Comment on "Binding Debye-Hückel theory for associative electrolyte solutions

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Comment on "Binding Debye–Hückel theory for associative electrolyte solutions", [J. Chem. Phys. 159, 154503 (2023)]

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It is argued that the Binding Debye-Hückel (BiDH) model proposed in [J. Chem. Phys. 159, 154503 (2023)] might not be appropriate for the description of Monte-Carlo simulation data obtained for primitive model electrolytes. The first reason is that the original Debye-Hückel (DH) theory is of low accuracy for describing deviations from ideality in concentrated solutions of strong salts. The DH framework is thus a poor basis for building a model including association. The second reason is that the mean-spherical approximation (MSA), without assumption of association, apparently predicts MC data for primitive electrolytes better than BiDH. Thus the BiDH model seems to be simply a way of compensating for the deficiencies of DH theory by assuming association.

An article recently published in this journal[1], hereafter denoted as R1, proposed the Binding Debye-Hückel (BiDH) model to describe Monte-Carlo (MC) data for deviations from ideality in primitive model electrolytes, i.e. systems of charged hard spheres in a continuum solvent of some relative permittivity. These solutions were assumed to exhibit association.

Bjerrum theory is used in R1 to describe ion-pairing, up to high salt concentration. However, it should be pointed out that this theory is valid only for dilute solutions[2,3]. At finite concentration, an estimation of the amount of ion pairs can no longer be done as suggested by Bjerrum. It requires a thorough examination, as was pioneered by Fuoss in a quantitative way[4]. A word of caution must therefore be issued regarding the use of Bjerrum theory for concentrated electrolytes.

A few months ago, we published an article[5] in which results from various theories for strong salts (DH, MSA, and hypernetted-chain (HNC) theory) were compared with MC data for the mean salt and individual activity coefficients, and osmotic coefficients, for 1:1, 2:1, 3:1, and 2:2 electrolytes[6,7]. MSA is superior to DH[5], and HNC is the most accurate integral equation theory[8,9] (more accurate than MSA).

The narrative underlying R1 is that the systems from which MC data were retrieved are subject to ion-pairing, and that the original DH theory needs being supplemented with ingredients that account for this association in order to correctly describe deviations from ideality in these solutions.

We want mainly to make two points in this comment. *(i)* The first point is that, as is well known, DH theory gives inaccurate results for strong salts in a waterlike solvent at room temperature[5]. Therefore, the DH theory is a weak basis for building a more elaborate theory to account for association effects in concentrated solutions. *(ii)* The second point is that MC data for solutions of multivalent salts are well described using the

MSA, and even more so using HNC, *without association*[5,7,10,11]. The excellent agreement with HNC is illustrated in Figure 1 in the case of a 2:2 salt with ions 4.25 Å in diameter[7].
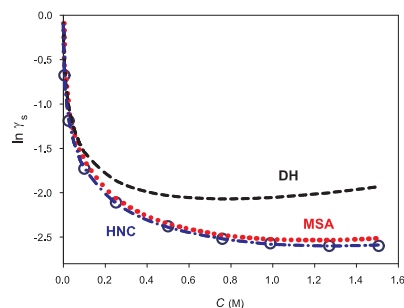
FIG. 1. Mean salt activity coefficient as a function of concentration for a 2:2 salt (plot of $\ln \gamma_s$). Symbols: MC data from Ref. 7; Dashed line: DH; Dotted line: MSA; Dash-dotted line: HNC.

These outcomes suggest that, contrary to many real aqueous solutions that are thought to exhibit ion association[12–14], primitive model electrolytes seem to behave as strong salts (at least in the case of ions of realistic size). To our best knowledge, evidence of associated species has never been reported in molecular dynamics simulations of these model solutions[15,16]. This method could have allowed one to look for 'long-lived' pairs by computing the residence times of unlike ions in, or near, contact[17], but such a study was apparently never undertaken.

The two points above are now illustrated by showing some results for systems (taken at random) that were considered in R1 and for which plots were provided. The latter were digitized using Engauge software. The DH and MSA results were computed using equations given in R1 and in Ref. 5, respectively. In both cases, a contribution from volume exclusion (arising from hard sphere repulsion) was added to the electrostatic part.

The results for the logarithms of the mean salt activity coefficient, $\ln \gamma_s$, are plotted in Fig. 2 for a 2:1 salt (sys-

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tem S42[7]), and in Fig. 3 for a 3:1 salt (system V21[18]). Figure 4 shows the variation of $\ln \gamma_s$ with the cation size σ_+ for a 1 M solution of a 1:1 salt in a solvent of relative permittivity $\varepsilon_r = 20$[18]. The result from BiDH for this system is shown in Fig. 15 of R1. The low value of ε_r makes this system the one most likely prone to association in this figure. In the figure captions is mentioned the value of the maximum salt concentration, C_{max}, and of the minimum mean interionic distance, d_{min}, defined by $\rho_t^{max} = 1/d_{min}^3$ with ρ_t the total ion number density.
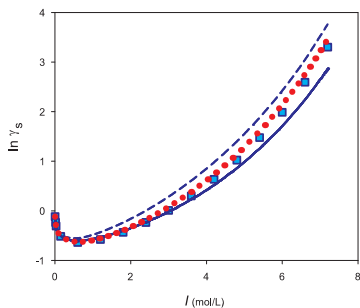

FIG. 2. Plot of $\ln \gamma_s$ as a function of ionic strength for the 2:1 electrolyte S42 ($\sigma_+ = 4.4$ Å, $\sigma_- = 6.18$ Å); $C_{max} = 2.4$ M, $d_{min} \sim 6.1$ Å. Symbols: MC data[7] used in Fig. 4 of R1; Dashed line: DH; Solid line: BiDH; Dotted line: MSA.
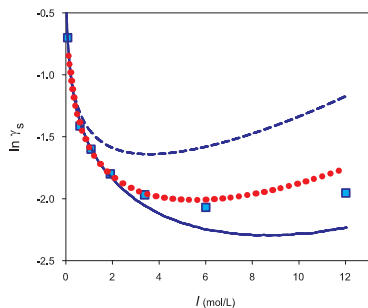

FIG. 3. Plot of $\ln \gamma_s$ as a function of ionic strength for the 3:1 electrolyte V21 ($\sigma_+ = 3$ Å, $\sigma_- = 4.5$ Å); $C_{max} = 2$ M, $d_{min} \sim 5.9$ Å. Symbols: MC data[18] used in Fig. 9 of R1; Dashed line: DH; Solid line: BiDH; Dotted line: MSA.

In Figs. 1-4, it is noted that the DH curves (and the MSA ones to a lesser extent) are located above the MC data. This outcome is caused by the fact that, contrary to HNC, they are linearized theories that do not fully account for the effect of attractive electrostatic interactions[5], especially near contact. Adding association to DH corrects this shortcoming because it introduces extra attractive interactions. Then as compared to DH, the BiDH curves are moved downward in Figs. 2 and 3, but BiDH overshoots the MC results to the downside. In Fig. 4 the BiDH result is not very different than the DH one (although the low value of ε_r should yield a high K^0 in Eq. (37)), and both are too high.

At the same time, it is seen in these figures that the simple MSA predicts the MC results better than the somewhat involved BiDH, and it does it without having to assume association. In Fig. 4, despite the low value of ε_r, the MSA result is quite in keeping with the MC, except for a slight deviation in the case of the smallest cation diameter where cation-anion attraction at contact is the strongest.

Lastly, it must be mentioned that some information seems to be missing in R1 about the actual expressions or values taken for some important parameters. This concerns the cut-off distance l_{mn} in Eq. (37) and the related parameter θ mentioned on page 14 (Section IV.C), as well as δ_j appearing in Eq. (24) and $\varepsilon_{in,j}$ in Eq. (25). It is also noted that the ion-dipole contribution A^{DI} of Eq. (24) is not included in Eq. (43) for A. It is not clear whether this is an omission. Moreover, the purpose of a "Born" term[19] in R1 is unclear since all systems seem to have a constant permittivity.

Data Availability Statement. Data sharing is not applicable to this article as no new data were created or analyzed in this study.

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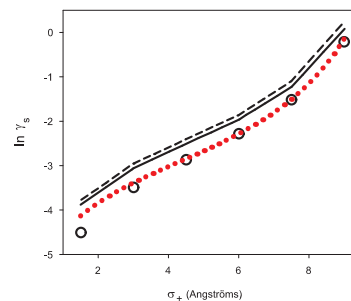[10] T. Mohorič, M. Lukšič, and B. Hribar-Lee, Acta Chim. Slov. **59**, 490 (2012).

FIG. 4. Plot of $\ln \gamma_s$ as a function of cation diameter for a 1 M 1:1 salt, with $\sigma_- = 3$ Å, and $\varepsilon_r = 20$ (see Fig. 15 of R1); $d_{min} \sim 9.4$ Å. Symbols: MC data[18] of Fig. 15 of R1; Dashed line: DH; Solid line: BiDH; Dotted line: MSA.

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