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Modelling a polyelectrolyte system in water to estimate the ion-conductivity

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Abstract

Atomistic molecular modelling has been utilized to construct a proton-conducting polymer electrolyte system consisting of poly(ethylene oxide) sulfonic acid anion (PEO sulfonic acid anion), water, hydronium ion and proton in an amorphous cell. The forcefield was parametrized to simulate proton transport as accurately as possible in an atomistic model. The coordination study was made and found to be mainly in accordance with experimental data. The diffusion coefficients for the PEO sulfonic acid anion, water, the proton and for the hydronium ion were determined. The ion conductivities of the whole system and of the ions were estimated and found to be in accordance with experimental values. The good correlation between the experimental and simulated results shows that the used model may provide guidance for evaluating new materials by experimentalists. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Ion-conductivity; Polyelectrolyte; Diffusion coefficient

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1. Introduction

Polymer electrolytes have been extensively investigated during the past two decades due to their potential applications in different types of electrochemical devices as solid non-corrosive electrolytes [1–3]. A primary goal is to find polymer materials with ion conductivities in the range of mS/cm at temperatures up to 100°C. Of special interest are proton-conducting materials. The conduction mechanisms are partly unknown at present and the experimental work has not, despite much effort, been able to resolve all the atomistic-level details. The rapid increase in computing resources and the progress of software offer new possibilities to rapidly gain new information by molecular modelling of conductivity phenomena.

There are two contributions to proton conductivity in water: the classical diffusion and the proton transfer from one water molecule to another (a proton hopping mechanism) [4]. The data for the calculation of the classical diffusion of the hydronium were collected by MD methods in the present work. It is possible to take into account also the hopping mechanism explicitly only in the framework of the quantum approach. However, this can only be applied for small systems usually consisting of up to some tens of atoms. In the present work, a new kind of particle was created to study proton-conductivity by classical molecular dynamics which can handle the polymers. This particle, which is called in this paper a proton, has the proton's mass and charge. However, its Van der Waals radius is derived based on condensed phase properties of molecules containing highly polarized hydrogen, (such as water or alcohol). Thus, this particle can, in the model, react constantly with surrounding molecules via a strong electrostatic interaction and can jump from one water molecule to another. This means that the proton in our system is not a true proton nor a proton in condensed phases, but it is a particle, with which the hopping mechanism can be described, partially by MD simulation [5]. The model, of course, is not perfect, (e.g., no bonds can be created between the proton and the water molecules). However, this provides a new interesting approach to a very difficult task.

In the present work MD atomistic simulations of an amorphous proton-conducting system, consisting of (1) one PEO sulfonic acid ($M_w = 436$) molecule, (2) one proton, (3) one hydronium ion and (4) 220 water molecules, were made to study the coordination of the ions, the diffusion of the ions and water and the conductivity of the system. The work was started by the determination of the parameters for the ions missing from the PCFF forcefield made by MSI (Molecular Simulations Inc.), to create a new forcefield, NJPCFF. The

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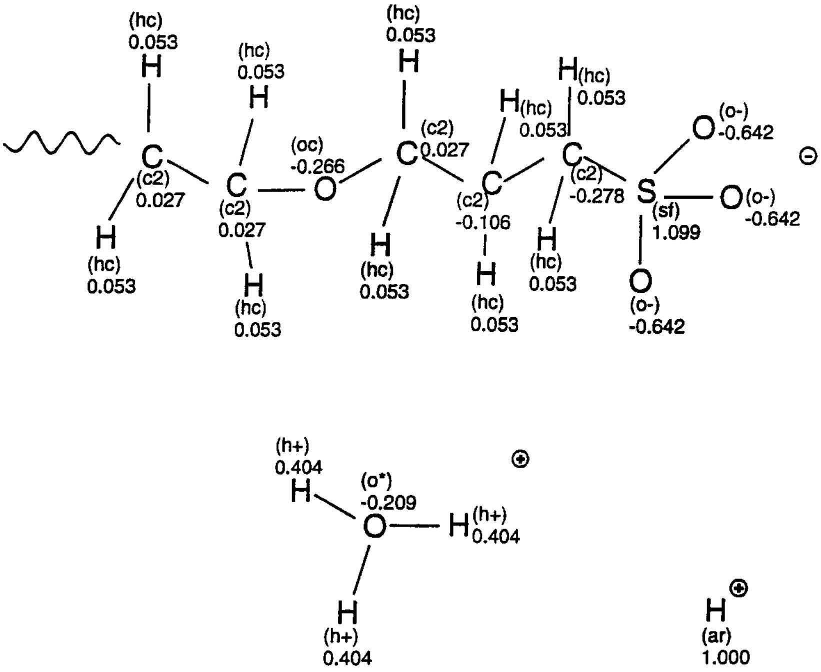

Fig. 1. Partial charges are shown next to the atoms for PEO sulfonic acid anion (on the top), and hydronium ion (below on the left), calculated using MP2 method and for proton (below on the right). The atom types are shown in parentheses.

coordination between the cations and the anion and between the cations and the oxygen in the chain of the PEO sulfonic acid anion, which have previously been studied in the real polymer system by Raman spectroscopy [3] were modelled by calculating the pair correlation functions. The diffusion coefficients were calculated with a new code. To evaluate the conductivity of the system a program was made to calculate the correlations of displacements of ions.

The goal of this work is to create a model which can give information that can be used when the applicability of a new material as a polyelectrolyte is predicted. The model and the system are still rather simple and they will be further developed to take account more explicitly of the hopping mechanism. The present work is part of a series where three systems were constructed with different concentrations of the PEO. In the present system, the concentration of PEO was zero and the number of the ions was kept as small as possible to obtain a dilute solution as a reference system for more complex systems. The calculations of the other systems in the series are still running and the results will be published later.

2. Theory

Pair correlation functions are used in simulations to give the probabilities of finding a pair of atoms at distance r apart, relative to the probabilities expected for a completely random distribution at the same density [6,7]. The coordination numbers were calculated by the equation

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

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, $< V >$ is the volume of the cell and $g_{x\ldots z}(s)$ is the radial distribution function between x and z.

The diffusion coefficient D, can be determined in the atomistic modelling by the following equation [8]

$$D_\alpha = \frac{1}{6N_\alpha} \lim_{t\to\infty} \frac{d}{dt} \sum_{i=1}^{N_\alpha} \left\langle [R_i(t) - R_i(0)]^2 \right\rangle \tag{2}$$

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 $R_i(t)$ 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, in other words, the Einstein diffusion is reached. It is easy to test the region in which Eq. (2) is valid by plotting log(MSD) against log(t). In the case of Einstein diffusion, the slope of the curve is one, (Eq. 3) [9].

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

The ionic conductivity σ, can be determined by using the Einstein equation

$$\sigma = \frac{e^2}{6tVkT} \left(\sum_i z_i^2 \left\langle [R_i(t) - R_i(0)]^2 \right\rangle + 2\sum_{j>i} z_i z_j \left\langle [R_i(t) - R_i(0)] \left[R_j(t) - R_j(0) \right] \right\rangle \right) \tag{4}$$

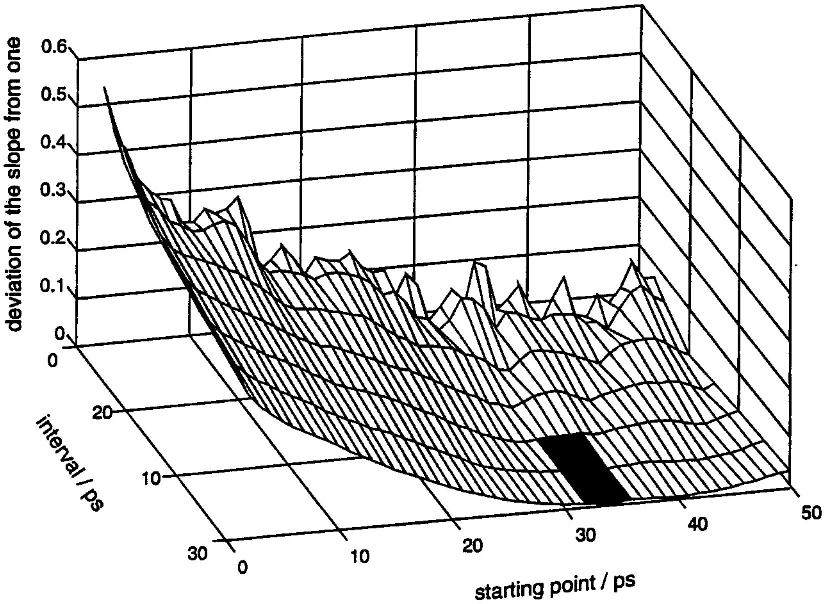

Fig. 2. The deviation from one of the slopes of log(MSD) as a function of log(t) on the $n1$,$n2$ surface where $n1$ is the length of the interval and $n2$ is the starting point of the interval used to determine the optimal region where the slope is near to one. Calculations are for the hydronium ion in one cell at simulation time of 1000 ps.

where t is time, V is the volume of the cell, k is the Boltzmann constant, T is the temperature and R is the position vector of the diffusing ion. The first term of the right-hand side is the sum over individual mean square displacements weighted with the charges and the second term is the sum of correlation of displacements of ions describing the interactions between different ions.

3. Computational details

The computational results were obtained using a Silicon Graphics Indigo 2 workstation, the SGI Power Challenge metacomputers of CSC, (Center for Scientific Computing Ltd, Espoo, Finland), and the software programs from MSI (Molecular Simulations Inc.) from San Diego [10]. Ten 3D amorphous cell starting structures with periodic boundary conditions were built. Each cell consists of one proton, one hydronium ion, 220 water molecules and one PEO sulfonic acid dianion, $^{-}O_3SCH_2CH_2CH_2O(CH_2CH_2O)_4CH_2CH_2CH_2SO_3^{-}$, corresponding to $M_w = 436$. The density of the system was 1.00 g/cm^3. The size of the system was 19.49 Å × 19.49 Å × 19.49 Å corresponding to $<V> = 7404.499$ Å^3. All calculations were made using the NJPCFF forcefield, a modification of the PCFF forcefield [11–15], which is suitable for the PEO sulfonic acid [16]. The modified charge distribution of the ions and the atom types used are shown in Fig. 1. The added parameters for PEO sulfonic acid anion were the bond parameters, K_2 is 500 and b_0 is 1.49. The term corresponding to the bond length agrees with the values 1.46 Å–1.44 Å calculated for different methylsulfonate and phenylsulfonate anions with ab initio methods [17]. The O–S–O angle was set to 115°. In the NJPCFF forcefield the proton has the mass 1.00797 u and the value 2.5 for constant r_i^* and 0.013 for ε_i in the non-bonding term.

All ten cells were first minimized with molecular mechanics using the steepest-descents method for 10000 steps. Six structures with the lowest total energy were selected and minimized with the conjugate-gradients method until the maximum derivate was less than 15 kcal/mol. After minimization, a molecular dynamics run of 860 ps–1000 ps was made using the NVT ensemble and the Andersen [8] method for temperature control. The temperature was 298 K in all calculations. The time step was 1 fs. The van der Waals and coulombic non-bonding interactions were calculated using both the Ewald summation method and the group-based summation method with cutoff 9.75 Å. No difference between the results was found, because the interactions between the ions were small due to the high dielectric constant of water and the small amount of ions. A new program was made for the calculations of the correlation of displacements of the ions and the ionic conductivity of the system. A new `matlab`® code was written in order to find the region in which the Einstein diffusion is valid in the plot of MSD as a function of time. This code allows reduction of the error of the calculation of the diffusion coefficient. In this code, the location of the interval on the time axis is the first variable ($n1$) and the length of each interval ($n2$) is the second. The response surfaces of the deviation of the slope in Eq. (3) from slope equal to one and the error of the diffusion coefficient by 3-dimensional plots, (see Fig. 2), were interactively studied. The error of

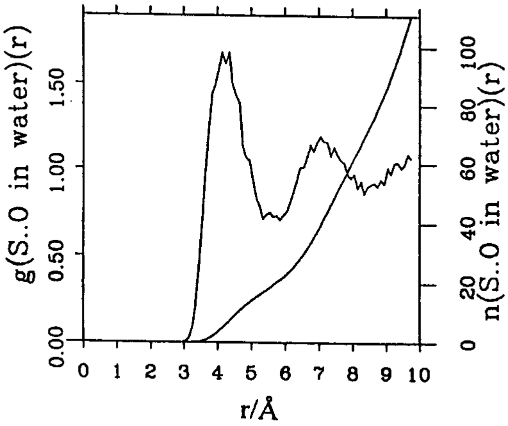

Fig. 3. Pair correlation function *g*(*r*), between the sulfur (S) in the sulfonic acid anion group and the oxygen in water. Coordination numbers *n*, as a function of the distance, *r*, are indicated in the figure.

the diffusion coefficients was calculated from the variation of the values of MSD on the selected *n*1,*n*2 plane.

4. Results

4.1. Coordination study

Pair correlation functions and coordination numbers were calculated to study the coordination. Analysis of the coordination of the sulfur atom in the sulfonic acid anion group and the oxygen of water gives the number of the water molecules coordinated to the sulfur atom; it is about 19 at the range 3 Å–5.5 Å and about 69 at the range 3 Å–8.5 Å, see Fig. 3. In the experimental study, the first coordination shell around the sulfonic acid group in Nafion boiled for 1 h in water is reported to contain about 22 water molecules [18], which corresponds well to the calculated value of 19. The coordination number, of course, depends on the concentration. It has been shown in the case of grafted and sulfonated poly(vinylidene fluoride) membranes that there should be more than 10 water molecules per sulfonic acid group to gain a significant proton conductivity [19].

The pair correlation function between the proton and the sulfur atom showed a very weak coordination between these particles. The coordination number at a separation of from 2.5 Å to 4 Å is very small, about 0.11. When the proton is coordinated to the sulfur atom, it is coordinated with all three oxygen atoms. The correlation between the sulfur in the anion and the proton ceases after 4 Å. When the system was animated on the screen it was seen that for most of the time the proton moves freely.

The simulated coordination number between the hydronium ion and the sulfur in the first coordination shell (at 5.5 Å) is 0.26. From the graphics it can be seen, that the hydronium ion is occasionally coordinated to both ends of the chain at the same time. In the experimental study of PEO sulfonic acid only a few or no uncoordinated SO_3^- end groups were detected and the dominant feature was found to be a contact ion pair between the cation and the sulfonic acid anion [3]. This agrees well with the results of the simulation where both of the SO_3^- end groups could be coordinated to the same hydronium ion while the proton moved freely.

In the pair correlation function between the ether oxygen in the PEO sulfonic acid chain and the oxygen of water, two coordination shells are seen. The first is at 3.5 Å where one water molecule is coordinated to one ether oxygen and the second is at about 5.6 Å where about 8 water molecules are coordinated to the ether oxygen. The water binding of the PEO chain has been extensively studied experimentally. In the earlier papers, the number of bound water molecules per PEO repeat unit was reported to be 2–4 [20,21], but in the latest papers it is usually reported to be one [22–24], which agrees with our result.

No coordination was found in the pair correlation function between the proton and the ether oxygen in the PEO sulfonic acid anion. Between the oxygen in the hydronium ion and the ether oxygen in the PEO sulfonic acid a coordination was found. The coordination number at a separation of 3.5 Å is 0.3 and at 4.5 Å it is about 1 indicating that the hydronium ion is coordinated to one oxygen in the chain. One is the largest possible coordination number in this system where only one hydronium ion is present. When the system is animated, it is clearly seen that the proton is jumping from one place to another rather freely, while the hydronium ion is close to one end of the chain for a long time and then slides along the chain to the other end. The coordination between the cation and the ether oxygen in PEO sulfonic acid has been experimentally studied by Raman spectroscopy [3]. In these studies, the vibrational behaviour of the C–O–C bands did not indicate any cation-ether oxygen coordination. However, several investigations have shown a coordination between metal cations and the ether oxygen of PEO [25–27].

The coordination of the water with water and water with the cations was studied by the intermolecular pair correlation function between the oxygens in water, the oxygen and the hydrogen in water, the proton and the oxygen in water and the oxygen in the hydronium ion and the oxygen in the water. In the pair correlation function between the oxygen and the hydrogen atoms in water there is a strong peak at 2.5 Å corresponding to the hydrogen bond. The experimental pair correlation function gives a little lower value, 1.85 Å [28]. The pair correlation functions between cations and oxygen in water and between oxygens in water all exhibit the same kind of pattern. The first strong peak is at 3.15 Å corresponding to the correlation between oxygen atoms or at 2.3 Å corresponding to the correlation between the proton and the oxygen in water. The second strong peak is about 3 Å from, and the third about 6 Å from the first peak. The experimental value of the correlation distance between the oxygen atoms for pure water is 2.9 Å for the first peak with an error of about 6% [29]. This indicates the same tendency

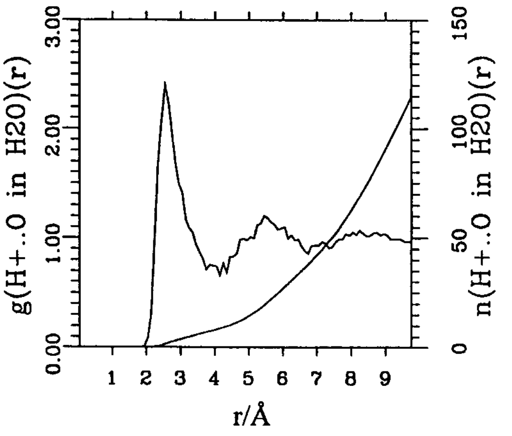

Fig. 4. Pair correlation function $g(r)$, between the proton (H^+), and the oxygen in water. Coordination numbers n, as a function of the distance, r, are indicated in the figure.

as above for the length of the hydrogen bond; the distances between the molecules in water are a little shorter in reality than in the model used. The experimental pair correlation function between the oxygens in pure water has one strong peak at 2.87 Å ending at 3.2Å with the coordination number 4.5 [29]. The experimental pair correlation function has a second peak before 5 Å. In our model, the first peak ends at 4.5 Å, where the coordination number between the oxygen atoms of water is about 12. The simulated coordination number between the hydronium ion and the oxygen atoms of water is about 10 in the first coordination shell, which ends at 4.5 Å, and about 50 in the second shell, which ends at 7.5 Å. The proton in our model is coordinated to 7 water molecules at a distance of 4 Å and to 50 water molecules at a distance of about 7 Å between proton and the oxygen of water (see Fig. 4).

Ab initio calculations with the gaussian 90 program show that the barriers for the proton transfer from the hydronium ion to a water molecule by a hopping mechanism are lower than the zero point energy of an O–H vibration, as long as the distance of the oxygen in water and the oxygen in the hydronium ion is less than 2.7 Å [30]. Although the distances between molecules in our simulation are longer than in the experimental studies, there are water molecules near enough to the hydronium ion to have a distance between the oxygen in the water molecule and the oxygen in the hydronium ion of less than 2.7 Å. Thus, if the classical MD program would have allowed a proton to hop from a hydronium ion to a water molecule then the hop would probably have happened. However, this was not possible in the present case and the hydronium ion was added to the system purely to study the classical diffusion of the hydronium ion.

4.2. Diffusion coefficients

The calculated diffusion coefficients of the proton, the water, the hydronium ion and the PEO sulfonic acid anion are shown in Table 1. The simulated average diffusion coefficient from the 1000 ps total simulation time for the proton is $(12 \pm 2) \times 10^{-9}$ m^2/s which is of the same order of magnitude as the value found in the literature, 9.31×10^{-9} m^2/s [31]. The simulated value of the diffusion coefficient from the 1000 ps run for the hydronium ion is $(1.9 \pm 0.4) \times 10^{-9}$ m^2/s and for water $(2.13 \pm 0.04) \times 10^{-9}$ m^2/s. The simulated value for water is close to the experimental value for the diffusion coefficient of pure water, 2.26×10^{-9} m^2/s [31]. The diffusion coefficient of the hydronium ion is very near the value of water, which can be explained by the similar sizes of the molecules and small concentration of ions in the system. The effective diffusion coefficient of the oxygen anion in the end of the polymer chain, $(0.6 \pm 0.1) \times 10^{-9}$ m^2/s, and of the ether oxygen in the polymer main chain, $(0.26 \pm 0.03) \times 10^{-9}$ m^2/s, are not the same due to the narrow time scale used in calculations of MSD. However, the values are very low compared to the other diffusion coefficients. This is due to the larger size of the polymer anion compared to the other penetrants. The Einstein diffusion was reached for the small ions and water in all the cases (the slopes of the curves log(MSD) as a function of log(t) varied from 0.96–1.03).

Calculations for the hydronium ion for six cells varying the duration of the dynamics run from 200 ps to 1000 ps were made. A special program to optimize the range where the Einstein diffusion is reached was constructed to optimize the simulation time for the hydronium ion. With this program, constant results within 1.6×10^{-9} m^2/s–2.2×10^{-9} m^2/s could be obtained for the hydronium ion from the longest runs to runs as short as 200 ps. Without the optimization procedure the calculation was very time consuming. From all the calculations, we conclude that the diffusion coefficients calculated with this novel method from different

Table 1
The average values for the calculated diffusion coefficients of hydronium ion (H_3O), with different simulation times, proton (H^+), water (H_2O) and the oxygen anion in the PEO sulfonic acid anion (O^-)

Penetrant	Total simulation time (ps)	Diffusion coefficient (10^{-9} m^2/s)	Literature values in pure water (10^{-9} m^2/s)
H^+	1000	12	9.31
H_3O	1000	1.9	9.31
H_2O	1000	2.13	2.26
O^-	1000	0.6	–
H_3O	200–900	1.6–2.3	–

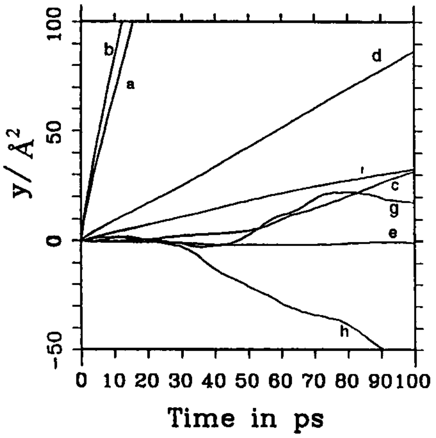

Fig. 5. The MSD for cell *g* as a function of time for the proton (a), the hydronium ion (d), the oxygen atom in the sulfonic acid anion group (f), and the correlations of displacements between the proton and the hydronium ion (h), between the proton and the anion (g), between the hydronium ion and the anion (c), and between the anions (e), and the total correlation function of ions displacements (b), where all other curves are included. The conductivity value σ calculated from curve *b* is (9.56 ± 0.90) S/m, from curve *a* for the proton σ is (8.00 ± 0.20) S/m, from curve *d* for the hydronium ion σ is (1.30 ± 0.30) S/m λ and from curve *f* for the anion σ is (0.5 ± 0.08) S/m.

starting configurations, in other words from different cells, differ more than the values calculated from shorter runs for the same cell. However, the order of magnitude of the diffusion coefficient is the same in all cases considered. The simulation time of 400 ps is probably sufficient for systems with a large amount of water. The error caused by the new code was about 3%. The total error, wherein is also the error caused by including the different starting structures, is about 15%–30% for systems containing only one penetrant. The total error of the diffusion coefficient for water was less than 2%. This is due to the great number of water molecules, 220, in the system.

4.3. Conductivity and interactions between the ions

Fig. 5 shows an example of the different contributions to the conductivity of the system: the MSD for one of the cells as a function of time for the proton, for the hydronium ion, for the oxygen atom in the sulfonic acid anion group and the correlation of displacements between the proton and the hydronium ion, between the proton and the anion, between the hydronium ion and the anion and between the anions, and the total correlation function of ions displacements, where all the other curves are included. The average values of the ion conductivity σ for all the cells calculated from the total correlation function of ions displacements is (12 ± 2) S/m. The average values of the conductivity σ calculated from the MSD as a function of time for the proton is (10 ± 2) S/m corresponding to $\lambda = (440 \pm 80)$ S cm^2/mol. Similarly for hydronium σ is (1.6 ± 0.3) S/m corresponding to $\lambda = (3.7 \pm 0.9)$ S cm^2/mol. The λ value for H^+ in the literature is about 349 S cm^2/mol at infinite dilution [32]. The value calculated based on the hydronium ion diffusion is smaller than the literature value. The value calculated for the proton is a little higher than the literature value, but the order of magnitude of the value of the conductivity is correct. This can be explained by the fact, that the hydronium ion described only the classical diffusion process and no hopping mechanism was included. The proton could move from one water molecule to another, but could not create a bond with any water molecule. So it proceeds faster in our model than in reality. The correlation of displacements between ions gives a very small contribution to the total correlation function in the range where the calculations are made. Also the MSD as a function of time for the hydronium ion is greater than the correlation of displacements between ions. The correlations of displacements between ions for different ions are small and nearly compensate each other for the present system having a low concentration of ions in water.

5. Conclusions

Systems consisting of PEO sulfonic acid anion, one proton, one hydronium ion and water were studied. An amorphous cell program was used to construct the system. Missing parameters were calculated and added to the PCFF forcefield to create a new NJPCFF forcefield. The proton was created with such non-bonding terms that, in the system, it could constantly jump from one water molecule to another forced by a strong electrostatic interaction. The coordinations between anions and cations were studied by calculating the pair correlation functions. The coordination between the cations and the sulfonic acid anion group was found. The hydronium ion was strongly coordinated to one or two sulfonic acid anion groups, while the proton was coordinated only to one end of the anion or moved freely. The hydronium ion was coordinated to the ether oxygen, while the proton had no coordination to the ether oxygen. Both the proton and the hydronium ion were coordinated to water molecules. Also, the sulfonic acid anion group was coordinated to water molecules. The diffusion coefficients for the proton, the hydronium ion, water and for the anion were calculated. A new procedure was developed to optimize the calculation of the diffusion coefficient for the hydronium ion. With this procedure the diffusion coefficients were obtained faster than before. The conductivity of the system was calculated and found to agree well with the results in the literature.

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References

[1] Chen-Yang YW, Hwang JJ, Chang FH. Macromolecules 1997;30:3825–3831.
[2] Odian G. Principles of polymerization. 3rd ed. Chichester, UK: Wiley, 1991, p, 172.
[3] Herranen J, Kinnunen J, Mattsson B, Rinne H, Sundholm F, Torell L. Solid State Ionics 1995;80:201–212.
[4] Eikerling M, Kornyshev AA, Stimming U. J Phys Chem B 1997;101(50):10807.
[5] Discussion with Dr Sun H, from MSI, San Diego.
[6] Allen MP, Tildesley DJ. Computer simulation of liquids. Oxford, UK: Clarendon Press, 1987.
[7] Raaska T, Niemelä S, Sundholm F. Macromolecules 1994;27:5751.
[8] Polymer user guide. Part 1. San Diego, CA: Biosym Technologies, 1993, p. 3–12.
[9] Müller-Plathé F. Acta Polym 1994;45:259.
[10] Insight II user guide. October 1995. San Diego, CA: MSI, 1995.
[11] Sun H. J Comp Chem 1994;15:752.
[12] Sun H. Macromolecules 1995;28:701.
[13] Hill J-R, Sauer J. J Phys Chem 1994;98:1238.
[14] Maple JA, Hwang MJ, Stockfisch TP, Dinur U, Waldman M, Ewig CS, Hagler AT. J Compt Chem 1994;15:162.
[15] Sun H, Mumby SJ, Maple JR, Hagler AT. J Am Chem Soc 1994;116:2978.
[16] Ennari J, Hamara J, Sundholm F. Polymer 1997;38:3733.
[17] Rozas I, Weaver DF. J Chem Soc, Perkin Trans 1996;2:461.
[18] Sondheimer SJ, Bunce NJ, Fyfe CA. J Macromol Sci-Rev Macromol Chem Phys 1986;C26(3):361.
[19] Hietala S, Holmberg S, Näsman J, Ostrovskii D, Paronen M, Serimaa R, Sundholm F, Torell L, Torkkeli M. Angew Macromol Chem 1997;253:151.
[20] Hager SL, MacRury TB. J Appl Polym Sci 1980;25:1559.
[21] de Vringer T, Joosten JGH, Junginger HE. Colloid Polym Sci 1986;264:623.
[22] Lüsse S, Arnold K. Macromolecules 1996;29:4251.
[23] Graham NB, Zulfiqar M, Nwachuku NE, Rashid A. Polymer 1989;30:528.
[24] Hey MJ, Ilett SMJ. Chem Soc, Faraday Trans 1991;87:3671–3675.
[25] Gray FM. Solid polymer electrolytes. New York: VCH, 1991, p. 45–55.
[26] Neyertz S, Brown D, Thomas JO. Electrochimica Acta 1995;40:2063.
[27] Catlow CRA, Mills GE. Electrochimica Acta 1995;40:2057.
[28] Laasonen K, Sprik M, Parrinello M. J Chem Phys 1993;99:5749.
[29] Soper AK, Philips MG. Chem Phys 1986;107:47.
[30] Schmidt RG, Brickmann J. Solid State Ionics 1995;77:3.
[31] Atkins PW. Physical chemistry. 2nd ed. Oxford: Oxford University Press, 1982, p. 905.
[32] Adamson AW. A textbook of physical chemistry. 2nd ed. New York: Academic Press, 1979.