Ion solvation in liquid mixtures: effects of solvent reorganization

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SUPPLEMENTARY MATERIAL

In this Supplementary Material, we provide some details of the derivation of the key equations in our theory [Eqs. (4)-(8) in the main text]. We first introduce the coarse-grained number density field $n_s(\vec{r})$ for the solvents ($s = A$ and $B$) via the identity

\[
1 = \int Dn_s \delta[\tilde{n}_s(\vec{r}) - n_s(\vec{r})] = \int Dn_s D\omega_s \exp\left\{ i \int d\vec{r}' \omega_s(\vec{r}) \{ \tilde{n}_s(\vec{r}) - n_s(\vec{r}) \} \right\}, \tag{S1}
\]

where the right-hand side of the equation arises from the Fourier representation of the $\delta$-function with $\omega_s(\vec{r})$ being the Fourier conjugate field to $n_s(\vec{r})$. A similar procedure is performed for the total charge density $\tilde{\rho}(\vec{r})$, which introduces the conjugate field $\psi(\vec{r})$.

The partition function $Z$ [Eq. (1) in the main text] can then be cast into a functional integral of the general form,

\[
Z = \int D\rho Dn_A Dn_B D\psi D\omega_A D\omega_B \delta \left[ \sum_{s=A,B} v_s n_s(\vec{r}) - 1 \right] \exp \left\{ -\frac{1}{2} \int d\vec{r} d\vec{r}' \rho(\vec{r}) v(\vec{r} - \vec{r}') \rho(\vec{r}') + i \int d\vec{r} \rho(\vec{r}) \psi(\vec{r}) - i z \psi(0) + i \sum_{s=A,B} \int d\vec{r} n_s(\vec{r}) \omega_s(\vec{r}) \right\} \prod_{N_A, N_B} \prod_{s=A,B} \int d\vec{r} d\vec{p} \exp \left\{ -i \sum_{s=A,B} \sum_{i=1}^{N_s} [\omega_s(\vec{r}_si) + \vec{p}_si \cdot \nabla \psi(\vec{r}_si)] \right\} \]. \tag{S2}

Note that because of the identity operator, Eq. (S1), the instantaneous particle density $\tilde{n}_s(\vec{r})$ is replaced by the coarse-grained (average) density $n_s(\vec{r})$. Furthermore, we have made use of the identity

\[
\int d\vec{r} \tilde{n}_s(\vec{r}) \omega_s(\vec{r}) = \int d\vec{r} \sum_{i=1}^{N_s} \delta(\vec{r} - \vec{r}_si) \omega_s(\vec{r}) = \sum_{i=1}^{N_s} \omega_s(\vec{r}_si), \tag{S3}
\]

and have performed the summation over the particle number using the identity, $\sum_{N=0}^{\infty} (x^N / N!) = e^x$.

Performing the Gaussian integral over the charge density fields $\rho(\vec{r})$ (the Hubbard-Stratonovich transformation) transforms the Coulomb interaction term to

\[
\int D\rho \exp \left\{ -\frac{1}{2} \int d\vec{r} d\vec{r}' \rho(\vec{r}) v(\vec{r} - \vec{r}') \rho(\vec{r}') + i \int d\vec{r} \rho(\vec{r}) \psi(\vec{r}) \right\} = N_v^{-1} \exp \left\{ \frac{1}{2} \int d\vec{r} d\vec{r}' v^{-1}(\vec{r} - \vec{r}') \psi(\vec{r}) \psi(\vec{r}') \right\}, \tag{S4}
\]

where $v^{-1}(\vec{r} - \vec{r}')$ is the inverse of the Coulomb operator $v^{-1}(\vec{r} - \vec{r}') = -(4\pi \varepsilon_0)^{-1} \nabla^2 \delta(\vec{r} - \vec{r}')$. $N_v$ is the thermodynamically inconsequential normalization term due to the Gaussian functional integral. Thus, Eq. (S2) can be written in the form,

\[
Z = \int Dn_A Dn_B D\psi D\omega_A D\omega_B \delta \left[ \sum_{s=A,B} v_s n_s(\vec{r}) - 1 \right] \exp(-F), \tag{S5}
\]
where the free energy functional of the system $F$ is

$$F = \frac{1}{8\pi l_0} \int d\vec{r} \psi(\vec{r}) \nabla^2 \psi(\vec{r}) + z\psi(0) - \sum_{s=A,B} \int d\vec{r} \left[ n_s \omega_s(\vec{r}) + \lambda_s e^{-\omega_s(\vec{r})} I_s(\vec{r}) \right]. \quad (S6)$$

In the above expression, we have replaced $i\psi(\vec{r})$ and $i\omega_s(\vec{r})$ by $\psi(\vec{r})$ and $\omega_s(\vec{r})$ in anticipation of the fact that the saddle point values of the original fields $\psi(\vec{r})$ and $\omega_s(\vec{r})$ are purely imaginary.

Making the saddle-point approximation, $\delta F/\delta \psi = 0$, using Eq. (S6) leads to the following self-consistent field equation,

$$\nabla^2 \psi(\vec{r}) - 4\pi l_0 \sum_{p=A,B} \int d\vec{r} \lambda_p e^{-\omega_p(\vec{r})} \frac{\delta I_p(\vec{r})}{\delta \psi(\vec{r})} = -4\pi l_0 z \delta(\vec{r}). \quad (S7)$$

After calculating the functional derivative of $I_s(\vec{r})$, Eq. (S7) can be cast into Eqs. (6) and (7) in the main text.

Because of the $\delta$-function in Eq. (S5), we have $\sum_{s=A,B} v_s n_s(\vec{r}) = 1$ for the incompressibility condition. This condition is used to solve for one of the density fields, say $n_B(\vec{r})$, in terms of the other density field $n_A(\vec{r})$, thus eliminating the functional integration over $n_B(\vec{r})$. For the remaining three field variables, we make the saddle-point approximation in evaluating the integral by setting $\delta F/\delta n_A = 0$ and $\delta F/\delta \omega_s = 0$ ($s = A, B$), to result in the equations, $\omega_B(\vec{r}) = (v_B/v_A) \omega_A(\vec{r})$ and $n_s(\vec{r}) = \lambda_s e^{-\omega_s(\vec{r})} I_s(\vec{r})$. Combining the latter equation for $n_s(\vec{r})$ with the incompressibility condition $\sum_s v_s n_s(\vec{r}) = 1$ leads to Eq. (8) in the main text.