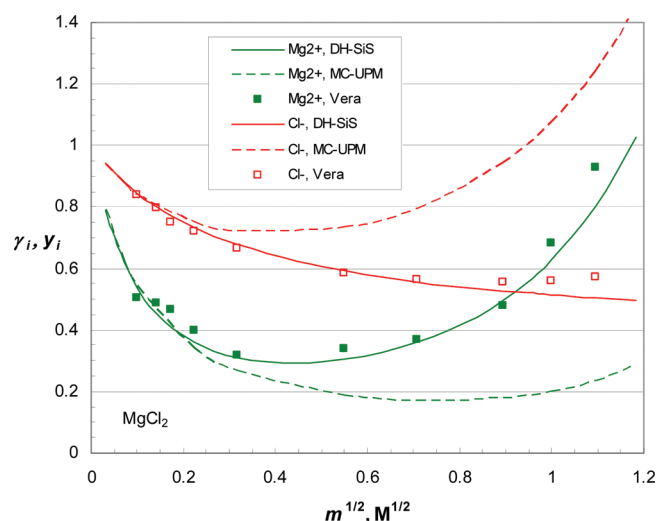
Figure 3. Single-ion activity coefficients of Mg^{2+} and Cl^- in aqueous $MgCl_2$ solution at 25 °C and their dependence on electrolyte concentration. As in Figure 1, experimental and DH−SiS data (symbols and full lines, respectively) are molal, that is, γ_i versus $m^{1/2}$, and MC−UPM data (broken lines) are molar, that is, y_i versus $M^{1/2}$. "Vera" stands for Wilczek-Vera et al.[3]
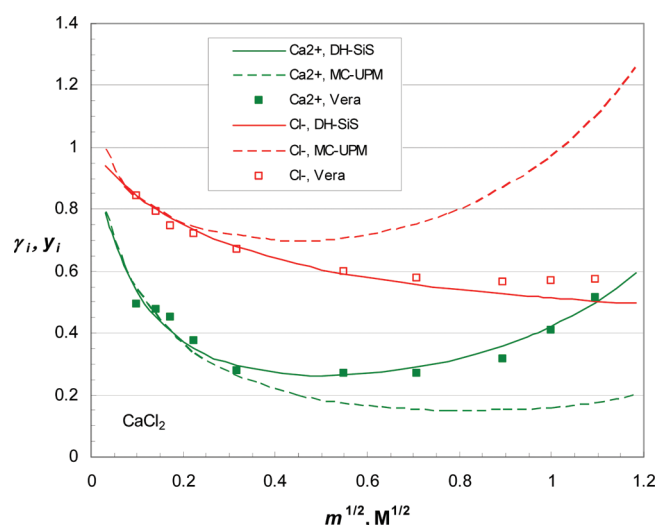

Figure 4. As Figure 3 but for Ca^{2+} and Cl^- in aqueous $CaCl_2$ solution.

Figure 5. Single-ion activity coefficients of K^+ and SO_4^{2-} in aqueous K_2SO_4 solution at 25 °C and their dependence on concentration. Lines are the DH−SiS computed functional behavior; symbols are experimental data. "Vera" stands for Wilczek-Vera et al.[3]

Table 1. Ion-Size Parameters (in pm) Giving the Best Fit of DH−SiS and MC−UPM with Experiment for the Change of the Mean Ionic Activity with Concentration[a]

			DH−SiS		MC−UPM	
electrolyte	family	d_+	b_+	a	b_+	a
LiCl	1−1	136[b]	120	348	420	391
NaCl	1−1	194	194 (194)	344 (352.5)	336	349
NaBr	1−1	194	194	364	336	364
MgCl₂	2−1	132	212	361	590	476
CaCl₂	2−1	198	226 (198)	361 (339)	548	455
K₂SO₄	1−2	266	266	317		

[a]In water, at 25 °C; b_- in both cases is 362 for Cl^- and 392 for Br^-, so $b_- = d_-$, d_- being the crystallographic diameter of the anion; for SO_4^{2-}, $b_- = 460$ (see ref 14); d_+ is the crystallographic diameter of the cation (see ref 14). ISPs of DH−SiS are derived from the best fit on molal scale except for the values in parentheses that are from the best fit on molar scale; for MC−UPM, all best-fit ISPs are on the molar scale (ref 13); experimental $\gamma_\pm$ values are from literature sources mentioned in refs 13 and 14. [b]Pauling's value, 120.

in the two cases; it is far stricter for DH−SiS. MC−UPM typically misses experiment initially downward (giving substantially lower $y_\pm$ values), then crosses experiment and rises steeply thereafter (giving increasingly higher $y_\pm$ values), due to the core effect. This is illustrated in Figure 6 for NaCl and CaCl₂. The explanation of Abbas et al. for the lack of fit at concentrations higher than 1 M for many halide electrolytes, among them NaCl, NaBr, MgCl₂, and CaCl₂, is strong ion association;[13] this explanation, however, seems to lack solid independent evidence. DH−SiS gives, in contrast, about constant fit quality that is very high at the effective fit range;[18] then, beyond this range, the fit is gradually lost, with computed $y_\pm$ values being lower than the experimental ones. (See Figure 6.) This may be due to core effects that are ignored in DH−SiS.

In all cases shown here (Figures 1−5), the experimental values of single-ion activity coefficients fit fairly well with the theoretical DH−SiS values but are in clear disagreement with values predicted by MC−UPM. In Figure 1, two sets of
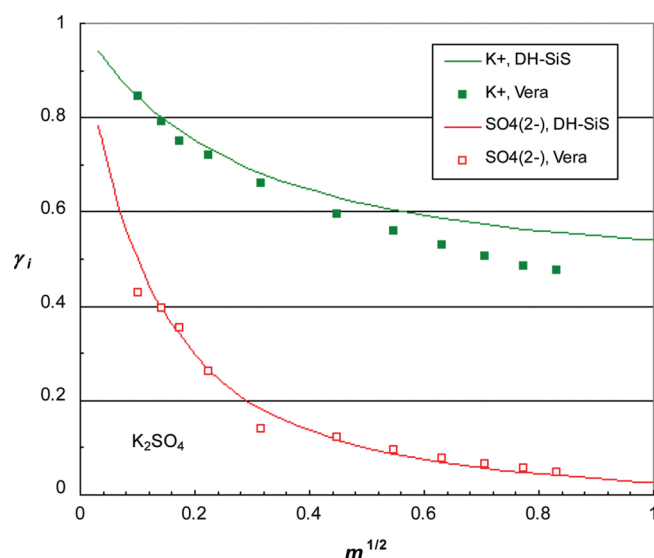
experimental results for NaCl from the two different literature sources are presented; they are in reasonable accord with each other and fit impressively with the predicted curves of the SiS analysis of this electrolyte, at least up to ~1 m. The "Vera set", that is, that of Wilczek-Vera et al.[3] (both γ_{Na+} and γ_{Cl-} based on eq 18 in ref 3) fits with poorer quality and appears less consistent and smooth as a function of concentration. The "Zhuo set", that is, that of Zhuo et al.[2] (comprising two separate experimental groups of measured data herein combined together) appears to be of higher quality and fits better with the SiS curve, especially for γ_{Cl-}. The γ_{Na+} versus $m^{1/2}$ function goes clearly through a minimum as, and where, expected from theory, and γ_{Cl-} declines monotonically with increase in concentration, again as predicted by DH−SiS. The MC−UPM prediction for both γ_{Na+} and γ_{Cl-} (broken lines) is at odds with the experimental results (and with the SiS prediction), both quantitatively and qualitatively.
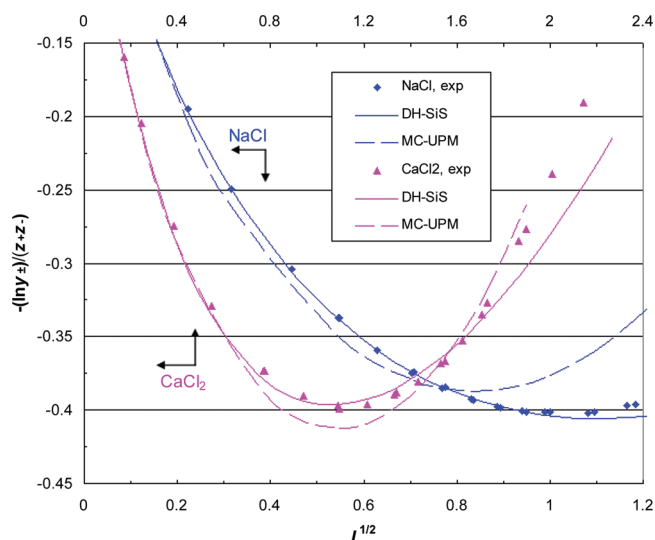
Figure 6. Best fit of DH−SiS (solid lines) and of MC−UPM (broken lines) with the experimental $\ln y_{\pm}$ versus $I^{1/2}$ behavior (symbols) of NaCl and CaCl$_2$. For better relative comparison of the two electrolyte systems, the effect of electrolyte family is eliminated by dividing $\ln y_{\pm}$ by $z_+ z_-$.

Figure 2 shows that experimental γ_i values of LiCl (Vera) and NaBr (Zhuo) agree very well with the parallel theoretical DH−SiS values, at least up to ~1 m, and as effectively as in the NaCl case. The respective MC−UPM curves are not shown to avoid crowdedness, but they are similar in nature to those of NaCl, thus again not agreeing with experiment.

Figures 3 and 4 demonstrate the behavior of 2−1 electrolytes; they depict a similar pattern, compared with 1−1 electrolytes, featuring a very good fit of experiment with DH−SiS and a clear lack of fit with MC−UPM. For the 2−1 electrolytes, as expected, γ_+ is considerably lower than γ_- over most of the concentration range of good fit; this is in contrast with the γ_i order of 1−1 electrolytes (Figures 1 and 2). The difference in γ_+ as a function of cation valency for electrolytes of different families and the lack of difference in γ_{Cl^-} have been discussed and explained previously.[14] Also, unlike 1−1 electrolytes, the 2−1 electrolytes MgCl$_2$ and CaCl$_2$ exhibit a crossover of the γ_+ and γ_- curves, with γ_+ becoming larger above a certain concentration. There are subtle, yet significant, variations, however, between these two 2−1 electrolytes. For example, the crossover occurs at 0.85 m for MgCl$_2$ and at 1.2 m for CaCl$_2$. The experimental data appear in good agreement with the theoretical MgCl$_2$ crossing point and seem to not contradict with theory for CaCl$_2$, even though in this case the DH−SiS calculated crossover point is beyond the concentration range of good fit.[14] As in the 1−1 electrolyte case, the MC−UPM prediction for the 2−1 systems strongly disagrees with experiment and with the prediction of DH−SiS. The MC−UPM y_- ($\approx \gamma_-$) values are considerably above γ_- values of the experiment and, unlike the latter, go through a low concentration deep minimum; the MC−UPM y_+ ($\approx \gamma_+$) values are considerably below those of the experiment and exhibit a weak minimum at higher concentration. MC−UPM predicts no γ_+−γ_- (or y_+−y_-) crossover points for the 2−1 electrolytes.

A clear advantage of the SiS treatment over the DH theory is that due to the ion-size dissimilarity in the SiS model and the consequent smaller-ion shell around the central ion there is a straightforward theoretical explanation for the different experimental behavior (activity vs concentration) of different asymmetric families sharing the same values of the $|z_+ z_-|$ and I/m factors; the DH theory and the RPM and theories based on it are all blind to this difference. Thus, as discussed previously,[14] the fundamental experimental difference between 2−1 and 1−2 electrolytes (as well as 3−1 and 1−3 electrolytes, etc.) is readily predicted by the SiS treatment (DH−SiS). This difference is *not* related to ion size changes or the different level of ion pairing between electrolytes of various families; instead, it is just the effect of the smaller-ion shell (missing in the DH theory and in the PM).

In Figure 5, the single-ion activity coefficients of K$^+$ and SO$_4^{2-}$ in K$_2$SO$_4$ solutions ($|z_+ z_-|$ = 2, I/m = 3) are shown as functions of concentration; as seen, the behavior is very different from that of the 2−1 electrolytes ($|z_+ z_-|$ = 2, I/m = 3), for example, CaCl$_2$ (Figure 4). Specifically, γ_+ is larger than γ_- over the entire concentration range of interest, and γ_- of the divalent anion (SO$_4^{2-}$) declines more strongly than γ_- of the univalent anion (Cl$^-$). Computed γ_i values, using DH−SiS, and the experimental values of Wilczek-Vera et al.[3] fit initially very well, but the experimental γ_+ shifts downward from theory at higher concentration, to ~10% lower values. In the experiment, only γ_+ (i.e., γ_i of K$^+$) was "measured" and γ_- (γ_i of SO$_4^{2-}$) was calculated from the relation with $\gamma_{\pm}$ (eq 3), using literature's $\gamma_{\pm}$ derived from experiment. Therefore, the downward shift of γ_+ is accompanied by a small upward shift of γ_-. Overall, the experiment−theory fit is good considering the approximate nature of the method of calculating γ_i by Wilczek-Vera et al., and experiment and theory show the same general trend of the change of γ_i values with concentration.

No MC−UPM data are available for K$_2$SO$_4$ because Abbas et al. analyzed mostly electrolyte systems that exhibit a clear minimum in the $y_{\pm}$ versus M curve. In the many other cases in which $y_{\pm}$ declines monotonically with the increase in concentration (e.g., electrolytes of the 1−2, 1−3, and 1−4 families[14]) it is difficult, if not impossible, to apply the UPM because no real core effect is observed despite the ions being usually very large (for instance, in potassium electrolytes of polyatomic anions). The only way to "justify" the use of the UPM in such systems, if not resorting to unphysically small ISPs, is to claim strong ion association; this limits the analysis to very small concentration at which the contribution of the electrostatic attraction to the thermodynamic nonideality of the electrolyte solution overwhelms the contribution of the hard-sphere repulsion.

4. DISCUSSION

The present Article is not meant to, nor can it, resolve the controversy on the physical validity of the experimentally "measured" single-ion activity and not even on whether it is conceptually feasible to separate the mean ionic activity, experimental or theoretical, into physically well-defined activities that uniquely and unequivocally represent individual ions.[19] Theoretical single-ion activities are obviously subject to the electrolyte model chosen and the method and assumptions applied in devising a model−theory and the mathematical solution involved. That being said, two important general findings of the current work, which are directly related to the above problem, deserve attention:

(1) Experimental estimation of γ_+ and γ_- of a few 1−1, 2−1, and 1−2 electrolytes that appear to be of good quality and consistency shows a compelling agreement with

theoretical values derived from the SiS treatment, even though an ionic activity data set derived from experiment and a parallel set derived from theory are completely independent of each other in the way by which they are arrived at; the current results support and complement the outcome of the recent study of Sakaida and Kakiuchi on aqueous HCl.[17]

(2) The prediction of single-ion activities using the PM is in clear disagreement with experiment as well as with the prediction of the SiS model. Therefore, if the PM is correct, being indeed an ideal physical presentation of electrolytes, then the SiS model and literature experimental data of a_i values are wrong and meaningless; if the SiS model and the experiment are correct, then the PM is obviously useless, being inadequate for real-world electrolytes, and so are all electrolyte theories based on this model (in both the RPM and UPM levels).

Malatesta has issued a strong warning to electrolyte scholars[4] to not rely on experimental γ_i values for justifying their theories by confusing conventional γ_i values with γ_i values of physical reality that, he argued, are unfeasible; in the current context, this may be interpreted as suggesting that even if the PM does not agree with the results of Wilczek-Vera et al., Zhuo et al., and Sakaida and Kakiuchi, then this is of no physical consequence whatsoever. By the same token, according to Malatesta, the "physical" validity of the SiS treatment is by no means related to whether or not it agrees with experimentally derived γ_i values. This, however, poses a dilemma. If the experimental γ_i values are indeed "conventional" and, as Malatesta has argued, there is an infinite number of $\gamma_+ - \gamma_-$ combinations that satisfy a given value of $\gamma_\pm$ (using, of course, an infinite number of different conventions), then we face a weird situation: Strangely, γ_i values obtained from experiment by different groups of researchers, using different electrochemical methods and employing different arbitrary conventions, all mysteriously generally agree with the DH–SiS theoretical prediction for various electrolytes of different families, in which another, totally different (and again, "arbitrary") convention is used. Possibly, conventional γ_i values are in fact quite close to "real" γ_i values that *do* have physical meaning because the other possibility is that experimental γ_i values of an arbitrarily chosen convention (e.g., of Vera's group) match theoretical γ_i values of another, unrelated arbitrary convention (SiS treatment); statistically, this seems very unlikely. Malatesta has indeed admitted,[4] as reiterated by Wilczek-Vera et al.,[20] that "for many purposes, there is no difference between the use of conventional values (of activity coefficients − DF) and the unknown real values." Wilczek-Vera et al. further pointed out correctly that "all activity coefficients are conventional" by being dependent on their standard state which is a convention.

Unsurprisingly, I favor the possibility that γ_i values of DH–SiS and of experiment *are* valid and those of the PM are not, regardless of the notional difference between "conventional" and "physical" ion activity, which may end up being mostly semantic. Figure 6 seems to support further my conclusion that the SiS model is more adequate than the UPM as representative of real-life electrolyte solutions. In view of this, caution is due in regarding the recommended ion sizes of Abbas et al. − unless fixed as the crystallographic (e.g., Pauling's) sizes − as anything other than just fitting parameters; as such, they may only serve to create the illusion that an imperfect model (the PM) agrees with experiment.

If the SiS equations, eqs 1 and 2, up to a certain electrolyte concentration limit, are indeed of physical significance, then the single-ion activity in a binary system is simply and straightforwardly related to the size of the ion (its b) and to the counterion's distance of closest approach (a). Apart from these two ISPs, a_i depends only on readily available system variables − concentration, temperature, solvent's density, and permittivity (but note that ISPs change with permittivity[16]) − and the universal constants mentioned in the Methods section. Furthermore, eqs 1 and 2, by including the conterion's ISP, a, show that a_i is dependent on the type and nature of the counterion in a well-understood and usually predictable manner. Therefore, a_i of a certain ion is not the same in different electrolytes in which this ion is combined with different counterions, except if a is accidentally the same in two (or more) such equi-ion electrolytes.

In contrast with the above dependence of a_i on system constants and variables if the SiS model is correct, assuming instead that the PM is the correct model makes ion activities much more complex physical functions. They then depend on all of the above factors and also on ion solvation and ion pairing and their specific details, and, of course, on the nonelectrostatic core effect. The latter three factors are complicated and vague, not easily comprehensible and predictable, and − worse − not commonly supported by hard independent evidence.

More high-quality experimental studies allowing the estimation of a_i values of many strong binary electrolytes in solution are needed, and they may show whether the experiment–theory agreement, as revealed in the current study and in the work of Sakaida and Kakiuchi,[17] is a mere coincidence or it emanates from the very nature of ionic solutions.

5. CONCLUSIONS

Selected literature data of individual ion activities of positive and negative ions in aqueous solutions of various electrolytes of different families, estimated from electrochemical measurements at 25 °C over a range of concentration up to ∼1 M (m), have been compared with theoretical computations. Summarizing the main findings of the current work

(1) Computations based on Monte Carlo (MC) simulations of the unrestricted PM (UPM) do not correlate with experiment.

(2) In contrast, computations based on the SiS analytic expressions do correlate with experiment.

(3) Therefore, the current work indicates that, to a first approximation, besides system variables and universal constants, only the size of the ion and the closest distance of the ion to its counterion are necessary individual factors in evaluating the single-ion activity.

(4) Consequently, if what is desired is a simplified, yet effective, correlation between theory and experiment, there is, in general, no need to consider ion solvation, ion pairing, and core effects in computing single-ion activities.

■ APPENDIX A: THE DEBYE–HÜCKEL PARAMETERS $\mathcal{A}$, $\mathcal{B}$, AND κ AND THEIR DEPENDENCE ON UNIVERSAL CONSTANTS AND RESPONSE TO ELECTROLYTE SOLUTION CONDITIONS

The purpose of Appendix A is to provide somewhat more elaboration on eqs 1−3 to facilitate their use for practical cases. The Appendix is intended for researchers who do not wish to

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Table 2. Parameters for the Calculation of Activity Coefficients at Different Temperatures (t, as °C); for Symbols, See Text[a,b]

t	σ	ε	δ	$\mathcal{B}$	$\mathcal{A}$	$\mathcal{A}/\mathcal{B}$
0	0.99984	87.87	696.20	0.0032459	0.49070	151.179
5	0.99996	85.90	699.39	0.0032535	0.49411	151.872
10	0.99970	83.96	702.89	0.0032612	0.49776	152.631
15	0.99910	82.06	706.68	0.0032690	0.50164	153.454
20	0.99820	80.20	710.74	0.0032769	0.50574	154.336
<u>25</u>	<u>0.99704</u>	<u>78.38</u>	<u>715.06</u>	<u>0.0032849</u>	<u>0.51006</u>	<u>155.273</u>
30	0.99565	76.66	719.60	0.0032930	0.51456	156.259
35	0.99403	74.86	724.35	0.0033012	0.51924	157.290
40	0.99221	73.17	729.28	0.0033094	0.52407	158.360
50	0.98803	69.88	739.95	0.0033264	0.53449	160.677
60	0.98320	66.74	751.54	0.0033442	0.54575	163.195
70	0.97777	63.75	763.79	0.0033620	0.55761	165.856
80	0.97181	60.92	776.75	0.0033801	0.57011	168.668
90	0.96535	58.24	790.13	0.0033977	0.58296	171.575
100	0.95839	55.73	803.55	0.0034141	0.59572	174.489

[a]σ (as g/cm^3) and ε of water are smoothed values obtained by polynomial regressions based on handbook data (see ref 14); ε values above 80 °C are larger than the handbook's by 0.1 to 0.2; δ, $\mathcal{B}$ and $\mathcal{A}/\mathcal{B}$ are in pm (100 pm = 1 Å). [b]Number underlining in the 25 °C line emphasizes the recommended parameters for this temperature at which most activity measurements have been, and still are, conducted.

spend time and effort searching the literature yet are still interested in learning more (or refreshing their memory) on the DH (and DH−SiS) model essentials. Here I give some background on the DH parameters, especially in regard to their use in the SiS treatment and, specifically, their presence in the above equations. I further concentrate on the dependence of the DH parameters on temperature (T as absolute) and on the permittivity (ε) and density (σ) of the solvent. The standard textbooks on electrolyte solutions may be consulted for more detail, but I especially recommend the excellent step-by-step presentation of the Debye−Hückel theory in Davidson, N. *Statistical Mechanics*; McGraw-Hill: New York, 1962; Chapter 21.

Equations 1 and 2 include the DH parameters in addition to the three ISPs and the ionic valences. To concentrate on the DH parameters, let us reduce DH−SiS to the conventional and simpler DH theory, where all ions are assumed to have the same size, and additivity is enforced for the distances of closest approach. For this, we simply apply in eqs 1 and 2 the condition $a = b_+ = b_-$ to obtain, respectively

$$\log \gamma_+ = -z_+^2 \frac{\mathcal{A}}{\mathcal{B}} \frac{\kappa}{1 + \kappa a} \tag{1A}$$

and

$$\log \gamma_- = -z_-^2 \frac{\mathcal{A}}{\mathcal{B}} \frac{\kappa}{1 + \kappa a} \tag{2A}$$

Equation 3 then becomes

$$\log \gamma_\pm = z_+ z_- \frac{\mathcal{A}}{\mathcal{B}} \frac{\kappa}{1 + \kappa a} \tag{3A}$$

Because by definition, $\mathcal{B}$ is the proportionality coefficient of the κ versus $I^{1/2}$ function (see below), that is, $\kappa = \mathcal{B}I^{1/2}$, we have

$$\log \gamma_\pm = -|z_+ z_-| \frac{\mathcal{A}I^{1/2}}{1 + \mathcal{B}aI^{1/2}} \tag{4A}$$

the well-known Debye−Hückel extended equation (DHEE).

The κ factor arises from the linearized Poisson−Boltzmann equation, $\nabla^2 \phi(r) = \kappa^2 \phi(r)$, where $\phi(r)$ (r being the distance from the coordinate origin) is the electrostatic potential at r, as

felt by the singled-out (or β) ion, that is, the ion placed at the coordinate origin. The explicit mathematical expression for κ is

$$\kappa = \left[4\pi\delta \left(\sum_\alpha \frac{N_\alpha}{V} z_\alpha^2 \right) \right]^{1/2} \tag{5A}$$

where $\delta = q^2/\varepsilon kT$, with q and k being the fundamental charge and the Boltzmann factor, respectively; δ is thus a characteristic length − the distance between two unit charges at which their electrostatic interaction energy equals the kinetic energy kT. The dimension of δ is [pm] when the ISPs are in pm. Subscript α in eq 5A denotes atmospheric ions, and N_α/V, with $V = 1000$ (see below), is the number density of the α-ions per 1 cm^3 volume. The DH and DH−SiS developments are in volume-molal terms; hence I is in fact I_v, but in theoretical analyses, it is more convenient to apply instead the weight-molal ionic strength, I_w, which, at sufficiently dilute solution, is related to I_v through the solvent's density, σ (i.e., $I_v \approx \sigma I_w$), and is defined by

$$I_w = \frac{1}{2} \sum_\alpha m_\alpha z_\alpha^2 \tag{6A}$$

Therefore, eq 5A transforms to a more convenient form

$$\kappa = \left(4\pi\delta \frac{2\sigma A_N}{1000} \times I_w \right)^{1/2} \tag{7A}$$

in which A_N is Avogadro's number. I further use σ as the density of the solvent even at ~1 m; this is a good practical approximation in aqueous solutions, and for 1−1 electrolytes it is still reasonable up to ~2 m. (See ref 15.)

From eq 7A, we have

$$\mathcal{B}_w = \left(8\pi\delta \frac{\sigma A_N}{1000} \right)^{1/2} \tag{8A}$$

(subscript w specifying that $\mathcal{B}$ is expressed in terms of I_w), so if the dimension of δ is [pm], then the dimension of $\mathcal{B}_w$ is [pm^{-1}(kg-solvent/mol-solute)$^{1/2}$].

The $\mathcal{A}/\mathcal{B}$ ratio in eqs 1 and 2 (and in this Appendix, in eqs 1A−3A) equals $\delta/(2 \ln 10)$; see eq 31 in ref 14. Therefore,

$$\mathcal{A}_w = \left(2\pi \frac{\sigma A_N}{1000}\right)^{1/2} \frac{\delta^{3/2}}{\ln 10} \qquad (9A)$$

The dimension of $\mathcal{A}_w$ is $[(\text{kg-solvent/mol-solute})^{1/2}]$, and the $\mathcal{A}/\mathcal{B}$ (or $\mathcal{A}_w/\mathcal{B}_w$) ratio is, like δ, a length parameter whose dimension is [pm] if the ISPs (and δ) are given in pm.

■ APPENDIX B: COMPUTATION OF THE DEBYE−HÜCKEL AND RELATED PARAMETERS AT DIFFERENT TEMPERATURES AND CALCULATION OF THE INDIVIDUAL ACTIVITY COEFFICIENTS OF AQUEOUS NaCl, AS TEST CASE, AT DIFFERENT TEMPERATURES AND CONCENTRATIONS

Appendix B demonstrates the usefulness of the DH parameters when incorporated in the SiS expressions, for the theoretical computation of γ_+ and γ_- as functions of T, ε, and concentration (or I). The classical electrolyte NaCl in aqueous solution is used, as a test case, at the temperature range of 0−100 °C. The parameters of the computations, σ, ε, δ, $\mathcal{A}_w$, $\mathcal{B}_w$, and $\mathcal{A}_w/\mathcal{B}_w$, at various temperatures, are presented in Table 2.

The δ, $\mathcal{A}$, and $\mathcal{B}$ values of Table 2 are numerically somewhat different than those provided in the literature (e.g., in Robinson, R. A.; Stokes, R. H. *Electrolyte Solutions*, 2nd ed.; Butterworths: London, 1959, p 468) in being computed from more current and accurate values of the universal constants (see source in refs 14 and 15) and also because $\mathcal{A}$ and $\mathcal{B}$ values of the present Appendix are on the weight-molal scale. In the computation program for $\gamma_{\pm}$ versus m, σ and ε are calculated from continuous polynomial functions of temperature. Therefore, in Table 2 the values of σ and ε are smoothed, being recalculated from the continuous $\sigma(T)$ and $\varepsilon(T)$ functions. For improved accuracy, two separate $\varepsilon(T)$ functions are used, one covering the temperature range 0−40 °C and the other most effective for the 40−100 °C range. With the latter polynomial function, ε values at >80 °C slightly (i.e., insignificantly) deviate from the tabulated literature values. (See footnote a in Table 2.)

For calculating γ_+ and γ_- of NaCl, we need to use, at each temperature, the ISPs that provide the best fit of calculated $\gamma_{\pm}$ ($\gamma_{\pm}{}^{clc}$) with experimental $\gamma_{\pm}$ ($\gamma_{\pm}{}^{exp}$) over a range of concentration. $\gamma_{\pm}{}^{exp}$ data for NaCl were taken from the compilation of Robinson and Stokes in the above-mentioned reference (on p 480) and from the compilation of Harned and Owen (Harned, H. S.; Owen, B. B. *The Physical Chemistry of Electrolytic Solutions*, 3rd ed.; Reinhold Publishing Corp.: New York, 1958, p 726). ISP optimization was done with a fixed Na+ radius of 97 pm (the crystallographic value) hence with $b_+ = 194$ pm and with b_- calculated from $b_{Cl-}[\text{pm}] = 316 + 3640/\varepsilon$, the recently reported expression correlating b_{Cl-} with ε based on HCl solutions; see ref 16. Thus, in the current optimization, the b values are unadjusted, and a is the only adjustable parameter. Optimized a values at different temperatures are listed in Table 3, which also shows the goodness of the fit in terms of $\Delta\gamma_{\pm} = \gamma_{\pm}{}^{clc} - \gamma_{\pm}{}^{exp}$. In the present analysis, the deviation of $\gamma_{\pm}{}^{clc}$ from $\gamma_{\pm}{}^{exp}$ at <1 m is usually very small, and it is still less than −1% up to at least 1.5 m, except at 100 °C. Best-fit a values of the current ISP optimization process are in the 322−352 pm range, increasing with temperature up to 60 °C, then declining with further temperature increase. Tables 4 and 5 list theoretical DH−SiS derived γ_{Na+} and γ_{Cl-} values, respectively, at different temperatures, for various molality values.

Table 3. DH−SiS Derived Best-Fit $\Delta\gamma_{\pm}$ Values and a Values (in pm) of Aqueous NaCl for Selected Values of m and Temperature

	$\Delta\gamma_{\pm}$ at various temperatures (shaded numbers, as °C)						
m	5	15	25	40	60	80	100
0.1	−0.0032	−0.0022	−0.0015	−0.0010	0.0003	0.0006	0.0007
0.2	−0.0015	−0.0011	−0.0030	0.0008	0.0007	0.0006	0.0004
0.5	0.0000	0.0005	−0.0003	0.0009	0.0003	0.0008	−0.0001
1.0	0.0006	−0.0009	−0.0002	0.0005	−0.0026	−0.0008	−0.0024
1.5	−0.0012	−0.0013	−0.0017	−0.0044	−0.0088	−0.0052	−0.0119
2.0	−0.0098	−0.0103	−0.0101	−0.0140	−0.0209	−0.0135	−0.0180
2.5	−0.0237	−0.0220	−0.0213	−0.0230	−0.0315	−0.0221	−0.0255
a	328.5	338.0	344.0	349.0	351.7	350.0	343.0

In a further effort, more γ_i data points have been computed at various temperatures and concentrations than those listed in Tables 4 and 5; for this, a was expressed as the following polynomial function of temperature (t, as degrees centigrade)

Table 4. DH−SiS Computed γ_{Na+} Values of Aqueous NaCl at Selected Values of m and Temperature[a]

	γ_{Na+} at various temperatures (shaded numbers, as °C)						
m	5	15	25	40	60	80	100
0.001	0.966	0.966	0.965	0.964	0.963	0.961	0.960
0.002	0.953	0.953	0.952	0.951	0.949	0.947	0.945
0.005	0.930	0.929	0.928	0.927	0.924	0.921	0.917
0.01	0.906	0.905	0.904	0.902	0.899	0.895	0.890
0.02	0.877	0.876	0.875	0.873	0.868	0.863	0.857
0.05	0.830	0.830	0.829	0.827	0.821	0.814	0.806
0.1	0.792	**0.793**	**0.793**	0.790	0.785	0.776	0.765
0.2	0.755	0.759	**0.760**	0.758	0.753	0.744	0.730
0.5	<u>0.721</u>	<u>0.731</u>	<u>0.735</u>	<u>0.738</u>	<u>0.735</u>	<u>0.725</u>	<u>0.706</u>
1.0	<u>0.721</u>	0.738	0.749	0.757	**0.759**	0.749	0.725
1.5	0.738	0.764	0.782	0.796	**0.803**	0.794	0.764

[a]Bold numbers are in the vicinity of the maximum on the temperature scale; underlined numbers are in the vicinity of the minimum on the molality scale.

Table 5. DH−SiS Computed γ_{Cl-} Values of Aqueous NaCl at Selected Values of m and Temperature

	γ_{Cl-} at various temperatures (shaded numbers, as °C)						
m	5	15	25	40	60	80	100
0.001	0.966	0.965	0.965	0.964	0.962	0.961	0.959
0.002	0.953	0.952	0.951	0.950	0.948	0.946	0.943
0.005	0.928	0.927	0.926	0.924	0.921	0.918	0.914
0.01	0.902	0.901	0.900	0.897	0.894	0.889	0.884
0.02	0.869	0.868	0.867	0.864	0.859	0.853	0.847
0.05	0.814	0.813	0.811	0.807	0.800	0.793	0.784
0.1	0.764	0.763	0.761	0.756	0.748	0.739	0.728
0.2	0.708	0.707	0.705	0.700	0.692	0.681	0.668
0.5	0.632	0.632	0.630	0.625	0.615	0.603	0.587
1.0	0.575	**0.577**[a]	0.576	0.571	0.561	0.547	0.529
1.5	0.545	**0.547**[a]	0.546	0.542	0.531	0.517	0.498

[a]See footnote in Table 4.

$$a = 344.0 + 0.45939(t - 25) - 1.066247$$
$$\times 10^{-2}(t - 25)^2 + 1.80944 \times 10^{-4}(t - 25)^3$$
$$- 2.5477 \times 10^{-6}(t - 25)^4 + 1.21 \times 10^{-8}(t - 25)^5$$
$$\qquad (1B)$$

The smoothed a values are almost identical with values obtained directly, that is, by manually adjusting this ISP for each experimental series of $\gamma_\pm$ versus m data at constant temperature. The deviation of smoothed a values from directly optimized a values is within ± 0.1 pm and hence insignificant. Using eq 1B, γ_+ and γ_- were calculated to provide the $\gamma_i−m−t$ mappings as presented in Figure 7. The Figure provides
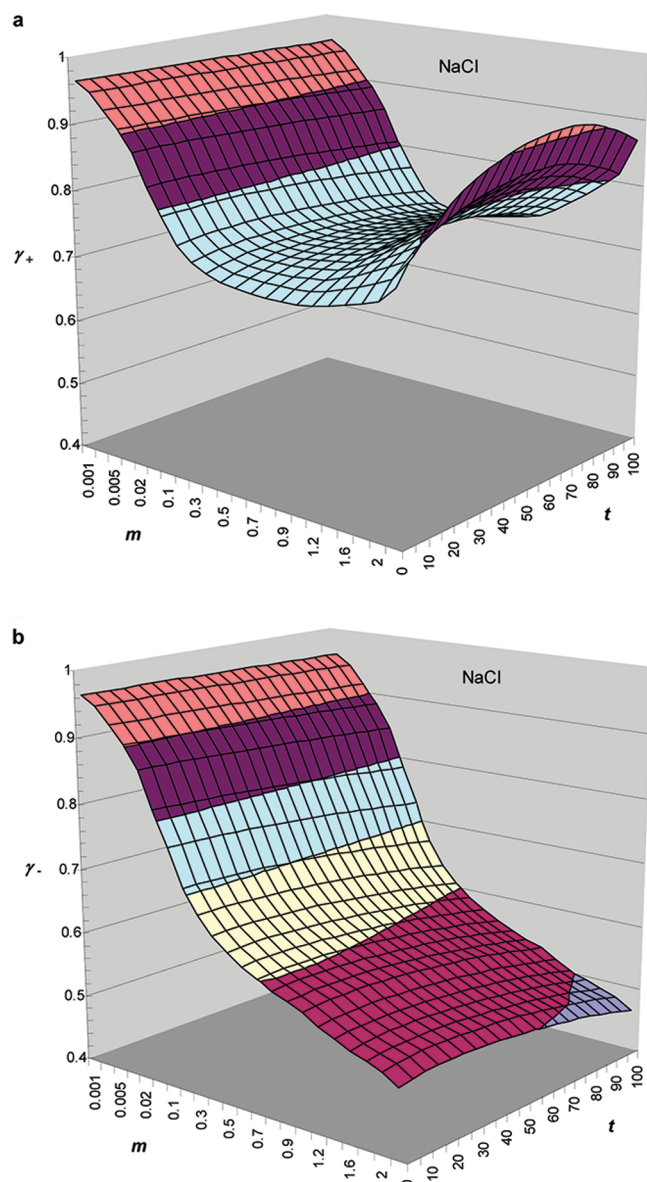
Figure 7. $\gamma_i−m−t$ contour maps for Na$^+$ (a) and Cl$^-$ (b) in aqueous NaCl (t is in °C).

contour lines of γ_i versus t at constant m, and γ_i versus m at constant t. Each line corresponds to a given m or t value, respectively. The constant-t lines are of temperatures between 0 and 100 °C with a constant increment of 5 °C. The m scale is not proportional to the m values, and the 22 constant-m lines are those of the m values 0.001, 0.002, 0.005, 0.01, 0.02, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, and 2.5. In this smoothed area presentation of γ_+ (Figure 7a) and γ_- (Figure 7b), different colors represent different 0.1 increments on the γ_i scale, thus facilitating the comprehension of the two maps as well as the comparison between the

behavior of Na$^+$ and Cl$^-$. For example, in Figure 7a, the sixth constant-m line, corresponding to 0.05 m, is within one color zone representing the 0.8 to 0.9 range of γ_+, but this line in Figure 7b goes from that color zone to another because γ_- is in the 0.8 to 0.9 zone at low temperature but above 60 °C, it is in the 0.7 to 0.8 zone.

The differences between γ_+ and γ_- are very apparent: At <0.1 m, γ_+ declines with increasing temperature over the entire range, but above 0.1 m, γ_+ first increases then passes a maximum and declines at higher temperature. The γ_+ maximum becomes more pronounced and shifts to higher temperature with increase in concentration, reaching 60 °C at 1.5 m. This behavior seems to parallel that of a (eq 1B). The minimum of γ_+ as a function of concentration occurs at ~0.5 m for all temperatures. It is also noteworthy that the γ_+ increase past the minimum is steeper for higher temperatures up to 80 °C. In contrast with γ_+, γ_- — in addition to not exhibiting a minimum as a function of m — declines steadily with increasing temperature over the entire range of the present analysis except above $m = 1$ where a shallow maximum is indicated at 15 °C; γ_- is, otherwise, about constant at any given m in the temperature range of 0−25 °C.

Finally, it should be noted that even though other, somewhat different, sets of ISPs can be chosen for the optimization of the $\gamma_\pm^{\text{clc}}−\gamma_\pm^{\text{exp}}$ fit, such ISP sets cannot substantially affect the calculation of γ_+ and γ_-. This is a general rule, so it applies not only for NaCl but also for many other electrolytes. Therefore, individual ion activity coefficients derived from DH−SiS are solid, reliable theoretical data.

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Notes
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