Ion Solvation in Liquid Mixtures: Effects of Solvent Reorganization

Issei Nakamura,[1] An-Chang Shi,[2] and Zhen-Gang Wang[1],[*]

[1]*Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, USA*
[2]*Department of Physics and Astronomy, McMaster University, Hamilton, Ontario L8S 4L8, Canada*

Using field-theoretic techniques, we study the solvation of salt ions in liquid mixtures, accounting for the permanent and induced dipole moments, as well as the molecular volume of the species. With no adjustable parameters, we predict solvation energies in both single-component liquids and binary liquid mixtures that are in excellent agreement with experimental data. Our study shows that the solvation energy of an ion is largely determined by the local response of the permanent and induced dipoles, as well as the local solvent composition in the case of mixtures, and does not simply correlate with the bulk dielectric constant. In particular, we show that, in a binary mixture, it is possible for the component with the lower bulk dielectric constant but larger molecular polarizability to be enriched near the ion.

PACS numbers: 77.84.Nh, 31.15.xr, 31.70.Dk, 78.20.Ci

Salt ions are essential in biology, colloidal science, electrochemistry, and many other areas of science and engineering. For example, protein stability and solubility are well known to be significantly affected by the addition of salts [1]. In the energy arena, there is much current interest in lithium salt-doped polymers as new battery materials [2].

The effects of salt ions on the properties of soft matter can often be understood in terms of translational entropy and electrostatic screening. However, recently it has been shown that the solvation energy of the salt ions can significantly affect the phase behavior [3,4] and interfacial properties of liquid mixtures [5–8]. For example, Ref. [4] showed that the dramatic increase in the order-disorder transition temperature of (polyethylene oxide)-b-polystyrene block copolymers upon adding a small amount of lithium salt can be explained on the basis of the preferential solvation energy of the anions. Physically, the tendency of an ion to be preferentially solvated by the more polarizable component in a two-component mixture provides a significant driving force for phase separation [3], as well as differential adsorption between the cation and anion at the interface [5–8].

While a very large body of theoretical literature exists for ion solvation in single-component liquids (See Refs. [9–13] for comprehensive reviews and Ref. [14] for recent developments of ion force fields for solvation.), we are not aware of any theory that predicts the composition dependence of ion solvation in liquid mixtures. In Refs. [3–6,8], the solvation energy is modeled phenomenologically at the linear dielectrics level by a crude Born expression: $\Delta G_{\text{Born}} = [(ze)^2/(8\pi a \epsilon_0)](1/\epsilon - 1)$, where e is the elementary charge, a is the radius of the ion, and z is the valency. The local dielectric constant is taken to be given by a simple composition weighted average $\epsilon = \epsilon_A \phi_A + \epsilon_B \phi_B$. The Born model has the virtue of being simple and intuitive in capturing the essential qualitative physics of solvation. However, quantitatively, the Born expression is known to

be a poor description of the solvation of small ions [11], even in a one-component uniform liquid, because of the dielectric saturation (due to saturated dipole orientation) [15–17] near the ion. In a spatially inhomogeneous liquid or mixture, there is the additional effect of local density or composition response to the electric field of the ion. For example, the more polarizable component is expected to be enriched near the ion relative to its bulk composition.

In this Letter, we study the solvation of salt ions in liquid mixtures using a field-theoretic molecular approach. Our approach draws upon several recent field-theoretical studies that treat the solvent as a lattice gas of dipoles [18–21]. In particular, Koehl *et al.* developed a Poisson-Boltzmann-Langevin approach for ion solvation in aqueous solutions [19–21], taking into account the permanent dipoles of water molecules and density variation near the ions; the theory contains adjustable parameters that are optimized to model aqueous systems. In earlier works, Warshel and co-workers [22,23] studied the charge solvation of biomolecules in an aqueous solution. Their work includes both the induced and permanent dipoles, but these two types of dipolar interaction are treated differently. Our approach is similar in spirit but differs from previous works in several important respects in the model and in the focus. First, instead of a lattice gas model as in Refs. [18–21], we consider a continuum model in which the liquid nature of the medium is accounted for by incompressibility and the volume of the molecules. Second, we include the molecular polarizability and permanent dipoles using the same unified framework. Third, in comparison to the systems considered by Warshel and co-workers where the molecular species have a fixed spacial distribution, we account for the translational degrees of freedom and the associated effects of the entropy of mixing in a liquid mixture. Furthermore, our theory contains no adjustable parameters. Finally, we focus on several new physical effects arising from the reorganization of the mixture around the solvated

ions. In particular, we show, for some combinations of the intrinsic dipole moment and molecular polarizability, that the component having a large molecular polarizability but lower bulk dielectric constant is enriched near the ion and that the identity of the enriched component can switch upon changing the valency and/or radius of the ion.

We consider an ion fixed at the origin immersed in a binary liquid mixture of N_A type-A molecules and N_B type-B molecules in a volume V. The ion is modeled as a cavity of radius a with a point charge ze at the center. The center of mass of the ith molecule of species s is denoted by $\vec{R}_{si}$; its dipole moment is $\vec{p}_{si}$. For convenience, we work in the grand canonical ensemble; the partition function is

$$Z = \sum_{N_A,N_B} \prod_{s=A,B} \frac{\lambda_s^{N_s}}{N_s!} \int \prod_{i=1}^{N_s} \mathcal{D}\vec{R}_{si} d\vec{p}_{si} \delta\left[\sum_s v_s \hat{n}_s(\vec{r}) - 1\right]$$
$$\times \exp\left[-\frac{1}{2}\int d^3r d^3r' \hat{\rho}(\vec{r})v(\vec{r}-\vec{r}')\hat{\rho}(\vec{r}') - V_H\right], \quad (1)$$

where $v(\vec{r}-\vec{r}') = e^2/(4\pi\epsilon_0|\vec{r}-\vec{r}'|)$ is the Coulomb potential in vacuum, λ_s is the fugacity of dipolar molecule s, and v_s is the molecular volume of solvent s ($s = A$ or B). We use $k_B T$ as the energy unit. The hard-core repulsion between the molecules is modeled by the δ function in Eq. (1) that enforces incompressibility for the liquid mixture outside of the ion, with $\hat{n}_s(\vec{r}) = \sum_{i=1}^{N_s} \delta(\vec{r}-\vec{R}_{si})$ being the number density for species s. The total charge density $\hat{\rho}(\vec{r})$ is given by [24]

$$\hat{\rho}(\vec{r}) = z\delta(\vec{r}) + \sum_{s=A,B} \hat{\rho}_s(\vec{r}),$$
$$\hat{\rho}_s(\vec{r}) = -\sum_{i=1}^{N_s} \vec{p}_{si} \cdot \nabla\delta(\vec{r}-\vec{R}_{si}), \quad (2)$$

where $\hat{\rho}_s(\vec{r})$ is the charge density due to the dipoles. The dipoles on the molecules consist of an intrinsic (permanent) contribution $\bar{p}_s$ and a contribution induced by the electric field. Thus, the Coulomb interaction in Eq. (1) includes the dipole-dipole interaction between the solvent molecules. Within the harmonic approximation, we ascribe a deformation energy for the induced dipole as [18,25]

$$V_H = \sum_{s=A,B}\sum_{i=1}^{N_s} \frac{1}{2\alpha_s}(|\vec{p}_{si}| - \bar{p}_s)^2, \quad (3)$$

where α_s is the molecular polarizability of species s.

In this work, we consider liquid components that are fully miscible. Thus, we ignore any differential energetic interactions (besides the dipolar interactions) between the two liquid species in the mixture; these additional interaction effects will be considered in future work.

Using standard field-theoretic techniques [26], we first integrate the solvent degrees of freedom. Ignoring an inconsequential term from normalization in the Hubbard-Stratonovich transformation, we write the free energy in terms of field variables,

$$F = \frac{1}{8\pi l_0}\int d\vec{r}\,\psi(\vec{r})\nabla^2\psi(\vec{r}) + z\psi(0)$$
$$- \sum_{s=A,B}\int d\vec{r}[n_s(\vec{r})\omega_s(\vec{r}) + \lambda_s e^{-\omega_s(\vec{r})}I_s(\vec{r})]. \quad (4)$$

In this equation, $l_0 = e^2/(4\pi\epsilon_0)$ is the vacuum Bjerrum length, n_s and ω_s are the density field and its conjugate field for species s, respectively, and ψ is the electrostatic potential scaled by the elementary charge. The function $I_s(\vec{r})$ is

$$I_s(\vec{r}) = 4\pi\int_0^\infty dp_s p_s^2 e^{-1/(2\alpha_s)(p_s-\bar{p}_s)^2} \frac{\sinh[p_s|\nabla\psi(\vec{r})|]}{p_s|\nabla\psi(\vec{r})|}. \quad (5)$$

Extremizing the free energy functional with respect to the field variable $\psi(\vec{r})$, we obtain

$$\nabla\cdot[\varepsilon(\vec{r})\nabla\psi(\vec{r})] = -4\pi l_0 z\delta(\vec{r}). \quad (6)$$

Equation (6) is just the Poisson equation for the solvated ion, where $\varepsilon(\vec{r})$ can be identified as the local dielectric function given by

$$\varepsilon(\vec{r}) = 1 + 4\pi l_0 \sum_{s=A,B}\lambda_s e^{-\omega_s(\vec{r})}$$
$$\times \int d\vec{p}_s e^{-1/(2\alpha_s)(|\vec{p}_s|-\bar{p}_s)^2} p_s^2 F[p_s|\nabla\psi(\vec{r})|]. \quad (7)$$

F_s is related to the Langevin function, $\mathcal{L}(x) = 1/\tanh x - 1/x$, by $F = \mathcal{L}(x)\sinh x/x^2$. Similarly, extremization with respect to other field variables leads to a set of equations for the incompressibility

$$1 = \sum_{s=A,B}n_s(\vec{r})v_s, \qquad n_s(\vec{r}) = \lambda_s e^{-\omega_s(\vec{r})}I_s(\vec{r}),$$
$$\omega_B(\vec{r}) = \frac{v_B}{v_A}\omega_A(\vec{r}). \quad (8)$$

Details of the derivation can be found in the Supplemental Material [27]. Equations (6)–(8) constitute a modified Poisson-Boltzmann equation, in which the incompressibility of the fluid is reflected through the conjugate field $\omega_s(\vec{r})$ associated with the volume of the solvents. For easy reference, we shall refer to our theory or Eqs. (6)–(8) as the dipolar self-consistent field theory (DSCFT). Without loss of generality, λ_s can be absorbed into ω_s, so we set $\lambda_s = 1$. From Eq. (6), we identify the electric field and electric displacement, respectively, as $\vec{E}(\vec{r}) \equiv -\nabla\psi(\vec{r})$ and $\vec{D}(\vec{r}) \equiv \varepsilon(\vec{r})\vec{E}(\vec{r})$.

Because of the spherical symmetry, Eq. (6) reduces to $d\psi(r)/dr = -zl_0/[\varepsilon(r)r^2]$ by integrating once with respect to the radial distance r. This equation is to be solved together with Eqs. (7) and (8).

The solvation energy upon transferring an ion from vacuum to a dielectric medium is given by

$$\Delta G = \frac{1}{2} \int d\vec{r} [\vec{D}(\vec{r}) \cdot \vec{E}(\vec{r}) - \vec{D}_0(\vec{r}) \cdot \vec{E}_0(\vec{r})],$$

$$= \frac{z^2 l_0}{2} \int dr \left[\frac{1}{\varepsilon(r)} - 1 \right] \frac{1}{r^2}, \qquad (9)$$

where the subscript 0 denotes the corresponding variables in the vacuum. Note that $\vec{D}(\vec{r})$ is unchanged from $\vec{D}_0(\vec{r})$ because the charge remains constant. For the spatially uniform bulk dielectric constant, Eq. (9) yields the standard Born expression. Here, however, $\varepsilon(r)$ is position dependent and also depends on the electric field through Eqs. (6) and (7) in a nonlinear manner.

We first illustrate our results with a single-component liquid, since many of the salient features of our theory are more easily explained for this simpler case. In Fig. 1, we show the solvation free energy ΔG in methanol (MeOH) for monovalent and divalent ions of varying radii. The molecular parameters for methanol, as well as for other liquids considered in this work, are listed in Table I. The agreement between the DSCFT and experiments is remarkably good for both monovalent and divalent ions [29]. For comparison, we include the standard Born energy using the measured value of the bulk dielectric constant given in Table I, which clearly shows substantial deviation from the experimental data, particularly at small ion radii and for divalent ions. Similarly good agreement is obtained between our DSCFT results and experimental data for ions in ethanol, 1-propanol, acetone, and acetonitrile. Even for water, which is complicated by the presence of hydrogen bonds, the theoretical values are within 20–35% of the experimental data for the monovalent ions and
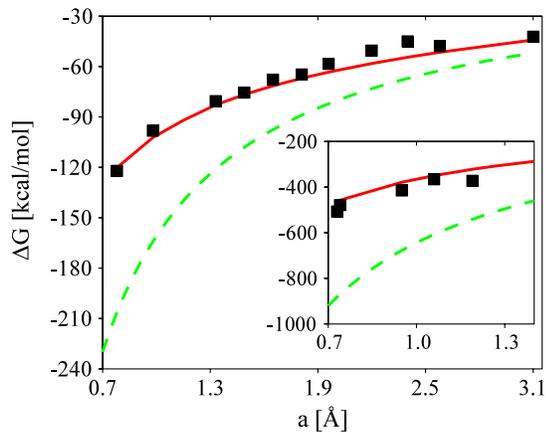
within 3–12% for the divalent ions (in both cases, the theory underestimates the solvation energy with more negative values).

As in previous work, Refs. [17,34], our calculation shows that $\varepsilon(\vec{r})$ has a sigmoidal shape as a function of the distance from the ion because of the dielectric saturation near the ion [35]. Because the primary contribution to the solvation energy arises from the local dielectric function near the ion, which is much reduced from the bulk value, the solvation energy is higher (less negative) than that predicted by the Born expression. Furthermore, while the Born expression predicts that the solvation energy is more negative in a liquid with a higher experimental bulk dielectric constant than in one with a lower experimental bulk dielectric constant, we find that it is possible to have a lower (more negative) solvation energy in a liquid that has a lower bulk dielectric constant but higher polarizability. For example, our calculation shows that ΔG for Na$^+$ ($a = 0.98$ [Å]) in chloroform is slightly more negative (by ~ 2 [kcal/mol]) than in ethyl acetate, even though chloroform has a lower experimental bulk dielectric constant (4.81) than ethyl acetate (6.08) (see Table I); this prediction awaits experimental validation.

We now consider ion solvation in a liquid mixture, starting with a Ag$^+$ ion ($a = 1.15$ [Å]) in a mixture of acetonitrile (MeCN) and MeOH. The measured bulk dielectric constants of these two liquids are, respectively, 36.64 and 33 (see Table I). Figure 2(a) shows the local composition as a function of the radial distance r from the Ag$^+$ ion. Even though the bulk composition of MeCN is quite low (0.0028), there is substantial enrichment of MeCN near the ion. In other words, upon adding even a very small amount of the higher-dielectric component, the structure of the first solvation shell is substantially altered. This result arises naturally from our DSCFT without assuming any mixing rule for the bulk dielectric constant of the mixture.

In Fig. 2(b), we show the transfer free energy ΔG^*— defined as the solvation free energy change relative to the pure MeCN liquid—as a function of the volume fraction of MeCN. Very good agreement between the theoretical prediction and experimental data is seen. The rapid decrease in the transfer free energy with ϕ_{MeCN} is a consequence of the local enrichment of this component near the ion.

FIG. 1 (color online). The solvation free energy ΔG of monovalent ions (Li$^+$, Na$^+$, K$^+$, Rb$^+$, Cs$^+$, Et$_4$N$^+$, Me$_4$N$^+$, Br$^-$, I$^-$, ClO$_4^-$, and Cl$^-$) and divalent (inset) ions (Ca^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, and Cu^{2+}) with different effective ionic radius a [38,39] in MeOH. (a) Filled squares represent experimental data [9,30–32]. (b) The solid red curves represent ΔG calculated by the DSCFT. (c) The dashed green curves represent the standard Born energy ΔG_{st} with the experimental value of the bulk dielectric constant.

TABLE I. Values of the solvent parameters [28] used in this work. $\bar{\varepsilon}$ is the experimental value of the bulk dielectric constant. $T = 293.15$ K for methanol and $T = 298.15$ K for all other substances.

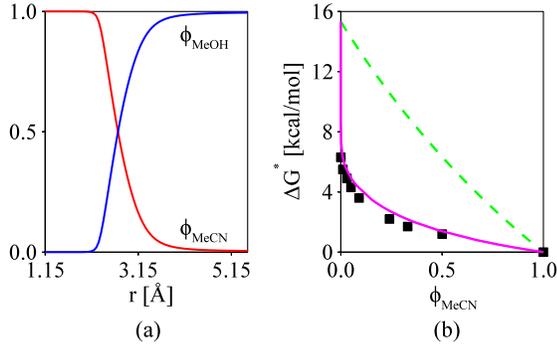| Solvent	$\bar{p}_s$ [D]	α_s [10^{-24} cm^3]	v_s [Å^3]	$\bar{\varepsilon}$
Methanol	1.70	3.29	67.3	33
Acetonitrile	3.84	4.4	87.7	36.64
Chloroform	1.04	9.5	133.7	4.81
Ethyl acetate	1.78	8.62	163.0	6.08

FIG. 2 (color online).   (a) Composition profile of MeCN and MeOH as a function of the radial distance r from a Ag^+ ion. (b) The transfer free energy ΔG^* as a function of the volume fraction of MeCN. Square points, experimental data [33]; solid purple line, ΔG^* calculated by the DSCFT; and dashed green line, result implied by the Born expression and linear mixing rule for the bulk dielectric constant.

For comparison, we also include the result for the transfer free energy as implied by the simple linear mixing rule for the dielectric constant of the mixture. This mixing rule, together with the simple Born expression for the solvation energy, implies the following expression for the transfer free energy: $\Delta G^*(\phi_A) = \{\phi_A[\Delta G_A + z^2 l_0/(2a)]^{-1} + \phi_B [\Delta G_B + z^2 l_0/(2a)]^{-1}\}^{-1} - \Delta G_A - z^2 l_0/(2a)$, where ΔG_s $(s = A, B)$ is the solvation energy in the pure liquids. That both the experimental data and our DSCF results lie considerably below this expression reflects the local reorganization of the solvent composition around the ion.

While the qualitative behavior shown in Fig. 2(a) is to be expected since MeCN has both a larger dipolar moment and polarizability (and hence an overall higher experimental bulk dielectric constant) than MeOH, for some combinations of the permanent dipole moment and molecular polarizability, it is possible that the component with the lower experimental bulk dielectric constant is enriched near the ion. In Fig. 3(a), we show that the low-dielectric-constant component chloroform (4.81) is enriched relative to ethyl acetate (6.08). This effect reflects the importance of molecular polarizability in determining the solvation structure and energy in the mixture. To better understand this effect, in Fig. 3(b) we show the change in the local dielectric function upon adding a small amount of chloroform. Because of the higher polarizability of this component, it gets enriched near the ion and this enrichment decreases the strength of the electrostatic field $E(r)$ and gives rise to a nonmonotonic behavior in the dielectric function $\varepsilon(r)$ in the vicinity of the ion.

More intriguingly, for a given binary mixture, it is possible that the identity of the locally enriched component can switch depending on the valency and radius of the ion. For example, for a hypothetical 50:50 binary mixture with parameter values $(\bar{p}_s[D], \alpha_s\ [10^{-24}\ cm^3], v_s\ [\mathring{A}^3], \bar{\varepsilon}) =$ (1.5, 1.0, 100, 3.4) and (1.2, 1.3, 100, 2.7), the component
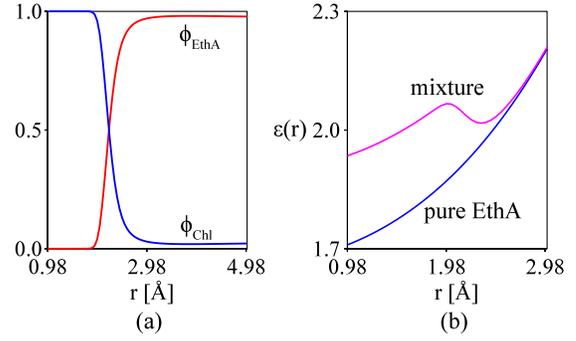

FIG. 3 (color online).   (a) Composition profile of chloroform and ethyl acetate as a function of the radial distance r from a Na^+ ion. (b) Profile for the local dielectric function. The bulk composition for the mixture is $\phi_{Chl} = 0.026$ and $\phi_{EthA} = 0.974$.

having a larger molecular polarizability but lower bulk dielectric constant becomes enriched near the ion with radius $a = 1.5\ \mathring{A}$, when a monovalent ion is changed to a divalent ion or a is decreased from 1.5 to 1.0 $\mathring{A}$.

In summary, we have developed a coarse-grained molecular theory, the DSCFT, for studying the solvation of salt ions in simple molecular liquids and liquid mixtures. The theory includes key molecular characteristics such as permanent and induced dipoles of solvents and their molecular volume, without any adjustable parameters. Effects such as dielectric saturation, excluded volume, and local solvent reorganization are naturally accounted for in a unified theoretical framework. The theoretical predictions for both single-component liquids and binary mixtures are in remarkable agreement with experimental data. Our study shows that the molecular polarizability plays a key role in ion solvation. The primary contribution to the solvation energy arises from the region near the ion where there is significant dielectric saturation of the permanent dipoles; thus, the bulk dielectric constant is a poor description for the ion solvation in polar liquids. Since the mean-field treatment in the DSCFT underestimates the reaction field, which is known to be important in determining the bulk dielectric constant [15,16], the good agreement between experimental data and our DSCFT results also suggests that this field plays a minor role in ion solvation.

The composition dependence of the ion solvation energy in liquid mixtures obtained in this work provides the first quantitative theory for such systems and serves as essential input for studying salt-induced phase separations in binary mixtures. In addition, the theory can be extended to study ion solvation at liquid-liquid interfaces. Finally, we expect many of the effects addressed in this work to be relevant to nonequilibrium charge solvation, as in the context of the Marcus theory for electron transfer [36,37].

*Corresponding author.
zgw@caltech.edu

[1] S. Kumar and R. Nussinov, Chembiochem **3,** 604 (2002).

[2] P. P. Soo, B. Y. Huang, Y. I. Jang, Y. M. Chiang, D. R. Sadoway, and A. M. Mayes, J. Electrochem. Soc. **146,** 32 (1999).

[3] Z.-G. Wang, J. Phys. Chem. B **112,** 16 205 (2008).

[4] I. Nakamura, N. P. Balsara, and Z.-G. Wang, Phys. Rev. Lett. **107,** 198301 (2011).

[5] A. Onuki, Phys. Rev. E **73,** 021506 (2006).

[6] A. Onuki, J. Chem. Phys. **128,** 224 704 (2008).

[7] W. Kung, F. J. Solis, and M. O. de la Cruz, J. Chem. Phys. **130,** 044502 (2009).

[8] R. Wang and Z.-G. Wang, J. Chem. Phys. **135,** 014707 (2011).

[9] J. Burgess, *Metal Ions in Solution* (Horwood, New York, 1978).

[10] Y. Marcus, *Ion Solvation* (Wiley, New York, 1985), 1st ed.

[11] J. O. Bockris and A. K. Reddy, *Modern Electrochemistry 1* (Springer, New York, 1998), 2nd ed.

[12] C. J. Cramer and D. G. Truhlar, Chem. Rev. **99,** 2161 (1999).

[13] Y. Marcus, Chem. Rev. **107,** 3880 (2007).

[14] D. Horinek, S. I. Mamatkulov, and R. R. Netz, J. Chem. Phys. **130,** 124 507 (2009).

[15] L. Onsager, J. Am. Chem. Soc. **58,** 1486 (1936).

[16] J. G. Kirkwood, J. Chem. Phys. **7,** 911 (1939).

[17] H. P. Gong, G. Hocky, and K. F. Freed, Proc. Natl. Acad. Sci. U.S.A. **105,** 11 146 (2008).

[18] R. D. Coalson and A. Duncan, J. Phys. Chem. **100,** 2612 (1996).

[19] C. Azuara, E. Lindahl, P. Koehl, H. Orland, and M. Delarue, Nucleic Acids Res. **34,** W38 (2006).

[20] C. Azuara, H. Orland, M. Bon, P. Koehl, and M. Delarue, Biophys. J. **95,** 5587 (2008).

[21] P. Koehl, H. Orland, and M. Delarue, J. Phys. Chem. B **113,** 5694 (2009).

[22] A. Warshel and M. Levitt, J. Mol. Biol. **103,** 227 (1976).

[23] A. Warshel and S. T. Russell, Q. Rev. Biophys. **17,** 283 (1984).

[24] A. Abrashkin, D. Andelman, and H. Orland, Phys. Rev. Lett. **99,** 077801 (2007).

[25] J. D. Jackson, *Classical Electrodynamics* (Wiley, New York, 1998), 3rd ed.

[26] G. H. Fredrickson, *The Equilibrium Theory of Inhomogeneous Polymers* (Oxford University, New York, 2006).

[27] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.109.257802 for the details of the derivation.

[28] W. M. Haynes, *CRC Handbook of Chemistry and Physics* (CRC Press, Boca Raton, FL, 2011), 92nd ed.

[29] Separating the experimentally measured values of the solvation energy of the salt ions into contributions by the cation and anion is nontrivial, and large discrepancies may result between different methods; see Refs. [9,11,13,14]. We have simply taken the published data reported in Refs. [9,30–32] for the single-component solvent and in Ref. [33] for the mixture. While there may be issues of uncertainty in the numerical values of the data because of the way they were obtained, there is no bias or prejudice in selecting these data for comparison.

[30] B. Case and R. Parsons, Trans. Faraday Soc. **63,** 1224 (1967).

[31] M. H. Abraham and J. Liszi, J. Chem. Soc., Faraday Trans. 1 **74,** 1604 (1978).

[32] J. R. Bontha and P. N. Pintauro, J. Phys. Chem. **96,** 7778 (1992).

[33] B. G. Cox, A. J. Parker, and W. E. Waghorne, J. Phys. Chem. **78,** 1731 (1974).

[34] L. Sandberg and O. Edholm, J. Chem. Phys. **116,** 2936 (2002).

[35] P. Debye, *Polar Molecules* (Dover, New York, 1929).

[36] R. A. Marcus, J. Chem. Phys. **24,** 966 (1956).

[37] R. A. Marcus, J. Chem. Phys. **24,** 979 (1956).

[38] R. D. Shannon, Acta Crystallogr. Sect. A **32,** 751 (1976).

[39] W. L. Masterton, D. Bolocofsky, and T. P. Lee, J. Phys. Chem. **75,** 2809 (1971).