Comment on "The Role of Concentration Dependent Static Permittivity of Electrolyte Solutions in the Debye–Hückel Theory"

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In their recent paper,[1] Shilov and Lyashchenko (SL) extended the Debye–Hückel (DH) theory (denoted as EDH in this work) for the case when the dielectric constant of the electrolyte can vary with salt concentration, $\varepsilon(c)$, which is a strong experimental evidence[2–5] (an idea advocated by Hückel[6] as early as 1925). They divide the thermodynamic functions into two parts representing interionic and ion–water (solvation) interactions denoted by numbers 1 and 2, respectively.

These terms clearly correspond to the II (ion–ion) and IW (ion–water) terms in the excess chemical potential introduced in our II+IW model:[7–10]

$$\mu_i^{\mathrm{EX}} = \mu_i^{\mathrm{II}} + \mu_i^{\mathrm{IW}}. \qquad (1)$$

The II term was computed from Grand Canonical Monte Carlo (GCMC) simulations on the basis of the Primitive Model (PM) of electrolytes using hard sphere ions with the Pauling radii (Table 1), while the IW term was

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computed from the Born equation.[11] The excess chemical potential is related to the activity coefficient through $\mu_i^{\mathrm{EX}} = kT \ln \gamma_i$, where k is Boltzmann's constant and T is temperature.

The purpose of this comment is fourfold. (1) We show that our IW term is equivalent with the solvation term of SL. (2) We show that the Born radii can and should be used in it instead of the Pauling radii. (3) We show that using the individual ionic radii in the equations (instead of the mean, $R_{\pm} = (R_+ + R_-)/2$) the theory of SL gives good results for the individual ionic activities too. (4) We also propose an alternative equation for the individual activity coefficient elaborated in the Supplementary Information (SI).

The IW term that we proposed in our 2010 publication[7] is

$$\mu_i^{\mathrm{IW}}(c) = \frac{z_i^2 e^2}{8\pi\varepsilon_0 R_i^*} \left(\frac{1}{\varepsilon(c)} - \frac{1}{\varepsilon_{\mathrm{w}}} \right), \qquad (2)$$

where μ_i^{IW} is the part of the excess chemical potential of species i that is associated with the

IW interactions, e is the unit charge, z_i is the valence of the ionic charge, ε_0 is the permittivity of vacuum, ε_w is the dielectric constant of water (of the solution at infinite dilution), $\varepsilon(c)$ is the dielectric constant of the solution at salt concentration c, and R_i^* is a yet unspecified ionic radius.

We briefly present SL's results keeping their notation (except that we drop the superscript E to denote "excess"). They started with the Gibbs free-energy

$$G_2 = \sum_i N_i \frac{z_i^2 e^2}{8\pi\varepsilon_0\varepsilon_w R_\pm} \tau_2(\kappa_0), \qquad (3)$$

where N_i is the number of ions of species i and

$$\tau_2(\kappa_0) = 2 \int_0^1 \frac{\lambda}{f(\kappa_0\lambda)} d\lambda. \qquad (4)$$

Function $f(\kappa_0)$ is defined through the equation

$$\varepsilon(c) = \varepsilon(\kappa_0) = \varepsilon_w f(\kappa_0) \qquad (5)$$

and expresses the c-dependence of the dielectric constant. In these equations, κ_0 is the inverse Debye screening length defined through

$$\kappa_0^2 = \sum_j N_j \frac{z_j^2 e^2}{\varepsilon_0\varepsilon_w kTV} \qquad (6)$$

expressing the concentration dependence (the relation of density and concentration is $N_i/V = 1000 N_A c_i$ with N_A being the Avogadro number and V the volume) but still containing the water dielectric constant (ε_w).

The solvation excess chemical potential is obtained from the differentiation $\mu_{i,2} = \partial G_2/\partial N_i$ and is expressed as

$$\mu_{i,2} = \frac{z_i^2 e^2}{8\pi\varepsilon_0 R_\pm\varepsilon_w} [\chi_2(\kappa_0) - 1] \qquad (7)$$

using the infinitely dilute electrolyte as refer-

ence. This equation corresponds to Eq. 29 of SL[1] in SI unit except that the second term of that equation is omitted here (it is small and can be neglected). The function $\chi_2(\kappa_0)$ is given by

$$\chi_2(\kappa_0) = \tau_2(\kappa_0) + \frac{\sigma_2(\kappa_0)}{2}, \qquad (8)$$

where

$$\sigma_2(\kappa_0) = -2 \int_0^1 \frac{f'(\kappa_0\lambda)\lambda^2}{f(\kappa_0\lambda)^2} d\lambda \qquad (9)$$

with $f'(\kappa_0\lambda) = df(\kappa_0\lambda)/d\lambda$ (note the definition of the derivative slightly different from that used by SL).

We can obtain an expression for the individual chemical potential if we use an ion-dependent radius, R_i^*, instead of the mean, $R_\pm$. We have two choices where to introduce the ion-specific radius. (1) We can introduce it in Eq. 7 after the differentiation $\mu_{i,2} = \partial G_2/\partial N_i$ (route 1), or (2) we can introduce it in the free energy:

$$G_2^\dagger = \sum_i N_i \frac{z_i^2 e^2}{8\pi\varepsilon_0\varepsilon_w R_i^*} \tau_2(\kappa_0), \qquad (10)$$

and perform the differentiation $\mu_{i,2}^\dagger = \partial G_2^\dagger/\partial N_i$ afterwards (route 2). The second route results in a slightly different formula for the chemical potential

$$\mu_{i,2}^\dagger = \frac{z_i^2 e^2}{8\pi\varepsilon_0\varepsilon_w R_i^*} \left[\chi_2^\dagger(\kappa_0) - 1\right], \qquad (11)$$

where

$$\chi_2^\dagger(\kappa_0) = \tau_2(\kappa_0) + \frac{1}{2}\left(\frac{\kappa_i^2}{\kappa_0^2}\right)\sigma_2(\kappa_0) \qquad (12)$$

and

$$\kappa_i^2 = \sum_j N_j \frac{z_j^2 e^2}{\varepsilon_0 \varepsilon_{\mathrm{w}} kTV} \frac{R_i^*}{R_j^*}. \qquad (13)$$

The derivation of this equation is found in the SI with some results that show that this equation gives slightly larger values for the bigger ion and slightly smaller for the smaller ion compared to route 1.

In the main text of this comment, therefore, we focus on the first route and show that Eqs. 2 and 7 (with replacing R_i^* for $R_\pm$) are equivalent. We can show this equivalence if we prove that

$$\chi_2(\kappa_0) = \frac{1}{f(\kappa_0)}. \qquad (14)$$

The function $\chi_2(\kappa_0)$ can be written in the form

$$\chi_2(\kappa_0) = \int_0^1 \frac{2\lambda f(\kappa_0\lambda) - \lambda^2 f'(\kappa_0\lambda)}{f(\kappa_0\lambda)^2} d\lambda. \qquad (15)$$

If we realize that

$$\left(\frac{\lambda^2}{f}\right)' = \frac{2\lambda f - \lambda^2 f'}{f^2}, \qquad (16)$$

the integral can be written simply as

$$\chi_2(\kappa_0) = \left[\frac{\lambda^2}{f}\right]_0^1 = \frac{1}{f} \qquad (17)$$

which concludes the proof (the function f is positive in the interval $0 \le \lambda \le 1$).

SL state that "If $f(\kappa_0\lambda) = 1$, then the function $\tau_2(\kappa_0) = 1$ and we arrive at the expression similar to that obtained in the Born theory of solvation." If $f = 1$, the IW term is zero, because the ion does not change its dielectric environment.

They also state that "Our solvation contribution to the ionic activity coefficient is different from a plain Born-like expression used by Vincze, Valiskó, and Boda[46,47]." We have proven above that this statement is wrong and that the solvation contribution of SL is equivalent to the "plain" Born-like expression proposed by us.

The derivation of SL, therefore, justifies our intuitive considerations that were based on identifying the solvation part of the excess chemical potential with the electrostatic interaction of a single ion with the surrounding dielectric medium in which it has been inserted. This electrostatic potential is the same that SL use in their charge-up process. Entropic terms are ignored in both approaches. To our best knowledge, other authors[12–14] also used the Born equation without strict justification.

SL use the mean of the Pauling radii, $R_\pm = (R_+ + R_-)/2$, to compute the mean excess chemical potential:

$$\mu_{\pm,2} = \frac{|z_+ z_-| e^2}{8\pi\varepsilon_0 \varepsilon_{\mathrm{w}} R_\pm} [\chi_2(\kappa_0) - 1]. \qquad (18)$$

We use the individual ionic radii and compute the excess chemical potentials of the individual ionic species from which the mean is obtained as

$$\mu_\pm^{\mathrm{EX}} = \frac{\nu_+ \mu_+^{\mathrm{EX}} + \nu_- \mu_-^{\mathrm{EX}}}{\nu_+ + \nu_-}, \qquad (19)$$

where ν_i is the stoichiometric coefficient (the same weighted average applies for the II and IW components too). For pure electrolytes, $\nu_+ = |z_-|$ and $\nu_- = z_+$. In the SI, we show that the mean excess chemical potentials computed from the individual ones obtained from the two routes are identical: $\mu_{\pm,2} = \mu_{\pm,2}^\dagger$.

In this work, we show detailed results for NaCl and CaCl$_2$. For the dielectric constant, the following equations[4,5] were used:

$$\varepsilon_{\mathrm{NaCl}}(c) = \varepsilon_{\mathrm{w}} - 15.45c + 3.76c^{3/2} \qquad (20)$$

and

$$\varepsilon_{\mathrm{CaCl_2}}(c) = \varepsilon_{\mathrm{w}} - 34c + 10c^{3/2} \qquad (21)$$
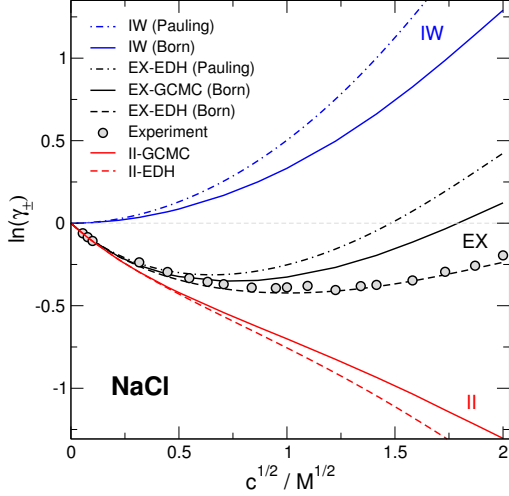
Figure 1: Mean activity coefficients of NaCl and its II and IW components (in molar scale). Solid and dot-dashed blue lines show the IW term as computed from Eq. 2 using either the Born (R_i^B) or the Pauling (R_i) radii for R_i^*. The radii can be found in Table 1. Solid and dashed red lines show the II terms as computed from either GCMC simulations[15] or the EDH theory (Eq. 29 of SL[1]). The black curves show the total activity coefficients as computed from different combinations – solid: GCMC for II and Born radius for IW; dashed EDH for II and Born radius for IW; dot-dashed: EDH for II and Pauling radius for IW. The experimental data are taken from Wilczek-Vera et al.[16] These notations will be used in other figures, therefore, the legend will not be repeated in those figures for clarity.

with $\varepsilon_w = 78.65$ at $T = 298.15$ K. The II term was computed either from GCMC simulations or the EDH theory (Eq. 18 of SL) using the Pauling radii (Table 1).

The mean IW term as calculated from Eq. 18 is a little bit smaller than the mean IW term calculated from Eq. 19. Therefore, we will show only the latter data. It is a more important question which ionic radius should be used
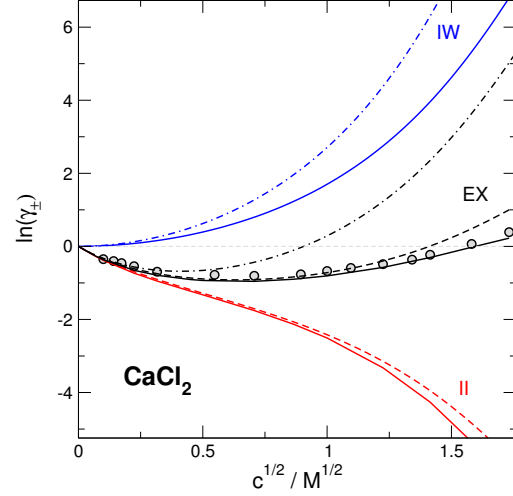

Figure 2: Mean activity coefficients of CaCl$_2$ and its II and IW components. The notations are the same as in Fig. 1.

in Eq. 2. SL used the Pauling radii. This considerably overestimates the IW term. In Figs. 1 and 2 we show the mean activity coefficients of NaCl and CaCl$_2$, respectively. The IW term as computed with the Pauling radii (blue dot-dashed lines) is considerably larger than that computed with the Born radii (blue solid lines). The total activity coefficients computed from the IW (Born) curve (black solid and dashed lines) are in much better agreement with experiment than the one computed from the IW (Pauling) curve (black dot-dashed).

We have proposed in our papers[7–10] that the calculation of the II and IW terms can be decoupled. The only quantity that couples them is the concentration dependent dielectric constant, $\varepsilon(c)$. To compute a decent IW term, we must be as close to experiments as possible. The Born radius can be considered as an experimental parameter, because it is related to the experimental hydration free energy through

$$\Delta G_i^s = \frac{z_i^2 e^2}{8\pi\varepsilon_0 R_i^B}\left(\frac{1}{\varepsilon_w} - 1\right). \qquad (22)$$
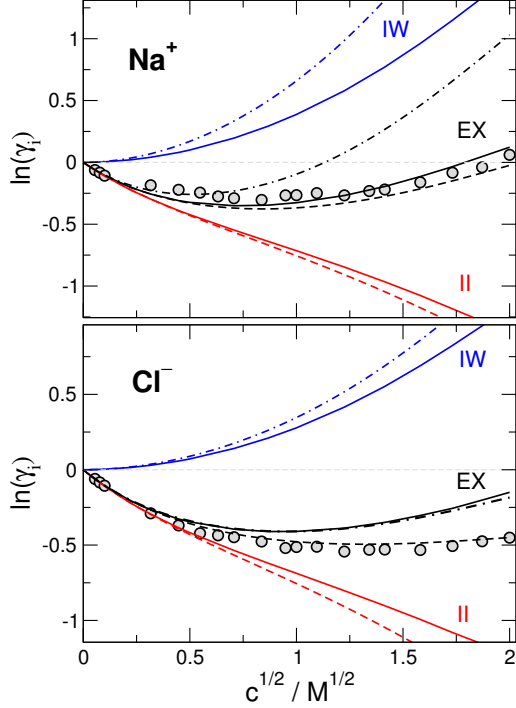
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Figure 3: Individual activity coefficients of Na^+ (top panel) and Cl^- (bottom panel) and their II and IW components in NaCl solutions of varying concentrations. The notations are the same as in Fig. 1.

Figure 4: Individual activity coefficients of Ca^{2+} (top panel) and Cl^- (bottom panel) and their II and IW components in CaCl$_2$ solutions of varying concentrations. The notations are the same as in Fig. 1.

It is important to note that the Born radius is not a physical radius. It is an effective parameter to make the results of a simple theory match the experimental data of a complex system. As a matter of fact, we can eliminate R_i^B from Eqs. 2 and 22 to obtain

$$\mu_i^{IW}(c) = \Delta G_i^s \frac{\varepsilon(c) - \varepsilon_w}{\varepsilon(c)\,(\varepsilon_w - 1)}, \qquad (23)$$

which equation contains only experimental parameters (see Table 1). It might be surprising that this simple electrostatic equation describes the IW term so well. The explanation, in our opinion, is that the main contribution to the change in solvation free energy while the ion is getting from the infinitely dilute solu-
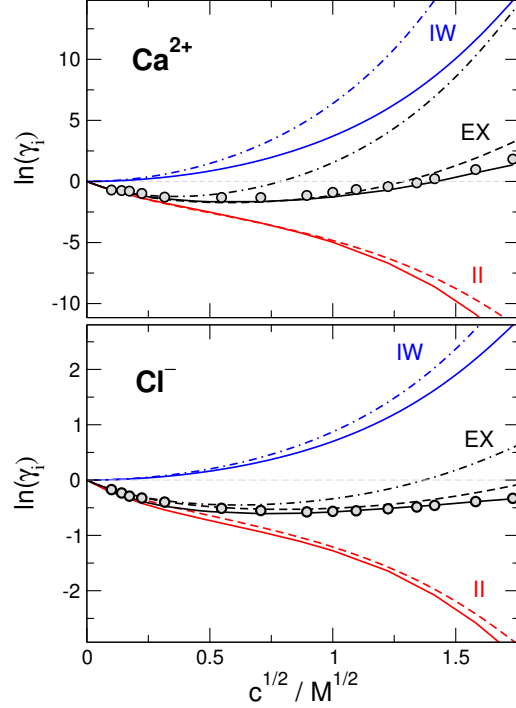
tion (ε_w) to a concentrated solution ($\varepsilon(c)$) is purely electrostatic. Both solutions are high-density and crowded, so entropic terms may cancel. The change in the dielectric environment is described by Eq. 23 seemingly well. The solvation free energy, ΔG_i^s, establishes the amplitude of the change, while $\varepsilon(c)$ establishes the c-dependence.

The problem with the procedure of SL is that this decoupling is not made in their work so they used the Pauling radii in the IW term too. The same thing was done by Abbas et al.[12]

SL cite the "discouraging opinion" of Fawcett and Tikanen.[17] The failure of the works of Fawcett and Tikanen[4,17,18] is due to the fact that they, similarly to earlier

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Table 1: Experimental parameters of ions studied in this work: the valence, z_i, the Pauling radius,[22] R_i, the hydration Gibbs free energy,[23] ΔG_i^s, and the Born radius, R_i^B.

Ion	z_i	$R_i/\text{Å}$	$\Delta G_i^s/\text{kJmol}^{-1}$	$R_i^B/\text{Å}$
Na^+	1	0.95	-424	1.62
Ca^{2+}	2	0.99	-1608	1.71
Cl^-	-1	1.81	-304	2.26

works,[19–21] ignored the IW term.

Inchekel et al.,[13] on the other hand, used the Born radii (they used a complex equation of state to estimate the II term). Liu and Eisenberg[14] used a concentration-dependent Born radius in their Poisson-Fermi theory.

Using the individual ionic radii in Eq. 2 (or, equivalently, in Eq. 7) makes it possible to compute the individual ionic activity coefficients from the EDH theory. Figures 3 and 4 show the results for NaCl and CaCl$_2$, respectively. As far as the experimental data[16] are reliable (this question is strongly debated in the literature; see the discussion in our earlier paper[10]) the agreement with them is quite good. Results for $\mu_{i,2}^\dagger$ obtained from Eq. 11 are found in the SI.

Two main conclusions can be drawn from Figs. 1-4. (1) The curves computed with the Pauling radii are off, which justifies the proposal of computing the IW term using purely experimental data (Eq. 23). (2) The estimate of the EDH theory for the II term (agreement of red solid and dashed curves) is surprisingly good. This is especially stunning for the 2:1 system. The EDH theory is a mean field theory for point ions, namely, it ignores electrostatics correlations between ions and, partly, volume exclusion effects between ions in the ionic cloud, while ionic size can be built into the theory with distance parameters between the cen-

tral ion and the ions around it. The explanation of the relatively good agreement is probably cancellation of errors from ignoring these two effects.[24] The EDH results are smaller than the GCMC results for NaCl, while the opposite trend is observed for CaCl$_2$. We hypothesize that in the case of NaCl the missing hard sphere correlations (that are positive) dominate, while in the case of CaCl$_2$ the missing ionic correlations in Ca^{2+}–Cl^-–Cl^- triplets (that are negative) dominate.

In any case, the EDH theory used together with Eq. 23 to compute the IW term seems like an attractive tool to estimate activity coefficients of electrolytes. We obtained results for other electrolytes (data are available from the authors) similar to NaCl and CaCl$_2$.

All these data have been obtained without using any adjustable parameter (a fact that we cannot emphasize enough). SL proposed a "modest parameter adjustment" by keeping parameter $a = R_+ + R_-$ (that appears in the II term) and adjusted the mean radius by $R_\pm = \eta a$, where η is a fitting parameter. They obtained that $\eta = 0.7$ and 0.8 give good results for NaCl and KCl, respectively. Such a fitting procedure was never our intention,[8] but if someone wants to fit, we would rather suggest the following procedure: use the Born radii in Eq. 7 (or, equivalently, use Eq. 23) and rather fit in the II term playing with the value of a that can be different for the two ions. Adjustable distance parameters can be built into the DH theory with which virtually perfect agreement with experiments can be achieved (see the critical assessment of various modifications of the DH theory in the work of Fraenkel[25]).

Supporting Information The Supporting Information is available free on the ACS Publications website at http://pubs.acs.org. It contains the derivation and discussion of route 2

with results for NaCl and $CaCl_2$.

Acknowledgement

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