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Molecular dynamics study of the hydrophobic 6,6-ionene oligocation in aqueous solution with sodium halides*

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Abstract: An explicit water molecular dynamics (MD) simulation is presented of a solution modeling aliphatic 6,6-ionene oligocations mixed with low-molecular-weight electrolytes. In all cases, the co-ions were sodium cations and the counterions were fluoride, chloride, bromide, or iodide anions. The simple point charge/extended (SPC/E) model was used to describe water. The results of the simulation at T = 278 K (the data for 298 K were obtained earlier) and T = 318 K are presented in the form of pair distributions between various atoms and/or between ions in the system. We were interested in how temperature variation modifies the ion-specific effects, revealed by the various pair distribution functions (PDFs). The results were compared with previous calculations for the less hydrophobic 3,3-ionene solutions. Simulations of 6,6-ionene solutions containing mixtures of fluoride and iodide counterions at T = 298 K were also presented.

Keywords: 3,3-ionene oligocations; 6,6-ionene oligocations; molecular dynamics; pair distribution functions; simple point charge/extended model.

INTRODUCTION

Polyelectrolytes are polymers containing groups that can ionize in an appropriate solvent (for a review, see refs. [1–6]). They have complex properties and find many applications in industry [7]. Their theoretical description is most often based on the cylindrical cell model; see, for example, [1,2] or the Manning condensation approach [8,9]. These macromolecules contain ionic and hydrophobic groups and can therefore serve as prototypes for biological materials, such as nucleic acids and proteins. In this paper, we model the properties of cationic polyelectrolytes called ionenes. Aliphatic *x*,*y*-ionenes can be prepared with varying degree of hydrophobicity; *x* and *y* refer to the numbers of methylene groups between the two quaternary ammonium atoms. Interestingly, even very hydrophobic 10,10-ionenes are soluble in water [10]. So far, the 3,3-, 4,5-, 6,6-, and 6,9-ionenes have been examined using different experimental methods [11–18]. The *x*,*y*-ionenes, therefore, form a homologous series, which allows the study of the effect of increasing hydrophobicity on the polyion–counterion interaction. A better understanding of this effect, accompanied by the hydration and dehydration of interacting ionic species, is of considerable importance for the biological sciences.

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Only a few explicit water molecular dynamics (MD) studies of charged oligomers have been published so far [19–24]. Recently, in a series of papers [25–27] we utilized this approach to gain a more molecular view of aqueous solutions of 3,3- and 6,6-ionene oligomers in mixtures with various sodium halides. Notice that the two polyelectrolytes differ widely in the length of the monomer unit, b, carrying one positive charge. For 3,3-ionenes, b = 0.498 nm, while for 6,6-ionene it is 0.879 nm. According to the condensation theory of Manning [8,9], the counterions of 3,3-ionene (in water at 298 K) undergo "condensation" on the polyion (b < 0.714 nm), which is not the case for the 6,6-ionene salts, where b > 0.714 nm. In the preceding contribution [27], we simulated aqueous solutions of 6,6-ionene oligoions (six monomer units long) neutralized with fluoride, chloride, bromide, or iodide counterions. In all cases, the sodium ion was present as co-ion. All these calculations applied to a single temperature of T = 298 K. The results for pair distribution functions (PDFs) between various sites were compared with the corresponding functions for the (more highly charged) 3,3-ionenes, and interesting differences were observed. This makes it of value to extend the study to other temperatures (in this paper to 278 and 318 K) to examine the influence of temperature on the hydration of counterions and oligoions, as well as on their mutual interaction. The results are then compared with the temperature dependence study of more highly charged 3,3-ionenes [25,26]. Notice that the short-range, water-induced interactions are expected to have a different temperature dependence than the long-range Coulomb forces prevailing in 3,3-ionenes. In addition, we present simulations of 6,6-ionene solutions containing mixtures of fluoride and iodide counterions at T = 298 K.

MODEL AND METHOD

The model for 6,6-ionene (Fig. 1) and its construction were described elsewhere [27]. The charges (Z) and the Lennard–Jones parameters (σ_i, ε_i) assigned to the various atoms or ions were the same as used in refs. [25–27]. The ionene molecules were represented by chains with six monomer units each, while every monomer unit consisted of six methylene groups and a quaternary nitrogen atom.

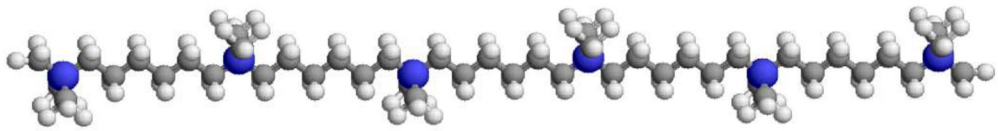

Fig. 1 Schematic representation of the 6,6-ionene 6-mer oligoion. Nitrogens are denoted by large blue circles, carbons by gray circles, and hydrogens by white circles.

MD 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). The standard DL_POLY package was used for the purpose. All the species were allowed to move freely across the basic simulation cell. The long-range Coulomb interactions were taken into account by the Ewald summation technique. The cut-off distance for short-range interactions was set to 15 Å. The concentration c_s of added simple electrolyte Na^+X^- (X^- stands for one of the halide anions) was about 0.28 mol/l, which was twice as large as the concentration of counterions. An excess of the low-molecular electrolyte was added to screen the interaction between the ionene oligoions. The conditions studied were equal to those for the 3,3- and 6,6-ionene solutions investigated in our previous studies [25–27]. The pressure (1 bar) and temperature were controlled by means of the Nose–Hoover baro- and thermostat in an isotropic N,P,T ensemble [28]. The relaxation times for thermo- and barostat were set to 0.05 and 1.0 ps, respectively. The particles were placed in a cubic box with periodic boundary conditions. The averaged box length for ionene solution with F^- counterions was ≈52.3 Å, in solution with Cl^- ions 52.6 Å in solution with Br^- ions 52.7 Å, and for I^- ions it was 52.9 Å. The equilibration pro-

cedure required 2×10^5 time steps, and the production runs were performed over 4×10^6 steps. We used the velocity Verlet algorithm with a time step of $\tau = 5 \times 10^{-16}$ s to integrate the classical equations of motion for the system under consideration [25–27].

The question can be raised to what extent the simulated molecules stretch and bend upon solvation. To answer this, one would need to monitor the N–N distances of neighboring as well as non-neighboring ammonium groups. Our observation is that the oligoion is slightly overstretched in comparison with Fig. 1; the effect seems to be due to the positive charges on the polymer backbone. In addition, we found that the angle between two consecutive monomer units fluctuates for about 3° around the theoretical value.

RESULTS

PDFs between the various charged sites on the ionene oligoions and those on ions and water represent the main result of this study. These functions for 6,6-ionene solutions, modeled as described above, are presented at T = 278, 298, and 318 K. The results for 298 K were recently published in ref. [27] but some of them, together with the results for the other two temperatures, are shown here for the sake of completeness.

Ionene hydration

First, we discuss the hydration of nitrogen atoms in 6,6-ionene solutions in the presence of various counterions and sodium ions as co-ions. In Fig. 2, we present the nitrogen–oxygen(water) PDFs. The correlation between water oxygen and nitrogen increases with decreasing temperature; the peaks of all nitrogen–oxygen PDFs are the highest at T = 278 K. Similar behavior was previously found for 3,3-ionenes under such conditions.

In Fig. 3, a comparison between nitrogen–oxygen(water) PDFs for three solutions (two different sodium halides and the "no salt" case) at T = 298 K is presented. By "no salt", we mean the results for a solution of ionene oligoion in pure water, i.e., without counterions and co-ions present. It can be seen that the nitrogen of the 6,6-ionene is most strongly solvated when no low-molecular-weight ions are present ("no salt" case) and in the presence of sodium fluoride solutions. The increase of counterion size leads to a slight decrease of the first peak with the sequence $F^- > (Cl^- > Br^- >) I^-$. This indicates that larger ions "bring" less water to the nitrogen. This conclusion coincides with our finding for 3,3-ionenes [25,26]. The results for bromide and chloride anions are not shown to make this figure easy to read.

In Fig. 4 we show the carbon (methylene group)–oxygen(water) distributions. The temperature effect is analogous to that observed for the nitrogen–oxygen PDFs. The height of the first peak decreases in the order $F^- > Cl^- > Br^- > I^-$. The result is consistent with the corresponding result for the 3,3-ionenes [25,26].

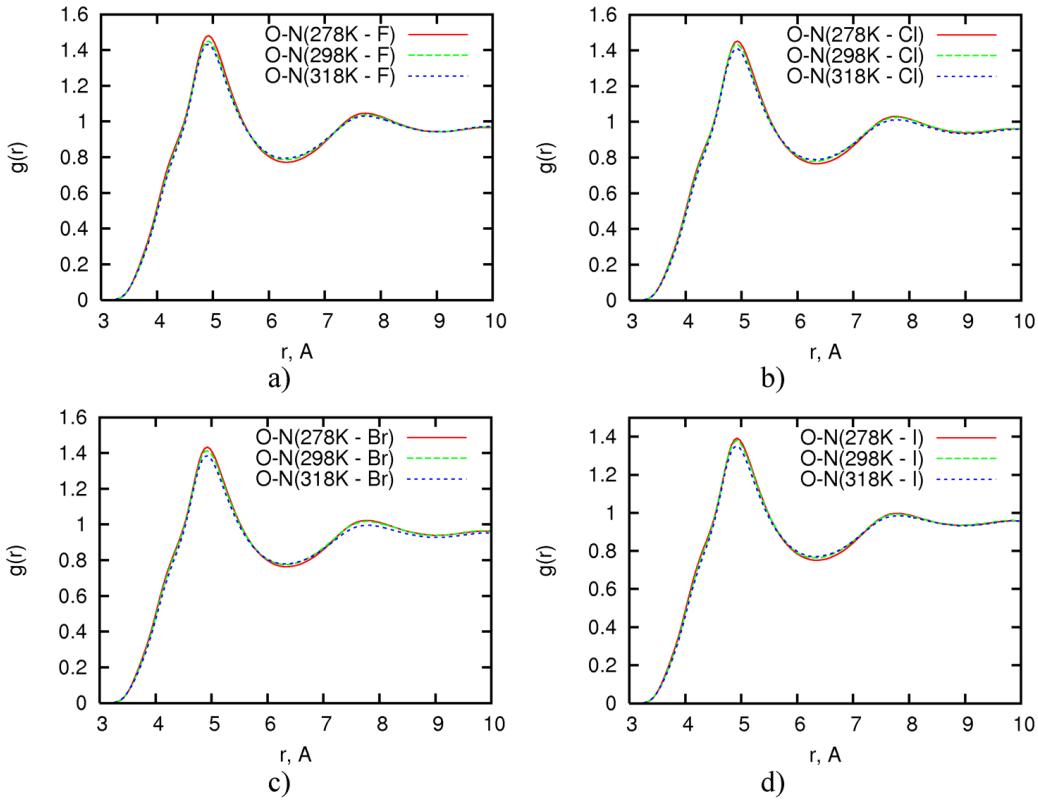

Fig. 2 Nitrogen–oxygen(water) PDFs for the 6,6-ionene in aqueous solution with sodium halides. Panel (a) represents results for solutions with F^-, (b) Cl^-, (c) Br^-, and (d) I^- counterions. The results for T = 278 K are denoted by continuous lines, for 298 K by long-dashed lines, and for T = 318 K by short-dashed lines.

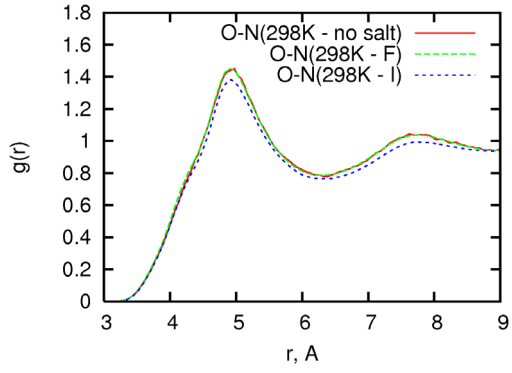

Fig. 3 Nitrogen–oxygen(water) PDFs at T = 298 K. The continuous line denotes results with no counterions and co-ions present ("no salt"), the long-dashed line (coinciding with the continuous one) applies to a solution with added NaF and the short-dashed line to the mixture with NaI.

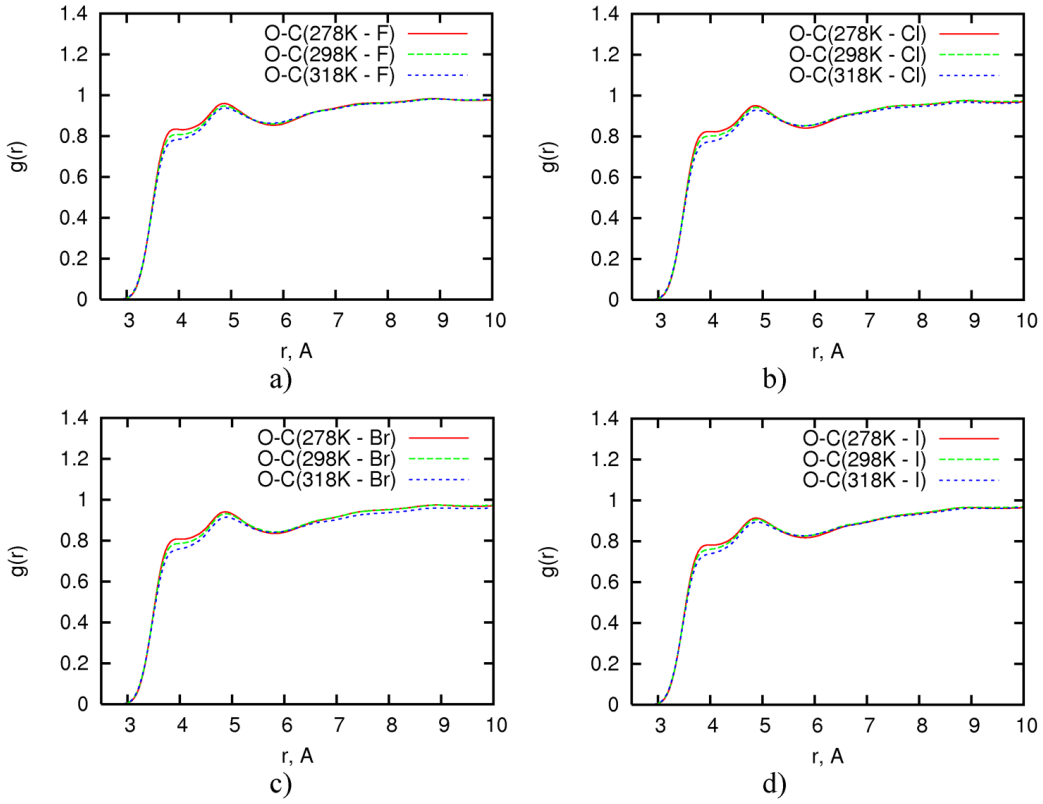

Fig. 4 Carbon (methylene group)–oxygen(water) PDFs for 6,6-ionene in aqueous solution with sodium halides. Panel (a) represents results for solutions with F^-, (b) Cl^-, (c) Br^- and (d) I^- counterions. The results for $T = 278$ K are denoted by continuous lines, for 298 K by long-dashed lines, and for $T = 318$ K by short-dashed lines.

Counterion–ionene distributions

The temperature dependence of the counterion–nitrogen distributions is discussed next. The corresponding PDFs are displayed in Fig. 5. As for the 3,3-ionenes, the temperature dependence of the PDFs varies from anion to anion. Let us focus on the fluoride and iodide ions first. The former is known to attract water very strongly (kosmotrope) while the latter is only poorly hydrated (chaotrope). According to Fig. 5 (panel a; continuous red line), the attraction between nitrogen and fluoride ions seems to be the strongest in a "cold" solution at 278 K. For the iodide ion, the temperature influence on PDFs is weak, but the ordering is similar: the peak of the PDF between the nitrogen and iodide ions is the highest for $T = 278$ K. The same also holds true for chloride counterions. Among the ions studied here, bromide ion is an exception to this ordering. The non-monotonic temperature dependence shown here seems to be a consequence of competition between the ionene–counterion electrostatic attraction and hydration effects.

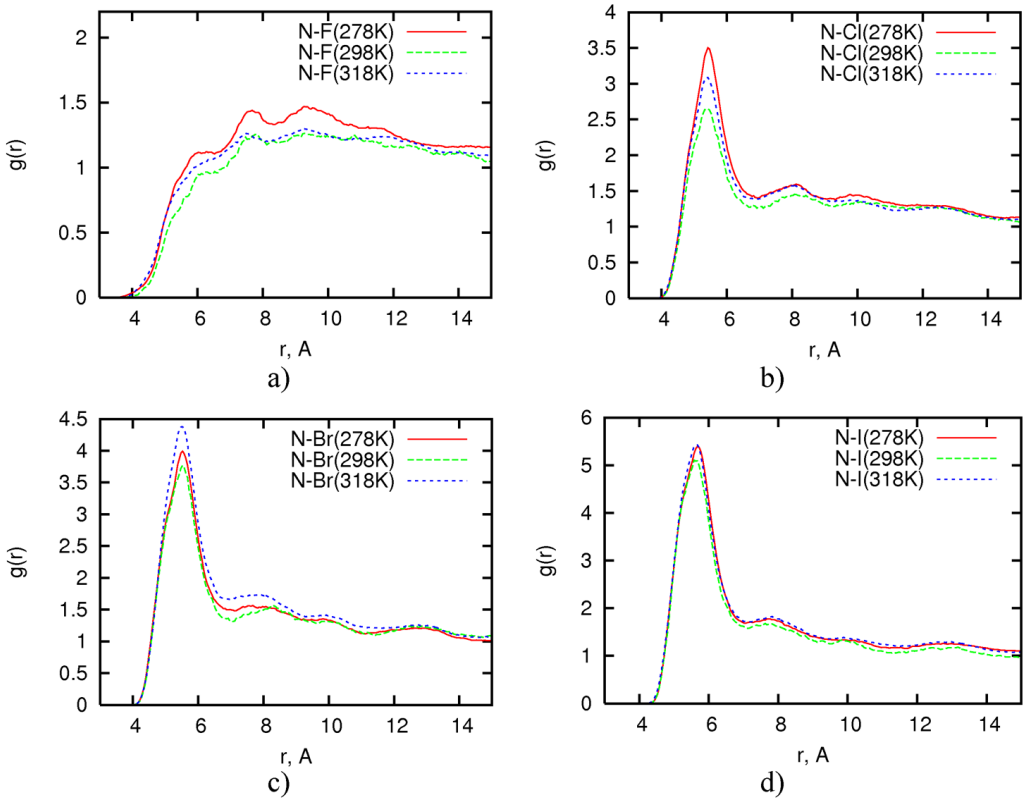

Fig. 5 Nitrogen–counterion PDFs for 6,6-ionene in aqueous solution with sodium halides. Panel (a) represents results for solutions with F^-, (b) Cl^-, (c) Br^-, and (d) I^- counterions. The results for T = 278 K are denoted by continuous lines, for 298 K by long-dashed lines, and for T = 318 K by short-dashed lines.

It is of considerable interest to analyze the counterion distributions near the methylene groups. Notice that 6,6-ionenes are only weakly charged; there are six methylene groups between two quaternary nitrogen atoms carrying positive charge. These results are shown in the next set of graphs, presented in Fig. 6. The temperature dependence of the fluoride–carbon(methylene group) distribution function is analogous to that of the fluoride–nitrogen distribution shown above: the fluoride–carbon attraction is the strongest in "cold" solution (T = 278 K) and weakens with temperature increase. Similar behavior is observed for the iodide–carbon pair distributions. Again, the bromide ion does not conform to this ordering, exhibiting the strongest correlation peak at 318 K.

Next we compare the results for 6,6-ionenes, presented in this paper, with the temperature dependence of PDFs for the 3,3-ionenes. The 3,3-ionenes are much less hydrophobic than their 6,6 counterparts since they only have three methylene groups between the two quaternary nitrogens. The nitrogen–counterion PDFs are shown in Fig. 5 of ref. [26]. Notice that the ordering with respect to temperature variation is different for 3,3-ionene fluoride solution than for the corresponding 6,6 salt. For the more highly charged 3,3-ionene fluoride solution, the nitrogen–counterion correlation is the strongest at T = 318 K, and the weakest at 278 K, just the opposite to the 6,6-ionene fluorides. The situation is, however, different for iodide ions. Here the correlation with nitrogen is the strongest for T = 278 K and the weakest for 318 K in both cases, that is for both the 3,3- and the 6,6-ionene salts.

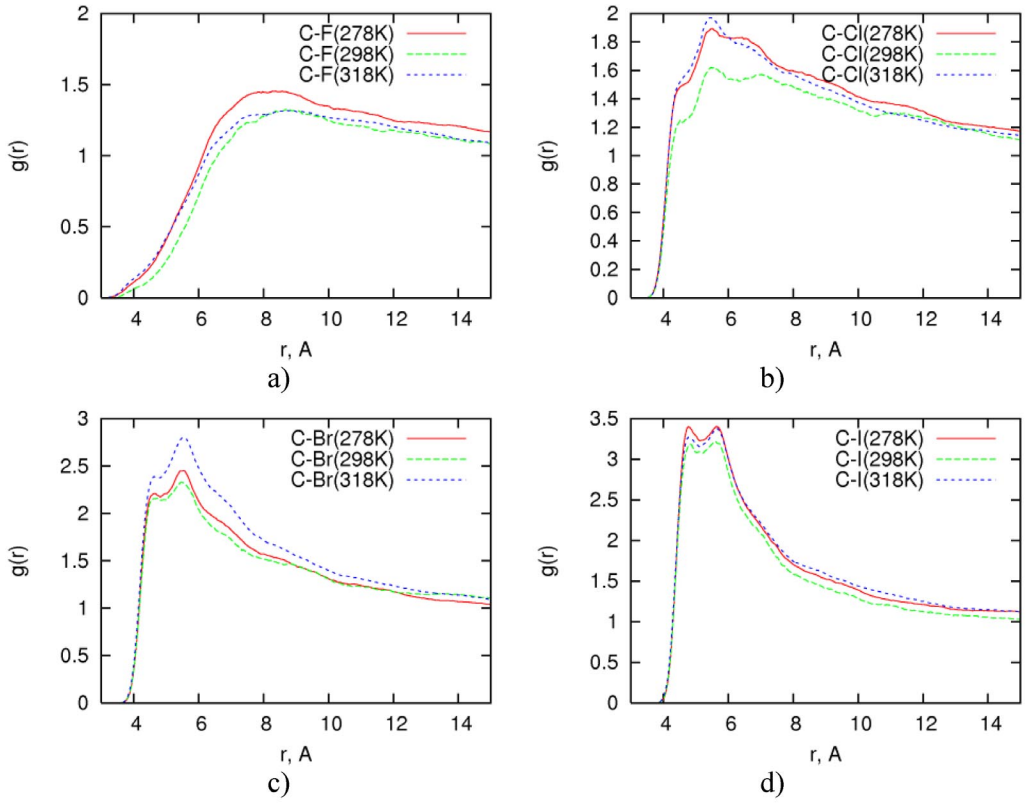

Fig. 6 Carbon(methylene group)–counterion PDFs for 6,6-ionene in aqueous solution with sodium halides. Panel (a) corresponds to solutions with F^-, (b) Cl^-, (c) Br^-, and (d) I^- counterions. The results for $T = 278$ K are denoted by continuous lines, for 298 K by long-dashed lines, and for $T = 318$ K by short-dashed lines.

Finally, to complement the picture, we discuss the temperature dependence of the carbon(methylene group)–counterion distribution functions for both types of ionenes. The simulation data for 3,3-ionenes are presented in Fig. 7 of ref. [26]. The temperature dependence is the same as in case of the nitrogen–counterion correlation discussed above; see Figs. 5 and 7 of ref. [26]. In summary: the temperature dependence of the fluoride–carbon(methylene group) correlation functions are different for 3,3- and 6,6-ionenes. On the other hand, the iodide–carbon(methylene group) correlation functions exhibit the same behavior in the case of 3,3- and 6,6-ionene solutions.

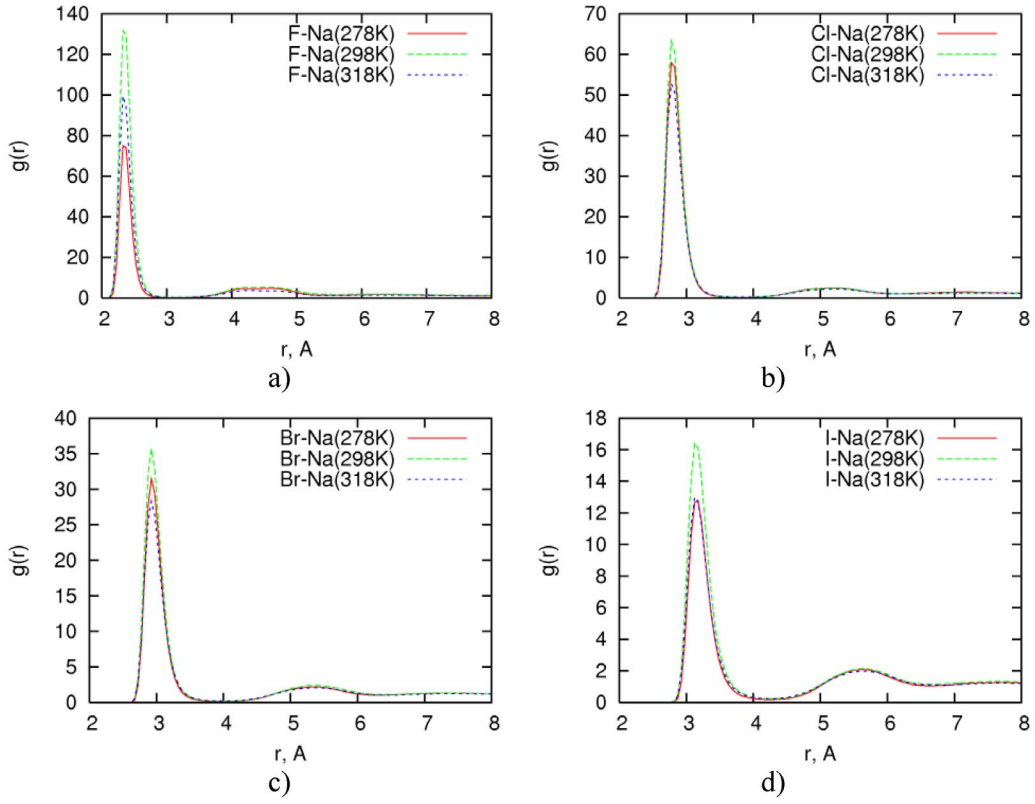

Fig. 7 Counterion–co-ion PDFs for 6,6-ionene in aqueous solution with sodium halides. Panel (a) corresponds to solutions with F^-, (b) Cl^-, (c) Br^-, and (d) I^- counterions. The results for $T = 278$ K are denoted by continuous lines, for 298 K by long-dashed lines, and for $T = 318$ K by short-dashed lines.

Counterion–co-ion distributions

The counterion–co-ion PDFs for 6,6-ionene in aqueous solution with sodium halides are shown in Fig. 7. These results reveal a strong correlation between the counterions and co-ions; especially in the case of fluoride counterions. This effect has been noticed before [27]; the co-ions compete with the ionene molecules for counterions and they are more successful in the case of the weakly charged 6,6-ionenes. The temperature dependence does not show a particular regularity, demonstrating the complexity of the system. The strongest correlation between sodium ions and different halide counterions is found at the intermediate temperature, $T = 298$ K. This seems to be a consequence of the relatively weak correlation between the counterions and ionene molecule at this temperature, as seen in Figs. 5 and 6. Obviously, at $T = 298$ K the net interaction between the species present favors the counterion–co-ion correlation at the expense of the counterion–ionene correlation.

Water- and/or sodium-assisted correlation between counterions

In this subsection, we analyze the counterion–counterion distribution functions. In Fig. 8 we present the F^-–F^-, Cl^-–Cl^-, Br^-–Br^-, and I^-–I^- PDFs at three different temperatures. A surprisingly strong F^-–F^- correlation has previously been noticed for 6,6-ionenes, and explained by the clustering of counterions via either water molecule or/and sodium ions (see Figs. 8–11 presented in ref. [27]). No such clustering has been noticed for iodide ions [27]. The effect has its origin in the fact that fluoride ions hold their

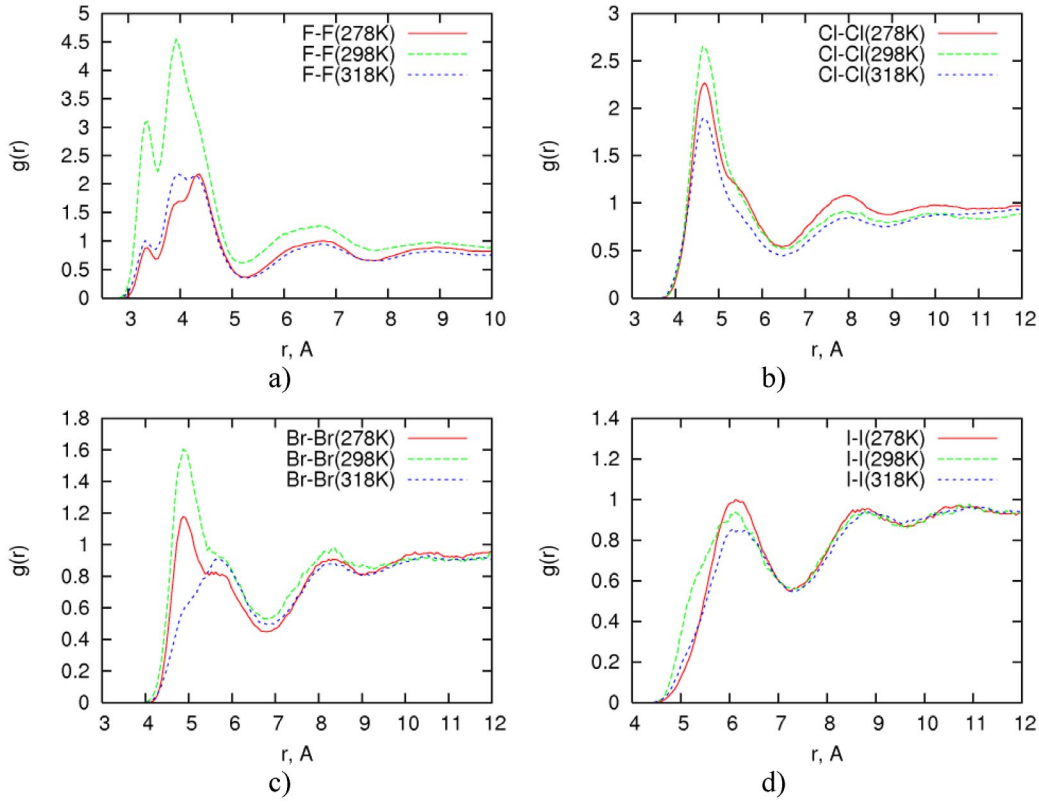

Fig. 8 Counterion–counterion PDFs for 6,6-ionene in aqueous solution with various sodium halides. Panel (a) corresponds to solutions with F^-, (b) Cl^-, (c) Br^-, and (d) I^- anions. The results for $T = 278$ K are denoted by continuous lines, for 298 K by long-dashed lines, and for $T = 318$ K by short-dashed lines.

waters tightly and are therefore not located immediately next to 6,6-ionene oligoion as the iodide ions are. For this reason, there must be a region in the bulk where F^- ions are in excess and can efficiently correlate with Na^+ ions. In Fig. 8, the temperature dependence of this effect is examined. Consistent with the results shown in Fig. 7, the temperature dependence indicates the strongest F^-–F^- correlation at $T = 298$ K. The results for other counterions differ; for iodide the temperature dependence is weak but clearly opposite to that exhibited by the other anions studied here.

The like–charge distributions

The co-ion–nitrogen and co-ion–co-ion PDFs are discussed next. First, in Fig. 9 we present the temperature dependence of co-ion–nitrogen distributions. Since the co-ions (sodium ions) carry the charge of the same sign as ionene chains the two species repel each other and are accordingly distributed at larger distances. All the co-ion–nitrogen distributions have characteristic peaks at 6 Å, indicating a weak penetration of the sodium ion into the ionene hydration shell. Similar peaks were for more highly charged 3,3-ionenes noticed at 5.5 Å (see Fig. 8 of [26]). The temperature produces rather small effect on the Na^+–nitrogen correlation functions in presence of Br^- and I^- counterions, while in the case of the F^- and Cl^- counterions, a tendency of weakening of correlations with the temperature increase is observed.

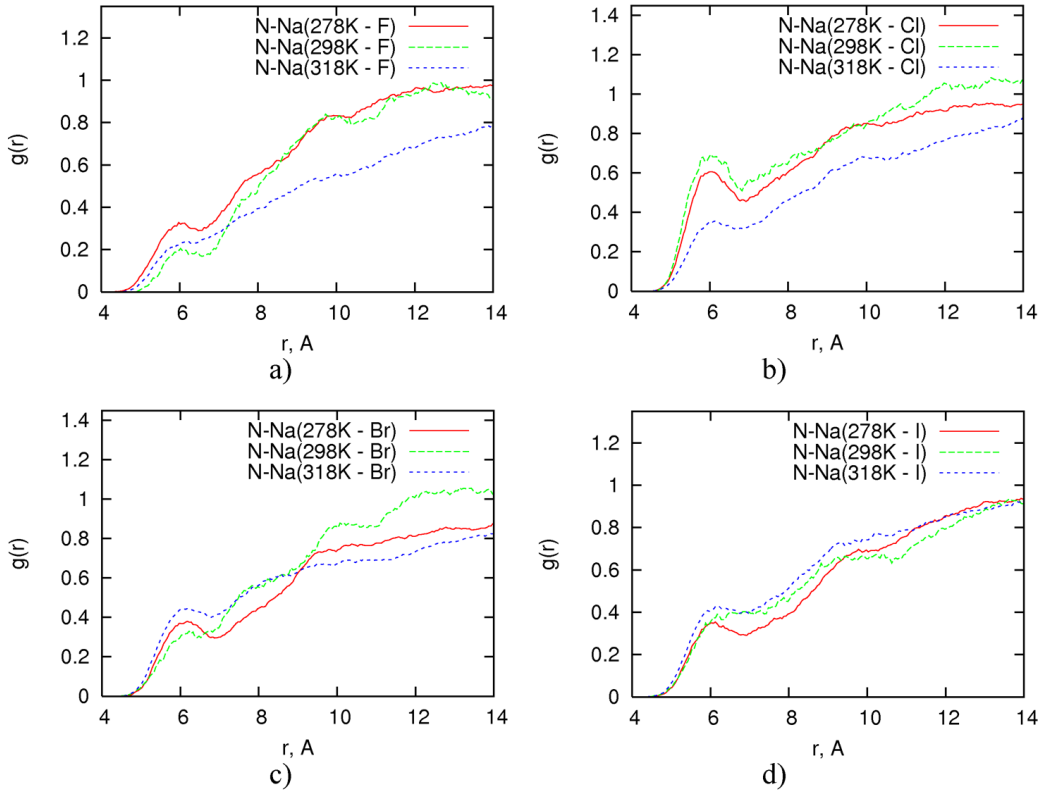

Fig. 9 Nitrogen–co-ion PDFs for 6,6-ionene in aqueous solution with sodium halides. Panel (a) shows results for solutions with F^-, (b) Cl^-, (c) Br^-, and (d) I^- counterions. The results for $T = 278$ K are denoted by continuous lines, for 298 K by long-dashed lines, and for $T = 318$ K by short-dashed lines.

The co-ion–co-ion PDFs are presented in four plots of Fig. 10. The shape of these distribution curves and their temperature variations depend strongly on the nature of the counterion present in the 6,6-ionene solution. A strong correlation between sodium ions is noticed in the presence of F^- ions; quite the opposite is true when I^- ions are counterions. These results are consistent with the counterion–counterion PDFs as discussed in the section "Water- and/or sodium-assisted correlation between counterions" (see also the snapshots shown in ref. [27]).

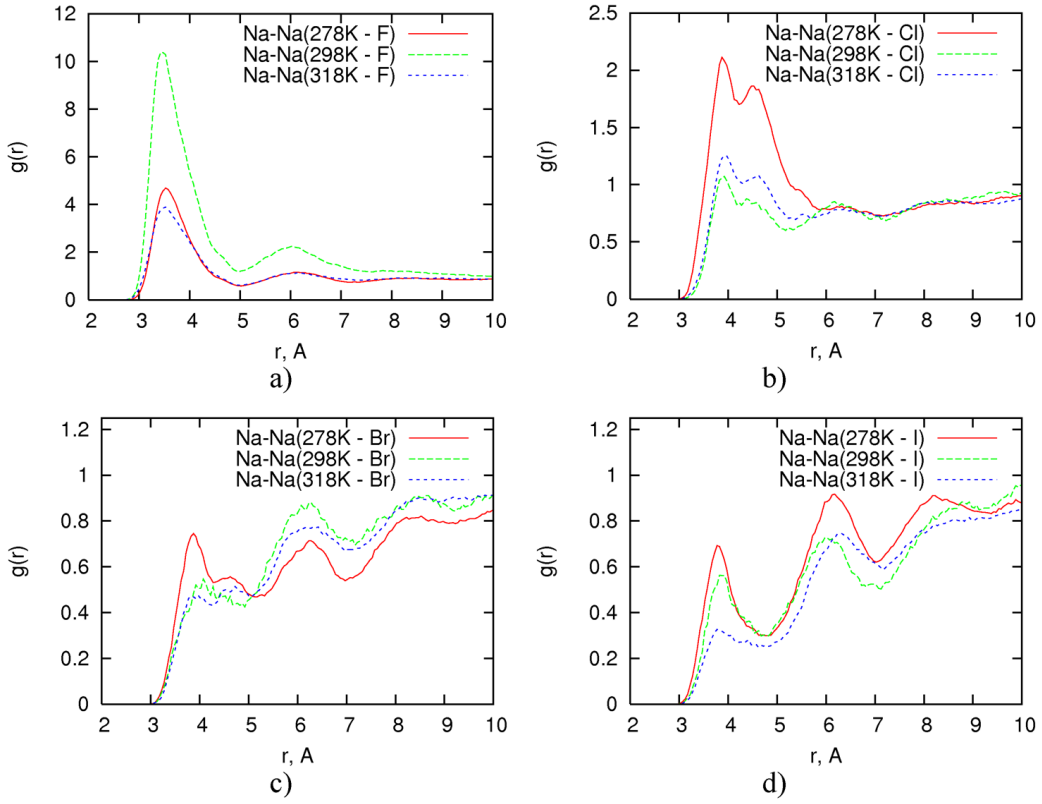

Fig. 10 Co-ion–co-ion (sodium–sodium) PDFs for 6,6-ionene in aqueous solution with sodium halides. Panel (a) presents the results for solutions with F^-, (b) Cl^-, (c) Br^-, and (d) I^- counterions. The results for $T = 278$ K are denoted by continuous lines, for 298 K by long-dashed lines, and for $T = 318$ K by short-dashed lines.

MIXTURE OF FLUORIDE AND IODIDE COUNTERIONS

It is well known that fluoride and iodide ions behave differently in water. The fluoride ion, small in crystal size, holds its waters tightly and is a strong kosmotrope, while "large" iodide loses its hydration waters easily and is an example of a chaotrope. To understand better the situation when two such anions compete for a position near the 6,6-ionene oligocation, we simulated solutions with equimolecular (1:1) mixtures of fluoride and iodide counterions. Sodium cations were present to the same concentration as in all previous examples studied in this paper.

The results are shown in Fig. 11. Red solid lines, labeled (6–6,F–I) denote the ionene–F^- ion distributions in solution with a 1:1 mixture of fluoride and iodide counterions. Blue short-dashed lines, labeled (6–6,F–I), represent the results for the ionene–iodide PDFs in the mixture. The other two curves, green dashed lines and magenta dotted lines (labeled 6–6), show the ionene–counterion distributions when only one counterion species (F^- or I^-) is present in the system. Let us focus on the left panel first. The presence of extra counterion species, as judged by the PDFs presented here, slightly suppresses the nitrogen–F^- interaction, but strongly increases the nitrogen–I^- interaction. The same holds true for the results shown in the right panel, where the carbon(methylene group)–counterion distributions are given. The impression is that addition of fluoride ions forces the iodide anions to occupy the space close to the oligoion. In this process, the iodide ions probably lose some hydrated water, as already found before (see Fig. 3 of ref. [27]).

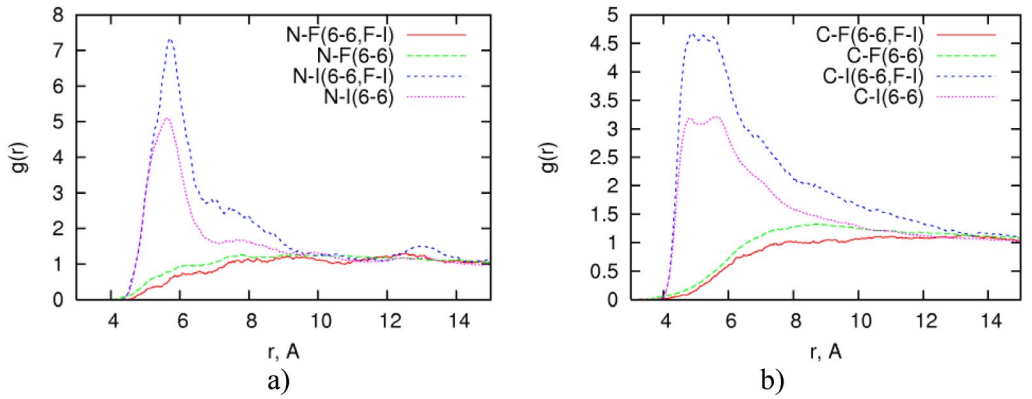

Fig. 11 Ionene–fluoride and ionene–iodide PDFs for 6,6-ionene in aqueous solution with a 1:1 mixture of fluoride and iodide ions at T = 298 K. Sodium ions are present as co–ions. Panel (a) shows the nitrogen–F^- (N–F) and nitrogen–I^- (N–I) correlation functions, and panel (b) the carbon(methylene group)–F^- (C–F) and carbon(methylene group) –I^- distributions (C–I). The curves labeled (6–6,F–I) denote PDFs obtained for the mixed counterion system.

CONCLUSIONS

The temperature dependence of the PDFs between the nitrogen and methylene groups on 6,6-ionene and low-molecular-weight halide ions in aqueous solution was examined. Water [simple point charge/extended (SPC/E) model] and all ionic species were described on the atomic level. The MD method was used to evaluate the relevant PDFs. The results are presented for three different temperatures and four different counterion species: fluoride, chloride, bromide, and iodide. Sodium ions were present in all calculations to screen the ionene–ionene interaction. It was found that the iodide–nitrogen and iodide–methylene group pair correlations increased with decreasing temperature, and the same held true for fluoride ions. The results were compared with the PDFs obtained for 3,3-ionene under otherwise identical thermodynamic conditions. Interestingly, the temperature dependence of fluoride–carbon (carbons belonging to the methylene groups) correlation function of the more charged 3,3-ionene was different from that of the equivalent 6,6-ionene solution in water. In general, the temperature dependencies exhibit a complicated interplay of Coulomb and solvation effects, associated with charged and hydrophobic groups present in this aqueous system. The simultaneous presence of F^- and I^- counterions in solution causes a redistribution of ions in favor of the iodide ions, which now occupy the place closer to the 6,6-ionene.

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