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Molecular dynamics simulation of the structure of PEO based solid polymer electrolytes

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Abstract

A water-free solid polymer electrolyte containing poly(ethyle oxide) (PEO) and poly(ethyle oxide) with sulfonic acid dianion end groups (PEO sulfonic acid dianion) is constructed using periodic boundary conditions by atomistic molecular modelling. The vibrational frequencies are calculated and found to be in agreement with the measured spectra. The structure of the PEO sulfonic acid dianion is studied by calculating the dihedral angle distributions and the intramolecular pair correlation functions between the carbon atoms and the ether oxygen atoms. The dimensional analysis is made. Results concerning the PEO sulfonic acid dianion in the water-free system are compared to the results obtained in the water containing systems and in vacuum. The structure of the PEO sulfonic acid dianion in water-free system is found to be rather similar to its structure in water and PEO containing system but different from its structure in vacuum. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(ethylene oxide) sulfonic acid; Polymer electrolyte; Modelling

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1. Introduction

Polymer-based conducting materials have stimulated considerable interest in the field of solid polymer electrolytes during the last two decades due to their potential applications in electronic equipments, medical devices and electrical vehicles [1–5]. The traditional attempts to develop ion-conducting polymers are to dissolve salts to a polymer matrix like poly(ethyle oxide) PEO [6,7]. Recently a new group of materials, namely the proton conducting polymers, have been studied because the possible use of these materials in electrochemical devices [8,9]. Molecular modelling has not yet been utilized widely to study polymer electrolytes, although it can offer an efficient way to get information about the conduction mechanisms in the proton conducting polymer electrolytes. The conduction mechanisms are still not completely understood despite many experimental and theoretical investigations. Molecular modelling shows the structure of the polymer matrix in detail as a function of time. This can provide insight and guidance for developing new polymer electrolytes.

Recently we reported the synthesis and testing of a proton-conducting membrane containing high molar mass poly(ethylene oxide) (PEO), sulfonated PEO (PEO sulfonic acid), and water [10]. Based on this experimental material three amorphous systems with different concentrations of the PEO and water have been constructed and studied by molecular modelling. We have recently reported the results concerning the first system, which contained one PEO sulfonic acid dianion molecule, ($M_w = 436$), two cations and 220 water molecules [11,12]. The second system contains four PEO sulfonic acid dianion molecules, ($M_w = 436$), eight cations, one PEO molecule and 74 water molecules. The third system contains four PEO sulfonic acid dianion molecules, ($M_w = 436$), eight cations and one PEO molecule. We have previously reported the dynamical behaviour of the particles in these two last mentioned systems [13]. In our latest paper, it was shown that the results of the second system obtained by using the traditional, but slow, Ewald summation method [14] and the new fast CMM method [15] to model the non bonding interactions gave the similar results [16]. Thus the results in this work are mainly calculated using the CMM method. The goal of this work is to study the structure of the PEO sulfonic acid dianion in water-free and in water containing polymer electrolytes. The structure of the PEO in the systems is also discussed.

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Table 1
The vibrational simulated absorptions from trajectory calculated with Ewald summation method (Ewald) or CMM. For simulated values *a* is the harmonic frequency, *b* is the anharmonic frequency ($0 \rightarrow 1$) and *c* is the anharmonic frequency ($0 \rightarrow 2$). The resolution of the experimental spectra is 1 cm^{-1}

	Frequency (cm^{-1})				
	Simulated		Measured	Assignments	
	Ewald	CMM			
a	3510	3510		<3500 (very broad)	O–H in H_3O^+
b	3510	3510			
c	7020	7020			
a	3550	3550	3440	3400–3600[b]	O–H Polymers
b	3440	3450			
c	6910	6920			
			1600–2800	1650–2800	H_3O^+
			1650	1680	
a	2940	2940	2925	2925[a]	C–H
b	2840	2840	2870	2890[a]	
c	5670	5670		2850–3000[b]	
a	1260	1260	1350	800–1300[b]	C–C
b	1260	1250			
c	2510	2510			
a	1240	1240	1110	1110[a]	C–O
b	1230	1230		1120[a]	
c	2450	2450		1070–1150[b]	
a				1150–1170[d]	S=O
b				1340–1350[d]	
				890–910[d]	S–O
a	1100	1100	610	600–700[c]	$SO_3^- H_3O^+$
b	1100	1100	1040	1010–1080[c]	
c	2200	2200	1190	1150–1260[c]	
a	1100	1100		1070–1140	$S–O^-$
b	1100	1100		1200–1220	
c	2200	2200			
a	1080	1090		1070–1100[b]	C–S
b	1080	1080			
c	2160	2170			

[a] Values are for PEO.
[b] General frequencies.
[c] Frequencies for hydrated sulfonic acid.
[d] Frequencies for dry, non-hydrated sulfonic acid.

2. Theory

The vibrational spectra were calculated by the local mode method. In this method the slow motions are calculated by using classical simulation techniques, (MD). To calculate the fast vibrations the MD run was stopped several times and during the stop the molecular vibrations were determined by quantum mechanical calculations for each vibration and configuration. Eq. (1) describes the local effective potential energy function, which is first calculated

$$V^{\mathrm{eff}}(Q) = K_0 + K_2Q^2 + K_3Q^3 + K_4Q^4 \tag{1}$$

Then this potential function is utilized to solve the 1D Schrödinger equation;

$$\frac{\hbar}{2M}\left[\frac{\mathrm{d}^2}{\mathrm{d}Q^2} + V^{\mathrm{eff}}(Q)\right]\Psi(Q) = E\Psi(Q) \tag{2}$$

where *M* is the G matrix of normal mode analysis in general [17]. The final results are obtained by calculating averages of the results determined from the different starting structures.

The characteristic ratio as a limit of C_n as $n \rightarrow \infty$ is defined [18]

$$C_n \equiv \langle r^2 \rangle / \sum_{i=1}^{n} l_i^2 \tag{3}$$

where $\langle r^2 \rangle$ is the mean square end-to-end distance of the chain, *n* is the number of bonds and l_i are the lengths of the bonds.

3. Computational details

The computational results were calculated on two Silicon Graphics Indigo 2 workstations, the SGI Power Challenge computers of CSC, (Centre for Scientific Computation Ltd, Espoo, Finland). In all calculations the software programs InsightII and Discover versions 3.0.0 and 4.0.0P from MSI (Molecular Simulations Inc.) were used [19]. A 3D system was studied by constructing ten water-free amorphous cells with periodic boundary conditions. Each cell contained four PEO sulfonic acid dianions, ($^-O_3SCH_2CH_2CH_2O(CH_2CH_2O)_4CH_2CH_2CH_2SO_3^-$), eight cations and one PEO molecule with degree of polymerization 60. Four of the cations were protons and four hydronium ions. The construction of the protons is reported earlier [12]. The cell size was $19.4454 \times 19.4454 \times 19.4454$ Å^3 corresponding to $\langle V \rangle = 7352.764$ Å^3. The density of this water-free system was 1.05 g/cm^3. We have previously reported results for a system containing one PEO sulfonic acid and cations in water, (only water containing system), and for a system containing four PEO sulfonic acid dianions, eight cations, 74 water molecules and one PEO molecule with degree of polymerization 60 (a water and PEO containing system) [11–13,16]. The size of the water and PEO containing system was $19.4028 \times 19.4028 \times 19.4028$ Å^3 corresponding to $\langle V \rangle = 7304.546$ Å^3 and density = 1.36 g/cm^3.

The PCFF forcefield [20–24] has been found to be suitable for modelling the PEO sulfonic acid [25]. However, the PCFF forcefield does not include ions. Thus it was modified to the NJPCFF forcefield, which can treat the ions [12]. The NJPCFF forcefield was utilized for all calculations. The cells were first minimized using molecular mechanics methods (Steepest descents and Conjugate gradients) until the maximum derivative reached the value 0.1 kcal/(mol Å). 200 ps long dynamics runs with the NVT ensemble at 298 K were performed for each cell. We have previously shown, that for the water and PEO containing system results

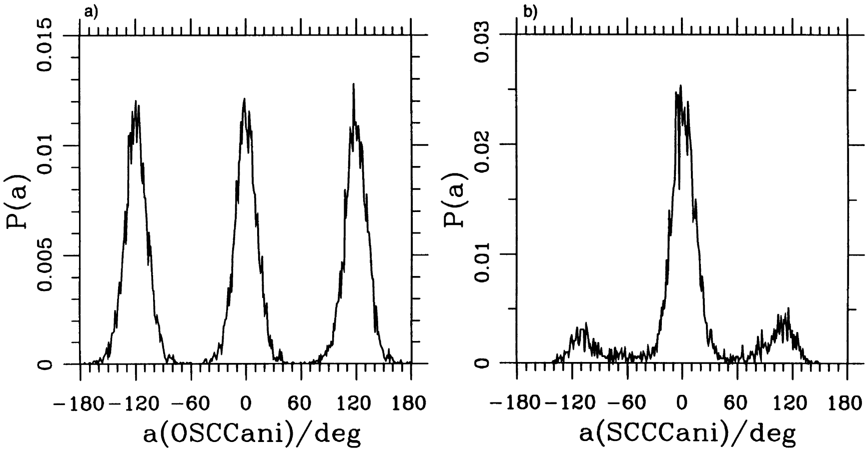

Fig. 1. The average of the: (a) OSCC dihedral angle distribution; and (b) SCCC dihedral angle distribution, for the PEO sulfonic acid dianion in the water-free system.

obtained using the Ewald summation method and the cell multipole method, CMM, did not differ remarkable [16]. The CMM was used in the present study to model the non-bonding interactions, because it is much faster than the Ewald summation method. We have previously used the Ewald summation method to model 800–1000 ps long runs with less statistics for this water-free system to study the dynamic behaviour of the particles in this system [13]. In the present study the structure of the PEO sulfonic acid dianion was studied in many small runs. This was done because it was previously seen, that the starting structures made by the amorphous_cell builder by MSI do not change much during a long run [16]. Thus better statistics is obtained when many small trajectories are used instead of a few long trajectories. The final properties were calculated utilizing only the 100 last ps from each trajectory.

4. Results

4.1. Spectral analysis

The simulated vibrational frequencies for all molecules in the system are shown in Table 1. Both the previously made simulations using the Ewald summation method and the CMM were used to obtain spectral frequencies. No remarkable differences were found between the results calculated using the Ewald summation method or the CMM. This was also the case for the system containing water and PEO [16].

The values from literature and the values from the experimental IR and Raman spectra for a membrane containing PEO sulfonic acid and PEO are also collected in Table 1 [26–31]. The local mode method is used to simulate the vibrational frequencies and its accuracy is about 50–100 cm^{-1}. Taking this accuracy into account the simulated vibrational frequencies for the C–C, C–S and C–H stretches in the PEO and for the PEO sulfonic acid dianion gave values in accordance with the corresponding vibrational absorptions assigned to PEO or PEO sulfonic acid or general sulfonic acid compounds, and with the measured data of the membrane consisting of the PEO sulfonic acid and PEO. The simulated value of the C–O stretch, (1240 cm^{-1}), was higher than the experimental value, (1110 cm^{-1}). This applied also for the simulation studies of the PEO sulfonic acid in vacuum [25], of the PEO sulfonic acid dianion in vacuum [11], and of water and PEO containing system [16]. This is found to appear when the PCFF forcefield is used for the calculation, but not when the CVFF forcefield is used [25]. Despite this the PCFF forcefield is used in all simulations, because it is more suitable for the calculations of the sulfonic acid group, than the CVFF forcefield [25].

From Table 1 it can be seen, that the simulated frequencies for the sulfonic acid group (1100 cm^{-1}) were very close to the experimental frequencies (1040 and 1190 cm^{-1}) and to the literature values for the coordinated sulfonic acid dianion (1010–1080 cm^{-1}), or the uncoordinated sulfonic acid dianion (1070–1140 cm^{-1}). The simulated value of the S=O stretch is also close to the frequency reported in the literature (the literature value is 1150–1170 cm^{-1} for harmonic and 1340–1350 cm^{-1} for anharmonic stretch) [30]. Thus it cannot be concluded from the frequencies whether the sulfonic acid group is coordinated or not.

The simulated values of the O–H stretch in the hydronium ions (3510 cm^{-1}) are close to the literature values for the hydronium ion (3500 cm^{-1}) when the accuracy of the local mode method is taken into account. The simulated frequencies of the O–H stretch of the end group of the PEO (3550 cm^{-1}), were in accordance with the assignments for the O–H stretch (3400–3600 cm^{-1}) in polymers.

Thus all simulated frequencies were close to the corresponding frequencies in the measured spectra for the PEO sulfonic acid containing membrane and in the literature. No remarkable difference was found between corresponding simulated frequencies in the studied systems containing the PEO sulfonic acid dianion only in water or containing

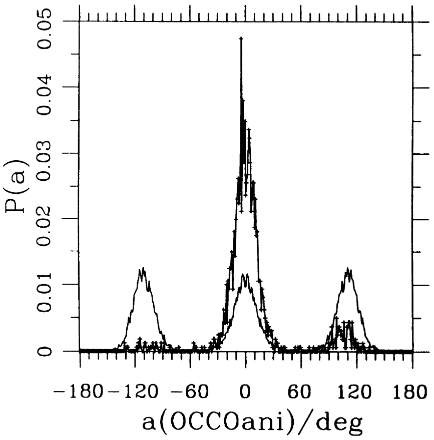

Fig. 2. The average of the OCCO dihedral angle distribution of the PEO sulfonic acid dianion in the water-free system (line), and in vacuum (cross).

PEO sulfonic acid dianion in water and in the PEO or containing PEO sulfonic acid dianion in water-free system [11,16].

4.2. Structure of polymers

The structure of the PEO sulfonic acid dianion and of the PEO in a water-free system was studied by calculating the OSCC, SCCC, CCCO, CCOC and OCCO dihedral angle distributions. The average of the OSCC dihedral angle distribution was calculated for the PEO sulfonic acid dianion, see Fig. 1a. Fig. 1a shows three maxima: the g^- (*gauche* minus) near −120°, the *t* (*trans*), near 0° and the g^+ (*gauche* plus) near +120° with nearly equal probabilities. This also applies for the OSCC dihedral angles in PEO sulfonic acid in systems containing one anion in water and for the anions, water and PEO containing system. The average of the SCCC dihedral angle distribution calculated for the PEO sulfonic acid dianion was almost completely in *trans* conformation, see Fig. 1b. The *trans* conformation was detected to be most favourable for the SCCC dihedral angle also in the system containing one anion in water and in the system containing the anions, water and PEO [11,16]. Thus the amount of water does not affect the main conformation of the average SCCC dihedral angle distribution. In the average of the CCCO dihedral angle distribution calculated for the PEO sulfonic acid dianion in the water-free system the *gauche* minus, *gauche* plus and *trans* conformations all have the same probability. This was also the case in the system containing one anion in water as well as in the system containing the anions, water and PEO [11,16].

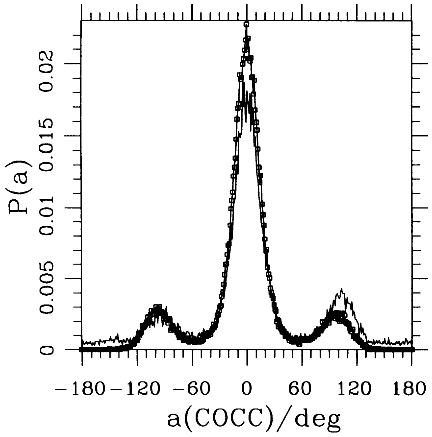

Fig. 3. The average of the COCC dihedral angle distribution in PEO sulfonic acid dianion (line), and in PEO (box) in the water-free system.

The average of the OCCO dihedral angle distributions was calculated both for the PEO and the PEO sulfonic acid dianion. For the PEO sulfonic acid dianion three maxima were detected; *gauche* minus, *trans* and *gauche* plus with similar probabilities, see Fig. 2. The *trans* conformation in present work is defined to cover the angles from −60 to 60°. The probability of the *trans* conformation in the PEO sulfonic acid was 34%. This is very close to the probabilities of the *trans* conformation of the OCCO dihedral angle distribution in the PEO sulfonic acid in a system containing water and PEO, which is 32% calculated with the CMM and 39% calculated with the Ewald summation method. In the system containing one PEO sulfonic acid dianion in water the probability of the *trans* conformation is about 16% indicating the so called *gauche* effect, which is well known for the PEO in water [32]. Thus the polymer matrix moderates the *gauche* effect in the PEO and water containing system. However, the probability to find the OCCO dihedral angles in *trans* conformation is still small in the polymer containing systems compared to its the probability for a PEO sulfonic acid dianion in vacuum, which is 88%, see Fig. 2. In the present study the OCCO dihedral angle distribution in the PEO was found to be in *trans* conformation with the probability of 43%, which is slightly higher than the probability of the *trans* conformation in the OCCO dihedral angle distribution in the PEO sulfonic acid dianion. The probability of 43% for the PEO is rather close to the probability of detecting the OCCO dihedral angle of PEO in *trans* conformation in a system containing water and PEO, which was 40% when the CMM is used for the calculation and 36% when the Ewald summation is used.

For the CCOC dihedral angle the probability of *trans* conformation is 69% for the PEO sulfonic acid dianion and 79% for the PEO, see Fig. 3. Thus, as in the case of OCCO dihedral angle distribution in polymer containing systems more *gauche* conformations are found for the CCOC dihedral angle distribution in PEO sulfonic acid than in the PEO. However, the *trans* is the main conformation for both the polymers in the water-free system. The probability of the *trans* conformation in the water and PEO containing systems is 66% for PEO calculated with CMM or with the Ewald summation method, and for the PEO sulfonic acid dianion it is 54% calculated using the CMM and 57% when the Ewald summation method is utilized for the calculation. Thus some more *trans* conformations are detected in the water-free system. In the system

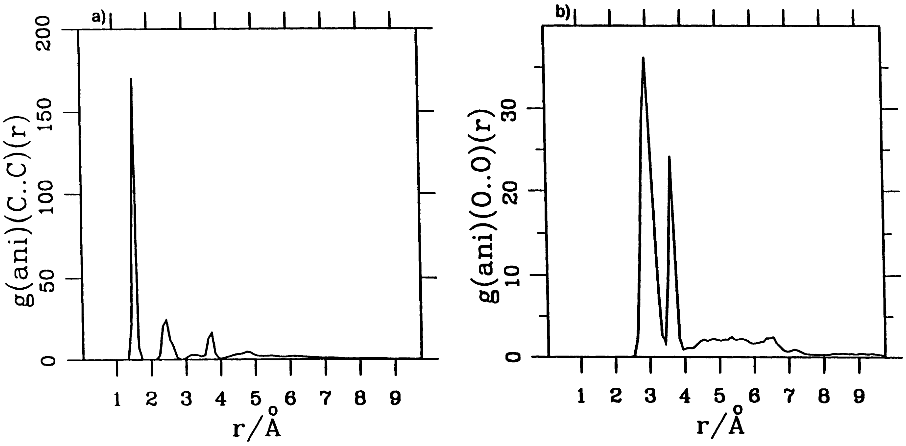

Fig. 4. (a) The intramolecular pair correlation function between the carbon atoms in PEO sulfonic acid dianion. (b) The intramolecular pair correlation function between the ether oxygen atoms in PEO sulfonic acid anion, in the water-free system.

containing one PEO sulfonic acid dianion in water the probability of the *trans* conformation was 85%, and in vacuum 82%.

4.3. Pair correlation study

Information on the structure of the polymers can be obtained from the intramolecular pair correlation function between the ether oxygen atoms and the carbon atoms in the PEO and PEO sulfonic acid dianion. The intramolecular pair correlation function between the carbon atoms in the PEO sulfonic acid dianion is seen in Fig. 4a. There is one very high peak at 1.55 Å corresponding to the average bond length between the carbon atoms in the anion, which is 1.54 Å in the water-free system. In Fig. 4a two smaller peaks are seen at 2.45 and 2.75 Å. The value at 2.45 Å corresponds to the distance of 2.3 Å between two carbon atoms, which are both bonded to the same ether oxygen and also to the carbons in the *gauche* conformation of the COCC dihedral angle. The value 2.75 Å corresponds to the carbons in the *trans* conformation of the COCC dihedral angle. Also the intramolecular pair correlation function between the carbon atoms in the PEO was studied. Three peaks at 1.55, 2.45 and at 3.75 Å, respectively, were found with a similar pattern as in the case of the PEO sulfonic acid dianion.

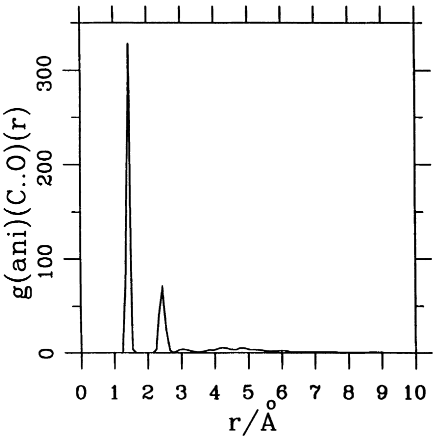

Fig. 5. The intramolecular pair correlation function between the carbon atoms and the ether oxygen atoms in PEO sulfonic acid dianion in the water-free system.

The intramolecular pair correlation function between the ether oxygen atoms in the PEO sulfonic acid dianion are seen in Fig. 4b. Two main peaks are seen. The peak at 3.00 Å is due to the *gauche* conformation of the OCCO dihedral angle and the peak at 3.70 Å is due to the *trans* conformation of the OCCO dihedral angle. The OCCO dihedral angle distribution shows that the probability of the *gauche* conformation is about 66% in the PEO sulfonic acid dianion, which agrees with the larger peak for the *gauche* conformation at 3.00 Å, than for the *trans* conformation at 3.70 Å. The intramolecular pair correlation function between the ether oxygen atoms in the PEO is similar to the results concerning the PEO sulfonic acid dianion.

The intramolecular pair correlation function between the carbon atoms and ether oxygen atoms in the PEO sulfonic acid dianion are seen in Fig. 5. The strongest peak is at 1.45 Å corresponding the average bond length between the carbon and the ether oxygen atoms, which is 1.43 Å in the water-free system. The peak at 2.45 Å corresponds to the distance between the carbon atoms and the ether oxygen atoms which are separated by a carbon in the PEO chain. Similar peaks were detected in the intramolecular pair correlation function between the carbon atoms and ether oxygen atoms in the PEO.

4.4. Dimensional analysis

The average values of the root mean square radius of gyrations and end-to-end distances for PEO sulfonic acid dianion in the water-free system, in water and in a PEO containing system and for the anion in vacuum [11] are seen in Table 2. For the PEO sulfonic acid dianion the radius

Table 2
The radius of gyration ($g(r)$) and the end-to-end distance (S) for PEO sulfonic acid dianion. The CMM means calculations made by using the Cell Multipole Method and Ewald means calculations made by using the Ewald summation method

System	$g(r)$ (Å)	S (Å)
Water-free cells	5.78 ± 0.18	12 ± 4
Water and PEO containing cells, CMM	5.38 ± 0.08	11 ± 2
Water and PEO containing cells, Ewald	5.22 ± 0.08	11 ± 3
One anion in vacuum	8.4 ± 0.4	22 ± 2

of gyration in the water-free system is (5.78 ± 0.18) Å, which is very close to the values in the water and PEO containing system, (5.38 ± 0.08) Å calculated using the CMM method and (5.22 ± 0.08) Å calculated using the Ewald summation method. These results agree with the rather similar results for the OCCO and CCOC dihedral angle distributions in the water-free and the water and PEO containing systems. In the vacuum the anion is more in an extended shape and the radius of gyration is (8.4 ± 0.4) Å. The radius of the gyrations for the PEO molecules in the water-free and water and PEO containing system are about 17 Å.

The average of the end-to-end distance of the PEO sulfonic acid dianion was (12 ± 4) Å in the water-free cells and (11 ± 3) Å in water and PEO containing cells. Nearly the same value, (12 ± 3) Å, was obtained for the system containing one PEO sulfonic acid dianion in water [11]. The end-to-end distance of the PEO sulfonic acid dianion in vacuum was much larger, (22 ± 2) Å [11]. The characteristic ratio of the PEO sulfonic acid dianion is 3.1 in the water-free system, 2.5 in the PEO and water containing system, 3.1 for the anion in water and 9.4 for the anion in vacuum. The characteristic ratio of the PEO is reported to be 3.9 in pure water [33]. This value is in accordance with the simulated values.

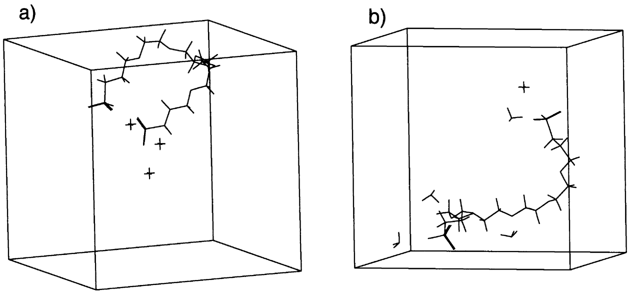

Fig. 6. The structure of the PEO sulfonic acid dianion in a water-free system: (a) when both the sulfonic acid end groups of the dianion are coordinated to the same cation; and (b) when the PEO sulfonic acid anion is coordinated to several cations and its end groups are not coordinated to same cation. The end-to-end distance of the PEO sulfonic acid dianion is 8 Å in case (a) and 12 Å in case (b) and the radius of gyration is 5.08 Å in case (a) and 6.35 Å in case (b). The protons are marked with cross and the hydronium ions with three lines.

4.5. Influence of the cations to the structure of the PEO sulfonic acid dianion

The structure of the PEO sulfonic acid dianion in the water-free system is highly dependent on its interactions with the cations. The coordination study between the cations, (protons and hydronium ions), and the PEO sulfonic acid dianion have been reported previously on a statistical level [13]. The main coordinations in the water-free system are the coordination between the sulfonic acid anion end group of the PEO sulfonic acid dianion and the cation and the coordination between the cation and the ether oxygen in PEO. Also the coordination between the cation and the ether oxygen in PEO sulfonic acid is found. A detailed coordination study of single coordinations shows many different variations. Opposite cases are found: the same cation is coordinated to both sulfonic acid end groups of the same dianion, (see Fig. 6a), or many cations are coordinated to the chain and to the other end of the PEO sulfonic acid dianion, while the other end of the dianion is not coordinated to same cation, (see Fig. 6b). The structure of the dianion in the former case is more coiled than in the latter case (see Fig. 6).

5. Conclusions

Ten amorphous polymer electrolyte systems containing four PEO sulfonic acid dianions, four hydronium ions, four protons and one PEO molecule were made to study the structure of the PEO sulfonic acid dianion. The vibrational spectra of the system calculated using the CMM and Ewald summation method to model the non-bonding interactions were in accordance with the experimental spectra. Previously the CMM method and Ewald summation method were reported to give results without any remarkable deviations for the water and PEO containing system [16]. Thus the CMM was used for further calculations for the water-free system since it is much faster than the Ewald summation method.

The structure of the PEO sulfonic acid dianion was studied by calculating all the averages of the dihedral angle distributions and the intramolecular pair correlation functions between the carbons and ether oxygens. The amount of the water in the system did not affect remarkably the OSCC, SCCC and CCCO dihedral angle distributions. The probability of the *trans* conformation in the OCCO dihedral angle distribution was lower in the system containing one PEO sulfonic acid dianion only in water than in the water-free systems, or in the systems containing PEO and water. The probability of the *trans* conformation in the OCCO dihedral angle distribution was similar in the water-free system and in the system containing PEO and water. This applied also for the PEO molecule in the systems. The highest probability of the *trans* conformation in the OCCO dihedral angle distribution was obtained for the PEO sulfonic acid dianion in vacuum. The *trans* conformation was found to dominate for the CCOC dihedral angle distribution in the PEO sulfonic acid dianion and in the PEO in all cases. The largest probability of the *trans* conformation in the CCOC dihedral angle distribution was found for the PEO sulfonic acid dianion in vacuum and for the system containing only one PEO sulfonic acid dianion in water. The results of the intramolecular pair correlation function study were in agreement with the results of the dihedral angle distributions. The dimensional analysis showed that the radius of the gyrations and the end-to-end distances of the PEO sulfonic acid dianion were similar in the cells containing water and PEO or only PEO. In the PEO containing cells the dianion was randomly coiled, while in vacuum the PEO sulfonic acid dianion was found to be in an extended shape. This was due to higher electrostatic repulsion between the negative end groups in the dianion in vacuum than in polymer matrix, which dielectric constant is higher than the dielectric constant of vacuum. The structure of the dianion is also dependent on its interactions with the cations. Because the coordinations between single cations and dianions show many different variations, this subset is discussed shortly in this paper and detailed studies on this subset will be published later.

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