Influence of Ion Solvation on the Properties of Electrolyte Solutions

Marat Andreev,[†] Juan de Pablo,[†] Alexandros Chremos,^{*,‡} and Jack F. Douglas^{*,‡}

[†]Institute of Molecular Engineering, University of Chicago

[‡]Materials Science and Engineering Division, National Institute of Standards and Technology, Gaithersburg, MD, 20899, USA

> E-mail: alexandros.chremos@nist.gov; jack.douglas@nist.gov Phone: [AC] +1 (301) 975 5891; [JFD] +1 (301) 975 6779

Abstract

It is widely appreciated that the addition of salts to water leads to significant changes in the thermodynamic and dynamic properties of these aqueous solutions that have great significance in biology and manufacturing applications. However, no theoretical framework currently exists that describes these property changes in an internally consistent fashion. In previous work, we developed a coarse-grained model of electrolyte solutions capable of reproducing basic trends on how salts influence the viscosity and water diffusion coefficient. The present work explores the predictions of this model for basic thermodynamic properties of electrolyte solutions, namely the density, isothermal compressibility, and surface tension. Based on our model, we find that ion-specific effects on thermodynamics properties, and by extension the dynamics of electrolyte solutions, derive primarily from ion solvation.

Introduction

The thermodynamic and transport properties of electrolyte solutions are crucial for a wide range of applications, including waste water treatment, chemical waste disposal, (bio) separation processes, and the production of energy sources such as scaling in production wells.^{1–3} These aqueous solutions are also essential for biological function, where ions are typically classified in terms of the Hofmeister series based on their influence on protein stability, enzyme activity, protein and polymer folding, and other basic biological properties.^{4–6} For a long time, it was thought that the microscopic mechanism of the Hofmeister series was associated with the capacity of the ions to "make" (kosmotropic) or "break" (chaotropic) water hydrogen-bonding structure, but recent experimental studies have cast doubt on the validity of this structural interpretation of the Hofmeister series.⁷⁻¹¹ In particular, Otma et al.⁷ reported that the ions primarily influence the structure and dynamics of the first hydration layer, but not the strength of the hydrogen bonding of the surrounding fluid. Later studies have shown that this effect can extend beyond the first hydration layer, but this interfacial layer is still localized to small distances around the ions.^{12,13} The emerging consensus¹⁴ is that Hofmeister effects are a result of direct ion-solvent interactions that give rise to extended hydration shells, and several studies have demonstrated the central role of solvation in influencing solution density,¹⁵ the modification of surface tension,^{2,16,17} the capacity of ions to segregate at the interfaces, ^{18–21} protein and polymer solubility, ²² and the effect of the water absorbency by fibers used in textile industry.²³ While this microscopic description has recently gained significant acceptance, there is still no satisfactory theory that can predict the mechanism by which ions modulate basic thermodynamic and dynamic electrolyte solution properties, such as density, isothermal compressibility, viscosity, and the water diffusion coefficient.

In principle, computer simulations provide an ideal tool for probing the microscopic structure of electrolyte solutions. Quantum mechanical based simulations and first principle molecular dynamics models^{24,25} can provide an accurate and detailed description of

the interactions in electrolyte solutions. However, such models are difficult to apply to the modeling of polyelectrolyte solutions because of the excessive computational burden associated with this type of "first principle" computation. Indeed, our own work on this problem is motivated by the desire to model polyelectrolyte solutions and aqueous block copolymer assemblies driven by complexation of polyelectrolyte blocks,²⁶ where large length and time scales are required for computational modeling. Unfortunately, classical coarse-grained pairpotential models fail to reproduce essential observed experimental trends in the dynamics of even the relative "simple" case of aqueous electrolyte solutions.²⁷

In a previous study,²⁸ we developed an explicit electrolyte solvent model by stripping down the molecular features of water to a minimal liquid model where the water-ion dispersion interaction parameter was determined by the ion solvation energy through the application of Born theory of ionic solvation. Molecular dynamics simulations utilizing this model captured semi-quantitatively observed changes in solution viscosity and water diffusion coefficient on ion type. We find these results to be encouraging for the development of a useful coarse-grained model of electrolyte and polyelectrolyte solutions, but further tests of the model are required to determine whether this type of model can also consistently reproduce the significant salt-specific changes in the thermodynamic properties of electrolyte solution upon adding salt. We then investigate how ion-water interactions influence basic thermodynamic properties (solvent density, isothermal compressibility, and surface tension) in order to further test the internal consistency of our coarse-grained model and to better understand the fundamental origin of Hofmeister series. We also calculate the ion-water and ion-ion pair correlation functions for different salts to better understand how the solvation effects influence the structure of electrolyte solutions.

Model and computational methods

We employ a model of charged Lennard-Jones (LJ) particles in an explicit solvent composed of uncharged LJ particles.^{28–33} All ions and solvent particles are assigned the same mass m, size σ , and self-interaction ϵ parameter. We set ϵ and σ as the units of energy and length; the cutoff distance for LJ interaction cut and shifted potential is $r_{\text{cut-off}} = 3 \sigma$. The size and energy parameters between i and j particles are set as $\sigma_{ii} = \sigma_{jj} = \sigma_{ij} = \sigma$ and $\epsilon_{ii} = \epsilon_{jj} = \epsilon$), except for the interaction parameter between the solvent particles and the ions, as we discuss below. The system is composed of a total of N = 10054 particles in a periodic cube of side L and volume V, periodic boundary conditions were applied in all three directions. There are N_+ and N_- positive and negative charged ions, respectively. All ions are monovalent and our systems are charge neutral $N_+ = N_-$. The fraction of charged particles in the solution is defined as $\varphi = (N_+ + N_-)/N$ and varied between 0 to 0.45, ranging from small to relatively large salt concentrations from $c = 0 \, \text{mol} / \text{L}$ to 4.77 mol /L.

The Bjerrum length was set equal to $l_{\rm B} = e^2/(\varepsilon_{\rm s}k_{\rm B}T) = 1.85 \,\sigma$, where T is the temperature, $k_{\rm B}$ is Boltzmann's constant, and $\varepsilon_{\rm s}$ is the dielectric constant of the medium. Coulomb interactions were treated by the particle-particle particle-mesh method. The timestep was set to $0.005 \,\tau$, where $\tau = \sigma \,(m/\epsilon)^{1/2}$ is the unit of time. System runs were performed at constant pressure and constant temperature conditions, i.e., reduced temperature $k_{\rm B}T/\epsilon = 0.75$ and reduced pressure $\langle P \rangle \approx 0.01$, maintained by Martyna-Tobias-Klein barostat-thermostat with time constants $\tau_T = 1.0 \,\tau$ and $\tau_P = 10.0 \,\tau$. Before any production run, there was equilibration for $2500 \,\tau$. Simulations were performed with a GPU-optimized molecular dynamics software package HOOMD.³⁴⁻³⁶

The van der Waals interaction parameters between the ions and the solvent ϵ_{\pm} are determined based on the methodology developed in our previous work.²⁸ Our coarse-grained modeling of electrolyte solutions is motivated by the observations of Collins^{5,37} and Ninham *et al.*⁶ indicating the importance of ion-size on the extent of ion solvation and the resulting dispersion interaction between ions and water, respectively. Given that the ion solvation en-



Figure 1: Particle density ρ normalized with the pure solvent density ρ_w as function of salt concentration c for ions having different salts. The values of the parameters describing the ion-water interaction for each type of ion are presented in Table 1. The errorbars represent one standard deviation.

ergy directly reflects a combination of Coulombic and dispersion interaction contributions³⁸ and that these solution energies are widely measured and tabulated, ^{39–41} we utilize measured values of ion solvation energies to set ϵ_{\pm} in our model. In particular, we use the Born model of ion solvation energy and measured ion solvation energies to determine ϵ_{\pm} . 41 We also assume that ϵ_{\pm} is proportional to the solvation energy and adopt the explicit relation for this quantity introduced by Born, so that we have $\epsilon_{\pm} = \epsilon (r_0/r_B)$, where the constant r_0 is fixed by a reference ion for which ϵ_{\pm} for the solvent and the ion are equal. To determine the Born radius, we took ions K⁺ and Cl⁻ ions for which the water diffusion coefficient D exhibits little or no change upon addition to water at low concentrations. This procedure results in $r_0 = 2.33$ Å for cations and $r_0 = 1.87$ Å for anions. The resulting cohesive interaction parameters determined by this coarse-grained model ϵ_{\pm} are summarized in Table 1. We note that water has a relative high cohesive energy due to the strong hydrogen bond interactions between the molecules and this aspect of water is incorporated into our model by equating the critical temperature of real water with that of our solvent model.

Results

The particle density ($\rho = N/V$) reflects the packing efficiency of the solvent particles and ions in the fluid, and it is perhaps the most basic thermodynamic property of electrolyte solutions.^{15,42} In a salt-free solvent, we find that the solvent density is $\rho_w = 0.76 \sigma^3$ near room temperature conditions (see Model and Computational Methods). The influence of different ion types at different salt concentrations (c in mol / L) is presented in Fig. 1, where the ion size and the interaction parameters for different salt types are assigned in Table 1. This list of salts is the same as in our previous study,²⁸ except for the addition of LiCl and NaF. As a starting point we consider the solution of KCl, which have $\epsilon_+ \approx \epsilon_- \approx 1$, as a reference point and label the density for these salts as ρ_0 . For KCl salts, we find that density increases linearly as the salt concentration increases $(\rho_0 \approx \rho_w + 0.002 c)$, which means that in the absence of any asymmetry in the dispersion interactions between the species composing the electrolyte solution the electrostatic contribution upon the addition of salt leads to a small increase in ρ ; these salts also lead to a small increase in the solution viscosity and diffusion coefficient of the water. We see that salts having stronger water-ion dispersion interaction strength result in an appreciable increase in ρ that depends on the magnitude of this interaction, see the cases of LiCl and NaF salts in Fig. 1. If the salt has a weaker ion-water interaction strength than KCl salts, then we expect it to reduce the ρ dependence

Ion	$r_{ m B}/{ m \AA}$	$\epsilon_{\pm}/k_{\rm B}T$
Na^+	1.87	1.25
K^+	2.33	1.00
Cs^+	2.75	0.85
Li^+	1.46	1.60
Cl^{-}	1.86	1.00
Br^-	2.00	0.93
I-	2.23	0.83
F-	1.39	1.34

Table 1: Born radii $r_{\rm B}$ taken from Ref. 41 and the strength of ion-water dispersion energy parameter ϵ_{\pm} for different ions in aqueous solutions.



Figure 2: Viscosity *B*-coefficient for different salt types as function of the relative partial salt volume α . The correlation is similar to the findings by Bramhall in Ref. 43. The errorbars represent one standard deviation.

on c, and, indeed KBr salts exhibit this trend for small salt concentrations (c < 2 mol / L). The specific volume of the solvent also exhibits a non-analytic $c^{1/2}$ variation at very low salt concentrations, but we neglect this type of contribution in our discussion below. Overall, we find that ion solvation can greatly influence the molecular packing as observed in experiments on aqueous solutions.¹⁵

To quantify how these trends in the solution density of aqueous salt solutions relate to solvent dynamics, we compare the Jones-Dole viscosity *B*-coefficients, defined from the ion concentration virial expansion of the salt solution shear viscosity (for more details see Ref. 28), and the relative partial salt volumes $\alpha = (1/\rho - 1/\rho_0)/c$. All salts fall onto a single line suggesting that the volume change upon the addition of salt is strongly correlated with the mobility change in the solvent; see Fig. 2. This observation accords with previous experimental observations by Bramhall,⁴³ but with some minor differences in the calculation. First, we do not split contribution of viscosity and partial volume for cation and ions. Second, Bramhall considered individual ionic van der Waals radii to determine $\alpha = 0$ point, whereas in our electrolyte model all ions have the same bare size and only their interaction strength ϵ_{\pm} is taken to vary. Despite these differences, our model semi-quantitatively captures the correlation between viscosity and density of ionic solutions as it was found in experimental findings by Bramhall,⁴³ suggesting that our model's embodies physical aspects of ion-water interactions of electrolyte solutions.

The agreement between our model with Bramhall findings has a number of consequences. First, the concept of "making" and "breaking" of the hydrogen bonding structure of water is not required since no hydrogen bonding interaction is involved in our model. Second, the formation of a local hydration layer around the ions greatly influences the average density of the fluid as a whole. Third, it is striking that ion-specific influences on aqueous solution properties, attributed to quantum mechanical or many-body polarization effects,^{24,25} can be described rather well by a classical molecular dynamics model and a coarse-grained pair potential. Finally, we note that ion-specific changes in solvent mobility can be understood in terms of the corresponding changes in the thermodynamic properties of the solvent derived from the ion solvation.

If the nature of ion solvation is responsible for the density and viscosity trends observed upon the addition of salt to water, then we may expect other thermodynamic properties to likewise become significantly affected through the addition of salt. Two additional basic thermodynamic properties of electrolyte solutions are the isothermal compressibility κ_T , which is a measure of the relative volume change of a fluid as a response to a pressure variation at fixed temperature, $\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T$, and the surface tension γ , which is the tension of the surface film of a liquid while the surface acquires the least surface area possible. We obtained κ_T by calculating the equilibrium volume at different pressure values that range from $0.01 \sigma^3/\varepsilon$ to $0.1 \sigma^3/\varepsilon$ while temperature was held constant. The surface tension was calculated for our solution by using the method of Shi *et al.*⁴⁴ (see Supplementary Information). We find that stronger ion-water dispersion interactions reduce κ_T , and correspondingly increase γ with the addition of salt to our solvent, while weaker ion-water dispersion interactions result in the opposite trend; see Fig. 3. Again, we obtain the same pattern as found before in the density and viscosity of aqueous salt solutions, reinforcing our view that the nature of ion solvation is central to understanding the thermodynamic and dynamic properties of the



Figure 3: (Top) Isothermal compressibility κ_T and (bottom) surface tension γ as function of salt concentration c and different salt types. Both κ_T and γ are normalized by their value as $c \to 0$. The errorbars for κ_T were smaller than the symbol size.



Figure 4: Viscosity *B*-coefficients of different salts as function of (left) isothermal compressibility the relative deviation from the pure solvent $\delta \kappa_T/c$ and (right) surface tension deviation $\delta \gamma/c$. The errorbars represent one standard deviation.

electrolyte solutions.

Since the character of the changes observed in κ_T and γ is similar to ion-specific changes



Figure 5: Pair distribution functions for ion-water for kosmotropic salt (NaF) and chaotropic salt (CsI) at c = 2 mol / L concentration. Water-water pair distribution shown for comparison. Inset: Water-ion radial distribution functions for different ions generated from both neutron and X-ray diffractions; the data were extracted from Ref. 46 and the x-axis is normalized by the corresponding Born radii r_{B} from Table 1.

in ρ , we compare κ_T and γ with viscosity *B*-coefficient in the spirit of Bramhall's approach. We first calculate the relative deviation from the pure solvent at low *c*, i.e., $\delta\kappa_T/c$ and $\delta\gamma/c$; a linear fit to determine the relative deviations was applied to data presented in Fig. 3 for salt concentrations upto $c = 2 \text{ mol } \text{L}^{-1}$. Our findings are presented in Fig. 4, where we again find the same trends as for ρ , compare Figs. 2 and 4. Since ρ , κ_T , and γ are correlated with the same quantity, i.e., viscosity *B*-coefficient, then ρ , κ_T , and γ , are all correlated with each other. We infer that ion solvation is the primary mechanism by which ions modulate thermodynamic and dynamic properties of electrolyte solutions. This conclusion is in agreement with several recent studies that have stressed this point of view.^{17,18,38,45}

It is also instructive to consider changes in the local density of aqueous solutions by the presence of ions to characterize the nature of ion solvation. In particular, we calculate the pair-correlation function g(r) for different ion types and compare these results to neutron and x-ray scattering measurements of g(r). In Fig. 5, we show the pair distribution function of some common ions (Na⁺, CS⁺, F⁻, and I⁻) and compare these to g(r) of pure water as a reference point. The height of g(r) at its first peak is evidently higher for "cosmotropic" ions (Na⁺ and F⁻) for which B > 0, and lower for "chaotropic" ions for which B < 0; this trend



Figure 6: Ion-ion pair distribution functions for ion pairs in electrolyte solutions having a salt concentration, c = 2 mol / L. The water-water pair correlation is provided for reference.

is in agreement with experimental observations, as illustrated in the inset of Fig. 5. Note that we have normalized the radial coordinate of the pair distribution by the ion size σ in our model, while in the corresponding neutron scattering estimates of q(r) the radial coordinate is normalized by the Born radius given in Table 1 as the appropriate experimental measure of ion size. We see that simulation and experimental observation of q(r) are consistent with the quantitative view of Collins, ^{5,37} indicating that the degree of ion solvation directly correlates with the ion size having smaller ions of a common valance have a higher charge density, and thus solvate better. These observable structural effects on q(r) are captured rather well by our model, even though we model water molecules by simple LJ particles having a high cohesive energy set by the observed critical temperature of water. The ion-water dispersion interaction, in turn, is set by the observed Born radius of the ions. This simple model ensures that ions with smaller r_B exhibit stronger solvation consistent with the intuitive reasoning of Collins. We also note that in the height of the first peak can be roughly interpreted in terms of change in the effective coordination number: The structure of the aqueous salt solution is approximately the same at long distances, which qualitatively accords with the conceptual picture of ions in water as being "sticky" in the sense described by Collins.³⁷

Ion-ion correlations are an another important aspect of structure in electrolyte solutions

and these correlations are related to the strength and frequency of "ion pairing" in aqueous solvents.⁴⁷ We note that the electrostatic interactions are much stronger in non-aqueous solutions, and thus ion clustering is dominated by electrostatic interactions, while in aqueous solutions the dielectric constant makes the strength of the electrostatic interactions comparable in magnitude to the associated solvation interactions dominated by dispersion interactions. In other words, the appearance of ion pairs in an aqueous electrolyte solutions is due to the balance of competitive interactions between different species and interaction types. In our model of aqueous electrolyte solutions, we can tune the solvent affinity due to dispersion interactions, we briefly probe how these interactions impact ion-ion correlations. Specifically, we compare the ion-ion pair correlations of different electrolyte solutions in Fig. 6, for a range of metal ions (Li⁺, Na⁺, and Cs⁺) but for a fixed co-ion Cl⁻. We find that weakly solvating ion pairs in our model, $\epsilon_{\pm}/k_{\rm B}T$ < 1, have stronger ion correlations compared to strongly solvating ions ($\epsilon_{\pm}/k_{\rm B}T > 1$), suggesting that the solvent affinity disrupts the formation of ion pairings since, as mentioned above, the electrostatic interactions are comparable with thermal energy and solvation interactions in aqueous solutions. On the other hand, weak solvation effectively enhances the formation of ion pairings. This same effect should greatly affect ion segregation at interfaces, giving rise to ion specific effects that influence polymer solubility and surface tension.

Conclusions

In summary, we use molecular dynamics simulations to investigate the effect of ion hydration on the thermodynamics properties of electrolyte solutions by using a recently developed coarse-grained model of electrolyte solutions that captures semi-quantitatively ion-specific effects on the dynamics of these solutions. While our model is not intended to be a highly precise model of the properties of electrolyte and polyelectrolyte solutions, it does captures, in a parameter-free method, many of the observed experimental trends regarding how ions modulate the thermodynamic and dynamic properties of these solutions. In particular, our model is in good agreement with observations of Bramhall linking solution density changes to the changes in solution viscosity, indicating that that salts that increase the solvent volume decrease the viscosity and vice versa. Similar correlations were constructed for isothermal compressibility and surface tension. Our findings support the view^{17,38,45} that the dispersion interactions between the ions and the solvent are primarily responsible for ion-specific changes in the thermodynamic properties of the electrolyte solutions, and by extension for changes in the diffusion of water and the viscosity of these solutions.

Of course, we do not mean to imply that directional hydrogen-bonding interactions are not important for understanding some of the unique properties of water. The competitive interactions of hydrogen bonding between water molecules, the associative interactions with polar molecules, and the mutual associative interactions between water and dissolved molecules lead to non-trivial patterns of molecular solubility and binding that collectively give rise to the "hydrophobic effect".⁴⁸ The treatment of such interactions will require a more sophisticated coarse-grained model of water that accounts for competitive directional interactions.

Associated Content

Supporting Information. Details of the surface tension calculation, including representative simulation box snapshot and representative stress profile.

Acknowledgement

We gratefully acknowledge the support of the NIST Director's Office through the NIST Fellows' postdoctoral grants program and additional financial assistance award 70NANB14H012 from U.S. Department of Commerce, National Institute of Standards and Technology as part of the Center for Hierarchical Materials Design (CHiMaD). Official contribution of the U.S. National Institute of Standards and Technology – not subject to copyright in the United States.

References

- Rogers, R. D.; Seddon, K. R. Ionic Liquids–Solvents of the Future. Science 2003, 302, 792–793.
- (2) Jungwirth, P.; Tobias, D. J. Specific Ion Effects at the Air/Water Interface. *Chem. Rev.* 2006, 106, 1259–1281.
- (3) Pham, T. P. T.; Cho, C. W.; Yun, Y. S. Environmental Fate and Toxicity of Ionic Liquids: A Review. *Water Res.* 2010, 44, 352–372.
- (4) Cacace, M. G.; Landau, E. M.; Ramsden, J. J. The Hofmeister Series: Salt and Solvent Effects on Interfacial Phenomena. Q. Rev. Biophys. 1997, 30, 241–277.
- (5) Collins, K. D.; W.Neilson, G.; Enderby, J. E. Ions in Water: Characterizing the Forces that Control Chemical Processes and Biological Structure. *Biophys. Chem.* 2007, 128, 95–104.
- (6) Salis, A.; Ninham, B. W. Models and Mechanisms of Hofmeister Effects in Electrolyte Solutions, and Colloid and Protein Systems Revisited. *Chem. Soc. Rev.* 2014, 43, 7358– 7377.
- (7) Omta, A. W.; Kropman, M. F.; Woutersen, S.; Bakker, H. J. Negligible Effect of Ions on the Hydrogen-Bond Structure in Liquid Water. *Science* 2003, 301, 347–349.
- (8) Batchelor, J. D.; Olteanu, A.; Tripathy, A.; Pielak, G. J. Impact of Protein Denaturants and Stabilizers on Water Structure. J. Am. Chem. Soc. 2004, 126, 1958–1961.
- (9) Marcus, Y. Effect of Ions on the Structure of Water: Structure Making and Breaking. Chem. Rev. 2009, 109, 1346–1370.

- (10) Marcus, Y. Effect of Ions on the Structure of Water. Pure Appl. Chem. 2010, 82, 1889–1899.
- (11) Ball, P.; Hallsworth, J. E. Water Structure and Chaotropicity: Their Uses, Abuses and Biological Implications. *Phys. Chem. Chem. Phys.* **2015**, *17*, 8297–8305.
- (12) O'Brien, J. T.; Prell, J. S.; Bush, M. F.; William, E. R. Sulfate Ion Patterns Water at Long Distance. J. Am. Chem. Soc. 2010, 132, 8248–8249.
- (13) Tielrooij, K. J.; Garcia-Araez, N.; Bonn, M.; Bakker, H. J. Cooperativity in Ion Hydration. Science 2010, 328, 1006–1009.
- (14) Record, M. T.; Guinn, E.; Pegram, L.; Capp, M. Faraday Discussion 160 Introductory Lecture: Interpreting and Predicting Hofmeister Salt Ion and Solute Effects on Biopolymer and Model Processes Using the Solute Partitioning Model. *Faraday Discuss.* 2013, 160, 9–44.
- (15) Hey, M. J.; Clough, J. M.; Taylor, D. J. Ion Effects on Macromolecules in Aqueous Solution. *Nature* **1976**, *262*, 807–809.
- (16) Weissenborn, P. K.; Pugh, R. J. Surface Tension and Bubble Coalescence Phenomena of Aqueous Solutions of Electrolytes. *Langmuir* **1995**, *11*, 1422–1426.
- (17) Borstöm, M.; William, D. R. M.; Ninham, B. W. Specific Ion Effects: Why DLVO Theory Fails for Biology and Colloid Systems. *Langmuir* 2001, 17, 4475–4478.
- (18) Gurau, M. C.; Lim, S. M.; Castellana, E. T.; Albertorio, F.; Kataoka, S.; Cremer, P. S. On the Mechanism of the Hofmeister Effect. J. Am. Chem. Soc. 2004, 126, 10522– 10523.
- (19) Pegram, L. M.; Record, M. T. Partitioning of Atmospherically Relevant Ions between Bulk Water and the Water/Vapor Interface. Proc. Nat. Acad. of Scie. 2006, 103, 14278– 14281.

- (20) Tobias, D. J.; Hemminger, J. C. Getting Specific About Specific Ion Effects. Science 2008, 319, 1197–1198.
- (21) Guo, F.; Friedman, J. M. Charge Density-Dependent Modifications of Hydration Shell Waters by Hofmeister Ions. J. Am. Chem. Soc. 2009, 131, 11010–11018.
- (22) Zhang, R.; Shklovskii, B. I. Long-Range Polarization Attraction between Two Different Like-Charged Macroions. *Phys. Rev. E* 2005, 72, 021405.
- (23) Lo Nostro, P.; Fratoni, L.; Ninham, B. W.; Baglioni, P. Water Absorbency by Wool Fibers: Hofmeister Effect. *Biomacromolecules* 2002, *3*, 1217–1224.
- (24) Yao, Y.; Kanai, Y.; Berkowitz, M. L. Role of Charge Transfer in Water Diffusivity in Aqueous Ionic Solutions. J. Phys. Chem. Lett. 2014, 5, 2711–2716.
- (25) Yao, Y.; Berkowitz, M. L.; Kanai, Y. Communication: Modeling of Concentration Dependent Water Diffusivity in Ionic Solutions: Role of Intermolecular Charge Transfer. J. Chem. Phys. 2015, 143, 211101.
- (26) Srivastava, S.; Andreev, M.; Levi, A. E.; Goldfeld, D. J.; Mao, J.; Heller, W. T.; Prabhu, V. M.; De Pablo, J. J.; Tirrell, M. V. Gel Phase Formation in Dilute Triblock Copolyelectrolyte Complexes. *Nat. Comm.* 2017, *8*, 14131.
- (27) Kim, J. S.; Wu, Z.; Morrow, A. R.; Yethiraj, A.; Yethiraj, A. Self-Diffusion and Viscosity in Electrolyte Solutions. J. Phys. Chem. B 2012, 116, 12007–12013.
- (28) Andreev, M.; Chremos, A.; de Pablo, J.; Douglas, J. F. Coarse-Grained Model of the Dynamics of Electrolyte Solutions. J. Phys. Chem. B 2017, 121, 8195–8202.
- (29) Chang, R.; Yethiraj, A. Strongly Charged Flexible Polyelectrolytes in Poor Solvents: Molecular Dynamics Simulations with Explicit Solvent. J. Chem. Phys. 2003, 118, 6634.

- (30) Lo, T. S.; Khusid, B.; Koplik, J. Dynamical Clustering of Counterions on Flexible Polyelectrolytes. *Phys. Rev. Lett.* **2008**, *100*, 128301.
- (31) Chremos, A.; Douglas, J. F. Influence of Higher Valent Ions on Flexible Polyelectrolyte Stiffness and Counter-Ion Distribution. J. Chem. Phys. 2016, 144, 164904.
- (32) Chremos, A.; Douglas, J. F. Counter-Ion Distribution Around Flexible Polyelectrolytes Having Different Molecular Architecture. Soft Matter 2016, 12, 2932–2941.
- (33) Chremos, A.; Douglas, J. F. Communication: Counter-Ion Solvation and Anomalous Low-Angle Scattering in Salt-Free Polyelectrolyte Solutions. J. Chem. Phys. 2017, 147, 241103.
- (34) HOOMD-blue. http://codeblue.umich.edu/hoomd-blue, (accessed July 20, 2017).
- (35) Anderson, J. A.; Lorenz, C. D.; Travesset, A. General Purpose Molecular Dynamics Simulations Fully Implemented on Graphics Processing Units. J. Comput. Phys. 2008, 227, 5342–5359.
- (36) LeBard, D. N.; Levine, B. G.; Mertmann, P.; Barr, S. A.; Jusufi, A.; Sanders, S.; Klein, M. L.; Panagiotopoulos, A. Z. Self-Assembly of Coarse-Grained Ionic Surfactants Accelerated by Graphics Processing Units. *Soft Matter* **2012**, *8*, 2385–2397.
- (37) Collins, K. D. Sticky Ions in Biological Systems. Proc. Natl. Acad. Sci. U.S.A. 1995, 92, 5553–5557.
- (38) Duignan, T. T.; Parsons, D. F.; Ninham, B. W. Collins's Rule, Hofmeister Effects and Ionic Dispersion Interactions. *Chem. Phys. Lett.* **2014**, *608*, 55–59.
- (39) Latimer, W. M.; Pitzer, K. S.; Slansky, C. M. The Free Energy of Hydration of Gaseous Ions, and the Absolute Potential of the Normal Calomel Electrode. J. Chem. Phys. 1939, 7, 108–111.

- (40) Rashin, A. A.; Honig, B. Reevaluation of the Born Model of Ion Hydration. J. Phys. Chem. 1985, 89, 5588–5593.
- (41) Schmid, R.; Miah, A. M.; Sapunov, V. N. A New Table of the Thermodynamic Quantities of Ionic Hydration: Values and Some Applications (Enthalpy-Entropy Compensation and Born Radii). *Phys. Chem. Chem. Phys.* **2000**, *2*, 97–102.
- (42) Millero, F. J. The Molal Volumes of Electrolytes. Chem. Rev. 1971, 71, 147–176.
- (43) Bramhall, A. D. A Viscosity/Density Relation for Solutions of Strong Electrolytes in Water. Nature 1963, 197, 967–968.
- (44) Shi, B.; Sinha, S.; Dhir, V. K. Molecular Dynamics Simulation of the Density and Surface Tension of Water by Particle-Particle Particle-Mesh Method. J. Chem. Phys. 2006, 124, 204715.
- (45) Ninham, B. W.; Yaminsky, V. Ion Binding and Ion Specificity: The Hofmeister Effect and Onsager and Lifshitz Theories. *Langmuir* 1997, 13, 2097–2108.
- (46) Skipper, N. T.; Neilson, G. W. X-Ray and Neutron-Diffraction Studies on Concentrated Aqueous-Solutions of Sodium-Nitrate and Silver-Nitrate. J. Phys.: Condens. Matter 1989, 1, 4141–4154.
- (47) Marcus, Y.; Hefter, G. Ion Pairing. Chem. Rev. 2006, 106, 4585–4621.
- (48) Dudowicz, J.; Freed, K. F.; Douglas, J. F. Mixtures of Two Self- and Mutually-Associating Liquids: Phase Behavior, Second Virial Coefficients, and Entropy-Enthalpy Compensation in the Free Energy of Mixing. J. Chem. Phys. 2017, 147, 064907.

TOC graphic

