Explicit-water molecular dynamics study of a short-chain 3,3 ionene in solutions with sodium halides

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Ionenes are alkyl polymer chains in which hydrophobic groups are separated by ionic charges. They are useful for studying the properties of water as a solvent because they demonstrate a sufficiently complex combination of hydrophobicity, charge interactions, and specific-ion effects that some properties cannot be predicted by implicit-solvation theories. On the other hand, they are simple enough that their molecular structures can be varied and controlled in systematic experiments. In particular, implicit-solvent models predict that all such solutes will have negative enthalpies of dilution, whereas experiments show that enthalpies of dilution are positive for the chaotropic counterions. Here, we study ionenes that are short chains (six monomer units) in solutions of different counterions, with sodium as the coion by molecular dynamics simulations in explicit water. We explore the pair distributions of various atoms within the system at three different temperatures: $T=278$, 298, and 318 K. We find (i) that the molecular dynamics simulations are consistent with the experimental trends for the osmotic coefficients and enthalpies of dilution, (ii) that the fluorine-nitrogen and fluorine-carbon correlations decrease with decreasing temperature, (iii) while the opposite behavior is found for iodine ions, and (iv) that in the counterion- Na^+ pair distributions, too, fluorine ions behave oppositely to iodine ions upon temperature increase. © 2009 American Institute of Physics. [DOI: 10.1063/1.3078268]

I. INTRODUCTION

Polyelectrolyte molecules are important in industry and biology.^{1–7} Yet, in many cases, their solution properties are poorly understood. For example, there are ion-specific effects^{8,9} (for review, see Ref. 10) that are clearly revealed in experiments on the enthalpy of dilution, ΔH_d .^{11–13} As a test bed for studying such properties our focus here is on aliphatic x,y ionene^{14–18} molecules. Here x and y are defined as numbers of methylene groups between the two quaternary nitrogen atoms and can assume values 3,3, 4,5, 6,6, or 6,9: for 3,3 ionenes the distance between two nitrogens is 0.498 nm. The 3,3 ionene polyion (poly[(dimethylimino)-1,3-propanediyl-(dimethylimino)-1,3-propanediyl dihalide]) is schematically shown in Fig. 1.

Implicit-solvent theories, which treat water as a dielectric continuum,^{2,19,20} predict that the enthalpies of dilution will be negative in all cases. In contrast, experiments show instead that ΔH_d values are positive when the counterions are “chaotropes,” such as Cs^+ and Br^- ions.¹³ On the other hand, ΔH_d results for counterions such as Li^+ , H^+ , or F^- (“kosmotropes”) are negative and generally in better agreement with the continuum-solvent theories.^{2,12,21} The deviations can probably be attributed to effects caused by restructuring of water around interacting charges not accounted for by the continuum-solvent theories.

Recently, explorations have begun of such subtle solvation properties by molecular dynamics simulations^{22–26} and by integral equation studies^{27,28} of oligoelectrolytes. Even though these chains are much shorter than the polymers they aim to mimic, for solvation properties, such models are expected to be fully sufficient. In our recent work,²⁶ hereafter referred as Ref. I, we examined solvation behavior of a model cationic oligoelectrolyte (6 monomer units long) in aqueous solution at 298 K. We simulated the interaction of the 3,3 aliphatic ionene with F^- , Cl^- , Br^- , and I^- ions in the SPC/E explicit model of water. An excess of low-molecular electrolyte, with Na^+ ions as coions, was present in the system. Using molecular dynamics, we calculated the pair distribution functions between various sites. The present study is much more extensive than the one presented before:²⁶ we now include simulations for multiple temperatures ($T=278$, 298, and 318 K), and we get deeper insights from looking at a broader range of pair correlation functions.

FIG. 1. Schematic representation of the 3,3 ionene polyion.

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TABLE I. Model parameters; 1 Å=0.1 nm.

Species		Z (e_0)	ϵ (kcal/mol)	σ (Å)
Water	O	-0.8476	0.1554	3.1656
	H	0.4238	0.0	0.0
Ionene	N	0.60	0.170	3.25
	C	-0.20	0.066	3.50
	C1	-0.25	0.066	3.50
	H1	0.10	0.030	2.5
	H2	0.13	0.030	2.5
Electrolyte	Na	1.00	0.0028	3.3304
	F	-1.00	0.0118	4.0
	Cl	-1.00	0.0403	4.86
	Br	-1.00	0.0645	5.04
	I	-1.00	0.0979	5.40

II. MODEL AND METHOD

We modeled the oligoelectrolyte-electrolyte mixture in water as explained in I. The model system consisted of water molecules, one molecule of ionene (six-mer, see Fig. 1 of Ref. I), the coions (Na^+) and an equivalent number of counterions (F^- , Cl^- , Br^- , or I^-) to satisfy the electroneutrality condition. The charges (Z) and the Lennard-Jones parameters (σ_i , ϵ_i) assigned to the various atoms or ions are given in Table I. For unlike sites the Lennard-Jones parameters were obtained using mixing rules in the form $\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j)$ and $\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j}$.

We modeled water using the SPC/E model,²⁹ where the hydrogens have effective charges $Z_{\text{H}} = 0.4238e_0$ (e_0 is the elementary positive charge) and the oxygens $Z_{\text{O}} = -2Z_{\text{H}}$. The 3,3 ionene oligoion simulated here was represented by a chain with six monomer units. Every monomer unit consists of three methylene groups and a quaternary nitrogen atom (see Fig. 1 of Ref. I). The geometry of the model ionene was optimized using the quantum mechanical semiempirical PM3 method³⁰ in implicit water (the COSMO model³¹ as implemented in the MOPAC program³² for QM semiempirical calculations). In order to preserve the internal geometry of ionene we imposed additional conditions for bond length and valence angles in the form: $E_{\text{bond}}(r) \sim (r - r_0)^2$ and $E_{\text{angle}}(\theta) \sim (\theta - \theta_0)^2$. Quantum chemical calculations^{30–32} of model parameters have shown differences between the carbons (and hydrogens as well) along the ionene chain. Carbons in CH_3 groups (denoted as C1) are characterized by a charge of $-0.25e_0$, while the carbons in CH_2 groups (denoted as C), have a charge of $-0.20e_0$. Hydrogens in CH_2 and CH_3 groups neighboring the nitrogen possess a charge $+0.13e_0$, while hydrogens in CH_2 of the in-between groups have a charge of $+0.10e_0$. The Lennard-Jones parameters for ionene particles were taken from the OPLS force field.³³ Besides the ionene and water molecules, the coion mimicking Na^+ and (different) counterions were present in solutions. The Lennard-Jones parameters for sodium³⁴ and the halide ions³⁵ were taken from literature.

Molecular dynamics simulations were performed on a box containing 2352 water molecules, one ionene oligomer,

12 Na^+ ions, and 18 counterions. The long-range interactions were taken into account by the Ewald summation technique. The concentration of added simple electrolyte $\text{Na}^+ X^-$, where X^- was one of the halide ions, was twice as large as the concentration of counterions, $c_s \approx 0.28$ mol/l. An excess of the low-molecular electrolyte should screen the interaction between the ionene oligoions (which would be present in real solution), making the cell model approximation less severe. The pressure (1 bar) and temperature were controlled by means of the Melchionna version of the Hoover algorithm in which the equations of motion incorporate Nose–Hoover barostat and thermostat.³⁶ The particles were placed in a cubic box with periodic boundary conditions. The equilibration procedure required 5×10^5 time steps and the production runs were performed over 2×10^7 steps. As in I we used the velocity Verlet algorithm with a time step $\tau = 5 \times 10^{-16}$ s to integrate the classical equations of motion of the system.

III. RESULTS

A. Water-counterion distributions

In the following sections, we show the pair distribution functions between the various atoms of the system at three temperatures, $T = 278$, 298, and 318 K. The first conclusion, shown in Fig. 2, is that smaller counterions are more tightly bound to their hydration shell waters than larger counterions are. This is consistent with results from our earlier study in Ref. I and is also well known from others.^{37–40} The trend for the first peak is to decrease with increasing temperature.

B. Distributions of water oxygen with ionene nitrogens and carbons

Next we focus on the nitrogen (on the ionene)-oxygen (on the water) distribution functions. By looking at the first peaks in Fig. 3, for the counterion sequence F^- , Cl^- , Br^- , and I^- , we see that the smaller ions help pull more water molecules close to the polymer nitrogens than the larger ions do. Interestingly, these results are practically temperature independent.

The temperature dependence is a little bit stronger in case of the carbon (C1)-oxygen (water) and carbon (C)-oxygen (water) distributions. Results in Fig. 4 apply to the ionene fluoride solutions. As expected the carbon (C1)-oxygen (water) correlation is, as judged by the height of the first peak, much stronger than the corresponding correlation of carbon (C) in CH_2 groups. Both correlation functions exhibit a weak dependence on the counterion type, similarly to that presented before for the nitrogen-oxygen (water) distribution functions.

C. Distributions of ionene nitrogen-counterion

Figure 5 shows the strong influence of the nature of counterion on the nitrogen-counterion pair distribution. The smeared first peak of the pair distribution for F^- suggests that this ion is not tightly restricted or tightly bound to the ionene. On the other hand, more pronounced peaks for Cl^- , Br^- , and I^- counterions indicate that these ions accumulate more strongly near the nitrogen atom of the ionene. The anion with

FIG. 2. (Color online) Temperature dependence of the counterion-oxygen (on the water) and the counterion-hydrogen (water) pair distribution functions in mixture.

the largest crystal radius (I^-) is attracted more strongly to the nitrogen than the smallest one, F^- , ion. Our interpretation is that the smallest ions hold hydration-shell waters most tightly, causing them to have the largest effective radii, and leading therefore to an inability to penetrate to near the ionene atoms. In contrast, the larger anions as Cl^- , Br^- , and I^- , partially desolvate, so they can approach the ionene backbone more closely. In polyelectrolyte terminology this is called “site binding”⁸ in contrast to the so-called territorial binding; the former is caused by a strong Coulomb interaction between the fixed charge and counterions.

In Fig. 5, we now look at how the counterions are distributed around the ionene nitrogens. For the nitrogen- F^- distribution the magnitude of the first peak decreases with the decreasing temperature. In other words, the nitrogen atom of the ionene backbone and the fluorine anion in solution are more strongly correlated at higher temperatures. Exactly the opposite behavior occurs for the nitrogen- I^- correlation, shown in the same figure. The two peaks of the nitrogen- I^- pair distribution function decrease with an increase in temperature.

The corresponding results for Br^- and Cl^- ions are also shown. As for the nitrogen- I^- pair distribution function, the first and second peaks are well defined for both systems. As

FIG. 3. (Color online) Temperature dependence of the nitrogen-oxygen (water) pair distribution functions in presence of various sodium halides.

far as the temperature dependence is concerned, the picture is less clear; for the nitrogen- Cl^- the height of the peak decreases in order $T=278>318>298$ K. In the case of nitrogen- Br^- distributions the highest first peak applies to 298 K, while the second peak gets the strongest at 278 K. Obviously, the result is a compromise of several competing effects and each of them may have different temperature dependence. Notice that dielectric constant of pure SPC/E water at 298 K is $\epsilon_r(298\text{ K})=71.0$.⁴¹

Figure 6 shows the corresponding predictions from an implicit-solvent simulation. In such a case the dielectric constant is a function of temperature. In order to consistently

FIG. 4. (Color online) Temperature dependence of the carbon (C1)-oxygen (water) and carbon (C)-oxygen (water) pair distribution functions in presence of sodium fluoride. By C1 we denote carbon atoms in CH_3 groups, and by C the carbons in CH_2 groups (see also Table I).

evaluate the temperature dependence of the nitrogen-counterion pair distribution functions we used the experimentally determined temperature coefficient for pure water [see Eq. 41 on p. 183 of Ref. 42] but with $\epsilon_r(273 \text{ K}) = 80.44$, instead of 87.740. This formula reproduces $\epsilon_r(298 \text{ K}) = 71.0$, and gives for the other two temperatures $\epsilon_r(278 \text{ K}) = 78.5$ and $\epsilon_r(318 \text{ K}) = 64.2$. For the F^- and Cl^- ions the implicit-solvent simulation predicts weaker, and for the Br^- and I^- stronger correlation of counterions with the nitrogen of ionene than those shown in Fig. 5. In addition, the temperature dependence is much weaker than in the explicit-solvent case.

D. Carbon (C)-counterion distributions

Now we look at the distributions of various ions around the ionene carbons (C); note again that these are the carbons in methylene groups on the oligoion backbone. Consistent with the results above, fluorine is not localized close to the chain, presumably because of its large size dictated by its tightly bound hydration shell of waters (see Fig. 7). On the other hand, the sawlike shape of the $\text{C}-\text{Cl}^-$, $\text{C}-\text{Br}^-$, and $\text{C}-\text{I}^-$ distributions in the same figure reflect the periodicity of the CH_2 groups on the ionene. The temperature dependence for this case is the same as for nitrogen-counterion correlation function shown before. For the $\text{C}-\text{F}^-$ pair distribution function the first peak decreases with decreasing temperature. The ordering in the $\text{C}-\text{I}^-$ case is different, with the highest peaks for 278 K.

FIG. 5. (Color online) Temperature dependence of the nitrogen-counterion pair distribution functions.

E. Nitrogen-Coion distributions

Figure 8 shows the distribution function for the ionene nitrogen relative to the Na^+ coion. These groups have the same charge sign, hence, the distribution functions show that the sodium ions are repelled by the chain, and are distant from it.

There are small peaks here indicating that some of the sodium ions penetrate into the electrical double-layer formed by counterions. Such an ion-specific behavior is not unknown in electrochemistry (see p. 394 of Ref. 42). For implicit water model simulations (results not shown here) the

(a)

(b)

(c)

(d)

FIG. 6. (Color online) Temperature dependence of the nitrogen-counterion pair distribution functions for implicit solvent case; ϵ_r is taken to be 78.5 at 278 K, and 64.2 at 318 K.

temperature dependence of the nitrogen- Na^+ pair distribution functions are very weak. In addition, these distribution functions are less structured, in particular, there is no visible first peak.

F. Counterion-Coion distributions

Another interesting way that explicit and implicit solvent simulations differ is shown in Fig. 9, of the distributions of counterions with respect to coions. We find for $\text{Na}^+ - \text{F}^-$ and $\text{Na}^+ - \text{Cl}^-$ case that the first peak of the pair distribution func-

(a)

(b)

(c)

(d)

FIG. 7. (Color online) Temperature dependence of the carbon (C)-counterion pair distribution functions.

tion, interestingly, increases with increasing temperature. However, we find the opposite for $\text{Na}^+ - \text{Br}^-$ and $\text{Na}^+ - \text{I}^-$ pair distributions. This is the same pattern we saw for the nitrogen-counterion distributions presented in Fig. 5. Note also that oxygen (water)-counterion (ion solvation) and oxygen (water)-oxygen (water) distribution functions (the latter one is not shown here) exhibit “normal” temperature dependence; in both cases the magnitude of the first peak increases with the decreasing temperature. As above (Fig. 6) the continuum solvent modeling predicts for the first peaks of all counterion- Na^+ distributions to increase with the temperature decrease.

FIG. 8. (Color online) Temperature dependence of the nitrogen-sodium pair distribution functions for 3,3 ionene in mixture with NaF (left) and NaI (right).

G. Small ions hydrate more tightly than larger ions

We calculated the differences in arbitrary defined hydration numbers of counterions in bulk solution and those in the “adsorbed” state, which is within a certain distance from the nitrogen atom. Minima of the pair distribution functions between water oxygens and various counterions, shown in Fig. 2 provided estimates for the radii, R_{hyd} , of the hydration shells of counterions. These values are approximately 3 Å for F^- , 4 Å for Cl^- and Br^- ions, and 4.3 Å in the case of iodine ions. We monitored the number of water oxygens within the R_{hyd} of counterions, as a function of the counterion distance from the nitrogen atom. As for our previous study²⁶ two regions were defined: (i) the counterion was assumed to be in the “adsorbed” state if it was located at the distance less than 6 Å from the nearest nitrogen atom, and (ii) the counterion was in the bulk region, if located at distances larger than that. The definition adopted here is based on the positions of the first minima of nitrogen-anion pair distribution functions (Fig. 5).

The results given in Fig. 10 confirm previous findings²⁶ that the counterions such as Cl^- , Br^- , and I^- lose one or two water molecules when approaching the ionene. In contrast to this the hydration shell of F^- ion remains intact in interaction with ionene. This seems to be valid for all temperatures studied here.

IV. RELATION WITH EXPERIMENTAL DATA

Ionene solutions have been characterized experimentally in several papers.^{13–18} Nagaya *et al.*^{15–17} measured the conductance and activity coefficients of 3,3, 4,5, 6,6, and 6,9 ionene solutions, while heats of dilution and osmotic coefficients were determined by Arh *et al.*^{13,18} All the measure-

FIG. 9. (Color online) Temperature dependence of the sodium-counterion pair distribution functions in presence of the 3,3 ionene molecule.

ments indicate strong deviations from theoretical predictions based on the continuum solvent models of polyelectrolyte solution. For example, the conductance of ionenes measured in the presence of additional electrolyte deviates from the “additivity rule;” i.e., the conductivity of the polyelectrolyte mixture cannot be described as a sum of the conductivities of the simple salt and salt-free polyelectrolyte solutions. The deviations depend on the ionene charge density (x, y values) and on the nature of the counterion.¹⁵ The ion-specific effects were noticed in viscosity measurements as well.¹⁵ Further, the measured activity¹⁵ and osmotic coefficients¹⁸ were much lower than theoretically predicted and the deviations were stronger for more hydrophobic (6,6 and 6,9) ionenes.

FIG. 10. (Color online) Coordination numbers of water oxygens within the R_{hyd} around counterions, as a function of the counterion distance from the nitrogen atom at $T=278$ K (top), 298 K (center), and 318 K (bottom).

Our molecular dynamics results are consistent with the experimental data for the osmotic pressures¹⁸ measured at 298 K. The counterion-nitrogen distribution functions presented in Fig. 5 indicate stronger correlation of the Br^- ions to the ionene oligoion in comparison with the Cl^- . This finding is confirmed by the carbon-counterion distribution functions (Fig. 7 discussed in Sec. III D). These results can explain stronger binding of Br^- (lower osmotic and activity coefficients) versus Cl^- ions (higher values of these coefficients) as revealed in thermodynamic measurements.^{15,18}

Even more interesting are the enthalpies of dilution, ΔH_d , results. The experiments for 3,3 ionenes bromides and chlorides indicate an endothermic effect for the enthalpy of dilution,¹³ just the opposite to predictions of the classical implicit-water theories.^{2,19,20} Heat is therefore consumed upon dilution of these salts, and the effect is much stronger for solutions where polyions are neutralized by bromide ions.¹³ In contrast to this, the enthalpies of dilution of 3,3 ionene fluoride are exothermic,⁴³ in quantitative agreement with the implicit-water models.^{2,19,20} A more detailed discussion of this effect in relation with the implicit water models and McMillan–Mayer theory is provided in Refs. 10, 20, and 21.

We believe that the molecular dynamics results presented here may provide a physical explanation for these experimental findings. Results shown in Fig. 10 indicate that weakly solvated counterions (for example, Br^-) lose some of the hydration shell water when interacting with the 3,3 ionene. This is not the case for F^- ions; it is evident from Figs. 5 and 7 that F^- ions in interaction with nitrogen and carbons behave as large rigid particles. The simulation results presented here therefore suggest that ionene fluorides should behave differently than corresponding chlorides and bromides; the latter ions should bind more strongly and yield more endothermic ΔH_d values than the equivalent chloride salts. This again is consistent with measurements¹³ as also with an approximate explicit solvent theory proposed recently.²⁸ Note that measurements of the dielectric relaxation spectrum of 3,3 ionene solutions⁴⁴ indicate a somewhat stronger binding of Br^- to ionene in comparison with F^- counterions, consistently with the present simulations.

Unfortunately, all the available experimental data for ionene solutions apply to a single temperature ($T=298$ K) and therefore we cannot test our predicted temperature dependencies. Osmotic coefficients for other polyelectrolytes, such as polystyrenesulfonic acid and its alkaline salts, show little temperature dependence.² ΔH_d values for the same solutions, on the other hand, become more exothermic with rising temperature (or more endothermic if the temperature is decreased).¹² The same study reveals that an agreement with the implicit-solvent model is considerably better at higher temperatures.

Amphiphilic quaternary ammonium salts have chemical structures similar to the alkyl ionenes. The counterion effects on the properties of amphiphilic quaternary ammonium salts have been investigated by Różycka-Roszak *et al.*^{45,46} The calorimetric measurements performed at 298 K revealed significant differences between dodecyltrimethylammonium chloride (DTAC) and dodecyltrimethylammonium bromide (DTAB); for DTAC the process of micelle dissociation was exothermic while for DTAB it was endothermic. In contrast to this, at 313 K both surfactants show exothermic effects, exhibiting in this way much smaller ion-specific effects as at lower temperature. In general we may expect for the ion-specific effects to be less pronounced at higher temperatures.

V. CONCLUSIONS

We studied six-mer ionene oligoion in mixture with sodium and halide ions by molecular dynamics simulations in explicit (SPC/E) water. We calculated the distributions of counterions, coions, and water molecules around these solute molecules at three different temperatures. We draw the following conclusions: (i) smallest counterions carry tight solvation shells, so they cannot penetrate close to the chain, whereas for larger counterions, waters are stripped away so the ions can come into contact with the ionene chain, (ii) increasing the temperature helps strip off some of these hydration-shell waters around the ions, (iii) temperature has weak effect on how waters form contacts with the ionene's charged nitrogens or the ionene's carbons, (iv) increasing temperature assists the association of fluorine with the ion-

ene chain, but assists dissociation of iodine with the ionene chain. Whereas implicit-solvent models miss some of these properties, for example, the sign on the enthalpies of dilution of ionene chains in water, the molecular dynamics simulations reported here appear to be consistent with experiments.

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- ¹Z. Alexandrowicz and A. Katchalsky, *J. Polym. Sci. A* **1**, 3231 (1963).
- ²D. Dolar, in *Polyelectrolytes*, edited by E. Selegny, M. Mandel, and U. P. Strauss (Reidel, Dordrecht, 1974), pp. 97–113.
- ³H. Dautzenberg, W. Jaeger, J. Kötz, B. Philipp, C. Seidel, and D. Stscherbina, *Polyelectrolytes Formation, Characterization and Application* (Hanser, Munich, 1994).
- ⁴J. Blaul, M. Wittemann, M. Ballauff, and M. Rehahn, *J. Phys. Chem. B* **104**, 7077 (2000).
- ⁵C. Holm, J. F. Joanny, K. Kremer, R. R. Netz, P. Reineker, C. Seidel, T. A. Vilgis, and R. G. Winkler, *Adv. Polym. Sci.* **166**, 67 (2004).
- ⁶R. Q. Yang, H. B. Wu, Y. Cao, and G. C. Bazan, *J. Am. Chem. Soc.* **128**, 14422 (2006).
- ⁷R. Q. Yang, A. Garcia, D. Korystov, A. Mikhailovsky, G. C. Bazan, and T. Q. Nguyen, *J. Am. Chem. Soc.* **128**, 16532 (2006).
- ⁸U. P. Strauss, in *Polyelectrolytes*, edited by E. Selegny, M. Mandel, and U. P. Strauss (Reidel, Dordrecht, 1974), pp. 79–85.
- ⁹W. Kunz, *Pure Appl. Chem.* **78**, 1611 (2006).
- ¹⁰V. Vlachy, *Pure Appl. Chem.* **80**, 1253 (2008).
- ¹¹P. W. Hales and G. Pass, *Eur. Polym. J.* **17**, 651 (1981).
- ¹²G. Vesnaver, M. Rudež, C. Pohar, and J. Škerjanc, *J. Phys. Chem.* **88**, 2411 (1984).
- ¹³K. Arh and C. Pohar, *Acta Chim. Slov.* **48**, 385 (2001).
- ¹⁴D. Casson and A. Rembaum, *Macromolecules* **5**, 75 (1972).
- ¹⁵J. Nagaya, A. Minakata, and A. Tanioka, *Langmuir* **15**, 4129 (1999).
- ¹⁶J. Nagaya, A. Minakata, and A. Tanioka, *Colloids Surf., A* **148**, 163 (1999).
- ¹⁷J. Nagaya, A. Minakata, and A. Tanioka, *Rep. Prog. Polym. Phys. Jpn.* **40**, 123 (1997).
- ¹⁸K. Arh, C. Pohar, and V. Vlachy, *J. Phys. Chem. B* **106**, 9967 (2002).
- ¹⁹G. S. Manning, *J. Chem. Phys.* **51**, 924 (1969).
- ²⁰J. Piñero, B. L. Bhuiyan, J. Reščič, and V. Vlachy, *J. Chem. Phys.* **127**, 104904 (2007).
- ²¹I. Lipar, P. Zalar, C. Pohar, and V. Vlachy, *J. Phys. Chem. B* **111**, 10130 (2007).
- ²²F. Molnar and J. Rieger, *Langmuir* **21**, 786 (2005).
- ²³A. A. Chialvo and J. M. Simonson, *J. Phys. Chem. B* **109**, 23031 (2005).
- ²⁴R. Chang and A. Yethiraj, *Macromolecules* **39**, 821 (2006).
- ²⁵B. Jerman, Č. Podlipnik, and K. Kogej, *Acta Chim. Slov.* **54**, 509 (2007).
- ²⁶M. Druchok, B. Hribar-Lee, H. Krienke, and V. Vlachy, *Chem. Phys. Lett.* **450**, 281 (2008).
- ²⁷V. Vlachy, B. Hribar-Lee, J. Reščič, and Yu. V. Kalyuzhnyi, in *Ionic Soft Matter: Modern Trends in Theory and Applications*, NATO Science Series II: Mathematics, Physics and Chemistry Vol. 206, edited by D. Henderson, M. F. Holovko, and A. Trokhymchuk (Springer, Dordrecht, 2005), pp. 199–231.
- ²⁸Yu. V. Kalyuzhnyi, V. Vlachy, and P. T. Cummings, *Chem. Phys. Lett.* **438**, 238 (2007).
- ²⁹H. J. C. Berendsen, J. R. Grigera, and T. P. Straatsma, *J. Phys. Chem.* **91**, 6269 (1987).
- ³⁰J. J. P. Stewart, *J. Comput. Chem.* **10**, 209 (1989).
- ³¹A. Klamt and G. Schuurmann, *J. Chem. Soc., Perkin Trans.* **1993**, 799.
- ³²J. J. P. Stewart, MOPAC 2002, Fujitsu Limited, Tokyo, Japan, 1999.
- ³³W. L. Jorgensen, D. S. Maxwell, and J. Tirado-Rives, *J. Am. Chem. Soc.* **118**, 11225 (1996).
- ³⁴J. Aqvist, *J. Phys. Chem.* **94**, 8021 (1990).
- ³⁵G. Palinkas, O. Riede, and K. Heinzinger, *Z. Naturforsch. A* **32**, 1197 (1977).
- ³⁶S. Melchionna, G. Ciccotti, and B. L. Holian, *Mol. Phys.* **78**, 533 (1993).
- ³⁷S. H. Lee and J. C. Rasaiah, *J. Phys. Chem.* **100**, 1420 (1996).
- ³⁸G. Lamoureux and B. Roux, *J. Phys. Chem. B* **110**, 3308 (2006).
- ³⁹R. Ayala, J. M. Martinez, R. R. Pappalardo, and E. S. Marcos, *J. Chem. Phys.* **119**, 9538 (2003).
- ⁴⁰G. Ahn-Ercan, H. Krienke, and W. Kunz, *Curr. Opin. Colloid Interface Sci.* **9**, 92 (2004).
- ⁴¹P. G. Kusalik and I. M. Svishev, *Science* **265**, 1219 (1994).
- ⁴²G. Kortüm, *Treatise on Electrochemistry*, 2nd ed. (Elsevier, Amsterdam, 1965).
- ⁴³C. Pohar (unpublished).
- ⁴⁴M. Lukšič, B. Hribar-Lee, V. Vlachy, and R. Büchner, “Dielectric relaxation spectroscopy of aliphatic ionene bromides and fluorides in water: The role of the polyion’s charge density and the nature of the counterions,” *Macromolecules* (in press).
- ⁴⁵B. Różycka-Roszak, R. Żyłka, and J. Sarapuk, *Z. Naturforsch. C* **55C**, 413 (2000).
- ⁴⁶B. Różycka-Roszak, R. Żyłka, and J. Sarapuk, *Z. Naturforsch. C* **56C**, 154 (2001).