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Modeling of water-free and water containing solid polyelectrolytes

J. Ennari*, M. Elomaa, I. Neelov, F. Sundholm

Laboratory of Polymer Chemistry, University of Helsinki, PB 55, FIN-00014 Helsinki, Finland

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Abstract

Atomistic molecular modeling was used to construct water-free and water-containing polymer electrolyte materials consisting of poly(ethylene oxide) (PEO), poly(ethylene oxide) with sulfonic acid anion end groups (PEO sulfonic acid anion) and cations. The coordination and the diffusion of the ions and water was studied and compared with experimental results of similar systems and the simulated results of a system containing only PEO sulfonic acid anion and cations in water. The coordination found in the systems was largely in accordance with the experimental results. The influence of the PEO and water concentration of the system on the coordination is discussed. The systems were not conducting, which also applies to similar real water-free materials. The good correlation between the experimental and simulated results shows, that the model may give atomistic information for evaluating new polyelectrolyte materials. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Polyelectrolyte; Coordination; Modeling

1. Introduction

Solid materials with high and pure protonic conductivity are candidates for electrolytes in sensors, batteries, fuel cells, electrolytes, etc. Different classes of materials have become increasingly important as proton conductors, among these oxide ceramics and intercalation compounds [1]. By most measures the leading solid proton conductors are the polymer based ones. The use of proton conducting polymer electrolytes in electrochemical applications has recently been reviewed [2,3]. These hydrated polyelectrolytes used as thin membranes have liquid-like regions of water, which carry protonic species towards the cathode. Despite numerous experimental and theoretical investigations, the basic features of the conduction mechanisms in these systems are still not very well understood. With the current availability of sophisticated software and increasingly powerful computers, it is instructive to evaluate the effect of ionic aggregation and coordination between the ions and the chain atoms of polymer electrolyte using molecular modeling. This may provide some insight and guidance for evaluating the polyelectrolytes and conduction mechanisms by experimentalists.

In this paper we use molecular dynamics (MD) simulations to study the coordination and conductivity of two polyelectrolyte systems. The coordination of a real similar system has been previously studied by IR and Raman spectroscopy [4]. The polymers in the system are poly(ethylene oxide) (PEO) and PEO chains of moderate molar mass substituted with sulfonic acid groups as end groups, PEO sulfonic acid. The first system contains about 20% water and the second system is water-free. We have recently reported a similar study for a conducting system containing only PEO sulfonic acid in water [5,6]. One of the goals is to study the influence of water on the conductivity and its mechanism. The proton conductivity in water can be due to classical diffusion or/and due to the proton transfer from one water molecule to another (a proton hopping mechanism) [7]. However, it is possible to study the hopping mechanism only in the framework of the quantum approach, which is not suitable for polymers. As a result of this, protons were created in the system with a Van der Waals radius derived from condensed phase properties [5]. Thus, the proton can interact constantly with surrounding molecules by electrostatic forces. This hopping procedure does not of course include any chemical reaction, (creating or breaking of bonds). To study the behavior and the classical diffusion of the hydronium ion, hydronium ions were placed in the system [5].

2. Theory

Pair correlation functions which also are called radial

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* Corresponding author. Tel.: +358-9-19140333; fax: +358-9-19140330.
E-mail address: ennari@csc.fi (J. Ennari)

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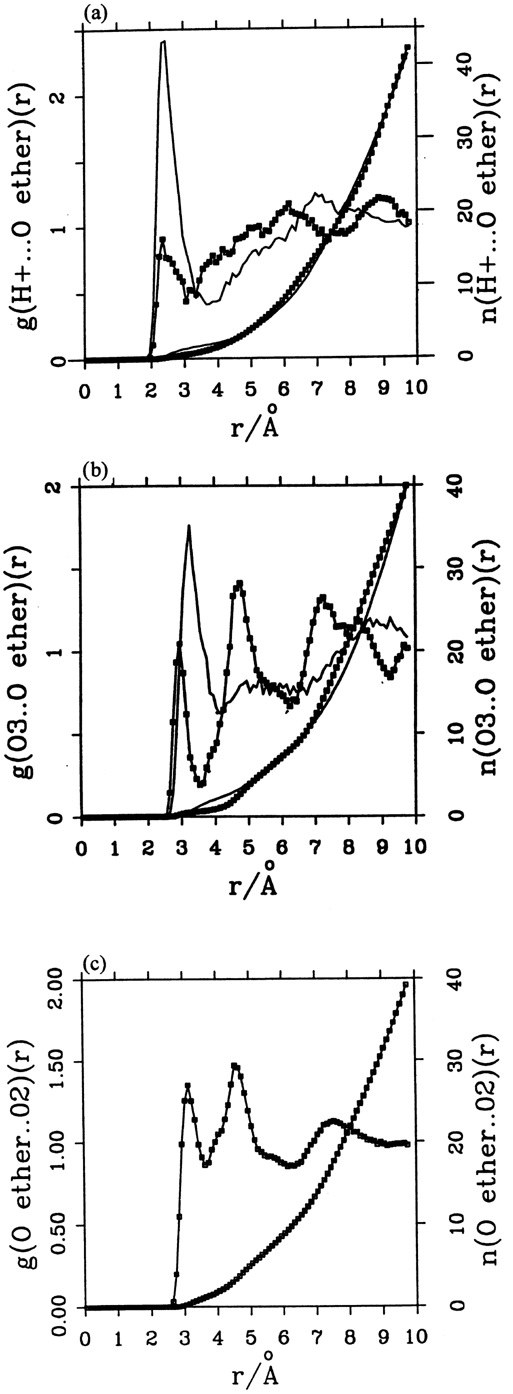

Fig. 1. The pair correlation function $g(r)$: (a) between the proton and the ether oxygen in the PEO and PEO sulfonic acid, (b) between the hydronium ion and the ether oxygen in the PEO and PEO sulfonic acid, and (c) between the oxygen atom in water and the ether oxygen in the PEO and PEO sulfonic acid. The coordination numbers $n(r)$ as a function of the distance are indicated in the figure. The results from the water containing system are marked with squares and the plot for the water-free system is marked with a full line.

distribution functions are used in simulation to give the probability of finding a pair of atoms at distance r apart, relative to the probabilities expected for a completely random distribution at the same density [8,9].

The coordination numbers were calculated from the pair correlation

$$n_{x\ldots z}(r) = 4\pi \frac{N_z}{\langle V \rangle} \int_0^r g_{x\ldots z}(s) s^2 \, \mathrm{d}s, \tag{1}$$

where n is the number of x particles coordinated to particle z within a radius r, N_z is the total number of the particles z in the system, $\langle V \rangle$ is the volume of the cell and $g_{x\ldots z}(s)$ is the pair correlation function between x and z.

To penetrate a membrane a substance should go through three stages: (1) absorption into the membrane, (2) diffusion through the membrane, and (3) desorption of the penetrant out from the opposite surface of the membrane. It is well known that the slowest and therefore the rate determining, stage is the diffusion [10]. In atomistic modeling the diffusion coefficient D can be determined by the following equation [11]

$$D_\alpha = \frac{1}{6N_\alpha} \lim_{t \to \infty} \frac{\mathrm{d}}{\mathrm{d}t} \sum_{i=1}^{N_\alpha} \langle [\mathbf{R}_i(t) - \mathbf{R}_i(0)]^2 \rangle. \tag{2}$$

The sum term on the right side divided by N_α is the mean square displacement (MSD). In Eq. (2) N_α is the number of diffusing particles, t is time and $\mathbf{R}_i(t)$ is the position vector of particle α at time event t. It is essential that Eq. (2) is valid only when the motion of the diffusing particle follows a random walk i.e. its motion is not correlated with its motion at any previous time, in other words the Einstein diffusion is reached. If the surroundings inhibit the free movement of the particle, (for instance if it is stuck for a while to a small space limited by the polymer chain) the diffusion is called anomalous diffusion. In this case $\langle |\mathbf{R}_i(t) - \mathbf{R}_i(0)|^2 \rangle \propto t^n$ where $n < 1$, and Eq. (1) is not valid. The movement of the particle is not by diffusion but by some other transport mechanism, if $n > 1$ in $\langle |\mathbf{R}_i(t) - \mathbf{R}_i(0)|^2 \rangle \propto t^n$. For instance if $n = 2$ the particle is in the so-called free flight in a low density medium without any interactions with the medium. It is easy to test the region in which Eq. (2) is valid by plotting log(MSD) against log(t). In the case of the Einstein diffusion, the slope of the curve is 1

$$\frac{\Delta \log(\mathrm{MSD})}{\Delta \log(t)} = 1. \tag{3}$$

If Einstein diffusion is reached the ionic conductivity, σ, can be determined by using the Einstein equation as the sum over individual mean square displacements weighted with the charges and the correlation of displacements of ions describing the interactions between different ions.

3. Computational details

The simulations were made on a Silicon Graphics Indigo

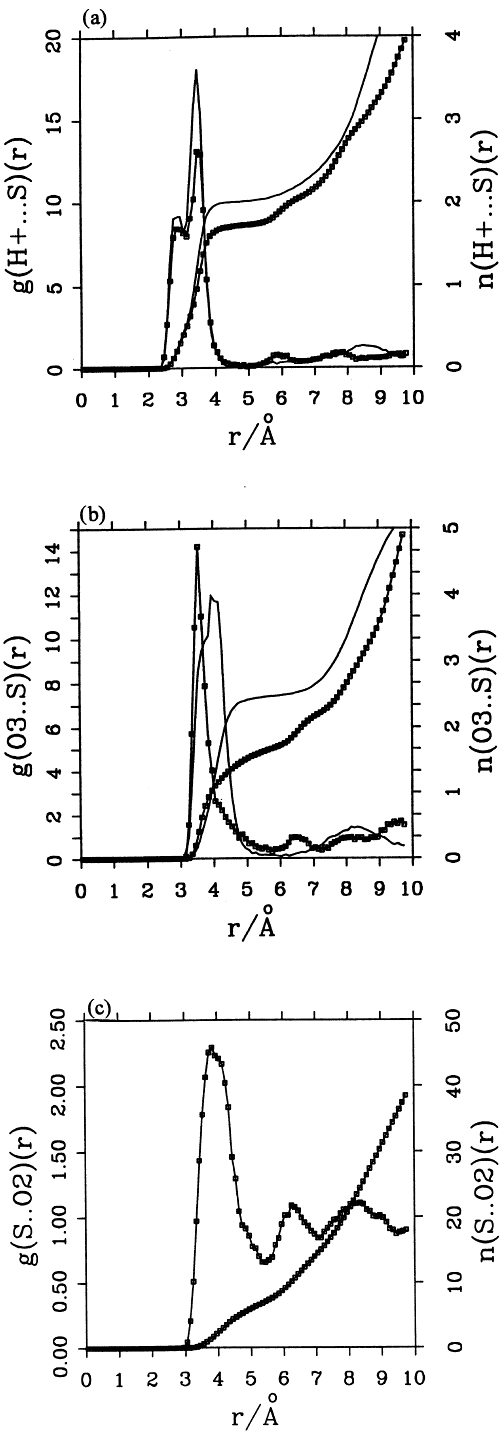

Fig. 2. The pair correlation function $g(r)$: (a) between the proton and the sulfur in PEO sulfonic acid anion, (b) between the oxygen atom in the hydronium ion and the sulfur atom in PEO sulfonic acid anion, and (c) between the sulfur atom in PEO sulfonic acid anion and the oxygen atom in water. The coordination numbers $n(r)$ as a function of the distance are indicated in the figures. The results concerning the water from the system are marked with squares and the plot for the water-free system is marked with a full line.

2 workstation, the SGI Power Challenge metacomputers of CSC, (Centre for Scientific Computation Ltd, Espoo, Finland), and the software programs InsightII and Discover 3.0.0 from MSI, (Molecular Simulations Inc.) [12]. Two different systems were studied by building 20 3D amorphous cells with periodic boundary conditions. Each cell had different starting conformations. The first system, 10 cells, consists of four protons, four hydronium ions, four PEO sulfonic acid dianions, $^{-}O_3SCH_2CH_2CH_2$ $O(CH_2CH_2O)_4$ $CH_2CH_2CH_2SO_3^{-}$, corresponding to $M_w = 436$, and of one PEO molecule with degree of polymerization is 60. The density of these systems was 1.05 g/cm^3. The cell size was $19.4454 \times 19.4454 \times 19.4454$ Å^3 corresponding to $\langle V \rangle = 7352.764$ Å^3. The second system, 10 cells, consists of four protons, four hydronium ions, four PEO sulfonic acid dianions, 74 water molecules and of one PEO molecule with degree of polymerization being 60. The density of these cells was 1.36 g/cm^3. The size of the cells was $19.4028 \times 19.4028 \times 19.4028$ Å^3 corresponding to $\langle V \rangle = 7304\ 546$ Å^3. Modifications were made to the PCFF forcefield [13–17] to be able to simulate the ions. The modified forcefield, the NJPCFF forcefield, was used in all calculations. It was presented recently [5]. The systems were minimized by the steepest-descent molecular mechanics method with 10 000 steps. The cell multipole method with constant dielectric constant value 1 was used to specify the non-bonding interactions. Three cells from the water containing cells and four cells from the water-free cells having the lowest total energy were selected for further calculations. The selected cells were minimized by the steepest-descents and conjugate-gradients methods until the maximum derivative was less than 15 kcal/mol. The dynamics runs were 800–1000 ps long. The NVT ensemble was used. The temperature was 298 K and it was controlled by the Andersen method [11]. The time step was 1 fs. The non-bonding interactions were simulated by the Ewald summation method with an accuracy of 0.01 and a constant dielectric value of 4 for the water containing system and 3 for the water-free system.

4. Results

4.1. Coordination study

The coordination was studied by calculating the pair correlation $g(r)$ and coordination numbers $n(r)$. The pair correlation function between the proton and the ether oxygen in the PEO and in the PEO sulfonic acid anion are seen in Fig. 1(a). For the water-free system one maximum peak is found in the range 1.9–3.7 Å with the coordination number 2. For the water containing system, (marked with squares), the coordination number at 2.5 Å is 0.7. However, the value of the pair correlation function in the water containing system is less than 1 indicating a very small

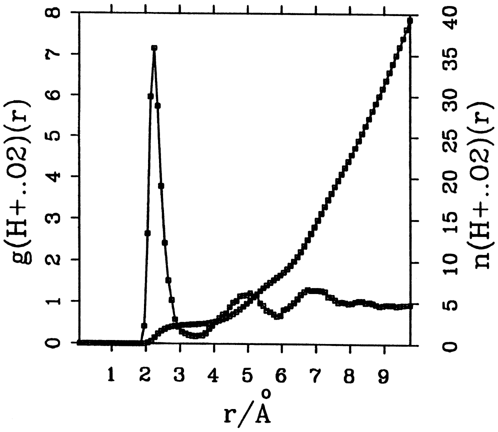

Fig. 3. The pair correlation function *g*(*r*) between the proton and the oxygen atom in water. The coordination numbers *n*(*r*) as a function of the distance are indicated in the figure.

correlation. The value of the pair correlation function in the water-free system is nearly 2.5, which means that the probability of the coordination is 2.5 times larger than the value of the average distribution would be. In the system containing water and PEO sulfonic acid anion but no water, there was no coordination between the proton and the ether oxygen [5]. Thus the coordination between the proton and the ether oxygen increases when the water content of the system decreases.

The pair correlation between the oxygen atom in the hydronium ion and the ether oxygen both in the PEO and in the PEO sulfonic acid anion are seen in Fig. 1(b). In the water containing system two main peaks are seen, the first at 3.3 Å with a coordination number of 0.65 and the second at 4.7 Å with a coordination number of 6.5. The third peak in the Fig.1(b) is very large (it is divided into two peaks, but it probably includes only one coordination shell, as is the case in the pair correlation function between water and ether oxygen in Fig. 1(c)). In the water-free system the pair correlation function between oxygen in the hydronium and the ether oxygen has only one clear coordination shell in the range 2.5–4.2 Å with the coordination number being 2.4. Also in the system containing only water one PEO sulfonic anion, the coordination between the hydronium ion and the ether oxygen of the PEO sulfonic acid chain was found [5]. Thus the cordination of the hydronium ion to the ether oxygen exists in all cases. In experimental Raman spectroscopic measurements for systems containing PEO and PEO sulfonic acid, no cation ether oxygen coordination was found [5,18]. However, in several investigations the coordination between metal cations and ether oxygen of PEO has been detected [19,20].

The pair correlation function between the ether oxygen both in PEO and PEO sulfonic acid anion and the oxygen atom of water is seen in Fig. 1(c). The coordination number at 3.15 Å is 1.2 and at 4.5 Å it is 8.5. In the latest papers the number of bound water molecules per PEO repeat unit is reported to be 1 [21–23], which is also the value from simulations of the system containing PEO sulfonic acid anion in water [5].

The pair correlation function between the proton and the sulfur atom in the PEO sulfonic acid anion has a maximum at 3.5 Å in both the systems (see Fig. 2(a)). The coordination number is 2 in the water-free system and 1.7 in the water containing system. In the system containing only PEO sulfonic acid anion in water, the coordination was very weak and the proton moved freely most of the time [5]. Thus the coordination between the proton and the sulfur atom in the PEO sulfonic acid anion decreases when the amount of water in the system increases.

The pair correlation function between the oxygen atom in the hydronium ion and the sulfur atom in the anion shows one strong peak (see Fig. 2(b)). For the water-free system the peak is rather broad (from 3 to 5 Å), while for the water containing system the peak is sharper (from 3 to 4 Å). The coordination number is 2.4 for the water-free system and 1.3 for the water containing system. Also in the system containing PEO sulfonic acid anion in water coordination between the oxygen atom in the hydronium ion and the sulfur atom in the PEO sulfonic acid anion was found [5]. The coordination between the cation and the sulfonic acid group increases when the amount of water in the system decreases. The Raman spectroscopic studies of the material containing PEO sulfonic acid and PEO show that there were only few or no uncoordinated SO_3^- end groups [4]. This is in accordance with the simulated results.

The pair correlation between the sulfur atom in the PEO sulfonic acid anion and the oxygen in water in the water containing system has a broad (from 3.0 to 5.5 Å), coordination shell at 3.8 Å with a coordination number of 7.0 and also a second coordination shell at 6.3 Å (see Fig. 2(c)). The coordination number should be more than 10 water molecules per sulfonic acid group to gain a significant proton conductivity [24]. Thus in both the systems containing PEO and water and in water-free system, the water content is so low, that the system cannot be conducting. In Nafion containing 20.2% water the number of water molecules per SO_3H group is 8.5 [25]. The coordination number between the sulfur atom in the PEO sulfonic acid anion and the oxygen in water was 19 in the system containing only PEO sulfonic acid anion and water [5]. This system was conducting.

In the water containing system the coordination between cations and the oxygen in water was studied. The pair correlation between the proton and the oxygen in the water showed a sharp peak at 2.3 Å with a coordination number 2.6 and at 5.9 Å with the coordination number 8.0, (see Fig. 3). The pair correlation between the oxygen in the hydronium ion and the oxygen atom in the water has the first broad peak (from 1.7 to 4.5 Å), at 3 Å with a coordination number of 5.5 and the second broad peak (from 4.5 to 8.6 Å), at 6 Å with a coordination number of 28. Also in the system containing only PEO sulfonic acid in water a coordination between the cations and oxygen in water was found [5]. The coordination between oxygen atoms in the water, in the water containing system had one maximum at 3.1 Å with the coordination number 3.6. Also in the system containing one PEO sulfonic acid anion in water coordination was detected between water molecules. In the experimental studies of pure water the distance between the oxygen atoms in the first coordination shell is reported to be 2.9 Å with an error of about 6% [26].

4.2. The motion of the particles

The diffusion of the proton, the hydronium ion, the water, the PEO sulfonic acid anion and the PEO was studied. The MSD as a function of time was plotted for the proton, the oxygen in hydronium ion, the oxygen in water, the ether oxygen in PEO and PEO sulfonic acid anion and the end group oxygen of the anion. No Einstein diffusion was found. The slopes of the curves log(MSD) as a function of log(t) were close to 0.2 (0.13–0.36), in all cases. Similar results were obtained for the MSD plots in different directions. This kind of anomalous diffusion of the small particles is caused by the polymers in their environment, which prevent the small particles from performing a random walk. It is well accepted that cation transport in high molecular-weight polyelectrolytes above the glass-transition temperature is closely associated with the dynamical relaxation modes of the polymer chain [27]. The glass transition temperatures of this kind of polyelectrolyte films have been measured to be in the temperature range between the glass transition temperature of high molar mass PEO, ($T_g = 207$ K) and of PEO sulfonic acids, ($T_g = 220$ K) [4], so the simulation was made above the glass transition temperature of the materials. In the systems both the proton and the hydronium ion moved with the same velocity as the PEO. Thus neither the classical diffusion nor the proton hopping type mechanism were found. This is probably due to the fact that both the mechanisms need more water than the 20% used to exist in the system. As was already mentioned the amount of water per sulfonic acid groups was low (less than 10). The dry or low water containing membranes are also not conductive. However, it must be remembered that, also the relatively short simulation time (1000 ps), the accuracy of the forcefield and other approximations embodied in the MD simulations can affect the diffusion of a particle in the system.

5. Conclusions

Amorphous water-free and water containing polyelectrolyte systems consisting of PEO, PEO sulfonic acid anion and cations were studied by atomistic molecular simulations. The cations used were hydronium ions and protons. The proton was described with non-bonding terms which enabled it to jump from one water molecule to another forced by a strong electrostatic interaction. In the previous paper [5] it was shown that the proton constructed in such a way could simulate the hopping mechanism as accurately as possible at the level of the simulation suitable for the polymer system. A coordination study was performed. It was mainly in good agreement with the experimental findings. The coordination between the proton and the ether oxygen in PEO and PEO sulfonic acid anion was found to increase when the water content of the system decreased. In addition, the hydronium ion was coordinated tighter to the ether oxygen when no water was present, than in the system containing water. Thus the cation, especially the proton, moved more in the water than close to the polymer when water was present. The coordination between the cations and the sulfur atom in PEO sulfonic acid increased when the amount of water in the system decreased. The small particles (water and cations), did not perform any Einstein diffusion in the systems, but they were stacked to the anions and moved with the anions. The number of water molecules coordinated to the sulfonic acid group was less than 10. It is assumed that this amount of water, cannot release the cation from the anion and transport it to the water phase, where the conducting could take place. The small amount of water quenched both the hopping and the classical diffusion mechanisms. Of course we have to remember, that the used model is still simple and results concerning the diffusion can also be affected by the used simulation time and other approximation of the method. Thus the situation must be further studied before any final conclusions can be made.

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