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Computer Simulations of Ionenes, Hydrophobic Ions with Unusual Solution Thermodynamic Properties. The Ion-Specific Effects

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Ionenes are alkyl polymer chains in which different numbers of methylene groups separate quaternary ammonium groups. They are ideal molecules for studying the balance between hydrophobic and charge effects in water. Implicit-solvent models predict osmotic coefficients that are too high (too low water vapor pressures), compared to experiments. We present a molecular dynamics simulation, in explicit SPC/E water, of a solution of aliphatic 6,6 ionene oligocations with sodium co-ions and fluorine, chlorine, bromine, or iodine counterions. In the 6,6 ionene solution, the latter polyion has more hydrophobic groups than its 3,3 counterpart, the waters are displaced more from the oligoion surface. Also, we find that the large ions, such as iodine, act like hydrophobic groups insofar as they bind to ionene's methylene groups. The water-mediated attraction between fluorine ions is enhanced in presence of weakly charged 6,6 ionene molecules. This effect may additionally reduce the osmotic pressure in such systems. Our results can explain some experimental trends in ionene solutions and weakly charged polyelectrolytes in general.

I. Introduction

Polyelectrolytes are by definition polymers containing groups that can ionize in an appropriate solvent. They possess very rich physical behavior, which together with theoretical advances, has been extensively reviewed.[1−8] Since they contain both ionic and hydrophobic groups, they resemble certain biological materials, such as nucleic acids and proteins. We study here the solution properties of ionenes, which are hydrophobic ions.[9−14] Ionenes are useful because they have the same solvation complexities as biologically important hydrophobic ions, such as proteins and nucleic acids, but their properties can be varied much more systematically in experimental studies. Aliphatic *x, y* ionenes can be prepared with varying degrees of hydrophobicity; for example the 3,3 ionene (poly[(dimethylimino)-1,3-propanediyl-(dimethylimino)-1,3-propanediyl dihalide]) contains three methylene groups between the quaternary nitrogen atoms. For the 6,6 ionene the hydrophobic part is twice as long (six methylene groups between the charges), which makes it a much weaker (in terms of Coulomb interaction) polyelectrolyte.

Aliphatic *x, y* ionenes are soluble in water and can therefore be studied by standard methods of the solution chemistry, such as osmometry, calorimetry, conductometry, and others. Experimental results are available for 3,3, 4,5, 6,6, and 6,9 ionenes in solutions with various halide anions.[9−14] These results are often analyzed by implicit-solvent theories of polyelectrolyte solutions, such as the cylindrical cell model[1−4,7] or the Manning condensation approach.[15,16] The principal parameter of these theories is the linear charge density parameter λ defined as

$$\lambda = \frac{e_0^2}{4\pi\epsilon_0\epsilon_r k_B T b} \tag{1}$$

where e_0 is the elementary charge, ε_0 is the permittivity of vacuum, ε_r is the relative permittivity of pure solvent at given temperature and pressure, k_B is Boltzmann's constant, T is the absolute temperature, and b is the distance between the two charges projected to the z-axis. For an aqueous solution of 3,3 ionene at 298 K, $\lambda = 1.43$ ($b = 0.498$ nm) and for 6,6 ionenes under these conditions, $\lambda = 0.81$ ($b = 0.879$ nm). According to the well-established Manning theory[15,16] the polyelectrolytes with $\lambda > 1$ (3,3 ionenes) behave qualitatively different than those with $\lambda < 1$ (6,6 ionenes). Implicit-solvent models[1−4,7,15,16] however, are not quantitatively accurate, and even more importantly they cannot describe the ion-specific effects, which are of great importance for biology and related sciences.

To better understand their solution properties, we perform an explicit-water molecular dynamics (MD) simulation of solutions of short 6,6 ionene oligomer with fluorine, chlorine, bromine, or iodine ions as counterions and sodium ions as co-ions. The work is a continuation of our previous studies,[17,18] where such calculations were performed for the higher charge density (3,3 ionene) oligoions. The possibility to vary the hydrophobic portion of the polyion makes ionene an ideal substance to study the influence of hydrophobic groups on interaction between the charge on the polyion and counterions in the solution.

There is already some theoretical evidence showing that presence of the electrical charges disrupts the interaction between the nonpolar solutes.[19−21] Here we are interested in effect of hydrophobic groups, note that the 6,6 ionene molecule has six methylene groups between the two charges on the potential of the mean force between charged sites in such systems. The purpose of the present study is to investigate how the increasing number of methylene groups affect interaction

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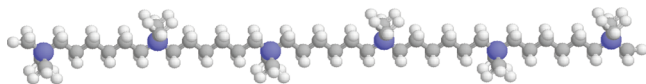
Figure 1. Schematic representation of the 6,6 ionene 6-mer oligoion. Nitrogens are denoted by blue, carbons by gray, and hydrogens by white circles.

TABLE 1: Model Parameters

	species	Z/e_0	$\varepsilon/$(kcal/mol)	$\sigma/$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

between the ionene oligocation and low-molecular counterions, such as, F^-, Cl^-, Br^-, and I^- in aqueous solution. Halide ions, proposed to be studied in combination with 6,6 ionene oligocation are important per se. They play an important role in biological phenomena and are of industrial importance. The calculations are extensively compared with previously published data for the corresponding 3,3 ionenes[17,18] and with experimental data for these solutions.

II. Model and Method

The ionene molecules were represented by chains with six monomer units each, and every monomer unit consisted of six methylene groups and a quaternary nitrogen atom (Figure 1). The model for 6,6 ionene was constructed in a similar way as previously described for 3,3 ionene (for more details see our previous works[17,18]). The charges (Z) and the Lennard-Jones parameters (σ_i, ε_i) assigned to the various atoms or ions (see Table 1) were the same as in refs.[17,18] Lennard-Jones parameters for ionene particles were taken from the OPLS force field.[22] Besides ionene and water molecules, co-ions modeling Na^+ and counterions were present in the solution. The Lennard-Jones parameters for Na^+ ions were taken from the literature.[23] Ionene solutions with four different counterions, F^-, Cl^-, Br^-, and I^- were considered. The Lennard-Jones parameters for the halide ions were taken from the work of Palinkas.[24] We modeled water using the SPC/E model.[25] For unlike sites the Lennard-Jones parameters were obtained using mixing rules in the form $\sigma_{ij} = (1/2)(\sigma_i + \sigma_j)$ and $\varepsilon_{ij} = (\varepsilon_i \varepsilon_j)^{1/2}$.

Molecular dynamics simulations of 6,6 ionene solutions were performed within a unit cell containing 4700 water molecules, two ionene oligomers, 24 Na^+ ions, and 36 counterions (F^-, Cl^-, Br^-, or I^-, respectively). All the species were allowed to move freely across the MD cell. The long-range Coulomb interactions were taken into account by the Ewald summation technique. The concentration c_s of added simple electrolyte Na^+X^- (X^- stands for one of the halide ions) was about 0.28 mol/L, which was two times larger than the concentration of counterions. An excess of the low-molecular electrolyte should screen the interaction between the ionene oligoions, making the model approximations acceptable. The pressure (1 bar) and temperature (298 K) were controlled by means of a Nose-Hoover barostat and thermostat in an isotropic N,P,T ensemble.[26] The particles were placed into a cubic box with periodic

boundary conditions. The equilibration procedure required 2×10^5 time steps and the production runs were performed over 4×10^6 steps. As in refs17 and 18, 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. Previous explicit water molecular dynamics studies of polyelectrolyte solutions are due to Chang and Yethiraj,[27] Chialvo and Simonson,[28,29] and Jerman and co-workers.[30]

III. Results

Our main results here are various calculated pair distribution functions (PDFs) between the interacting sites on the 6,6 ionenes and the surrounding ions and water. The results are compared with the MD calculations we performed before for various 3,3 ionene alkaline salts.[17,18] Some snapshots are also presented helping to visualize the results.

A. Iodine, Bromine, and Chlorine, but not Fluorine Ions, Stay Close to Ionenes. Figure 2 shows that MD simulations predict significant differences in the counterion-nitrogen and counterion-carbon pair distribution functions for 6,6 ionene. The results indicate that iodine, the largest considered anion (cf Table 1), has the strongest affinity for the polymer while fluorine, the smallest anion, has the smallest affinity for the ionene oligocation.

Experimentally obtainable quantities, such as the osmotic coefficient, depend strongly on how the counterions distribute around polyions. In dilute solutions, as most often studied experimentally, the polyion-counterion interaction term makes the dominant contribution to the osmotic coefficient.[31,32] Strong polyion-counterion attraction decreases the osmotic coefficient (increases the solvent vapor pressure). The experiments show that Br^- ionene solutions have lower osmotic coefficients than their Cl^- counterparts.[13] This is consistent with the results for the Br^-- and Cl^--ionene pair distribution functions, presented in Figure 2. In view of the osmotic pressure data, our molecular dynamics results will be further discussed in Section IV.

B. Fluorine Ions Have Large Negative Free Energy of Solvation. Minima of the pair distribution functions between water oxygens and various counterions, shown in Figure 2 of ref 18, provide 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^-, and 4.3 Å in the case of I^- counterions. We monitored the number of water oxygens within the R_{hyd}, as a function of the counterion distance from the nitrogen atom. These results are shown in Figure 3. The plots for 6,6 ionenes shown here are not much different from those obtained before for 3,3 ionenes,[18] except that the counterions approach slightly closer to the nitrogen in case of the 3,3 ionenes. Fluorine ions hold their waters tightly, regardless of the charge on the ionene.

The results presented in Figure 3 are consistent with the experimental and theoretical studies of hydration of halogen ions; see, for example, ref 33 and the references therein. Standard free energy of solvation becomes more negative with the decreasing crystal size of an ion. For F^-, this quantity is considerably lower than for other halogen ions (cf. Figure 2 of ref 33). We will encounter important consequence of this fact in later sections.

C. Methylene Group-Water Correlation. In this section, we show the effects of increased hydrophobicity of the polyion on the correlation functions between various species in system. The nitrogen−oxygen(water) pair distribution functions for oligoion-Na halide mixtures are shown in Figure 4. Here we only show the results for F^- and I^- counterions; the results for the other two ions (Br^- and Cl^-) are similar. The positions of the first peaks of the PDFs for the case of 6,6 ionene are shifted
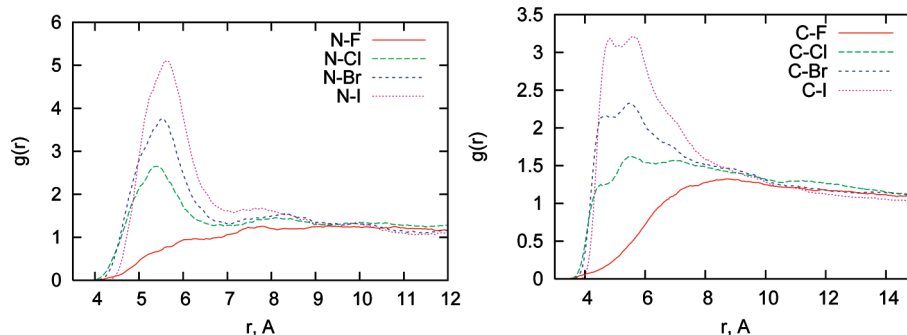
Figure 2. Counterion-nitrogen and counterion-carbon (C) pair distribution functions for the 6,6 ionene with different counterions. From top to bottom: solutions with I^-, Br^-, Cl^-, and F^- counterions. Note that C denotes the carbon of methylene group.
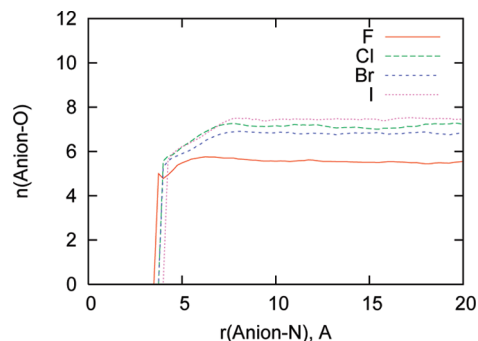
Figure 3. Coordination numbers of water oxygens within the R_{hyd} around counterions, as a function of distance between counterion and nearest nitrogen atom.

(for about 0.3 Å) toward larger distances for all four counterion species studied here. The peaks are lower for 3,3 ionenes and the periodicity of the curves is different; the distance between the first and the second peak is shorter in the case of the 6,6 ionene. The height of the peak decreases (for both 3,3 and 6,6 ionenes) in order from F^- to I^-. The same conclusion follows from the nitrogen-water(hydrogen) pair distribution functions. In a separate simulation, we calculated the hydration of the nitrogens on ionenes in the absence of counterions and co-ions. The resulting nitrogen−oxygen(water) pair distribution function was practically identical to that obtained in presence of F^- ions (cf. Figure 4), and therefore not shown here.

To complete the picture, we show in Figure 5 that waters around methylene groups of the 6,6 ionene distribute differently than in the 3,3 ionene solutions. For 6,6 ionene salts, the carbon−oxygen pair distribution functions demonstrate a shoulder near 3.9 Å, while the position of the first peak is at ∼4.9 Å. As above for Figure 4, the peaks of pair distribution functions decrease in order from fluorine to iodine, while the positions of the peaks seem to be independent of the counterion nature. These plots also indicate removal some of the water molecules from the 6,6 ionene oligomer surface.

D. Iodine Has an Affinity for the Methylene Group. Next we focus on the counterion-nitrogen distribution functions shown in Figure 6. The comparison reflects a weaker attraction between the counterions and the ionene backbone in the 6,6 case than for 3,3. We have simulated also the solutions with Br^- and Cl^- counterions but their behavior falls between that of F^- and I^-, so only the results for the latter ions are presented. For all the counterion species studied, the 3,3 ionene pair distribution function is considerably higher and shifted closer to the oligoion. This result is consistent with the available thermodynamic data for 298 K; the osmotic coefficients of the 6,6 ionenes are higher than those of the corresponding 3,3 ionene solutions.[13]

Figure 6 also shows the counterion-carbon(C) distribution functions for the 3,3 and 6,6 ionenes. As a consequence of the weaker Coulomb attraction of counterions to oligoions (smaller value of the linear charge density parameter λ) the pair distributions for the 6,6 ionenes are considerably less structured than found for their 3,3 counterparts. It seems that the counterions in 6,6 ionene solutions do not feel individual methylene groups in contrast to 3,3 ionene case (see iodine−carbon(C) distributions in Figure 6), but rather some average field. Notice also that F^-−nitrogen and F^-−carbon(C) distribution functions for 3,3 ionene case do not differ very much from each other.

In Figure 6 we see how the I^-−nitrogen and I^-−carbon(C) pair distributions change with the increasing hydrophobicity. The difference between the 3,3 and 6,6 ionene I^-−carbon(C) pair distribution functions is considerably smaller than in case of the adequate I^-−nitrogen distributions. This contrasts with the F^- ion (cf. left panels of Figure 6) results. This result, together with the observations discussed above, indicates some affinity of the large iodine ion for methylene groups. Our finding agrees with observations of other groups (see refs 34 and 35) that large anions can be attracted to nonpolar groups. The effect, however, is not as strong as described in the Cl^-−I^- "selectivity" simulation of Lund and co-workers.[35] Part of the reason might be that different co-ions were used in these studies, as discussed further below.

E. Is the Nature of the Co-ion Important? The negative counterions in our system are attracted both to the positive ionene ions and also to the co-ions, which are sodium ions in this case.

Figure 7 reflects this competition for counterions. These curves indicate stronger attraction between the counterion and co-ion in the case of the 6,6 ionene than for 3,3 ionene solutions. This was to be expected, the weakly charged 6,6 ionene competes less successfully for counterion than the 3,3 ionene oligoion. In short, the nature of co-ion is not completely irrelevant here. Computer simulations and experimental data show (see, for example, ref 36) that Li^+ pairs with F^- ions in solution, which would cause withdrawal of some counterions (F^-) from the surface of the ionene. This would in turn decrease the electrostatic screening between the oligoions, causing their stabilization in solution. On the other hand, the replacement of Na^+ by Cs^+ ion should have an opposite effect. An extensive investigation of the co-ion effect on the counterion distributions among polar and nonpolar sites on a model macromolecule is underway.

F. Water is Able to Correlate Equally Charged Ions. In this section, we look at the counterion−counterion distribution functions. The left panel of Figure 8 shows F^-−F^- correlations. For the more hydrophobic 6,6 ionenes, there is a strong correlation in the F^-−F^- pair distribution function. Two distinct peaks can be noticed in the F^-−F^- PDF for the 6,6 ionene, one (broken green

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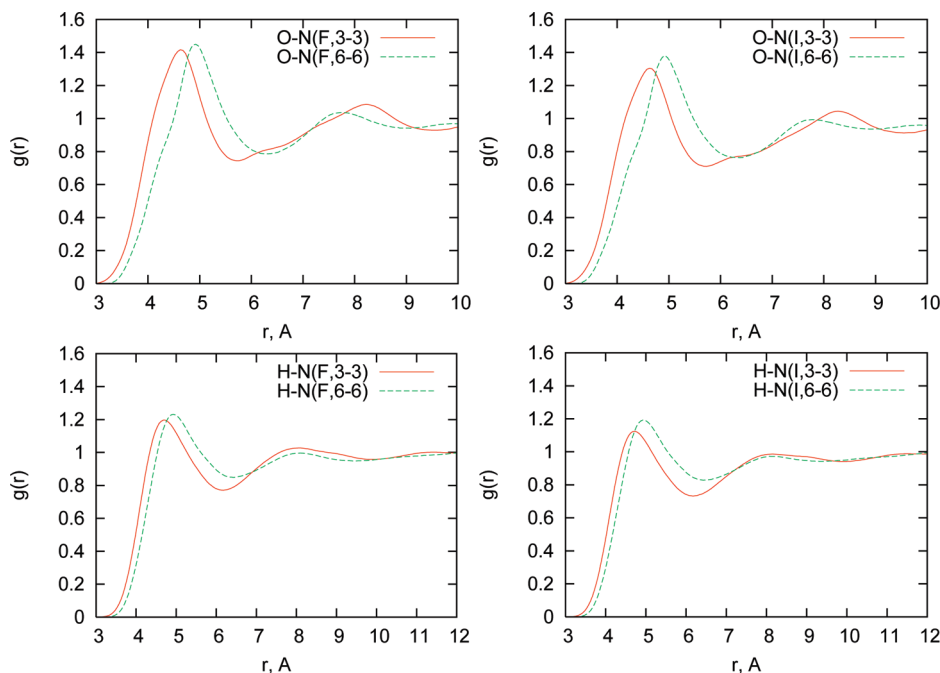
Figure 4. Nitrogen−oxygen (top) and nitrogen−hydrogen(water) (bottom) pair distribution functions for 3,3 (continuous red) and 6,6 ionene (broken green). Left panels show solutions with fluorine and the right ones show it with iodine ions.
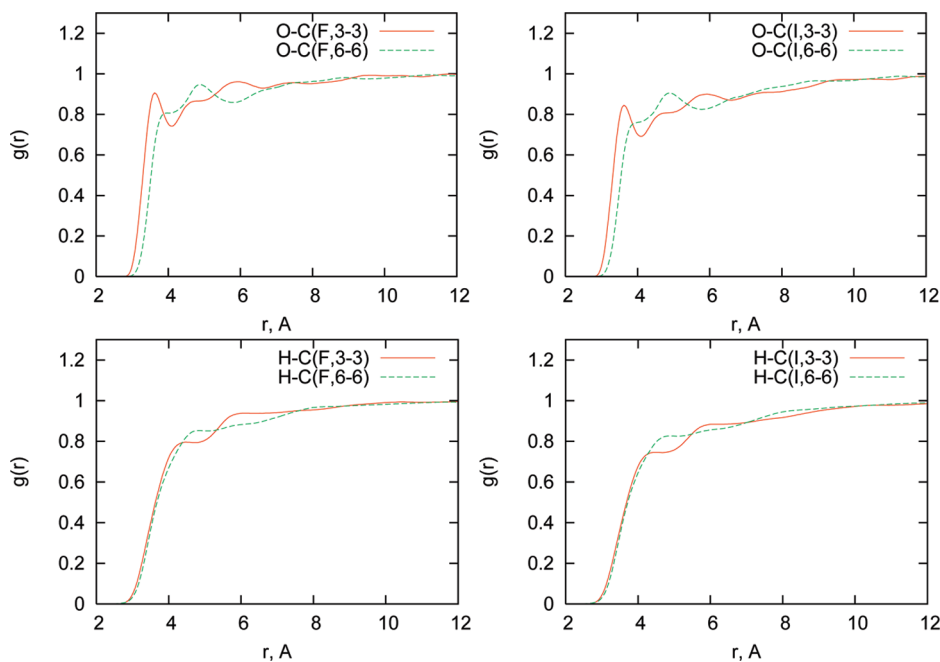

Figure 5. Same as Figure 4 but for carbon−oxygen and carbon−hydrogen(water) distributions.

line) at around 3.4 Å and the other at ∼4.0 Å. Snapshot analysis leads to the conclusion that the first (smaller) peak arises from the correlation of fluorine ions via Na^+ ions, caged by water molecules; the situation is schematically presented in Figure 9. For 3,3 ionene solutions, the 3.4 Å peak degenerates into the tiny shoulder.

The peak at 4.0 Å is water mediated, similarly as found before by Keasler and co-workers[37] (see also the references therein). We show the arrangement of particles (cf. Figure 3a of ref 37) in Figure 10. The water-mediated attraction between fluorine ions is for 3,3 ionenes reflected in a shoulder at 4.0 Å, which means that such structures are less frequent here. The main peak of the $F^-−F^-$ PDF, located at 4.4 Å, is lower in case of the 3,3 ionenes (full red line) and even lower for pure NaF solution in water at this concentration (0.28 mol/L). The arrangement of particles contributing to this peak is schematically shown in Figure 11.

Why is the $F^-−F^-$ correlation stronger for the more hydrophobic 6,6 than the 3,3 ionenes? The correlation functions shown in Figure 6 indicate that 6,6 ionene molecule is not "neutralized" at short distances and that there must be a region away from the ionene where there is an "excess" of the fluorine ions. Such a situation seems to favor Na^+ and/or water mediated correlation between the fluorine ions. The fluorine ions are attracted to the 3,3 ionene more strongly than to the 6,6 ionene (Figure 6, full lines). A possible explanation for a decrease of the 3,3 ionene correlation peak in Figure 8 may be related to the fact that relative "excess" of the F^- ions in the bulk region, which stimulates the $F^-−F^-$ attraction, is smaller for 3,3 ionene. This is supported by the fact that such an attraction is almost completely lost in pure NaF solution (dotted blue line in Figure 8).
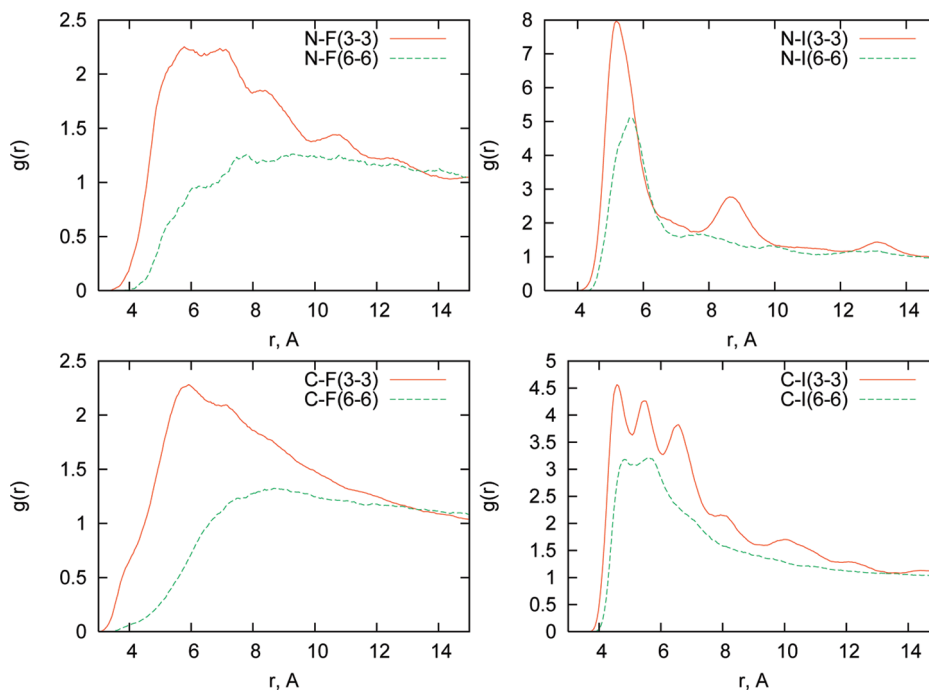
Figure 6. Counterion-nitrogen (top) and counterion-carbon(C) pair distribution functions (bottom) for 3,3 (continuous red lines) and 6,6 ionene (broken green lines).
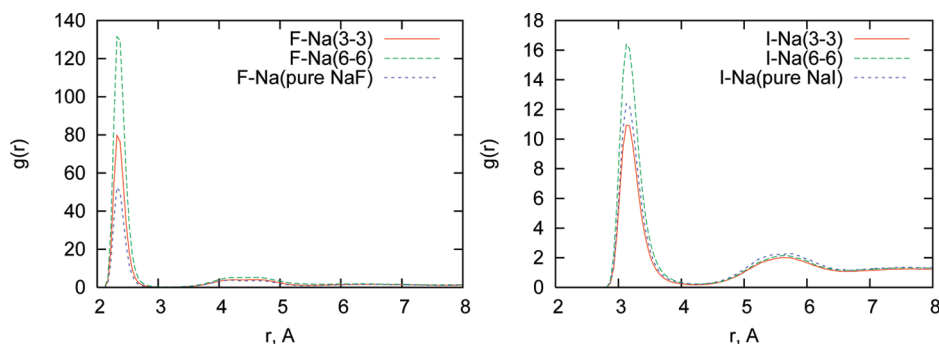

Figure 7. $F^- - Na^+$ (left panel) and $I^- - Na^+$ (right panel) pair distribution functions. The 3,3 ionene results are denoted by continuous red lines and the 6,6 ionene by broken green lines. The simulations of pure NaF and NaI solutions (dotted blue lines) correspond to the concentration 0.28 mol/L.
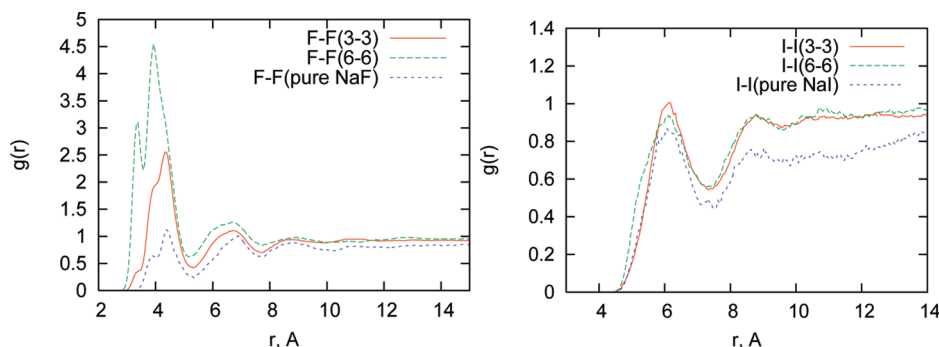

Figure 8. $F^- - F^-$ (left panel) and $I^- - I^-$ (right panel) PDFs. Notation as for Figure 7.

Iodine ions accumulate in the region close to the oligoion; as expected, they are less attracted by the 6,6 than 3,3 ionene (see right panels of Figure 6). In the right panel of Figure 8, we present the $I^- - I^-$ correlation functions for the 6,6 (broken green line), for the 3,3 (full red line) ionenes, as also for pure aqueous solution of NaI (dotted blue line). These plots do not show strong correlation among iodine ions as seen before for fluorines. Our snapshot analysis indicates that the cluster structures are much more open (see Figure 12) than

for fluorine ions. This is in our view a result of the iodine anions being weakly hydrated in comparison with fluorine ions. According to the data presented here the correlation between iodine ions results from high accumulation (Figure 6) of these ions around ionenes. The conclusion is supported by simulations of pure 3,3 and 6,6 ionene-iodine solutions (the results are not shown here); we found a higher $I^- - I^-$ peak in absence than in presence (more screening) of sodium ions.

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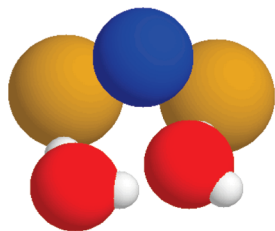
Figure 9. The configuration (schematically) of two fluorine ions (yellow) correlated by waters and a Na^+ ion (blue). For 6,6 ionene solution, the arrangement belongs to the first peak, positioned at 3.4 Å (cf. Figure 8). Notice that the sizes of the particles on the picture do not correspond the van der Waals size parameters.
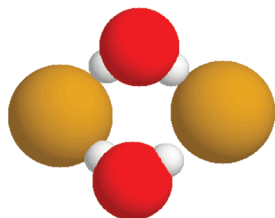
Figure 10. 6,6 ionenes (schematically). Two fluorine ions correlated by water molecules. The arrangement belongs to the peak position 4.0 Å in Figure 8. For 3,3 ionenes such an arrangement is indicated by a shoulder in the PDF at this distance.
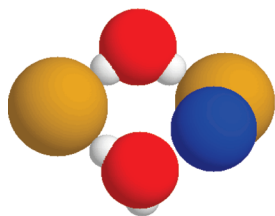
Figure 11. 3,3 ionenes (schematically). The configuration of two fluorine ions (yellow) correlated by waters and a Na^+ ion (blue); the arrangement belongs to the peak at 4.4 Å (Figure 8). Such an arrangement of particles can also be found in pure NaF solution.
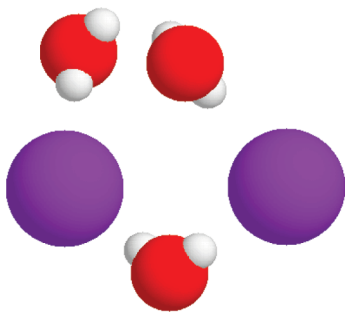
Figure 12. An arrangement (schematically) of two iodine ions (violet) correlated via water molecules, contributing to the peak at 6.0 Å.

IV. Comparison with Experimental Data

Extensive studies have been carried out of the thermodynamic and transport properties of 3,3, 4,5, 6,6, and 6,9 ionenes in aqueous solutions with various halide anions.[9–13] The results are summarized as follows: (i) The osmotic and activity coefficients are considerably lower than predicted by the implicit-solvent cell-model theory (cf. Figure 5 of ref 13). (ii) A similar disagreement between theory and experiment holds true also for the conductivity measurements.[11] (iii) The enthalpies of dilution (ΔH_D) of 3,3 and 4,5 ionene solutions with bromide and chloride counterions (these counterions are chaotropes) are endothermic,[12] while the corresponding solutions of more hydrophobic 6,6 and 6,9 ionenes produce exothermic

effect. (iv) Further, for 3,3 ionene fluoride (F^- is strong kosmotrope) solutions we found that heat is released upon dilution.[38] The well-established polyelectrolyte theories, such as the cylindrical cell model based on the Poisson–Boltzmann equation[1–3] or the Manning theory,[15,16] have been used to analyze these data. In these two approaches, the solvent is treated as a dielectric continuum. Both predict $\Delta H_D < 0$, the sign of which is the opposite from the experimental data. Ion-specific effects were also revealed in our recent dielectric relaxation study.[14]

How do our simulation results compare with the unusual physicochemical behavior of ionene solutions? Here we discuss the osmotic coefficient measurements published in ref 13. Thermodynamically the osmotic coefficient ϕ is defined as

$$\varphi = -\frac{n_1}{n_2} \ln a_1 \qquad (2)$$

where n_1 is the number of moles of solvent, n_2 is the number of moles of solute, and a_1 is the activity of solvent. The latter is proportional to the vapor pressure (more exactly fugacity) of the solvent $a_1 \propto P_1$. Low osmotic pressure is therefore a reflection of a high solvent vapor pressure, that is, an increased tendency of solvent molecules to escape into the vapor phase. As found in our previous study (see, Figure 5 of ref 13), the disagreement between the ϕ values, calculated by the implicit-solvent Poisson–Boltzmann approach, and the experimental data increases with increasing hydrophobicity of the ionene chain. This finding is confirmed by experimental studies of the activity coefficient[10,11] at 298 K; in summary, the 6,6 (and 6,9) ionenes exhibit stronger deviations from the electrostatic theory than the 3,3 ionenes. To show that this is not an isolated result for weakly charged macromolecules, we presented in Figure 6 of ref 13 a compilation of the osmotic coefficient data for various polyelectrolytes as a function of their charge density parameter λ.

In summary, the measured osmotic coefficients for 6,6 ionenes are considerably lower than calculated by the continuum-solvent approaches. According to eq 2 this indicates high vapor pressure of the solvent. The experimental result can be explained by the water-ionene interaction presented in the form of the site–site distribution functions in Figures 4 and 5 where we see a shift in the water(oxygen)-6,6 ionene distribution functions toward the larger distances. The extra hydrophobic groups in 6,6 ionene enhance the escaping tendency of water molecules, leading to a somewhat higher water vapor pressures and accordingly to lower osmotic pressures. Of course, the osmotic coefficients of the less charged 6,6 ionenes are higher than the corresponding 3,3 ionenes due to the weaker Coulomb interaction. However, as described above, this increase is not as strong as predicted by the implicit-solvent approach.[13]

The values of the enthalpy of dilution[3,12,39–42] are, as amply documented in the literature, sensitive to the nature of the counterion-polyion combination. It has been found experimentally that cosmotropic ions, such as Li^+, H^+, or F^-, yield exothermic effect, $\Delta H_D < 0$, upon dilution in good agreement with electrostatic theories.[3,41] On the other hand, chaotropes, like Cs^+ (at lower temperatures[41]), or Cl^- and Br^- ions[12] exhibit strong deviations from the theory[3,15] and yield $\Delta H_D > 0$. Unfortunately the enthalpy of dilution, that is, the difference in enthalpy between the diluted and concentrated states, cannot be calculated accurately by the simulation procedure used here. Numerical errors of the individual enthalpy simulations are

simply too large to allow a meaningful calculation of the enthalpy difference upon dilution, ΔH_D.

V. Conclusions

Here, we performed molecular dynamics simulations in explicit water of the pair correlation functions between various ions or sites on water on the one hand, and the ionene oligoion on the other hand. New results are presented for 6,6 ionenes with the F^-, Cl^-, Br^-, and I^- counterions, and sodium ions as co-ions. These results are compared with corresponding data, obtained previously for more highly charged 3,3 ionenes. The extra methylene groups present on the 6,6 ionenes cause water molecules to shift away from the oligoion, causing a small "gap" in water population near the 6,6 ionene. The model simulations are consistent with the osmotic measurements for these solutions, which can be summarized as (i) the Br^- counterion yields lower osmotic coefficients in aqueous solutions than its Cl^- counterpart, (ii) the osmotic coefficient increases in the direction from strongly charged 3,3 to weakly charged 6,6 ionenes, and (iii) the increase in the osmotic coefficient is considerably less than suggested by the continuum-solvent theories. The latter effect is probably due to the fact that hydrophobic groups contribute to the decrease of the osmotic pressure. Another important outcome of this simulation is the result that water and co-ion mediated attraction between the counterions may be enhanced in the presence of the weakly charged polyelectrolyte. The effect is ion-specific. The results presented in this study explain some discrepancies between the continuum-solvent polyelectrolyte theories and experimental data found for weakly charged polyelectrolyte solutions.

References and Notes

(1) Alexandrowicz, Z.; Katchalsky, A. *J. Polymer Sci., Part A: Polym. Chem.* **1963**, *1*, 3231–3260.
(2) Katchalsky, A. *Pure Appl. Chem.* **1971**, *26*, 327–373.
(3) Dolar, D. Thermodynamic properties of polyelectrolyte solutions. In *Polyelectrolytes*; Selegny, E., Mandel, M., Strauss, U. P., Eds.; D. Reidel Publishing Co.: Dordrecht, Holland, 1974; pp 97–113.
(4) Schmitz, K. S. *Macroions in Solution and Colloidal Suspension*; VCH: New York, 1993.
(5) Dautzenberg, H.; Jaeger, W.; Kötz, J.; Philipp, B.; Seidel, C.; Stscherbina, D. *Polyelectrolytes. Formation, Characterization and Application*; Hanser: Munich, 1994.
(6) Forster, S.; Schmidt, M. Physical Properties of Polymers. *Adv. Polym. Sci.* **1995**, *120*, 51–133.
(7) Vlachy, V.; Hribar Lee, B.; Reščič, J.; Kalyuzhnyi, Yu. V. Ionic Soft Matter: Modern Trends in Theory and Applications. In *NATO Science Series II: Mathematics, Physics and Chemistry*; Henderson, D.; Holovko, M.; Trokhymchuk, A., Eds.; Springer: New York, 2005; p 206.
(8) Yethiraj, A. *J. Phys. Chem. B* **2009**, *113*, 1539–1551.
(9) Casson, D.; Rembaum, A. *Macromolecules* **1972**, *5*, 75–79.
(10) Nagaya, J.; Minakata, A.; Tanioka, A. *Langmuir* **1999**, *15*, 4129–4134.
(11) Nagaya, J.; Minakata, A.; Tanioka, A. *Colloids Surf., A* **1999**, *148*, 163–169.
(12) Arh, K.; Pohar, C. *Acta Chim. Slov.* **2001**, *48*, 385–394.
(13) Arh, K.; Pohar, C.; Vlachy, V. *J. Phys. Chem. B* **2002**, *106*, 9967–9973.
(14) Lukšič, M.; Hribar Lee, B.; Vlachy, V.; Büchner, R. *Macromolecules* **2009**, *42*, 4337–4342.
(15) Manning, G. S. *J. Chem. Phys.* **1969**, *51*, 924–933.
(16) Manning, G. S. *J. Chem. Phys.* **1969**, *51*, 934–938.
(17) Druchok, M.; Hribar Lee, B.; Krienke, H.; Vlachy, V. *Chem. Phys. Lett.* **2008**, *450*, 281–285.
(18) Druchok, M.; Vlachy, V.; Dill, K. A. *J. Chem. Phys.* **2009**, *130*, 134903–1134903–8.
(19) Bulone, D.; Martorana, V.; San Biagio, P. L.; Palma-Vittorelli, M. B. *Phys. Rev. E* **2000**, *62*, 6799–6809.
(20) Dzubiella, J.; Hansen, J.-P. *J. Chem. Phys.* **2004**, *121*, 5514–5530.
(21) Chorny, I.; Dill, K. A.; Jacobson, M. P. *J. Phys. Chem. B* **2005**, *109*, 24056–24060.
(22) Jorgensen, W. L.; Maxwell, D. S.; Tirado-Rives, J. *J. Am. Chem. Soc.* **1996**, *118*, 11225–11236.
(23) Aqvist, J. *J. Phys. Chem.* **1990**, *94*, 8021–8024.
(24) Palinkas, G.; Riede, O.; Heinzinger, K. *Z. Naturforsch., A: Phys. Sci.* **1977**, *32*, 1137–1145.
(25) Berendsen, H. J. C.; Grigera, J. R.; Straatsma, T. P. *J. Phys. Chem.* **1987**, *91*, 6269–6271.
(26) Melchionna, S.; Ciccotti, G.; Holian, B. L. *Mol. Phys.* **1993**, *78*, 533–544.
(27) Chang, R.; Yethiraj, A. *Macromolecules* **2006**, *39*, 821–828.
(28) Chialvo, A. A.; Simonson, J. M. *J. Phys. Chem. B* **2005**, *109*, 23031–23042.
(29) Chialvo, A. A.; Simonson, J. M. *J. Mol. Liq.* **2007**, *134*, 15–22.
(30) Jerman, B.; Podlipnik, C.; Kogej, K. *Acta Chim. Slov.* **2007**, *54*, 509–516.
(31) Chang, R.; Yethiraj, A. *Macromolecules* **2005**, *38*, 607–616.
(32) Vlachy, V. *J. Chem. Phys.* **1982**, *77*, 5823–5825.
(33) Lamoureux, G.; Roux, B. *J. Phys. Chem. B* **2006**, *110*, 3308–3322.
(34) Zhang, Y.; Cremer, P. *Curr. Opin. Chem. Biol.* **2006**, *10*, 658–663.
(35) Lund, M.; Vrbka, R.; Jungwirth, P. *J. Am. Chem. Soc.* **2008**, *130*, 11582–11583.
(36) Fennell, C. J.; Bizjak, A.; Vlachy, V.; Dill, K. A. *J. Phys. Chem. B* **2009**, *113*, 6782–6791.
(37) Keasler, S. J.; Nellas, R. B.; Chen, B. *J. Chem. Phys.* **2006**, *125*, 144520–1144520–5.
(38) Čebašek, S.; Lukšič, M.; Pohar, C.; Vlachy, V., unpublished material.
(39) Daoust, H.; Chabot, M.-A. *Macromolecules* **1980**, *13*, 616–619.
(40) Hales, P. W.; Pass, G. *Eur. Polym. J.* **1981**, *17*, 651–659.
(41) Vesnaver, G.; Rudež, M.; Pohar, C.; Škerjanc, J. *J. Phys. Chem.* **1984**, *88*, 2411–2418.
(42) Vlachy, V. *Pure Appl. Chem.* **2008**, *80*, 1253–1266.

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