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Simulation of a PEO based solid polyelectrolyte, comparison of the CMM and the Ewald summation method

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Abstract

Modeling of polyelectrolytes is very time consuming because of the strong long-range interactions between ions. Traditionally the Ewald summation method is used to calculate the non-bonding Van der Waals and Coulombic interactions. Recently a new much faster method called the cell multipole method (CMM), has been developed to model the non-bonding interactions. The use of the CMM makes the calculations dramatically faster compared to the duration of the calculation when the Ewald summation method is used. In this paper we compare the results of a spectral analysis, pair correlation study and dihedral angle study made for a solid amorphous polyelectrolyte by using both the Ewald summation method and the CMM. The simulated system contained poly(ethylene oxide) sulfonic acid anions, poly(ethylene oxide) (PEO), cations and water. There was no remarkable difference between the results obtained by using Ewald summation method or the CMM. Thus in future the calculations of similar systems can be made applying the fast CMM. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: CMM and Ewald summation method; Poly(ethylene oxide) sulfonic acid; Polyelectrolyte

1. Introduction

Polyelectrolytes have received considerable attention during the last two decades because of their potential applications in electronic equipment, medical devices and electrical vehicles [1–4]. The possibility of using polymer based proton conductors in electrochemical devices has been recently reviewed [5,6]. The conduction mechanisms of the proton conducting polyelectrolytes are not yet known despite many theoretical and experimental investigations. Molecular modeling with the sophisticated software of today and increasingly powerful computers offers new ways to get information of this complex phenomenon and opens possibilities to predict the suitability of polyelectrolyte materials in various applications.

However, one of the main problems in applying molecular modeling to study ion-conductivity is the long duration of the calculations. This is mainly due to two facts. The first reason is that the systems contain ions. This leads to long-range interactions between the particles in the system. Secondly the conduction is a relatively slow process. Usually simulation times of 1–2 ns are needed for polymer systems to reach the Einstein diffusion region. The non-bonding Van der Waals and Coulombic interactions are traditionally calculated for the ion containing systems using the Ewald summation method [7]. However, the Ewald summation method is very time consuming. Recently a much faster method called cell multipole method (CMM) has been developed to treat the non-bonding interactions [8–10]. The time saving effect of the CMM is dramatic compared to the Ewald summation method. The aim of this study is to compare the results obtained by using the Ewald summation method and the CMM. Similar results obtained with both methods leads to the important possibility of choosing the quickest method, CMM, in future simulations.

We have reported the synthesis and testing of a proton-conducting membrane consisting of high molar mass poly(ethylene oxide) (PEO), sulfonated PEO (PEO sulfonic acid), and water [11]. To model this system 10 amorphous systems containing four PEO sulfonic acid anion molecules ($M_w = 436$), eight cations, one PEO molecule and 74 water molecules were built. The systems were relaxed by molecular mechanics and molecular dynamics by using both the Ewald summation method and the CMM. We have previously reported the dynamical behavior of the particles in this system simulated by the Ewald summation method [12]. We have also recently reported simulation studies of

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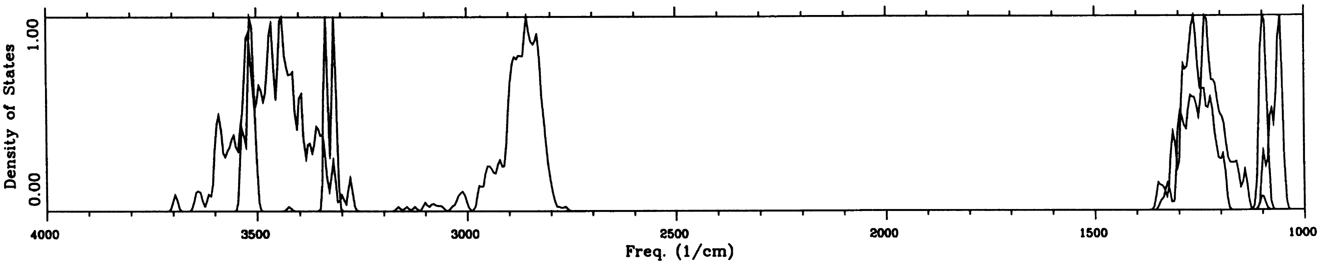

Fig. 1. Simulated vibrational spectrum of an amorphous cell containing the PEO sulfonic acid anion with $M_w = 436$, PEO, water and a hydronium ion.

Table 1
The simulated vibrational absorptions from trajectories calculated with the Ewald summation method (Ewald), or the 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	3670	3630		3710[a]	O–H, water not hydrogen bonded
b	3470	3440			
c	6930	6870			
			3440	3400–3600[a]	Hydrogen bonded
a	3510	3520		< 3500 (very broad)	O–H in H_3O^+
b	3510	3520			
c	7020	7030			
a	3550	3500	3440	3400–3600[a]	O–H polymers
b	3450	3400			
c	6930	6830			
			1600–2800	1650–2800	H_3O^+
			1650	1680	
a	2980	2980	2925	2925[b]	C–H
b	2880	2880	2870	2890[b]	
c	5750	5750		2850–3000[a]	
a	1270	1270	1350	800–1300[a]	C–C
b	1270	1270			
c	2540	2530			
a	1250	1250	1110	1110[b]	C–O
b	1240	1240		1120[b]	
c	2480	2480		1070–1150[a]	
a				1150–1170[c]	S=O
b				1340–1350[c]	
				890–910[c]	S–O
a	1100	1100	610	600–700[d]	$SO_3^-H_3O^+$
b	1100	1100	1040	1010–1080[d]	
c	2190	2200	1190	1150–1260[d]	
a	1100	1100		1070–1140	$S–O^-$
b	1100	1100		1200–1220	
c	2190	2200			
a	1090	1080		1070–1100[a]	C–S
b	1090	1080			
c	2170	2170			

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

the PEO sulfonic acid anion in pure water [13,14]. The construction of the ions is explained in detail in those papers.

2. Theory

The local mode method was used to calculate the vibrational spectra. The slow motions are modeled by using classical simulation techniques (molecular dynamics MD). The fast vibrations are treated separately by stopping the MD run several times and determining the molecular vibrations by quantum mechanical calculations for each vibration and configuration. First a local effective potential energy function (Eq. (1)), is calculated:

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

Then this potential function is used to solve a 1D Schrödinger equation (Eq. (2))

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

where M is the G matrix of normal mode analysis in general. The final results are averages of the values obtained from three different configurations from all different starting systems. The results of one configuration are collected as a histogram, which represents a Boltzmann averaged, inhomogeneously broadened vibrational density of states (Fig. 1).

3. Computational details

The computational results were calculated using two Silicon Graphics Indigo 2 workstations, the SGI Power Challenge computers of CSC (Centre for Scientific Computation Ltd, Espoo, Finland), and the software programs InsightII and Discover versions 3.0.0 and 4.0.0P from MSI (Molecular Simulations Inc.) [15].

Ten 3D amorphous cells were constructed with periodic boundary conditions. Each cell contained four PEO sulfonic acid anions ($^-O_3SCH_2CH_2CH_2O(CH_2CH_2O)_4CH_2CH_2CH_2SO_3^-$), four hydronium ions and four protons [14], one PEO molecule with degree of polymerization 60 and 74 water molecules. The size of each system was $19.4028 \times 19.4028 \times 19.4028$ Å^3 corresponding to $\langle V \rangle =$ 7304.546 Å^3. The density of these systems was 1.36 g/cm^3.

We have previously shown that the PCFF force-field [16–20] is suitable for modeling the PEO sulfonic acid [21]. We have recently reported the NJPCFF force-field in detail, which is a modification of the PCFF force-field [14]. The NJPCFF force-field includes also the ions and it was used for all calculations. All cells were first minimized by molecular mechanics methods (steepest descents and conjugate gradients), until the maximum derivative 0.1 kcal/(mol Å) was reached. Using NVT ensemble 200 ps long dynamics runs were made for each cell using the Ewald summation method and using the CMM. In all Ewald summation calculations the Ewald accuracy of convergence of the Ewald energy summation was 0.01 kcal/mol and the value of the update width parameter was 1.0 Å. In all CMM calculations the update width parameter was 1.0 Å and the accuracy parameter was set to Fine to use fourth order in the Taylor series expansion and explicit interactions for more neighboring cells. In all calculations the Van der Waals and Coulombic non-bonding interactions were modeled with the same cutoff methodology. Previously 800–1000 ps long runs using the Ewald summation method have been made for the same systems with the smaller number of trajectories [12]. Only one to two conformational changes were detected during these long runs. This means that the starting structures created by the amorphous_cell builder made by MSI do not change much during the simulation. Thus it was concluded, that by using many short runs a better statistical average is obtained than using a few long runs. The temperature was 298 K in all simulations and the Andersen method [22] was used to control it. For the calculation of the final properties only the 100 last picoseconds were used from each trajectory.

4. Results

4.1. Spectral analysis

The simulated vibrational frequencies for the simulated molecules are collected in Table 1. Table 1 also includes the values from literature and the values of the measured IR and Raman spectra for a membrane containing the PEO sulfonic acid and PEO [23–28]. The accuracy of the local mode method is about 100 cm^{-1}. The simulated vibrational frequencies for C–C, C–S and C–H stretch for PEO and for PEO sulfonic acid anion gave similar values with the corresponding vibrational absorptions assigned to PEO sulfonic acid, PEO or sulfonic acid compounds, and with the experimental data of the membrane containing the PEO sulfonic acid and PEO within the accuracy of the local mode method. There was no difference between the results calculated using the Ewald summation method or the CMM.

No difference was found between the simulated values of the C–O stretch calculated with the Ewald summation method or with the CMM. The simulated values of the C–O stretch were higher (1250 cm^{-1}) than the experimental value (1110 cm^{-1}). This was also found in the simulation studies of the PEO sulfonic acid in vacuum [21] and of PEO sulfonic acid anion in vacuum [13]. The phenomenon was not present when the CVFF force-field was used to study the PEO sulfonic acid [21]. However, the PCFF force-field was selected for the calculations, because it is more suitable for the calculations of the sulfonic acid group than the CVFF force-field [21].

The simulated frequencies for the sulfonic acid group

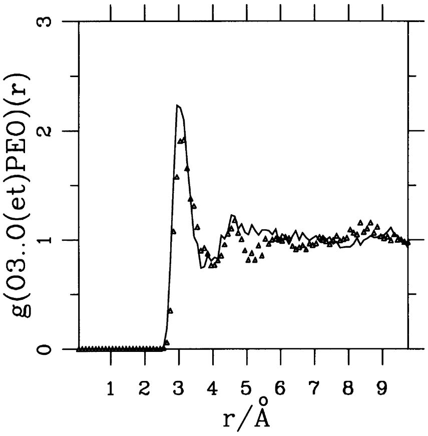

Fig. 2. The intermolecular pair correlation function $g(r)$ between the oxygen atom in the hydronium ion and the ether oxygen in PEO calculated using the CMM (line) and the Ewald summation method (triangle).

(1100 cm^{-1}), were very close to both the measured frequencies (1040 and 1190 cm^{-1}) and the frequencies found in the literature for the uncoordinated sulfonic acid anion (1070–1140 cm^{-1}) or the coordinated sulfonic acid anion (1010–1080 cm^{-1}), and for the S=O stretch (the literature value is 1150–1170 cm^{-1} for harmonic and 1340–1350 cm^{-1} for anharmonic stretch). Thus no conclusions can be drawn from the frequencies whether the sulfonic acid group is coordinated or not. The Ewald summation method and CMM gave the same results.

The simulated value of the O–H stretch in water (3630–3670 cm^{-1}), is very near the O–H stretch in hydrogen bonded water (3400–3600 cm^{-1}). The simulated values for the O–H stretch in hydronium ions (3510–3520 cm^{-1}) is in accordance with the assignments for the hydronium ion (3500 cm^{-1}) within the accuracy of the local mode method. The simulated value of the O–H stretch in the end of the PEO chain (3500–3550 cm^{-1}) is similar to the assignment for the O–H stretch (3400–3600 cm^{-1}). There was no difference between the results obtained using the CMM or the Ewald summation method that would be larger than the accuracy of the local mode method.

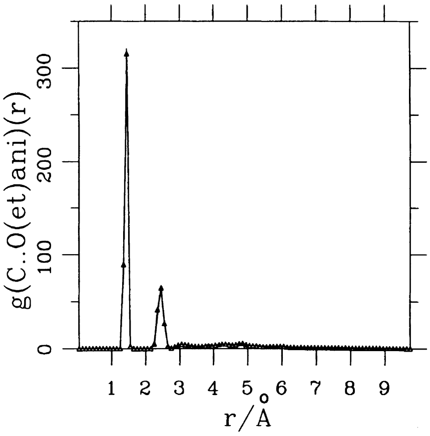

Fig. 3. The intramolecular pair correlation function $g(r)$ between the carbon atoms and ether oxygen atoms in PEO sulfonic acid anion calculated using the CMM (line) and the Ewald summation method (triangle).

Thus a good correlation between the simulated and measured spectra and between the simulated frequencies and the frequencies from the literature was found. Similar results were obtained with the Ewald summation method and with the CMM. All the stretching frequencies calculated were close to the values calculated previously for the system containing sulfonic acid anion and hydronium ion in water [13].

4.2. Pair correlation study

The coordination between the cations and the ether oxygen in the polymers was studied by calculating the intermolecular pair correlation functions between the oxygen atom in hydronium ion and the ether oxygen in PEO, between the oxygen atom in hydronium ion and the ether oxygen in PEO sulfonic acid anion, between the proton and the ether oxygen in PEO and between the proton and the ether oxygen in PEO sulfonic acid anion. In Fig. 2 the average pair correlation functions between the oxygen atom in the hydronium ion and the ether oxygen in PEO calculated using the CMM (line) or the Ewald summation method (triangle) are plotted. From Fig. 2 it can be seen that there is no remarkable difference between the results obtained using the CMM or the Ewald summation method in the pair correlation function between oxygen in hydronium and ether oxygen in PEO. One coordination shell is found at 3.2 Å. Also in the average pair correlation function between proton and ether oxygen in PEO one clear coordination shell was found at 2.5 Å. The results obtained using the CMM and the Ewald summation method were similar. The pair correlation function between the proton and the ether oxygen in PEO sulfonic acid calculated with CMM and Ewald summation method gave similar results. Of course a larger deviation was found than in the results concerning the proton and the ether oxygen in PEO, because the statistical number was not as large as in the case of PEO. One clear coordination shell was found at 2.5 Å. The pair correlation function between the oxygen atom in the hydronium ion and the ether oxygen in PEO sulfonic acid calculated with the CMM and the Ewald summation method gave rather similar results. There was a coordination shell at 3.2 Å. Results obtained using the Ewald summation method gave slightly larger values for the coordination between the oxygen atom in the hydronium ion and the ether oxygen in PEO sulfonic acid anion than the CMM, but the difference was in the range of the simulating error.

The intermolecular pair correlation function between oxygen in water and the ether oxygen in PEO and between oxygen in water and the ether oxygen in PEO sulfonic acid anion was calculated. Both the Ewald summation method and the CMM gave similar results. The results concerning PEO and PEO sulfonic acid were also similar. Two main coordination shells were found. The first coordination shell

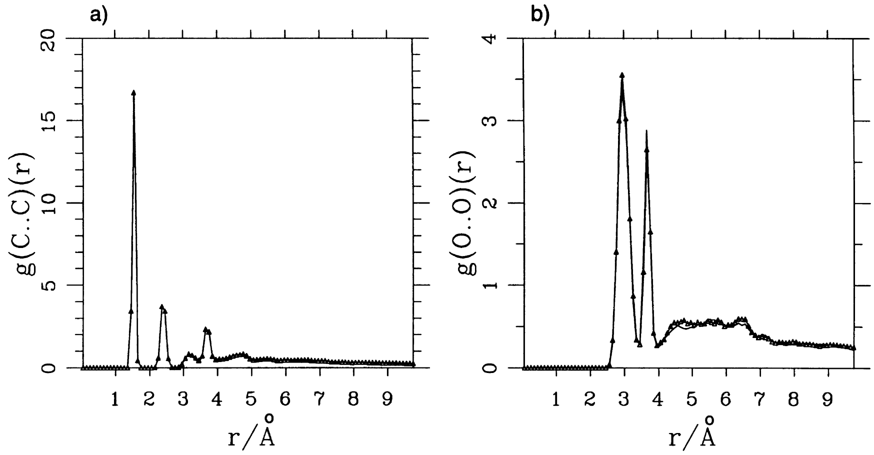

Fig. 4. The intramolecular pair correlation function $g(r)$ between: (a) the carbon atoms in the PEO chain; and (b) the ether oxygen atoms in PEO chain calculated using the CMM (line) and the Ewald summation method (triangle).

was at 3.1 Å (with $g(r)$ about 1.4) and the second coordination shell was at 4.6 Å (with $g(r)$ about 1.3).

The intramolecular pair correlation function between carbon and ether oxygen in the PEO chain (see Fig. 3) and between carbon and ether oxygen in the PEO sulfonic acid anion chain show coordinations at 1.5 Å corresponding to the bond length between an ether oxygen and a carbon atom in the chain and at 2.5 Å corresponding to the distance between an ether oxygen atom and a carbon atom next to the carbon atom bonded to the ether oxygen atom. There was no difference between the results obtained using the CMM or the Ewald summation method. In the intramolecular pair correlation function between carbons in the PEO chain (Fig. 4(a)), there was no difference between the curve calculated using the CMM or the Ewald summation method. The situation was the same for the intramolecular pair correlation function between carbons in the PEO sulfonic acid anion chain. The peaks were at the same distances for PEO and PEO sulfonic acid anion. The largest peak was found at 1.5 Å corresponding to the bond length between carbon atoms. The second largest peak was at 2.5 Å corresponding to the average distance of the carbon atoms separated by an ether oxygen molecule and the third largest was at 3.7 Å. The smallest peak detected was at 3.2 Å. The intramolecular pair correlation function between ether oxygens in the PEO chain (see Fig. 4(b)) and in the PEO sulfonic acid anion chain show correlations at 3.0 Å corresponding to the *gauche* conformation of the OCCO dihedral angle and at 3.6 Å corresponding to the *trans* conformation corresponding to the average distance between the carbon atoms separated by an ether oxygen molecule. Results obtained using the CMM or the Ewald summation method were similar.

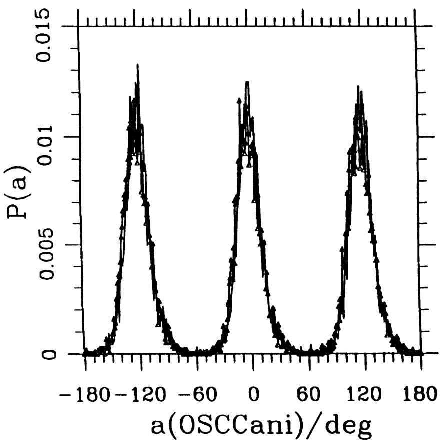

Fig. 5. The OSCC dihedral angle distribution $P(a)$ in the PEO sulfonic acid anion calculated using the CMM (line) and the Ewald summation method (triangle).

The intermolecular pair correlation function between the oxygen atom in water and the sulfur atom in the PEO sulfonic acid anion calculated using the Ewald summation method and the CMM were similar (a coordination shell was found at 4 Å). The intermolecular pair correlation function between the proton and sulfur atom in the PEO sulfonic acid anion were similar calculated using the Ewald summation method and the CMM (the coordination shell was at 3.4 Å). This also applies for the intermolecular pair correlation functions between the oxygen atom in the hydronium ion and the sulfur atom in the PEO sulfonic acid anion (a coordination shell was found at 3.8 Å). Also the results calculated by the Ewald summation method and the CMM were similar for the intermolecular pair correlation functions between the cations and the oxygen atom in water and for the intermolecular pair correlation function between oxygen atoms in water.

4.3. Dihedral angle study

The structure of the PEO and the PEO sulfonic acid anion was studied by calculating the OSCC, SCCC, CCCO, CCOC and OCCO dihedral angle distribution with both the Ewald summation method and the CMM.

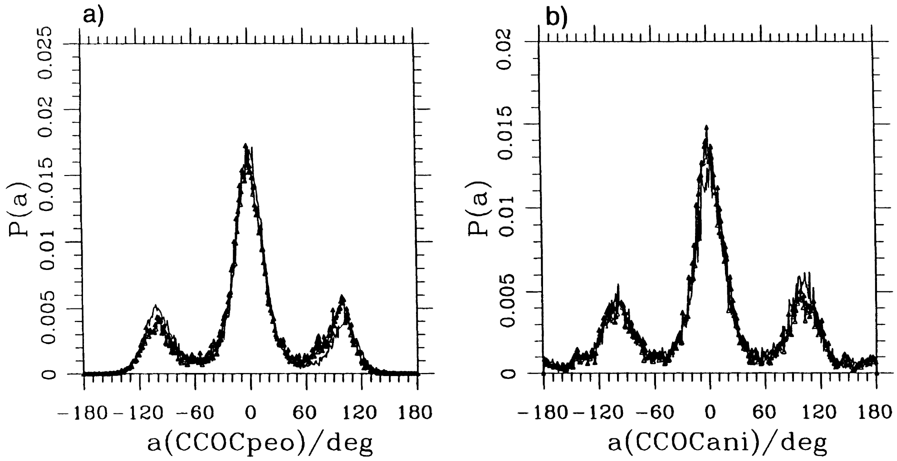

Fig. 6. The CCOC dihedral angle distribution *P*(*a*): (a) in PEO; and (b) in the PEO sulfonic acid anion calculated using the CMM (line) and Ewald summation method (triangle).

For the OSCC dihedral angle in PEO sulfonic acid anion three maxima were found: the g^- (*gauche* minus) near $-120°$, the *t* (*trans*), near 0° and the g^+ (*gauche* plus) near $+120°$ with similar probabilities (see Fig. 5). The OSCC dihedral angle distributions calculated with the CMM and the Ewald summation method are similar. Also in the OSCC dihedral angle distributions calculated for PEO sulfonic acid anion in vacuum and in water equal probabilities of the *trans* and *gauche* minus and *gauche* plus states were found [13].

We have previously reported that in the SCCC dihedral angle distribution of PEO sulfonic acid anion in vacuum and in water the *trans* conformation is dominating [13]. Also the SCCC dihedral angle distribution calculated in the present study with the CMM method is almost completely *trans*. In the Ewald summation method calculation for the SCCC dihedral angle distribution shows that the *trans* form was also dominating, but some more *gauche* forms were also detected than in the calculation with the CMM. Because the deviation is not large and especially only the probability of the *gauche* minus near $-120°$ is larger in the Ewald summation method calculation, this can be due to a statistical error. A similar small difference is seen for the CCCO dihedral angle distribution, although in all cases there are three maxima at *gauche* minus, *trans* and *gauche* plus with almost similar probabilities. The statistics is smallest in the SCCO and CCCO dihedral angles because their number is small and they cannot rotate as freely as the end of the PEO sulfonic acid chain, which gives better statistics for the OSCC dihedral angle.

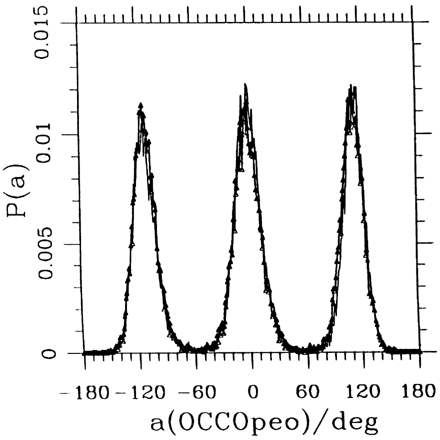

Fig. 7. The OCCO dihedral angle distribution *P*(*a*) in PEO calculated using the CMM (line) and Ewald summation method (triangle).

The CCOC dihedral angle distributions were studied separately for CCOC in PEO (see Fig. 6(a)), and for CCOC in the PEO sulfonic acid anion (see Fig. 6(b)). From Fig. 6 it can be seen that the CCOC dihedral angle distribution is similar for PEO and for PEO sulfonic acid anion. The CCOC dihedral angle distribution calculated with the Ewald method and the CMM are very similar. In all cases the *trans* conformation is dominating. This was also the case for the CCOC dihedral angle distribution in PEO sulfonic acid in vacuum and in water [13].

Also the OCCO dihedral angle distributions were studied separately for OCCO in PEO (see Fig. 7), and for OCCO in the PEO sulfonic acid anion. The results calculated for PEO and for PEO sulfonic acid were similar. Also the same results were obtained when the Ewald summation method or the CMM were used. There was the same portion of *gauche* minus, *gauche* plus and *trans* states, respectively. The OCCO dihedral angle distribution in PEO sulfonic acid anion has previously been found to be almost completely in *trans* conformation in vacuum and more in *gauche* form than in *trans* form in pure water [13].

5. Conclusions

Ten amorphous polyelectrolyte systems containing four PEO sulfonic acid anions, eight cations, one PEO molecule and 74 water molecules were constructed. For each system a

200 ps long molecular dynamics run using the Ewald summation method and using the CMM to calculate the non-bonding Van der Waals and Coulombic interactions was performed. The non-bonding interactions are usually treated with the Ewald summation method. This method is very slow. The new CMM is dramatically faster than the Ewald summation method. Results obtained for the spectral analysis, pair correlation study and dihedral angle distripution study by using the Ewald summation method or the CMM were compared. No remarkable difference was found. Thus the fast CMM can be used in further calculations of similar systems to obtain results faster.

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