From Solvent-Free to Dilute Electrolytes: Essential Components for a Continuum Theory

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ABSTRACT: The increasing number of experimental observations on highly concentrated electrolytes and ionic liquids show qualitative features that are distinct from dilute or moderately concentrated electrolytes, such as self-assembly, multiple-time relaxation, and underscreening, which all impact the emergence of fluid/solid interfaces, and the transport in these systems. Because these phenomena are not captured by existing mean-field models of electrolytes, there is a paramount need for a continuum framework for highly concentrated electrolytes and ionic liquid mixtures. In this work, we present a self-consistent spatiotemporal framework for a ternary composition that comprises ions and solvent employing a free energy that consists of short- and long-range interactions, along with an energy dissipation mechanism obtained by Onsager’s relations. We show that the model can describe multiple bulk and interfacial morphologies at steady-state. Thus, the dynamic processes in the emergence of distinct morphologies become equally as important as the interactions that are specified by the free energy. The model equations not only provide insights into transport mechanisms beyond the Stokes–Einstein–Smoluchowski relations but also enable qualitative recovery of three distinct regions in the full range of the nonmonotonic electrical screening length that has been recently observed in experiments in which organic solvent is used to dilute ionic liquids.

Concentrated electrolytes are being examined for a broad range of applications1–14 and specifically for energy-related devices, examples of which include dye-sensitized solar cells, fuel cells, batteries, and supercapacitors.3–7 Optimizing the design of these devices requires mechanistic understanding of the spatial ionic arrangement and charge transport in electrolytes. Although the physicochemical aspects of electrolyte solutions have been extensively studied, a series of recent experimental and computational results8–19 exposes knowledge gaps in the underlying basic science.3,16,20–24 A robust spatiotemporal framework is thus required to advance industrial applications of highly concentrated electrolytes, e.g., fuel cells ~1 M (mol/liter) and batteries ~10 M.

Theoretical formulation of electrolytes’ spatiotemporal behavior goes back to the 1890s with the formulation of the continuum mean-field Poisson–Nernst–Planck (PNP) equations.25,26 The PNP model describes ions as isolated point charges that obey drift-diffusion transport under an electric potential and is a well-established theory for dilute electrolytes.27 This description is valid for electrolytes with concentrations typically below ~0.01 M but is oversimplified for concentrated electrolytes where, for example, the finite size of the ions should be taken into account.28,29 Consequently, extensive studies during the past centennial have led to major modifications of the mean-field approach in order to tackle steady state electrical double layers (EDLs) or electrokinetic properties; see representative reviews20,21,24,30 and references therein. Among the broad family of modified PNP and Poisson–Boltzmann (PB) models, we highlight for our purposes the steric-PNP (SPNP) approach that has been employed for studying permeability and selectivity in ion channels,31 where ion concentrations exceed 10 M. This approach accounts for Lennard-Jones-type interactions between the ions, which are similar to the interactions employed in molecular dynamics (MD) simulations.

Theoretically (i.e., excluding the ion-pairing question22), the upper limit of “concentrated electrolytes” corresponds to molten salts, i.e., solvent-free electrolytes which at about room temperature, are also being referred to as ionic liquids (ILs).5,6 Besides their multiple applications, ILs, both with and without dilution, may exhibit several intriguing properties: (i) multiple time scales,27,32 (ii) self-assembly,33–35 and (iii) nonmonotonic variation (exhibiting qualitatively three distinct regions) of EDL with concentration,15,36 a.k.a., the phenomenon of underscreening. These phenomenologies clearly indicate that, despite the vast progress in concentrated electrolytes, a framework that unifies all these phenomena is still missing.24

Here we present a dynamical and thermodynamically consistent, unified continuum framework, based on SPNP and Onsager’s relations, for ternary media (i.e, solutions of anions, cations, and solvent). Our goal is to present a theoretical framework by outlining the essential features that

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are designed to pave the road toward a realistic description of concentrated electrolytes: (i) explicit densities of electrically positive, negative, and neutral subsets (aqueous or organic carriers), (ii) finite-size (steric) effects, and (iii) selective energy dissipation to reflect mass transport. While we follow the SPNP formulation, the starting point originates with ILSs37,38 and introduces explicitly the solvent density. Our testing of the qualitative model results, appears to capture and relate, in broad parameter regimes, the aforementioned phenomena to effects of polarization3 and self-assembly,23 and to explain the origins of nonmonotonic electrical screening length variation.15,36 In particular, at high concentrations, the system is expected to form different morphologies, in both the EDL and bulk region, that are strongly dictated by spatiotemporal instabilities that drive the self-assembly process in the bulk, as indeed observed in models for pure ILSs37,40 and charged diblock copolymers.41

Model Equations for a Ternary Composition. In general, PNP-type models consider the solvent as an effective background medium. This assumption, however, breaks down in the high-concentration limit, e.g., in ILSs. Therefore, we derive a ternary model by considering first model equations for asymmetric pure ILSs38 and introducing the solvent as an explicit field. Specifically, we assume a monovalent electrolyte composed of cations (p), anions (n), and solvent (s), identified by their respective concentrations in terms of the partial volume that is occupied by each species

\[
\frac{p}{P_{\text{max}}} + \frac{n}{n_{\text{max}}} + \frac{s}{s_{\text{max}}} = 1
\]  

(1)

where \(P_{\text{max}}, n_{\text{max}},\) and \(s_{\text{max}}\) are the maximal concentrations (packing densities) of the cations, anions, and solvent molecules, respectively. Following Onsager’s model, cf. ref 37, the transport equations are given by

\[
\frac{\partial}{\partial t} \begin{pmatrix} n \\ p \\ s \end{pmatrix} = \nabla \cdot \left( \begin{pmatrix} p J_p^\phi \\ n J_n^\phi \\ s J_s^\phi \end{pmatrix} \right)
\]

(2a)

and the Coulombic interactions obey the standard Poisson’s equation

\[
\nabla (\epsilon \nabla \phi) = q(n - p)
\]

(2b)

where \(q\) is the elementary charge and \(\epsilon\) is the dielectric permittivity (assumed here to be constant). The respective fluxes are obtained from the variation (functional derivative) of the free energy

\[
J_p^\phi = \frac{\mu_b}{\epsilon_{\text{max}}} \nabla \delta F_p, \quad J_n^\phi = \frac{\mu_b}{\epsilon_{\text{max}}} \nabla \delta F_n, \quad J_s^\phi = \frac{\mu_b}{\epsilon_{\text{max}}} \nabla \delta F_s
\]

where

\[
\delta F = \int \phi (p \nabla \phi / \epsilon + q n \nabla \phi / \epsilon + q p \nabla \phi / \epsilon) \, dx
\]

(3)

\[
\delta F = \int dx \frac{\mu_b P_{\text{max}}}{2} \left( p \nabla p + n \nabla n + s \nabla s \right) + \frac{q (p - n)}{2} \nabla \phi \nabla \phi + c_m \left( \frac{\beta}{n_{\text{max}}} + \frac{\gamma}{P_{\text{max}}} \right) \left( \nabla \frac{p}{P_{\text{max}}} \nabla + \nabla \frac{n}{n_{\text{max}}} \nabla \right)
\]

\( \Omega \) is the considered physical domain, \( \mu_b \) is the mobility coefficient, \( \beta \) is the interaction parameter (a.k.a., Flory parameter in the context of mixing energy for polymers) for the anion/cation mixture, \( \mathcal{E}_0 \| \kappa^2 \) is the gradient energy coefficient with units of energy for the former and units of length for the latter, \( \gamma \) is the average concentration of ionic species, and \( s \) is the average concentration of solvent molecules

\[
\gamma := \frac{1}{|\Omega|} \int_p dx = \frac{1}{|\Omega|} \int_n dx, \quad s := \frac{1}{|\Omega|} \int_s dx
\]

Notably, global charge neutrality and the equal valence of the anions and cations ensure that the average concentration of cations equals the average concentration of anions. This implies, together with the electrolyte incompressibility assumption (eq 1), that the maximal average concentration (achieved when \( s = 0 \)), equals the harmonic average of \( p_{\text{max}} \) and \( n_{\text{max}} \)

\[
\frac{1}{\gamma_{\text{max}}} = \frac{1}{p_{\text{max}}} + \frac{1}{n_{\text{max}}}
\]

Model Interpretation. To reveal the physical properties of the key parameters of the model equations (eq 2), we rewrite the equations in their dimensionless form (see the SI for details) and for simplicity present only the equation for cations while the equation for anions is given in the SI

\[
\frac{\partial p}{\partial t} = \nabla \cdot (J_p^\text{PNP} + c J_p^\text{st}}{3} + c^2 J_p^\text{st}}{2} + c^3 J_p^\text{st}}{1})
\]

(4)

where

\[
J_p^\text{PNP} = \nabla (p \nabla \phi)
\]

(5a)

\[
J_p^\text{st}}{1} = \frac{2 \gamma}{1 + \gamma} p \nabla (p + n)
\]

(5b)

\[
J_p^\text{st}}{2} = - \frac{1}{1 + \gamma} \frac{1}{\gamma} \frac{1}{\gamma} p \nabla n
\]

(5c)

\[
J_p^\text{st}}{3} = \frac{\sigma}{1 + \gamma} p (p \nabla^3 p + n \nabla^3 n)
\]

(5d)

The normalized global ion concentration \( 0 \leq \gamma \leq 1 \) is a key parameter that relates the ions to the solvent via \( (1 - c)s = 1 - c(p + n) \). In particular, \( c \) is scaled such that \( c = 0 \) corresponds to the vanishing concentration of ions (dilute limit), while \( c = 1 \) corresponds to the absence of solvent (IL); powers of \( c \) describe equal contributions of terms in the equations and do not imply a perturbative expansion. Here, \( \sigma \) is a measure of the ratio between relative strength of short-range steric and long-range Coulombic interactions, \( \chi \) is also related to steric interactions rescaled to the ambient temperature, \( \gamma \) is the size ratio between cations and anions, and \( \gamma \) is the complementary size asymmetry between the solvent and ions. In particular, \( \gamma \approx 1 \) for solvent molecules whose size is similar to the size of the ions (e.g., DMF), and \( \gamma \gg 1 \) for solvent molecules that are much smaller than the ions (e.g., water).

It is instructive to consider the ionic flux term-by-term to reveal the impact of different mechanisms on electrolyte behavior as concentration is varied. For the simplicity of
At higher orders, the combined effect of all terms can be comprehended in one space dimension (1D) by neglecting the boundary conditions and considering the case $\gamma = Y = 1$. In this case, substituting eq 2b into eq 5b, the flux takes the form of high-order corrections for the drift $\mathbf{J}_p = p \nabla \phi$, and thus, $\nabla \cdot \mathbf{J}_p$ gives rise to a fourth-order derivative of the electric potential that addresses short-range correlations (we note that originally the high-order operator was introduced phenomenologically for ILs by Bazant–Storey–Kornyshev through a displacement field in eq 2b). In the next section, we show that, under appropriate conditions, these short-range interactions give rise to self-assembled nanopatterns near charged interfaces and/or in the bulk.

**Analysis: Nonmonotonic Screening Length.** The broad family of generalized PNP models describes electrolyte solutions with a spatially uniform bulk. Equation 4 gives rise to a richer picture of bulk and interfacial behavior, which is consistent with the picture arising in recent experimental and numerical studies. Indeed, using spatial linearization methods (see the SI for details), we map the qualitatively distinct bulk and interfacial behaviors and the corresponding regions in the parameter space spanned by ion size asymmetry $\gamma$ and normalized concentration $c$; see Figure 1. The results have been obtained in one space dimension ($V \to \partial_x$) and with no-flux boundary conditions (inert electrodes) for ions and Dirichlet boundary conditions for the potential (constant applied voltage): $f(x = \pm L/2) = 0$ and $\phi(x = \pm L/2) = \pm V/2$, where $L$ is the physical domain size and $V$ is the applied voltage.

Figure 1. Parameter space spanned by the concentration ($c$) and ion size asymmetry ($\gamma$), showing the transitions from a monotonic EDL as described by the PNP or PB model (dark shaded region), the region of the oscillatory EDL giving rise to underscreening (light shaded region), and the region of self-assembled bulk. Parameters: $Y = 4$, $\sigma = 10$, $\chi = 30$.

Notably, these decaying oscillations have also been referred to as overscreening, although the phenomenon of self-assembly has been observed in many other compositions.

Region B corresponds to a homogeneous bulk with an oscillatory potential and charge density profiles near a charged interface (a.k.a, a spatially decaying oscillatory EDL), as shown in the middle inset. The onset of this region is computed using spatial dynamics methods, as detailed in the SI. Notably, these decaying oscillations have also been referred to as over-screening.

The three regions in Figure 1 imply that as an IL or concentrated electrolyte solution with relatively weak ion-size asymmetry ($\gamma \approx 1$) is diluted it exhibits a transition from a nanostructured bulk and a layered EDL at high ionic concentration (i.e., at region A) to a layered EDL with homogeneous bulk (region B), and finally, at low concentrations, to a monotonic EDL structure. Insets A–C in Figure 2 present steady-state solutions of eq 4 with parameters corresponding to the IL $\text{[C}_6\text{C}_{12}\text{Pyr}]\text{[NTf}_2\text{]}$, diluted with propylene carbonate ($\text{C}_6\text{H}_{12}\text{O}_3$). Indeed, a transition from layered to monotonic EDL has been observed using high-energy X-ray reflectivity and in situ AFM within the range...
of parameters considered here. The molecular origin for the transition from monotonically decaying Debye–Hückel approximation, \(\lambda_S\), (dotted red curve), the hypernetted chain correction \(\gamma\) (dashed curve), and the curve \(2/3\sqrt{c}\) (dashed curve) to allow comparison with the recently presented scaling argument.9 Inset A–C present spatial profiles of the electric potential \(\phi\) at different concentrations (solid curve, \(\bullet\)) and the exponential envelop (dashed curve) that is computed by the real part of the spatial eigenvalues (eq 6), which is being used as a measure for the screening length. Dimensionless parameters: \(\gamma = 1\), \(\varphi = 1\), \(\sigma = 28\), \(\kappa = 35\), \(V = 1\), and \(L = 200\).

Figure 2 presents the computed screening length as a function of concentration for parameters corresponding to a specific IL, \([C_4C_1Pyrr][NTf_2]\), diluted with propylene carbonate. In accordance with experimental observations, at low concentrations where the EDL structure monotonically decreases, the screening length becomes identical to the Debye length. As the electrolyte concentration is increased above the Kirkwood point, \(c_\kappa = 4(\chi - 4\sigma)/(\chi^2 - 16\sigma) \approx 0.077\), the envelope tail length increases and exceeds the Debye length. Switching to dimensional units, the transition is at \(0.48\sqrt{c}\) (which corresponds to the minimum in the IL screening length (Figure 2)). Accordingly, the increase in the concentration leads to the phenomenon of underscreening.5,15

As introduced by Lee et al.,55 in a regime of concentration beyond the Kirkwood point, we observe that the screening length roughly scales as \(c^{1/2}\) with respect to the Debye screening length.

While the transition from regions C and B can be formulated using near-equilibrium methods21,30,57, it is not true for the transition from region B to A. Here, the significance of the spatiotemporal approach (eq 2) in the context of screening length structure becomes fundamental as the temporal bulk instability is approached, i.e., region A. At the instability onset, the real part of the relevant eigenvalues \(\text{Re}(\mu_{\lambda}) \to 0\) and hence the screening length in a pure 1D system should extend to infinity, \(\lambda_S \to \infty\). This onset is in fact an analogue of the (temporal) finite wavelength instability bifurcation point, as discussed in more detailed by Gavish et al.37,41 However, in reality, the system is higher than 1D representation, so that secondary time-dependent zigzag instabilities36 of the bulk self-assembly become dominant in an appropriate parameter regime.37,41 In this case, spatial oscillations of the screening length are being used as a measure for the screening length. Dimensionless parameters: \(\gamma = 1\), \(\varphi = 1\), \(\sigma = 28\), \(\kappa = 35\), \(V = 1\), and \(L = 200\).
length are destroyed and the screening length effectively follows instead a decreasing spatially oscillatory profile, cf. ref 40. Indeed, the second decay in screening length has been reported at high concentrations; cf. refs 15 and 36 and Figure 2. The asymptotic methods applied in regions B and C cannot treat this phenomenon, and spatiotemporal framework is therefore required for a mechanistic explanation of this behavior.24,30,57,58

Consequently, as summarized in Figure 2, the above results qualitatively capture the experimental observation of all three regions of the nonmonotonic screening length dependence on concentration, as well as reducing to the PNP theory at low concentrations.19 We have also tested the consistency of our results with parameters that correspond to aqueous NaCl and have again obtained a good qualitative comparison, as shown in Figure 1 in the SI.

In this work, we have introduced a spatiotemporal thermodynamically consistent continuum mean-field framework for electrolytes that ranges from solvent-free to dilute concentrations with explicit treatment of the solvent medium and finite size (steric) effects of both ion and solvent components. These two components introduce, by consistency, an additional transport mechanism of interdiffusion and bulk nanostructuring by self-assembly. We conjecture that these are the essential features that mean-field models for electrolytes should aim to include, in order to provide a comprehensive description at a wide range of concentrations, including the approach to a solvent-free case. While it is true that other approaches (such as, a repulsive Yukawa potential, the hard sphere potential in Rosenfeld’s density functional theory of fluids, and asymptotic PB-type models) may be efficient in some specific cases,19,30,45,49,59,60 the existing approaches cannot capture the screening length behavior at a full range of concentrations. We therefore chose to focus on the screening length to emphasize the importance of including the energy dissipation and self-assembly features, and specifically on secondary transverse instabilities that explain the experimentally observed second decay at high concentrations.15,36 Notably, the advantage of the spatiotemporal framework is apparent in cases where understanding of temporal and/or morphological bulk effects is required, such as in self-assembly. A detailed analysis of secondary instabilities is beyond the scope of this Letter and will be presented elsewhere.

The advantage of the framework we developed is not only its consistency with different previous continuum approaches,9,26,51,37,39,40,58,61 but also its amenability to potential extensions to account for additional effects, e.g., ion–solvent interactions, ion-pairing,19,23,63–64 or other electrostatic corrections.65 These extensions should be advanced via quantitative comparisons with experimental observations, beyond the qualitative trends depicted in Figure 2. Consequently, we expect that the current spatiotemporal framework will stimulate experiments that combine temporal methods with structural analysis;66 for example, comparisons to transport properties via multiple time scale relaxations that have been already shown to be present for pure ILs due to interdiffusion and saturated mobility57 (not addressed here in detail) as systematic (for comparison purposes) experimental data is presently limited at large.17,32

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.7b03048.

Additional details of the dimensional form, the dimensionless equation for anions, spatial analysis and distinct regions, screening length and comparison, parameters for diluted ionic liquid, and parameters and comparison with NaCl aqueous electrolyte (PDF)

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**Notes**

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