

**Supporting Information**

**to**

**Comment on “The Role of Concentration Dependent Static**

**Permittivity of Electrolyte Solutions in the Debye–Hückel**

**Theory ”**

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The second free energy term (in SI unit) corresponding to solvation as defined by Shilov and Lyashchenko (their Eq. 21) is

$$G_2 = \sum_i N_i \frac{z_i^2 e^2}{8\pi\epsilon_0\epsilon_w R_{\pm}} \tau_2(\kappa_0), \quad (1)$$

where  $N_i$  is the number of ions of species  $i$ ,  $e$  is the unit charge,  $z_i$  is the valence of the ionic charge,  $\epsilon_0$  is the permittivity of vacuum,  $\epsilon_w$  is the dielectric constant of water (of the solution at infinite dilution),  $R_{\pm} = (R_+ + R_-)/2$  is the mean ionic radius,

$$\kappa_0 = \left( \frac{e^2}{\epsilon_0\epsilon_w kTV} \sum_i N_i z_i^2 \right)^{1/2} \quad (2)$$

is the inverse Debye screening length expressing the concentration dependence ( $k$  is Boltzmann's constant,  $T$  is temperature,  $V$  is volume),

$$\tau_2(\kappa_0) = 2 \int_0^1 \frac{\lambda}{f(\kappa_0 \lambda)} d\lambda, \quad (3)$$

and function  $f(\kappa_0)$  is defined through

$$\epsilon(c) = \epsilon(\kappa_0) = \epsilon_w f(\kappa_0), \quad (4)$$

where  $\epsilon(c)$  is the experimental  $c$ -dependent dielectric constant. Function  $f(\kappa_0)$  expresses the  $c$ -dependence of the dielectric constant, where concentration is related to density through  $N_i/V = 1000N_A c_i$  with  $N_A$  being the Avogadro number. For the 1:1 and 2:1 electrolytes considered in this paper the salt concentration is equal to the cation concentration:  $c = c_+$ .

The excess chemical potential (that is related to the logarithm of the activity coefficient,  $\gamma_{i,2}$ , is obtained from the derivation

$$\mu_{i,2} = kT \ln \gamma_{i,2} = \frac{\partial G_2}{\partial N_i}. \quad (5)$$

If we leave  $R_{\pm}$  in  $G_2$ , and perform the derivation, we can obtain the expression developed by Shilov and Lyashchenko for the infinite dilution as reference:

$$\mu_{i,2} = \frac{z_i^2 e^2}{8\pi\epsilon_0 R_{\pm}\epsilon_w} \left[ \tau_2(\kappa_0) + \frac{1}{2} \kappa_0 \frac{\partial \tau_2(\kappa_0)}{\partial \kappa_0} - 1 \right] = \frac{z_i^2 e^2}{8\pi\epsilon_0 R_{\pm}\epsilon_w} \left[ \tau_2(\kappa_0) + \frac{1}{2} \sigma_2(\kappa_0) - 1 \right], \quad (6)$$

where

$$\sigma_2(\kappa_0) = \kappa_0 \frac{\partial \tau_2(\kappa_0)}{\partial \kappa_0}. \quad (7)$$

This equation corresponds to Eq. 29 of Shilov and Lyashchenko except that the second term originating from the concentration dependence of  $V$  is omitted here (it is small and can be neglected).

In the main text, we showed that changing  $R_{\pm}$  for  $R_i^*$ , this equation is equivalent with the Born-like expression proposed by us<sup>1-4</sup>

$$\mu_i^{\text{IW}}(c) = \frac{z_i^2 e^2}{8\pi\epsilon_0 R_i^*} \left( \frac{1}{\epsilon(c)} - \frac{1}{\epsilon_w} \right), \quad (8)$$

using the infinite dilution as reference. This equivalence, however, stands only if we perform the  $R_{\pm} \rightarrow R_i^*$  replacement only after the differentiation  $\partial G_2 / \partial N_i$  (called route 1 in the main text). We obtain a slightly different result if we define the free energy with  $R_i^*$  right at the beginning

$$G_2^{\dagger} = \sum_i N_i \frac{z_i^2 e^2}{8\pi\epsilon_0 \epsilon_w R_i^*} \tau_2(\kappa_0) \quad (9)$$

and perform the differentiation  $\partial G_2^{\dagger} / \partial N_i$  afterwards (called route 2 in the main text):

$$\begin{aligned} \frac{\partial G_2^{\dagger}}{\partial N_i} &= \frac{\partial}{\partial N_i} \left( \sum_j N_j \frac{z_j^2 e^2}{8\pi\epsilon_0 \epsilon_w R_j^*} \tau_2(\kappa_0) \right) \\ &= \sum_j \delta_{ij} \frac{z_j^2 e^2}{8\pi\epsilon_0 \epsilon_w R_j^*} \tau_2(\kappa_0) + \sum_j N_j \frac{z_j^2 e^2}{8\pi\epsilon_0 \epsilon_w R_j^*} \frac{\partial \tau_2(\kappa_0)}{\partial N_i}, \end{aligned} \quad (10)$$

where  $\delta_{ij}$  is the Kronecker delta (1 if  $i = j$  and 0 otherwise). In this equation

$$\begin{aligned}
\frac{\partial \tau_2(\kappa_0)}{\partial N_i} &= \frac{\partial \tau_2(\kappa_0)}{\partial \kappa_0} \frac{\partial \kappa_0}{\partial N_i} \\
&= \frac{\partial \tau_2(\kappa_0)}{\partial \kappa_0} \frac{1}{2\kappa_0} \frac{\partial}{\partial N_i} \left[ \frac{e^2}{\epsilon_0 \epsilon_w k T V} \sum_k N_k z_k^2 \right] \\
&= \frac{\partial \tau_2(\kappa_0)}{\partial \kappa_0} \frac{1}{2\kappa_0} \left[ \frac{e^2}{\epsilon_0 \epsilon_w k T V} \sum_k \delta_{ik} z_k^2 + \frac{e^2}{\epsilon_0 \epsilon_w k T} \left( \sum_k N_k z_k^2 \right) \frac{\partial(1/V)}{\partial N_i} \right]. \quad (11)
\end{aligned}$$

The second term in the square brackets is similar to that of Shilov and Lyashchenko, but is small so we neglect it. The first term is

$$\frac{\partial \tau_2(\kappa_0)}{\partial N_i} = \frac{\partial \tau_2(\kappa_0)}{\partial \kappa_0} \frac{1}{2\kappa_0} \frac{e^2}{\epsilon_0 \epsilon_w k T V} z_i^2 \quad (12)$$

using the definition of  $\delta_{ij}$ . Writing it into the second term of Eq. 10 and rearranging we obtain

$$\begin{aligned}
\sum_j N_j \frac{z_j^2 e^2}{8\pi \epsilon_0 \epsilon_w R_j^*} \frac{\partial \tau_2(\kappa_0)}{\partial N_i} &= \sum_j N_j \frac{z_j^2 e^2}{8\pi \epsilon_0 \epsilon_w R_j^*} \frac{\partial \tau_2(\kappa_0)}{\partial \kappa_0} \frac{1}{2\kappa_0} \frac{e^2}{\epsilon_0 \epsilon_w k T V} z_i^2 \\
&= \left( \sum_j N_j \frac{z_j^2 e^2}{\epsilon_0 \epsilon_w k T V} \frac{R_i^*}{R_j^*} \right) \frac{z_i^2 e^2}{8\pi \epsilon_0 \epsilon_w R_i^*} \frac{1}{2\kappa_0} \frac{\partial \tau_2(\kappa_0)}{\partial \kappa_0} \\
&= \frac{z_i^2 e^2}{8\pi \epsilon_0 \epsilon_w R_i^*} \frac{\kappa_i^2}{2\kappa_0} \frac{\partial \tau_2(\kappa_0)}{\partial \kappa_0} \quad (13)
\end{aligned}$$

where we introduced the notation

$$\kappa_i^2 = \sum_j N_j \frac{z_j^2 e^2}{\epsilon_0 \epsilon_w k T V} \frac{R_i^*}{R_j^*} \quad (14)$$

that differs from  $\kappa_0$  in the fraction of  $R_i^*/R_j^*$  that can be considerable in some cases. Here we investigate the effect of that difference.

Replacing Eq. 13 in the second term of Eq. 10, for the solvation (IW) excess chemical potential

in route 2 we obtain that

$$\mu_{i,2}^\dagger = \frac{z_i^2 e^2}{8\pi\epsilon_0\epsilon_w R_i^*} \left( \tau_2(\kappa_0) + \frac{\kappa_i^2}{2\kappa_0} \frac{\partial \tau_2(\kappa_0)}{\partial \kappa_0} - 1 \right) \quad (15)$$

or (using Eq. 7)

$$\mu_{i,2}^\dagger = \frac{z_i^2 e^2}{8\pi\epsilon_0\epsilon_w R_i^*} \left( \tau_2(\kappa_0) + \frac{1}{2} \left( \frac{\kappa_i^2}{\kappa_0^2} \right) \sigma_2(\kappa_0) - 1 \right) \quad (16)$$

with the infinitely dilute electrolyte as reference. The difference between this equation (route 2) and Eq. 6 (route 1) is the presence of the  $\kappa_i^2/\kappa_0^2$  multiplication factor before the  $\sigma_2$ -term. Although the two equations in routes 1 and 2 differ for the individual chemical potentials, the mean computed as

$$\mu_\pm^{\text{IW}} = \frac{1}{\nu} (\nu_+ \mu_+^{\text{IW}} + \nu_- \mu_-^{\text{IW}}) \quad (17)$$

is the same no matter whether we use route 1 or route 2 ( $\nu = \nu_+ + \nu_-$ ). For pure electrolytes,  $\nu_+ = |z_-|$  and  $\nu_- = z_+$ . The proof follows.

The first term containing  $\tau_2(\kappa_0)$  is the same in Eq. 16 and 6. We can prove the statement if we show the equality of the second terms containing  $\sigma_2(\tau_0)$ . By collecting the ion-dependent quantities in square brackets, these terms can be written in the form

$$\frac{A}{\nu} \left[ \nu_+ \frac{z_+^2}{R_+^*} \frac{\kappa_+^2}{\kappa_0^2} + \nu_- \frac{z_-^2}{R_-^*} \frac{\kappa_-^2}{\kappa_0^2} \right] = \frac{A}{\nu} \left[ \nu_+ \frac{z_+^2}{R_+^*} + \nu_- \frac{z_-^2}{R_-^*} \right], \quad (18)$$

where  $A = e^2 \sigma_2(\kappa_0) / 16\pi\epsilon_0\epsilon_w$ . We prove the equality by developing the square bracket on the left hand side until we get the square bracket on the right hand side. Using the definition of  $\kappa_+^2$  and  $\kappa_-^2$  (Eq. 14), we obtain

$$\left[ \nu_+ \frac{z_+^2}{R_+^*} \frac{1}{\kappa_0^2} \left( BN_+ z_+^2 \frac{R_+^*}{R_+^*} + BN_- z_-^2 \frac{R_+^*}{R_-^*} \right) + \nu_- \frac{z_-^2}{R_-^*} \frac{1}{\kappa_0^2} \left( BN_+ z_+^2 \frac{R_-^*}{R_+^*} + BN_- z_-^2 \frac{R_-^*}{R_-^*} \right) \right], \quad (19)$$

where  $B = e^2/\epsilon_0\epsilon_w kTV$ . After rearranging, we obtain

$$\frac{B(v_+z_+^2 + v_-z_-^2)}{\kappa_0^2} \left[ \frac{z_+^2 N_+}{R_+^*} + \frac{z_-^2 N_-}{R_-^*} \right]. \quad (20)$$

Using the equations  $N_+ = \frac{v_+}{v}N$  and  $N_- = \frac{v_-}{v}N$  with  $N$  being the total number of ions, we can write that

$$\frac{B \left( \frac{N_+ v}{N} z_+^2 + \frac{N_- v}{N} z_-^2 \right)}{\kappa_0^2} \left[ \frac{z_+^2 \frac{v_+ N}{v}}{R_+^*} + \frac{z_-^2 \frac{v_- N}{v}}{R_-^*} \right]. \quad (21)$$

In this equation,  $N$  and  $v$  drop out, so we obtain

$$\frac{B(N_+z_+^2 + N_-z_-^2)}{\kappa_0^2} \left[ \frac{z_+^2 v_+}{R_+^*} + \frac{z_-^2 v_-}{R_-^*} \right]. \quad (22)$$

Since  $\kappa_0^2 = B(N_+z_+^2 + N_-z_-^2)$ , the equality in Eq. 18 is proven.

Because the results obtained from the two routes differ only for the individual excess chemical potentials, we show results only for them. As in the main text, we use NaCl and CaCl<sub>2</sub> as examples. We do not show results for using the Pauling radii in the IW term, because we proved in the main text that they overestimate the IW term.

The results (Figs. 1 and 2) show that route 2 (dashed line) gives a little bit larger values for the bigger ions (the anion, in these cases) than route 1 (solid line). The reverse is true for the smaller ion (the cation, in these cases). The difference is quite small. Furthermore, route 2 does not give any systematic improvement over route 1. For example, it improves the prediction for Na<sup>+</sup>, but makes it worse for Cl<sup>-</sup>. The same is true for CaCl<sub>2</sub>.

Therefore, we suggest using route 1. There are other reasons for this suggestion. We showed in the main text, that route 1 is equivalent with using just the “plain” Born-expression (Eq. 8) for the IW term. Moreover, this simple expression can be the basis of eliminating the Born radius by

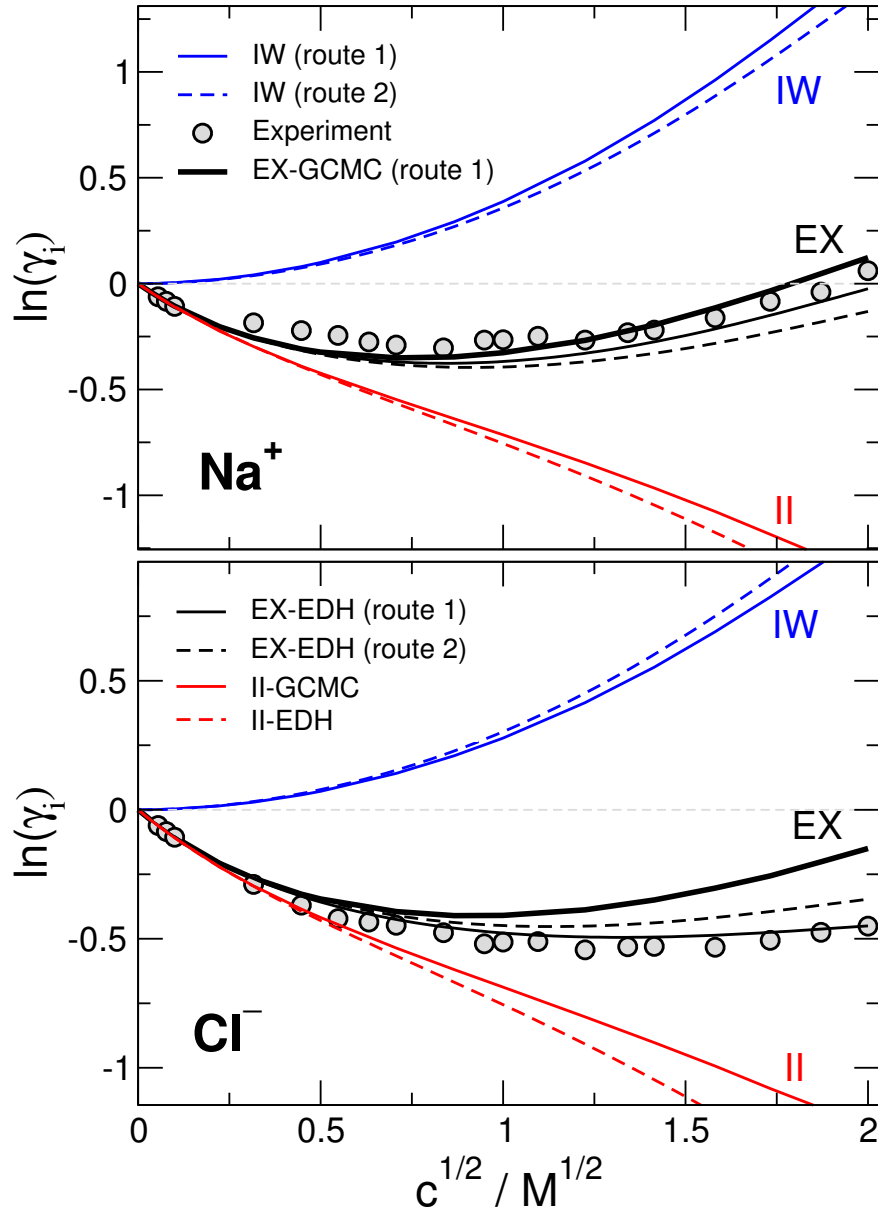


Figure 1: Individual activity coefficients of NaCl and its II and IW components (in molar scale). Solid and dashed blue lines show the IW term as computed from route 1 (Eq. 8) and route 2 (Eq. 16), respectively, using the Born ( $R_i^B$ ) radii for  $R_i^*$ . The radii can be found in Table 1 of the main text. Solid and dashed red lines show the II terms as computed from either GCMC simulations or the EDH theory (Eq. 18 of Shilov and Lyashchenko<sup>5</sup>). The black curves show the total activity coefficients as computed from different combinations – thick solid: GCMC for II and route 1 for IW; solid: EDH for II and route 1 for IW; dashed: EDH for II and route 2 for IW (the Born radius is used in all cases). The experimental data are taken from Wilczek-Vera et al.<sup>6</sup>

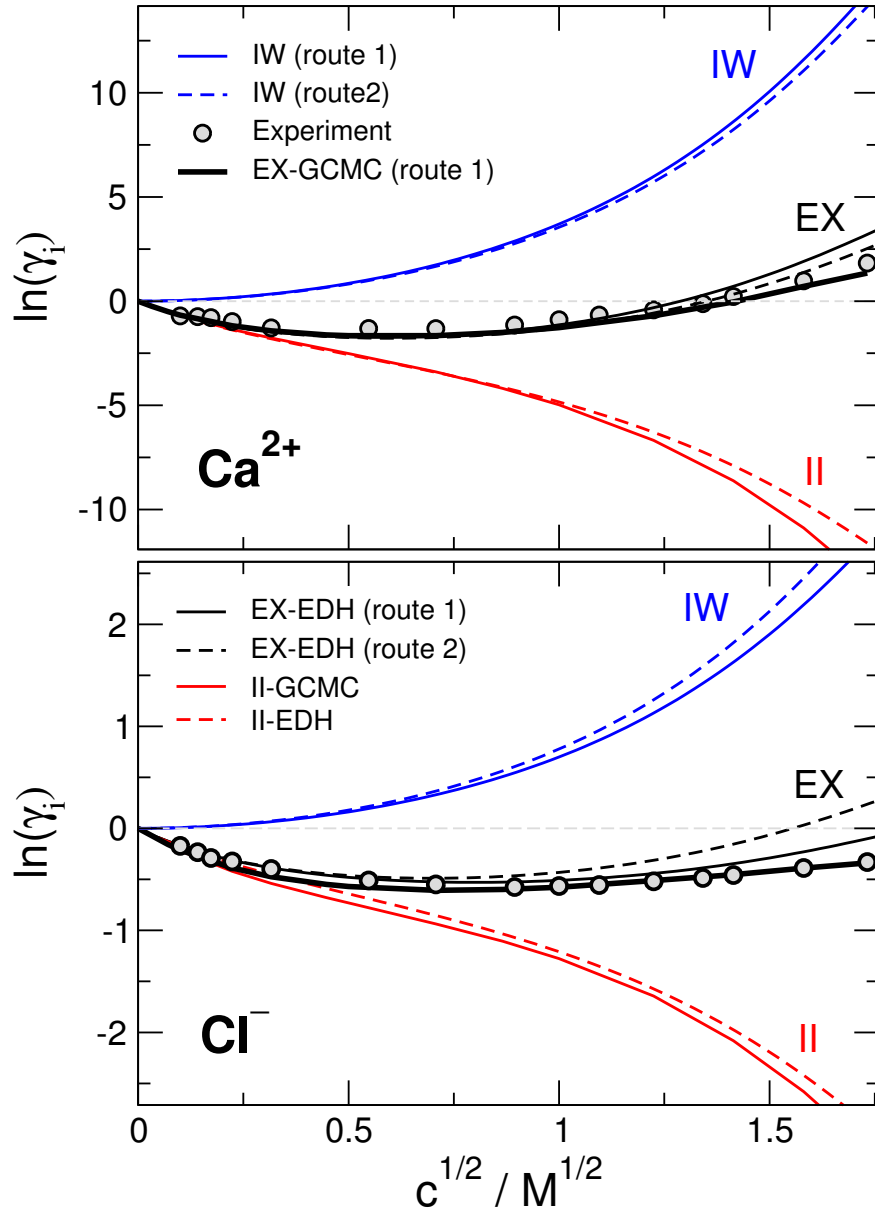


Figure 2: Individual activity coefficients of  $\text{CaCl}_2$  and its II and IW components (in molar scale). Solid and dashed blue lines show the IW term as computed from route 1 (Eq. 8) and route 2 (Eq. 16), respectively, using the Born ( $R_i^B$ ) radii for  $R_i^*$ . The radii can be found in Table 1 of the main text. Solid and dashed red lines show the II terms as computed from either GCMC simulations or the EDH theory (Eq. 18 of Shilov and Lyashchenko<sup>5</sup>). The black curves show the total activity coefficients as computed from different combinations – thick solid: GCMC for II and route 1 for IW; solid: EDH for II and route 1 for IW; dashed: EDH for II and route 2 for IW (the Born radius is used in all cases). The experimental data are taken from Wilczek-Vera et al.<sup>6</sup>



introducing the hydration free energy,  $\Delta G_i^s$ :

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

In this way, we obtain an equation that contains only experimentally attainable parameters. Parameter  $\Delta G_i^s$  gives the amplitude of the IW term, while function  $\varepsilon(c)$  describes the  $c$ -dependence of the IW term.

The Born radius drops out. It is not a loss, because the Born radius is not a physical radius; it is just a fitting parameter to reproduce the experimental hydration free energy with the Born equation. Getting rid of the Born radius, we also get rid of the confusion of using different radii in the II (ion-ion) and IW terms. The Pauling radius used in the II term is a real physical radius defining the distance of closest approach of ions in the simulations. The Born radius has no such a molecular meaning.

A relation similar to that in Eq. 23 can also be developed in the case of route 2 with a slightly different  $c$ -dependence. Route 1, nevertheless, results in simpler formulas so we do not pursue route 2 further.

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