Supporting Information: Theory for Gas Solubility and Hydrophobic Interaction in Aqueous Electrolyte Solutions

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SI-A Inversion of I^{ij} for small $n_{\rm h}$

For small $n_{\rm h}$ we can easily invert the 3×3 matrix I^{ij} to obtain I_{ij}. First, from Eq. (7), we obtain $I^{ij} = I_{\rm s}^{ij} + O(n_{\rm h})$ for $i, j = {\rm w}, {\rm I}$, $I^{i{\rm h}} = \partial \nu_{\rm h}^{\rm s}/\partial n_i + O(n_{\rm h})$ for $i = {\rm w}, {\rm I}$, and $I^{\rm hh} = 1/n_{\rm h} + U_{\rm hh}^{\rm s} + O(n_{\rm h})$. Here $I_{\rm s}^{ij}$ has been defined below Eq. (27). We expand I_{ij} as

$$I_{ij} = I_{ij}^{\rm s} + O(n_{\rm h}) \quad (i, j = {\rm w}, {\rm I}) \tag{SI-1}$$

$$I_{i{\rm h}} = A_i n_{\rm h} + O(n_{\rm h}^2) \quad (i = {\rm w}, {\rm I}) \tag{SI-2}$$

where 2×2 matrix $\{I_{ij}^{\rm s}\}_{i,j={\rm w},{\rm I}}$ is the inverse matrix of $\{I_{\rm s}^{ij}\}_{i,j={\rm w},{\rm I}}$. In Eq. (SI-2) we can easily confirm the zeroth order term identically vanishes. The relation $\sum_j I_{{\rm w}j} I^{j{\rm h}} = \sum_j I_{{\rm I}j} I^{j{\rm h}} = 0$ then yields

$$A_i = -\sum_{j={\rm w},{\rm I}} I_{ij}^{\rm s} (\partial \nu_{\rm h}^{\rm s}/\partial n_j). \tag{SI-3}$$

Inverting this, we obtain

$$\partial \nu_{\rm h}^{\rm s}/\partial n_i = -\sum_{j={\rm w},{\rm I}} I_{\rm s}^{ij} A_j \tag{SI-4}$$

$$= \begin{cases} \Delta_0^{-1}(-I_{\rm II}^{\rm s} A_{\rm w} + I_{\rm wI}^{\rm s} A_{\rm I}) & (i = {\rm w}) \\ \Delta_0^{-1}(I_{\rm wI}^{\rm s} A_{\rm w} - I_{\rm ww}^{\rm s} A_{\rm I}) & (i = {\rm I}). \end{cases} \tag{SI-5}$$

Substituting Eq. (SI-5) into Eq.(34) and using Eqs. (15) and (29), we obtain

$$g_{\rm h} = (1/n^2 \chi_{\rm I})(A_{\rm w} n_{\rm I} - A_{\rm I} n_{\rm w}). \tag{SI-6}$$

Similarly, substitution of Eq. (SI-4) into (21) yields

$$v_{\rm h}^{\rm s*} = -(v_{\rm w}^{\rm s} A_{\rm w} + v_{\rm I}^{\rm s} A_{\rm I}), \tag{SI-7}$$

where use has been made of Eq. (15). We can readily invert Eqs. (SI-6) and (SI-7) to have

$$A_{\mathrm{w}} = n^2\chi_{\mathrm{I}}g_{\mathrm{h}}v_{\mathrm{I}}^{\mathrm{s}} - n_{\mathrm{w}}v_{\mathrm{h}}^{\mathrm{s}*} \tag{SI-8}$$

$$A_{\mathrm{I}} = -n^2\chi_{\mathrm{I}}g_{\mathrm{h}}v_{\mathrm{w}}^{\mathrm{s}} - n_{\mathrm{I}}v_{\mathrm{h}}^{\mathrm{s}*}. \tag{SI-9}$$

Next, neglecting the terms of order n_{h} in $\sum_i I^{\mathrm{h}i}I_{i\mathrm{h}} = 1$, we obtain

$$\begin{aligned} 1/I_{\mathrm{hh}} =& 1/n_{\mathrm{h}} + U_{\mathrm{hh}}^{\mathrm{s}}/k_{\mathrm{B}}T + \sum_{i=\mathrm{w,I}} A_i(\partial\nu_{\mathrm{h}}^{\mathrm{s}}/\partial n_i) \\ =& 1/n_{\mathrm{h}} + U_{\mathrm{hh}}^{\mathrm{s}}/k_{\mathrm{B}}T - \sum_{i=\mathrm{w,I}} I_{\mathrm{s}}^{ij}A_iA_j, \end{aligned} \tag{SI-10}$$

where Eq. (SI-4) has been used in the second line. Setting $n_{\mathrm{h}} = 0$ in Eqs. (15) and (17), we have

$$\sum_{i,j=\mathrm{w,I}} I_{ij}^{\mathrm{s}}v_i^{\mathrm{s}}v_j^{\mathrm{s}} = k_{\mathrm{B}}T\kappa_T^{\mathrm{s}} = 1/\sum_{i,j=\mathrm{w,I}} I_{\mathrm{s}}^{ij}n_in_j. \tag{SI-11}$$

Substituting Eqs. (SI-8) and (SI-9) into (SI-10) and using (15) and (SI-11), we obtain

$$1/I_{\mathrm{hh}} = 1/n_{\mathrm{h}} + U_{\mathrm{hh}}^{\mathrm{eff}}/k_{\mathrm{B}}T, \tag{SI-12}$$

where the terms of order n_{h} have been neglected.

SI-B Calculation of $C_{\mathrm{I}}^{(1)}$

In this section we can set $n_{\mathrm{h}} = 0$. From Eq. (25) we find

$$(\partial n_{\mathrm{w}}/\partial X_{\mathrm{I}})_{T,p} = -n^2v_{\mathrm{I}}^{\mathrm{s}}, \quad (\partial n_{\mathrm{I}}/\partial X_{\mathrm{I}})_{T,p} = n^2v_{\mathrm{w}}^{\mathrm{s}}. \tag{SI-13}$$

Then for an arbitrary function $w(n_{\mathrm{w}}, n_{\mathrm{I}})$, we have

$$\lim_{n_{\mathrm{I}}\to 0}\left(\frac{\partial w}{\partial X_{\mathrm{I}}}\right)_{T,p} = n_{\mathrm{w}}\frac{\partial w}{\partial n_{\mathrm{I}}}\Big|_{n_{\mathrm{I}}\to 0} - n_{\mathrm{w}}^2 v_{\mathrm{I}}\frac{\partial w}{\partial n_{\mathrm{w}}}\Big|_{n_{\mathrm{I}}\to 0}. \tag{SI-14}$$

From Eq. (10), we have $(\kappa_T^{\mathrm{s}})^{-1} = k_{\mathrm{B}}T\sum_{i,j=\mathrm{w,I}} n_i n_j I_{\mathrm{s}}^{ij}$. Substituting $w = (\kappa_T^{\mathrm{s}})^{-1}$ into Eq. (SI-14), we obtain

$$\begin{aligned}\lim_{n_{\mathrm{I}}\to 0}\left(\frac{\partial(\kappa_T^{\mathrm{s}})^{-1}}{\partial X_{\mathrm{I}}}\right)_{T,p} =& k_{\mathrm{B}}Tn_{\mathrm{w}}(1 + 2n_{\mathrm{w}}I_0^{\mathrm{wI}} + n_{\mathrm{w}}^2 I_0^{\mathrm{wwI}}) - k_{\mathrm{B}}Tn_{\mathrm{w}}^2 v_{\mathrm{I}}[\partial(n_{\mathrm{w}}^2 I_0^{\mathrm{ww}})/\partial n_{\mathrm{w}}]\\ =& n_{\mathrm{w}}\kappa_{\mathrm{w}}^{-1}[\partial(v_{\mathrm{I}}n_{\mathrm{w}})/\partial n_{\mathrm{w}}],\end{aligned} \tag{SI-15}$$

where we have defined $I_0^{\mathrm{w}i} \equiv \lim_{n_{\mathrm{I}}\to 0} I_{\mathrm{s}}^{\mathrm{w}i}$ and $I_0^{\mathrm{w}ij} \equiv \lim_{n_{\mathrm{I}},n_{\mathrm{h}}\to 0}(\partial I^{\mathrm{w}i}/\partial n_j) = I_0^{\mathrm{w}ji}$. This readily yields

$$\lim_{n_{\mathrm{I}}\to 0}(\partial\kappa_T^{\mathrm{s}}/\partial X_{\mathrm{I}})_{T,p} = -n_{\mathrm{w}}\kappa_{\mathrm{w}}[\partial(v_{\mathrm{I}}n_{\mathrm{w}})/\partial n_{\mathrm{w}}]. \tag{SI-16}$$

Similarly, from Eqs. (15) and (SI-14), we obtain

$$\begin{aligned}\lim_{n_{\mathrm{I}}\to 0}\left(\frac{\partial v_{\mathrm{h}}^{\mathrm{s}}}{\partial X_{\mathrm{I}}}\right)_{T,p} =& (v_{\mathrm{h}}/\kappa_{\mathrm{w}})\lim_{n_{\mathrm{I}}\to 0}\left(\frac{\partial\kappa_T^{\mathrm{s}}}{\partial X_{\mathrm{I}}}\right)_{T,p} + k_{\mathrm{B}}T\kappa_{\mathrm{w}}[n_{\mathrm{w}}(I_0^{\mathrm{hI}} + n_{\mathrm{w}}I_0^{\mathrm{hwI}}) - n_{\mathrm{w}}^2 v_{\mathrm{I}}(I_0^{\mathrm{hw}} + n_{\mathrm{w}}I_0^{\mathrm{hww}})]\\ =& k_{\mathrm{B}}T\kappa_{\mathrm{w}}n_{\mathrm{w}}\frac{\partial[n_{\mathrm{w}}(K_{\mathrm{S}}/2 - v_{\mathrm{I}})]}{\partial n_{\mathrm{w}}}.\end{aligned} \tag{SI-17}$$

Using Eqs. (18) and (SI-16), we have

$$\lim_{n_{\mathrm{I}}\to 0}\left(\frac{\partial v_{\mathrm{h}}^{\mathrm{s}*}}{\partial X_{\mathrm{I}}}\right)_{T,p} = k_{\mathrm{B}}T\kappa_{\mathrm{w}}n_{\mathrm{w}}\frac{\partial(n_{\mathrm{w}}K_{\mathrm{S}}/2)}{\partial n_{\mathrm{w}}}. \tag{SI-18}$$

Substitution of $w = U_{\mathrm{hh}}^{\mathrm{s}}$ into Eq. (SI-14) yields

$$\lim_{n_{\mathrm{I}}\to 0}\left(\frac{\partial U_{\mathrm{hh}}^{\mathrm{s}}}{\partial X_{\mathrm{I}}}\right)_{T,p} = k_{\mathrm{B}}T(n_{\mathrm{w}}I_0^{\mathrm{hhI}} - n_{\mathrm{w}}^2 v_{\mathrm{I}}I_0^{\mathrm{hhw}}), \tag{SI-19}$$

where we have defined $I_0^{\mathrm{hh}i} \equiv \lim_{n_\mathrm{I},n_\mathrm{h}\to 0}(\partial I^{\mathrm{hh}}/\partial n_i) = \lim_{n_\mathrm{I},n_\mathrm{h}\to 0}(\partial I^{\mathrm{h}i}/\partial n_\mathrm{h})$ for $i = \mathrm{w}, \mathrm{I}$. Using Eqs. (SI-15), (SI-17), and (SI-19), one can calculate $C_\mathrm{I}^{(1)}$ in Eq. (41).

SI-C Expressions for salts of general valence numbers

For a salt with general valence numbers, i.e., $X_aY_b \to aX^{Z_1} + bY^{Z_2}$ with $b = -aZ_1/Z_2$, the relation between the the salt density n_s and the ion density n_I in Eq. (5) becomes $n_\mathrm{s} = n_\mathrm{I}/\mathcal{N}$ with $\mathcal{N} = a + b = a(1 - Z_1/Z_2)$. In this case Eq. (40) becomes

$$C_\mathrm{I} \equiv -\lim_{n_\mathrm{I}\to 0}\left(\frac{\partial B}{\partial n_\mathrm{s}}\right)_{T,p} = \frac{-\mathcal{N}/2}{k_\mathrm{B}Tn_\mathrm{w}}\lim_{n_\mathrm{I}\to 0}\left(\frac{\partial U_\mathrm{hh}^{\mathrm{eff}}}{\partial X_\mathrm{I}}\right)_{T,p}. \tag{SI-20}$$

Furthermore, Eqs. (31) and (35) are generalized to

$$K_\mathrm{S} = (\mathcal{N}/k_\mathrm{B}T)(U_{\mathrm{hI}} - v_\mathrm{h}^* v_\mathrm{I}/\kappa_\mathrm{w}) \tag{SI-21}$$

$$\lim_{n_\mathrm{I}\to 0} g_\mathrm{h} = n_\mathrm{w}K_\mathrm{S}/\mathcal{N}, \tag{SI-22}$$

while Eq. (28) remains unchanged. Then Eq. (42) becomes

$$C_\mathrm{I}^{(2)} \equiv \frac{\mathcal{N}}{2n_\mathrm{w}}\lim_{n_\mathrm{I}\to 0}(\partial[\chi_\mathrm{I}g_\mathrm{h}^2]/\partial X_\mathrm{I})_{T,p} = K_\mathrm{S}^2/(2\mathcal{N}). \tag{SI-23}$$

SI-D Long-wavelength density fluctuations

We discuss the long-wavelength density fluctuations, which shall make the physical meanings of χ_I and $U_\mathrm{hh}^{\mathrm{eff}}$ (or B) clearer. The Bjerrum length ℓ_B and the Debye wavenumber κ are defined as

$$\ell_B = e^2/k_\mathrm{B}T\varepsilon, \quad \kappa = \sqrt{4\pi\ell_B n_\mathrm{I}}. \tag{SI-24}$$

As in the previous paper,[S1] we study equilibrium density fluctuations on the scales larger than the Debye length κ^{-1}.

The deviations of the densities from their average values are denoted by δn_i,

$$\delta\hat{n}_i(\boldsymbol{r}) \equiv \hat{n}_i(\boldsymbol{r}) - \langle \hat{n}_i \rangle \quad (i = \mathrm{w}, \mathrm{c}, \mathrm{a}, \mathrm{h}). \tag{SI-25}$$

where $\langle \hat{n}_i \rangle$'s are given by Eqs. (4) and (5). We expand the free energy functional $\mathcal{F}$ defined in Eq. (43) with respect to $\delta\hat{n}_i$ about the homogeneous equilibrium values $\langle \hat{n}_i \rangle$. The second order term, which governs the density fluctuations, is given by

$$\delta^2 \mathcal{F} = \frac{1}{2} \int \sum_{i,j=\mathrm{w,c,a,h}} \hat{f}_{ij} \delta\hat{n}_i \delta\hat{n}_j d\boldsymbol{r} + \int \frac{\varepsilon |\nabla \Phi|^2}{8\pi} d\boldsymbol{r}, \tag{SI-26}$$

where $\hat{f}_{ij} = \partial^2 \hat{f} / \partial\hat{n}_i \partial\hat{n}_j |_{\{\hat{n}_k = \langle \hat{n}_k \rangle\}}$. The probability distribution of the density fluctuations is proportional to $\exp[-\delta^2 \hat{F} / k_{\mathrm{B}} T]$.

For any fluctuating variables $\delta\hat{A}(\boldsymbol{r})$ and $\delta\hat{B}(\boldsymbol{r})$ of zero mean $\langle \delta\hat{A} \rangle = \langle \delta\hat{B} \rangle = 0$, we define

$$\langle \delta\hat{A} \circ \delta\hat{B} \rangle \equiv \int d\boldsymbol{r} \langle \delta\hat{A}(\boldsymbol{r}) \delta\hat{B}(0) \rangle. \tag{SI-27}$$

Let $\delta\hat{A}_{\boldsymbol{q}}$ and $\delta\hat{B}_{\boldsymbol{q}}$ be the Fourier components of $\delta\hat{A}$ and $\delta\hat{B}$, respectively, where $\boldsymbol{q}$ is the wave vector. Then we have[S2] $\lim_{\boldsymbol{q}\to 0} \langle \delta\hat{A}_{\boldsymbol{q}} \delta\hat{B}_{-\boldsymbol{q}} \rangle / V = \langle \delta\hat{A} \circ \delta\hat{B} \rangle$.

SI-D.1 Fluctuations in electrolyte solvent without solute

We first study the density fluctuations in the electrolyte solvent without the hydrophobic solute,

$$n_{\mathrm{h}} = 0.$$

Then $\hat{f}$ in Eq. (43) is replaced by $\hat{f}^{\mathrm{s}}(\hat{n}_{\mathrm{w}}, \hat{n}_{\mathrm{c}}, \hat{n}_{\mathrm{a}}) \equiv \hat{f}(\hat{n}_{\mathrm{w}}, \hat{n}_{\mathrm{c}}, \hat{n}_{\mathrm{a}}, 0)$. In the previous paper,[S1] the ion-specific fluctuations in dilute electrolyte solutions have been studied. Here we slightly generalize the previous theory to a one that is (at least formally) valid for more concentrated electrolyte solutions.

It will turn out that the following combinations are convenient:

$$\delta\hat{\phi} \equiv \sum_{i=\mathrm{w,c,a}} v_i^{\mathrm{s}} \delta\hat{n}_i, \quad \delta\hat{X}_\rho \equiv n^{-1}(\delta\hat{n}_{\mathrm{c}} - \delta\hat{n}_{\mathrm{a}}), \tag{SI-28}$$

$$\delta\hat{X}_{\mathrm{I}} \equiv n^{-2}[n_{\mathrm{w}}(\delta\hat{n}_{\mathrm{c}} + \delta\hat{n}_{\mathrm{a}}) - n_{\mathrm{I}}\delta\hat{n}_{\mathrm{w}}]. \tag{SI-29}$$

Here, $\delta\hat{\phi}$ is the volume deviation, $\delta\hat{X}_\rho$ the deviation of the ion molar fraction difference, and $\delta\hat{X}_{\mathrm{I}}$ the deviation of the total ion molar fraction. For an electrolyte solvent without solute Eqs. (44) and (SI-26), respectively, become

$$f^{\mathrm{s}}(n_{\mathrm{w}}, n_{\mathrm{I}}) = \hat{f}^{\mathrm{s}}(n_{\mathrm{w}}, n_{\mathrm{I}}/2, n_{\mathrm{I}}/2) \tag{SI-30}$$

$$\delta^2\mathcal{F} = \frac{1}{2}\int \sum_{i,j=\mathrm{w,c,a}} \hat{f}_{ij}^{\mathrm{s}} \delta\hat{n}_i \delta\hat{n}_j d\boldsymbol{r} + \int \frac{\varepsilon|\nabla\Phi|^2}{8\pi} d\boldsymbol{r}. \tag{SI-31}$$

where $\hat{f}_{ij}^{\mathrm{s}} = \partial^2\hat{f}/\partial\hat{n}_i\partial\hat{n}_j|_{\{\hat{n}_k=\langle n_k\rangle\}}$. Inverting Eqs. (SI-28) and (SI-29), we can express $\{\delta\hat{n}_i\}_{i=\mathrm{w,c,a}}$ as linear combinations of $\hat{\phi}$, $\delta\hat{X}_\rho$, and $\delta\hat{X}_{\mathrm{I}}$. Substituting the result into $\sum_{i,j=\mathrm{w,c,a}} \hat{f}_{ij}^{\mathrm{s}} \delta\hat{n}_i \delta\hat{n}_j$ and using Eqs. (45)–(47), we find

$$\sum_{i,j} \hat{f}_{ij}^{\mathrm{s}} \delta\hat{n}_i \delta\hat{n}_j = \delta\hat{\phi}^2/\kappa_T^{\mathrm{s}} + \sum_{i,j=\rho,\mathrm{I}} \gamma_{ij} \delta\hat{X}_i \delta\hat{X}_j, \tag{SI-32}$$

where the terms proportional to $\delta\hat{\phi}\delta\hat{X}_i$ ($i = \rho, \mathrm{I}$) identically vanish. We do not discuss the coefficients $\gamma_{\rho\rho}$ and $\gamma_{\rho\mathrm{I}}$ as they are not relevant to the fluctuations in the long wavelength limit. The coefficient γ_{II} is calculated as

$$\begin{aligned}\gamma_{\mathrm{II}} =& n^4\Big[(v_{\mathrm{I}}^{\mathrm{s}})^2\hat{f}_{\mathrm{ww}}^{\mathrm{s}} + (v_{\mathrm{w}}^{\mathrm{s}}/2)^2\sum_{i,j=\mathrm{c,a}}\hat{f}_{ij}^{\mathrm{s}} - v_{\mathrm{I}}^{\mathrm{s}}v_{\mathrm{w}}^{\mathrm{s}}\sum_{i=\mathrm{c,a}}\hat{f}_{\mathrm{w}i}^{\mathrm{s}}\Big]\\ =& k_{\mathrm{B}}Tn^4[(v_{\mathrm{I}}^{\mathrm{s}})^2I_{\mathrm{s}}^{\mathrm{ww}} + (v_{\mathrm{w}}^{\mathrm{s}})^2I_{\mathrm{s}}^{\mathrm{II}} - 2v_{\mathrm{I}}^{\mathrm{s}}v_{\mathrm{w}}^{\mathrm{s}}I_{\mathrm{s}}^{\mathrm{Iw}}]\\ =& k_{\mathrm{B}}Tn^4\Delta_0^{-1}\sum_{i,j=\mathrm{w,I}}v_i^{\mathrm{s}}v_j^{\mathrm{s}}I_{ij}^{\mathrm{s}}\\ =& k_{\mathrm{B}}T\chi_{\mathrm{I}}^{-1}.\end{aligned} \tag{SI-33}$$

Here the second line follows from Eq. (SI-30), and the last line from Eqs. (SI-11) and (29). The second term of Eq. (SI-31) is rewritten as

$$\int\frac{\varepsilon|\nabla\Phi|^2}{8\pi}d\boldsymbol{r} = k_{\mathrm{B}}T\int\frac{d\boldsymbol{q}}{(2\pi)^3}2\pi\ell_B n^2q^{-2}|\delta\hat{X}_{\rho\boldsymbol{q}}|^2 \tag{SI-34}$$

The long-range Coulombic interaction is bilinear only in $\delta\hat{X}_\rho$, and thus from Eq. (SI-32) we obtain

$$\langle\delta\hat{X}_{\rho\boldsymbol{q}}\delta\hat{\phi}_{-\boldsymbol{q}}\rangle = \langle\delta\hat{X}_{\mathrm{I}\boldsymbol{q}}\delta\hat{\phi}_{-\boldsymbol{q}}\rangle = 0 \tag{SI-35}$$

$$\langle|\delta\hat{\phi}_{\boldsymbol{q}}|^2\rangle = k_{\mathrm{B}}TV\kappa_T^{\mathrm{s}}. \tag{SI-36}$$

Furthermore, as $\boldsymbol{q}\to 0$, the coefficient in front of $|\delta\hat{X}_{\rho\boldsymbol{q}}|^2$ diverges, suppressing the fluctuations of $\delta\hat{X}_{\rho\boldsymbol{q}}$. Therefore, combining Eqs. (SI-32)–(SI-34), we obtain

$$\langle\delta\hat{X}_{\mathrm{I}}\circ\delta\hat{X}_{\mathrm{I}}\rangle = \chi_{\mathrm{I}} \tag{SI-37}$$

$$\langle\delta\hat{X}_\rho\circ\delta\hat{X}_\rho\rangle = \langle\delta\hat{X}_\rho\circ\delta\hat{X}_{\mathrm{I}}\rangle = \langle\delta\hat{X}_\rho\circ\delta\hat{\phi}\rangle = 0. \tag{SI-38}$$

where χ_{I} is the solvent composition susceptibility defined below Eq. (26). The fluctuation variance in Eq. (SI-37) has the same form as the composition fluctuation variance in a nonionic binary solvent.[S3] From Eq. (SI-38), we have $\langle\delta\hat{X}_\rho\circ\delta\hat{A}\rangle = 0$, where $\delta\hat{A}$ is an arbitrary linear combination of $\delta\hat{\phi}$, $\delta\hat{X}_\rho$, and $\delta\hat{X}_{\rm I}$ (hence, of $\delta\hat{n}_{\rm w}$, $\delta\hat{n}_{\rm c}$, and $\delta\hat{n}_{\rm a}$). In particular, setting $\delta\hat{A} = \delta\hat{n}_i$ ($i = {\rm w, c, a}$), we obtain the well-know relations

$$\langle \delta\hat{n}_{\rm c} \circ \delta\hat{n}_{\rm c} \rangle = \langle \delta\hat{n}_{\rm a} \circ \delta\hat{n}_{\rm a} \rangle = \langle \delta\hat{n}_{\rm c} \circ \delta\hat{n}_{\rm a} \rangle \tag{SI-39}$$

$$\langle \delta\hat{n}_{\rm w} \circ \delta\hat{n}_{\rm c} \rangle = \langle \delta\hat{n}_{\rm w} \circ \delta\hat{n}_{\rm a} \rangle. \tag{SI-40}$$

The result in Eqs. (SI-36), (SI-37), and (SI-38) indicates that in the limit $\boldsymbol{q} \to 0$ the probability distribution of $\delta\hat{\phi}_{\boldsymbol{q}}$ and $\delta\hat{X}_{{\rm I}\boldsymbol{q}}$ is proportional to $\exp[-\delta^2 \hat{f}^{\rm s}_{\boldsymbol{q}}/k_{\rm B}T]$ with

$$\delta^2 \hat{f}^{\rm s}_{\boldsymbol{q}} = (1/2V)\left[|\delta\hat{\phi}_{\boldsymbol{q}}|^2/\kappa^{\rm s}_T + k_{\rm B}T|\delta\hat{X}_{{\rm I}\boldsymbol{q}}|^2/\chi_{\rm I}\right]. \tag{SI-41}$$

Note that the above expression can be obtained by minimizing $\delta^2\hat{F}$ in Eq. (SI-31) with respect to $\delta\hat{X}_{\rho\boldsymbol{q}}$ for $\boldsymbol{q} \to 0$.

For small ion densities, we may expand the local free energy for the electrolyte solvent $\hat{f}^{\rm s}(\hat{n}_{\rm w}, \hat{n}_{\rm c}, \hat{n}_{\rm a})$ as[S1]

$$\begin{aligned}\hat{f}^{\rm s} =& f_{\rm w}(\hat{n}_{\rm w}) + k_{\rm B}T\sum_{i={\rm c,a}} \hat{n}_i\{\ln(\hat{n}_i\lambda_i^3) - 1 + \nu_i(\hat{n}_{\rm w})\} \\ &- \frac{k_{\rm B}T}{12\pi}\hat{\kappa}^3 + \frac{1}{2}\sum_{i={\rm c,a}} U_{ij}(\hat{n}_{\rm w})\hat{n}_i\hat{n}_j + \cdots .\end{aligned} \tag{SI-42}$$

In the above, the third term ($\propto \hat{\kappa}^3$) is the DH free energy that arises from the ion density fluctuations on the scales smaller than the Debye length, where $\hat{\kappa}$ (without solute) is defined in accordance with Eq. (SI-24) as

$$\hat{\kappa}(\hat{n}_{\rm w}, \hat{n}_{\rm c}, \hat{n}_{\rm a}) = [4\pi\ell_B(\hat{n}_{\rm w})(\hat{n}_{\rm c} + \hat{n}_{\rm a})]^{1/2}. \tag{SI-43}$$

The effective ion-ion (short-range) interaction, which is the counterpart to Eqs. (1) and (32), is defined as

$$U_{\mathrm{II}}^{\mathrm{eff}} \equiv \frac{1}{4}\sum_{i,j=\mathrm{c,a}}\Big(U_{ij} - \frac{v_i^* v_j^*}{\kappa_{\mathrm{w}}}\Big) = U_{\mathrm{II}} - \frac{(v_{\mathrm{I}}^*)^2}{\kappa_{\mathrm{w}}}, \tag{SI-44}$$

where $U_{\mathrm{II}} = \sum_{i,j=\mathrm{c,a}} U_{ij}/4$. As shown in the previous paper,[S1] $U_{\mathrm{II}}^{\mathrm{eff}}$ is the key quantity to explain the ion-specificity in the salt activity coefficient, osmotic coefficient, and the deviation coefficient for the salt partial volume[1].

From Eqs. (46) and (SI-42), the ionic partial volumes in the dilution limit $n_{\mathrm{I}} \to 0$ are given by

$$v_i^* = k_{\mathrm{B}} T \kappa_{\mathrm{w}} n_{\mathrm{w}} \nu_i' \quad (i = \mathrm{c, a, I}), \tag{SI-45}$$

where $\nu_{\mathrm{I}} = (\nu_{\mathrm{c}} + \nu_{\mathrm{a}})/2$ and $\nu_i'(n_{\mathrm{w}}) = \partial \nu_i(n_{\mathrm{w}})/\partial n_{\mathrm{w}}$. For small n_{I}, Eqs. (SI-42) and (SI-30) yield

$$I_{\mathrm{s}}^{\mathrm{ww}} = 1/k_{\mathrm{B}} T n_{\mathrm{w}}^2 \kappa_{\mathrm{w}} + O(n_{\mathrm{I}}) \tag{SI-46}$$

$$I_{\mathrm{s}}^{\mathrm{II}} = 1/n_{\mathrm{I}} + U_{\mathrm{II}}/k_{\mathrm{B}} T - \kappa^3/16\pi n_{\mathrm{I}}^2 + O(n_{\mathrm{I}}) \tag{SI-47}$$

$$I_{\mathrm{s}}^{\mathrm{wI}} = \nu_{\mathrm{I}}' + O(n_{\mathrm{I}}^{1/2}), \tag{SI-48}$$

where U_{I} and ν_{I} are defined below Eqs. (SI-44) and (SI-45), respectively. We also have $v_{\mathrm{I}}^{\mathrm{s}} = v_{\mathrm{I}} + O(n_{\mathrm{I}}^{1/2})$ and $v_{\mathrm{w}}^{\mathrm{s}} = (1 - v_{\mathrm{I}} n_{\mathrm{I}})/n_{\mathrm{w}} + O(n_{\mathrm{I}}^{3/2})$, where the latter follows from Eq. (17). Substituting these and Eqs. (SI-46)–(SI-48) into Eq. (27), we obtain

$$\chi_{\mathrm{I}}^{-1} \simeq \frac{n^3}{n_{\mathrm{w}} n_{\mathrm{I}}}\Big[\frac{1}{2\chi} - (v_{\mathrm{I}} + v_{\mathrm{I}}^*) n_{\mathrm{I}} + \frac{n_{\mathrm{I}}}{n_{\mathrm{w}}}\Big] \tag{SI-49}$$

with $\chi^{-1} = 2 - \ell_B \kappa/2 + 2 n_{\mathrm{I}} U_{\mathrm{II}}^{\mathrm{eff}}/k_{\mathrm{B}} T$. In the square bracket of Eq. (SI-49), the terms of order $n_{\mathrm{I}}^{3/2}$ have been neglected. Substitution of Eqs. (SI-28), (SI-29), and (SI-49) into Eq. (SI-41)

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[1] To be precise, the defined in the previous paper[S1] were U_{eff} and U, that were twice the present definitions, i.e., $U_{\mathrm{eff}} = 2U_{\mathrm{II}}^{\mathrm{eff}}$ and $U = 2U_{\mathrm{II}}$.

yields

$$\delta^2 \hat{f}^{\mathrm{s}}_{\boldsymbol{q}} \simeq (1/2V) \left[|\delta\hat{\phi}_{v\boldsymbol{q}}|^2/\kappa_{\mathrm{w}} + k_{\mathrm{B}}T|\delta\hat{n}_{\mathrm{I}\boldsymbol{q}}|^2/2n_{\mathrm{I}}\chi \right], \tag{SI-50}$$

where $\delta\phi_v = n_{\mathrm{w}}^{-1}\delta\hat{n}_{\mathrm{w}} + v_{\mathrm{c}}^*\delta\hat{n}_{\mathrm{c}} + +v_{\mathrm{a}}^*\delta\hat{n}_{\mathrm{a}}$ and $\delta\hat{n}_{\mathrm{I}} = \delta\hat{n}_{\mathrm{c}} + \delta\hat{n}_{\mathrm{a}}$. From Eqs.(SI-39) and (SI-50), we reproduce the previous result for dilute electrolyte solutions,[S1]

$$\langle \delta\hat{n}_{\mathrm{c}} \circ \delta\hat{n}_{\mathrm{c}} \rangle = \langle \delta\hat{n}_{\mathrm{a}} \circ \delta\hat{n}_{\mathrm{a}} \rangle = \langle \delta\hat{n}_{\mathrm{c}} \circ \delta\hat{n}_{\mathrm{a}} \rangle \simeq n_{\mathrm{I}}\chi/2. \tag{SI-51}$$

SI-D.2 Solute-solute correlation

Now we add a small amount of hydrophobic solute. In accordance with Eqs. (7) and (44), we have

$$\begin{aligned} \hat{f} =& \hat{f}^{\mathrm{s}} + k_{\mathrm{B}}T\hat{n}_{\mathrm{h}}\{\ln(\hat{n}_{\mathrm{h}}\lambda_{\mathrm{h}}^3) - 1 + \hat{\nu}_{\mathrm{h}}^{\mathrm{s}}(\hat{n}_{\mathrm{w}}, \hat{n}_{\mathrm{c}}, \hat{n}_{\mathrm{a}})\} \\ &+ \frac{1}{2}\hat{U}_{\mathrm{hh}}^{\mathrm{s}}(\hat{n}_{\mathrm{w}}, \hat{n}_{\mathrm{c}}, \hat{n}_{\mathrm{a}})\hat{n}_{\mathrm{h}}^2 + \cdots, \end{aligned} \tag{SI-52}$$

where $\hat{\nu}_{\mathrm{h}}^{\mathrm{s}}$ and $\hat{U}_{\mathrm{hh}}^{\mathrm{s}}$ satisfies

$$\hat{\nu}_{\mathrm{h}}^{\mathrm{s}}(n_{\mathrm{w}}, n_{\mathrm{I}}/2, n_{\mathrm{I}}/2) = \nu_{\mathrm{h}}^{\mathrm{s}}(n_{\mathrm{w}}, n_{\mathrm{I}}) \tag{SI-53}$$

$$\hat{U}_{\mathrm{hh}}^{\mathrm{s}}(n_{\mathrm{w}}, n_{\mathrm{I}}/2, n_{\mathrm{I}}/2) = U_{\mathrm{hh}}^{\mathrm{s}}(n_{\mathrm{w}}, n_{\mathrm{I}}). \tag{SI-54}$$

We define the total volume deviation $\delta\hat{\phi}_{\mathrm{tot}}$ as[S3]

$$\delta\hat{\phi}_{\mathrm{tot}} \equiv \sum_{i=\mathrm{w,c,a}} v_i^{\mathrm{s}}\delta\hat{n}_i + v_{\mathrm{h}}^{\mathrm{s}*}\delta\hat{n}_{\mathrm{h}} = \delta\hat{\phi} + v_{\mathrm{h}}^{\mathrm{s}*}\delta\hat{n}_{\mathrm{h}}. \tag{SI-55}$$

Expanding Eq. (SI-52) with respect to the density deviations $\delta\hat{n}_i$, and neglecting the terms of order n_h, we obtain

$$\sum_{i,j=\mathrm{w,c,a,h}} \hat{f}_{ij}\delta\hat{n}_i\delta\hat{n}_j = \sum_{i,j=\mathrm{c,a}} \hat{f}^\mathrm{s}_{ij}\delta\hat{n}_i\delta\hat{n}_j + \delta^2\hat{f}^\mathrm{h}. \tag{SI-56}$$

Here the second term is the bilinear form including $\delta\hat{n}_\mathrm{h}$,

$$\delta^2\hat{f}^\mathrm{h} = (k_\mathrm{B}T/n_\mathrm{h} + U^\mathrm{s}_\mathrm{hh})\delta\hat{n}_\mathrm{h}^2 + 2k_\mathrm{B}T\sum_{i=\mathrm{w,c,a}} \hat{\nu}^\mathrm{s}_{\mathrm{h}i}\delta\hat{n}_i\delta\hat{n}_\mathrm{h} \tag{SI-57}$$

with $\hat{\nu}^\mathrm{s}_{\mathrm{h}i} = \partial\hat{\nu}^\mathrm{s}_\mathrm{h}/\partial\hat{n}_i|_{\{\hat{n}_i=\langle\hat{n}_i\rangle\}}$. Using Eqs. (21), (34), (SI-28), (SI-29) (SI-32), (SI-33) (SI-56), and (SI-57), we find

$$\begin{aligned}\sum_{i,j=\mathrm{w,c,a,h}} \hat{f}_{ij}\delta\hat{n}_i\delta\hat{n}_j =& \frac{\delta\hat{\phi}^2_\mathrm{tot}}{\kappa^\mathrm{s}_T} + \frac{k_\mathrm{B}T(\delta\hat{X}_\mathrm{I} + \chi_\mathrm{I}g_\mathrm{h}\delta\hat{n}_\mathrm{h})^2}{\chi_\mathrm{I}} \\ &+ (k_\mathrm{B}T/n_\mathrm{h} + U^\mathrm{eff}_\mathrm{hh})\delta\hat{n}_\mathrm{h}^2 + \gamma_{\rho\rho}\delta\hat{X}^2_\rho \\ &+ 2\gamma_{\rho\mathrm{I}}\delta\hat{X}_\rho\delta\hat{X}_\mathrm{I} + \gamma_{\rho\mathrm{h}}\delta\hat{X}_\rho\delta\hat{n}_\mathrm{h}\end{aligned} \tag{SI-58}$$

where we have introduced the coefficient $\gamma_{\rho\mathrm{h}}$, but it is irrelevant to the long wavelength fluctuations. As in SI-D.1, the long-range electrostatic interaction suppresses the fluctuations of X_ρ for small $\boldsymbol{q}$. Hence, in the limit $\boldsymbol{q} \to 0$, Eqs. (SI-38), (SI-39) and (SI-40) still hold in the presence of solute. In addition we have $\langle\delta\hat{X}_\rho \circ \delta\hat{n}_\mathrm{h}\rangle = 0$, or, equivalently,

$$\langle\delta\hat{n}_\mathrm{h} \circ \delta\hat{n}_\mathrm{c}\rangle = \langle\delta\hat{n}_\mathrm{h} \circ \delta\hat{n}_\mathrm{a}\rangle. \tag{SI-59}$$

The long-wavelength ($\boldsymbol{q} \to 0$) fluctuations of $\delta\hat{\phi}_\mathrm{tot}$, $\delta\hat{X}_\mathrm{I}$, and $\delta\hat{n}_\mathrm{h}$ are governed by the probability distribution proportional to $\exp[-\delta^2\hat{f}_{\boldsymbol{q}}/k_\mathrm{B}T]$ with

$$\delta^2\hat{f}_{\boldsymbol{q}} = (1/2V)\Big[\frac{|\delta\hat{\phi}_{\mathrm{tot}\boldsymbol{q}}|^2}{\kappa^\mathrm{s}_T} + \frac{k_\mathrm{B}T|\delta\hat{X}_{\mathrm{I}\boldsymbol{q}} + \chi_\mathrm{I}g_\mathrm{h}\delta\hat{n}_{\mathrm{h}\boldsymbol{q}}|^2}{\chi_\mathrm{I}} + |\delta\hat{n}_{\mathrm{h}\boldsymbol{q}}|^2(k_\mathrm{B}T/n_\mathrm{h} + U^\mathrm{eff}_\mathrm{hh})\Big], \tag{SI-60}$$

where the terms of order n_h have been neglected, and $U^\mathrm{eff}_\mathrm{hh}$ has been defined in Eq. (39). The fluctuation variance of the solute is then given by

$$\langle \delta\hat{n}_{\mathrm{h}} \circ \delta\hat{n}_{\mathrm{h}} \rangle = (1/n_{\mathrm{h}} + U^{\mathrm{eff}}_{\mathrm{hh}}/k_{\mathrm{B}}T)^{-1}. \tag{SI-61}$$

This result also follows from Eq. (SI-12) and the well-known relation $I_{\mathrm{hh}} = \langle \delta\hat{n}_{\mathrm{h}} \circ \delta\hat{n}_{\mathrm{h}} \rangle$ (see also sentences below Eq. (39)). The results in Eqs. (39), (SI-60) and (SI-61) are the same as the previous ones for a ternary mixture composed of a non-ionic binary solvent and a solute;[S3] this is because in the present ionic case the long wavelength fluctuations of $\delta\hat{X}_\rho$ are suppressed by the long-range Coulombic interaction, and thus in the limit $\boldsymbol{q} \to 0$ the cations and anions can be treated as a single indistinguishable component.[S1,S4]

SI-E Kirkwood-Buff integrals

Let $g_{ij}(r)$ denote the radial distribution function associated with species i and j. Its space integral is called the Kirkwood-Buff integral (KBI):[S5] $G_{ij} \equiv 4\pi \int_0^\infty dr\, r^2[g_{ij}(r) - 1]$. Since in Eqs. (SI-39), (SI-40) and (SI-59) cations and anions are indistinguishable, the cations and anions are regarded as indistinguishable, single species when KBIs are discussed in the literature.[S6–S13] In the present case we define the KBIs for species w (water), I (ion), and h (solute). For convenience we define $\delta\hat{n}_{\mathrm{I}} \equiv \delta\hat{n}_{\mathrm{c}} + \delta\hat{n}_{\mathrm{a}}$. The well-known relation $I_{ij} = \langle \delta\hat{n}_i \circ \delta\hat{n}_j \rangle$ combines the thermodynamics and the KBIs. Integrating the general relation $\langle \delta\hat{n}_i(\boldsymbol{r})\delta\hat{n}_j(0) \rangle = n_i n_j [g_{ij}(r) - 1] + n_i \delta_{ij} \delta(\boldsymbol{r})$, we have

$$I_{ij} = \langle \delta\hat{n}_i \circ \delta\hat{n}_j \rangle = n_i n_j G_{ij} + n_i \delta_{ij} \tag{SI-62}$$

First we discuss KBIs for the electrolyte solvent without solute. From Eqs. (SI-37)–(SI-40) and (SI-62) (or, from Eqs. (29) and (SI-62)), we obtain

$$\chi_{\mathrm{I}} = n_{\mathrm{w}} n_{\mathrm{I}}/n^3 + (n_{\mathrm{w}}^2 n_{\mathrm{I}}^2/n^4)(G^{\mathrm{s}}_{\mathrm{ww}} + G^{\mathrm{s}}_{\mathrm{II}} - 2G^{\mathrm{s}}_{\mathrm{wI}}). \tag{SI-63}$$

where G^{s}_{ij}'s are KBIs evaluated at $n_{\mathrm{h}} = 0$. The determinant $\Delta_0 = \det\{I^{\mathrm{s}}_{ij}\}$ can be expressed in terms of KBIs. Hence, The isothermal compressibility κ^{s}_T can also be expressed in terms of KBIs by using Eqs. (29) and (SI-63). At $n_{\mathrm{h}} = 0$, Eqs. (15), (29) and (SI-62) yield

$$v^{\mathrm{s}}_{\mathrm{I}} = (n_{\mathrm{I}} n^2_{\mathrm{w}}/n^4 \chi_{\mathrm{I}})(n^{-1}_{\mathrm{w}} + G^{\mathrm{s}}_{\mathrm{ww}} - G^{\mathrm{s}}_{\mathrm{wI}}) \tag{SI-64}$$

$$v^{\mathrm{s}}_{\mathrm{w}} = (n^2_{\mathrm{I}} n_{\mathrm{w}}/n^4 \chi_{\mathrm{I}})(n^{-1}_{\mathrm{I}} + G^{\mathrm{s}}_{\mathrm{II}} - G^{\mathrm{s}}_{\mathrm{wI}}). \tag{SI-65}$$

For a vanishing salt density $n_{\mathrm{I}} \to 0$ we substitute Eq. (SI-49) into (SI-64), and obtain

$$v_{\mathrm{I}} = -G^0_{\mathrm{wI}} + k_{\mathrm{B}} T \kappa_{\mathrm{w}}, \quad v^*_{\mathrm{I}} = -G^0_{\mathrm{wI}}, \tag{SI-66}$$

where G^0_{ij} is the KBI in the limit $n_{\mathrm{h}}, n_{\mathrm{I}} \to 0$. In the same limit, Eq. (SI-65) correctly reduces to Eq. (23). These formal results for electrolyte solvents are exactly the same as those for non-ionic binary fluids,[S3] but in the present ionic case one needs to be careful when taking the limit $n_{\mathrm{I}} \to 0$ for ion-ion KBI, $G^{\mathrm{s}}_{\mathrm{II}}$. For small n_{I} Eq. (SI-51) yields[S1,S14] $G^{\mathrm{s}}_{\mathrm{II}} \simeq (2\chi - 1)/n_{\mathrm{I}} \simeq \ell_B \kappa/4n_{\mathrm{I}} \propto n^{-1/2}_{\mathrm{I}}$, which diverges as $n_{\mathrm{I}} \to 0$; this divergence stems from the Debye-Hückel free energy, which is specific to electrolyte solutions.

Now we discuss the KBIs in the presence of a small amount of solute. First, Eqs. (SI-61) and (SI-62) yield

$$G_{\mathrm{hh}} = -\frac{U^{\mathrm{eff}}_{\mathrm{hh}}/k_{\mathrm{B}}T}{1 + n_{\mathrm{h}} U^{\mathrm{eff}}_{\mathrm{hh}}/k_{\mathrm{B}}T} = \frac{G^{\mathrm{s}}_{\mathrm{hh}}}{1 - n_{\mathrm{h}} G^{\mathrm{s}}_{\mathrm{hh}}}, \tag{SI-67}$$

where $G^{\mathrm{s}}_{\mathrm{hh}} = -U^{\mathrm{eff}}_{\mathrm{hh}}/k_{\mathrm{B}}T$ is the solute-solute KBI in the limit $n_{\mathrm{h}} \to 0$. The relation (SI-67) shows that KBI G_{hh} at finite n_{h} noticeably deviates from its dilute limit $G^{\mathrm{s}}_{\mathrm{hh}}$ when $|G^{\mathrm{s}}_{\mathrm{hh}}| \sim n^{-1}_{\mathrm{h}}$; this observation is sometimes not negligible when one attempts to compute $G^{\mathrm{s}}_{\mathrm{hh}}$ from MD simulations of small but finite n_{h}. Using Eq. (38), we obtain

$$U^{\mathrm{eff}}_{\mathrm{hh}}/k_{\mathrm{B}}T = -G^{\mathrm{s}}_{\mathrm{hh}} = 2B. \tag{SI-68}$$

Next, Eqs. (SI-62) and (SI-2) yield $A_i = G^{\mathrm{s}}_{i\mathrm{h}} n_i$ $(i = \mathrm{w}, \mathrm{I})$. Substituting this into Eqs. (SI-6) and (SI-7), we obtain

$$g_{\mathrm{h}} = (n_{\mathrm{w}} n_{\mathrm{I}} / n^2 \chi_{\mathrm{I}})(G^{\mathrm{s}}_{\mathrm{wh}} - G^{\mathrm{s}}_{\mathrm{Ih}}) \tag{SI-69}$$

$$v^{\mathrm{s}*}_{\mathrm{h}} = -(v^{\mathrm{s}}_{\mathrm{w}} n_{\mathrm{w}} G^{\mathrm{s}}_{\mathrm{wh}} + v^{\mathrm{s}}_{\mathrm{I}} n_{\mathrm{I}} G^{\mathrm{s}}_{\mathrm{Ih}}). \tag{SI-70}$$

In the limit $n_{\mathrm{I}} \to 0$, these reduce to

$$K_{\mathrm{S}} = 2(G^0_{\mathrm{wh}} - G^0_{\mathrm{Ih}}), \quad v^*_{\mathrm{h}} = -G^0_{\mathrm{wh}} \tag{SI-71}$$

where use has been made of Eqs. (35) and (SI-49) in deriving the first relation. Finally, Eqs. (33) and (SI-71) yield

$$U^{\mathrm{eff}}_{\mathrm{hI}} / k_{\mathrm{B}} T = -G^0_{\mathrm{Ih}}. \tag{SI-72}$$

SI-F Debye-McAulay theory and Eq. (52)

Debye and McAulay[S15] have studied effective solute-salt (electrostatic) interaction on the basis of Born theory.[S16] The idea is that the effective solute-salt interaction $U^{\mathrm{DM}}_{\mathrm{hs}}$ is given by the Born energy difference $\Delta\mu_{\mathrm{Born}} = U^{\mathrm{DM}}_{\mathrm{hs}} n_{\mathrm{h}} + O(n^2_{\mathrm{h}})$ between a pair of ions in pure water and that in water containing the solute. One can expand the dielectric permittivity with respect to n_{h}, $\varepsilon = \varepsilon^0(1 + D n_{\mathrm{h}} + O(n^2_{\mathrm{h}}))$, where ε^0 is the dielectric permittivity of pure water and D is a coefficient of proportionality. Then from the Born model one readily obtain

$$U^{\mathrm{DM}}_{\mathrm{hs}} = -(k_{\mathrm{B}} T \ell_B D/2)(R^{-1}_{\mathrm{c}} + R^{-1}_{\mathrm{a}}). \tag{SI-73}$$

In isobaric condition and without salt, meanwhile, the water density varies according to $(\partial n_{\mathrm{w}} / \partial n_{\mathrm{h}})_{T,p} = -\bar{v}_{\mathrm{h}} / \bar{v}_{\mathrm{w}}$ as the solute density varies (we can derive this relation as in the same manner for Eq. (25)). We thus have $n_{\mathrm{w}} - n_{\mathrm{w}}^0 = -v_{\mathrm{h}} n_{\mathrm{h}} n_{\mathrm{w}}^0 + O(n_{\mathrm{h}}^2)$ where n_{w}^0 is the water density without solute. Since we have assumed the dielectric permittivity explicitly depends only on n_{w}, we expand $\varepsilon(n_{\mathrm{w}}) = \varepsilon^0 + (\partial\varepsilon/\partial n_{\mathrm{w}})(n_{\mathrm{w}} - n_{\mathrm{w}}^0) + \cdots$. We thus have

$$D = -a_{\varepsilon} v_{\mathrm{h}}, \tag{SI-74}$$

where $a_{\varepsilon} = n_{\mathrm{w}} \varepsilon^{-1} (\partial\varepsilon/\partial n_{\mathrm{w}})$. Substituting Eq. (SI-74) into (SI-73) and using Eq. (53), we obtain

$$U_{\mathrm{hs}}^{\mathrm{DM}} = -2 v_{\mathrm{h}} v_{\mathrm{I}}^{\mathrm{B}} / \kappa_{\mathrm{w}} \simeq -2 v_{\mathrm{h}}^* v_{\mathrm{I}}^{\mathrm{B}} / \kappa_{\mathrm{w}}. \tag{SI-75}$$

The right hand side is indeed the same as $K_{\mathrm{S}}^{\mathrm{el}}$ in Eq. (52) with $v_{\mathrm{I}}^{\mathrm{el}}$ being replaced by $v_{\mathrm{I}}^{\mathrm{B}}$.

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