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Vibrational spectra as experimental probes for molecular models of ion-conducting polyether systems

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Atomistic molecular modelling has been used to construct polymer electrolyte materials consisting of poly(ethylene oxide) (PEO), poly(ethylene oxide) with sulfonic acid end groups (PEO sulfonic acid) and water in an amorphous cell with periodic boundary conditions. A conformational analysis of PEO sulfonic acid was made using the PCFF forcefield, and for one linkage also the CVFF forcefield was used in molecular mechanics calculations. In addition, the energy contour map for the bond connecting the sulfonic acid group to the polyether chain and the next carbon–carbon bonds was constructed using RIS theory. The results obtained with the different forcefields were fairly similar. For all linkages several minima with low energy barriers were found. The relative energies of the minima vary very little. The maxima are due to steric effects. The conclusion is drawn that all rotations in PEO sulfonic acid are restricted at room temperature. Two polymer electrolyte systems were constructed, one water-free, and one containing water. The relevance of the model, and the most suitable forcefield, were tested by comparing the calculated vibrational spectra with experimental i.r. and Raman spectra. Very good agreement between measured and calculated vibrational frequencies was found with both forcefields for the modes attributed to the PEO chain. There was a significant difference between values for the S=O stretch calculated in the CVFF forcefield and in the PCFF forcefield, respectively. Since the S=O stretch calculated with the PCFF forcefield corresponds very well with literature values, the conclusion was drawn that the PCFF forcefield is better suited to model PEO sulfonic acid than is the CVFF forcefield. In the modelling studies, hydrogen bonds between the sulfonic acid group and water molecules were formed. In the experimental system an absorption was found which is attributed to a hydronium sulfonate ion pair. The correlation of this finding with experimental measurements of water transport in proton-conducting membranes is discussed. The proton coordination study shows that the model can be developed by adding sulfonic acid anions to the amorphous cell. The model will be further developed for studies of proton conducting mechanisms. © 1997 Elsevier Science Ltd.

(Keywords: modelling; conformational analysis; ion conducting; polyelectrolyte; vibrational spectra)

INTRODUCTION

Polymer electrolytes are extensively studied because of their potential applications in electrochemical devices as solid non-corrosive electrolytes. Traditionally, metal salts are dissolved in polyether-based hosts to produce solid polymer electrolytes with possible applications in rechargeable batteries[1]. Recently a new area of possible technical applications has been suggested for similar materials; namely, proton-conducting polyether membranes are potentially useful as solid electrolytes in electrochemical cells. Several experimental methods have been used to characterize polymer electrolytes, but some of the details are hard to resolve, among them conduction mechanisms, hydration mechanisms and water transport. In contrast, molecular modelling techniques provide atomic-level structural details such as chain conformation, chain packing in amorphous cells, and free volume distribution in the bulk. Availability of commercial software has played a significant role in increasing the utilization of molecular simulations to characterize polymeric materials. So far the simulations of polymer electrolytes have mostly concerned systems of polyethers with metal ions included[2] and are usually done by simulating crystal structures to obtain general information[3], although it is well known that the amorphous materials have better conductivities[4,5]. It has been earlier reported that molecular dynamics is the best tool to simulate ionic conductivity in an amorphous system[6].

Recently we reported the synthesis and testing of poly(ethylene oxide) with sulfonic acid end groups (PEO sulfonic acids) as proton-conducting electrolytes[7]. The oligomeric electrolytes were embedded in high molar mass PEO to obtain a mechanically stable electrolyte membrane. Ionic conductivities up to 1.5×10^{-3} S cm^{-1} were reached. The polymer electrolytes were characterized by thermal analysis, impedance spectroscopy, n.m.r. and i.r. spectroscopy. In addition, Raman spectroscopy was used to study the ionic interactions of the charge carriers, and the Raman results were correlated with features of the morphology of the polymer electrolytes.

In the present study an atomistic simulation is used

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for modelling an amorphous proton-conducting polymer. The simulations were done for a material consisting of PEO sulfonic acid with $M_w = 438$ mixed into PEO molecules with $M_w = 1366$ (degree of polymerization $n = 31$). Since no specific information about the conformation of the PEO sulfonic acid was available, a conformational analysis was performed for this molecule. One of the most important steps in atomistic simulations is the selection of the forcefield, since this has an enormous effect on most results. The modelling of the vibrational spectra is a very accurate method of testing the forcefield, and therefore vibrational spectra are used in the present case. The aim of the present work is to form a good model of the proton-conducting polymer electrolyte corresponding to actual materials with known properties, and to be able later to study mechanisms of proton conductivity and water transport in polyether systems and other polymeric systems.

EXPERIMENTAL

Materials

The preparation of low molar mass PEO sulfonic acids ($\langle M_w \rangle = 446$, 646, 846, 2246 and 4246) has been described previously[7]. High molar mass polyelectrolyte membranes containing the PEO sulfonic acids were prepared by dissolving the PEO sulfonic acid in acetonitrile, and mixing with a solution of PEO ($\langle M_w \rangle = 5 \times 10^6$) in acetonitrile[7]. The thickness of the membranes so obtained was in the range 40–55 μm.

Measurements

I.r. spectra were recorded on a Nicolet 205 FT instrument. The samples were dissolved in chloroform and spread on potassium bromide pellets, and the chloroform was evaporated. Raman spectra were recorded at room temperature using a triple spectrometer (SPEX 1877) equipped with microscope collection optics (Nikon) and a CCD detector (Wright Instruments). The 514.5 nm line of an argon laser (Spectra Physics model 2060) was employed for excitation. Backscattering geometry was used for detection. Results of these measurements have been reported in reference 7.

THEORETICAL CONSIDERATIONS AND COMPUTATIONAL DETAILS

The PEO, $H-(CH_2CH_2O)_n-H$, chosen for the single molecule studies had $M_w = 5458$, corresponding to a degree of polymerization = 124. The PEO chosen as matrix material for the polymer electrolyte had $M_w = 1366$, corresponding to a degree of polymerization = 31. The chain had an ethyl group as one end group and a hydroxyl group as the other end group. The starting conformation of PEO was obtained from the literature[8]. To obtain different starting conformations the helix was set with different torsion angles for each PEO molecule. The ranges used for the angles were 170°–190° for the <(CCOC) and <(COCC) while the <(OCCO) was set to 60°–90°. The PEO sulfonic acid used in single molecule studies and in the simulated polymer electrolyte material was $HO_3SCH_2CH_2CH_2O(CH_2CH_2O)_4CH_2CH_2CH_2SO_3H$, corresponding to $M_w = 438$. No helix was set for the PEO sulfonic acid.

All calculations were performed using the molecular modelling package InsightII (Biosym/MSI) (release 237) and a Silicon Graphics Indigo 2 workstation. The molecular mechanics and dynamics calculations were made in the Discover module of the software. Both the CVFF and PCFF forcefields were used. The conformational analysis for the –C3 linkage was also made using the RIS module, which is an implementation of Flory's original RIS theory. The polymer electrolyte amorphous cells were constructed and the spectra were simulated in the Amorphous_cell module. Different frames from the molecule dynamics simulation were selected for spectra simulation using the Analysis module.

In order to carry out RIS calculations, all the groups in the polymer must be present in an RIS groups database[9]. However, the sulfonic acid group was missing from the database. To be able to calculate the conformational energy map for the –C3 linkage (*Figure 1*), the original database was copied and the sulfonic acid group was added to the copy. The bond length between the sulfur atom and the carbon atom was estimated to be 1.78 Å[10] and this value was added to the database. The numbering of the bonds corresponding to the –C3 linkage are shown in *Figure 2* in which also the dihedral angles used are marked. According to RIS theory long range excluded-volume interactions are neglected.

The contour map for each pair of dihedral angles was constructed by calculating the total energy $E^{tot}(\varphi, \psi)$ as a function of the two torsion angles. The map is divided into regions and the minima are located. To calculate the statistical weights from the map, which includes all first- and second-order interactions, the energy E^{seg} corresponding to the first-order interactions dependent on the first torsional angle must be determined and subtracted. The energy E^{seg} is calculated for

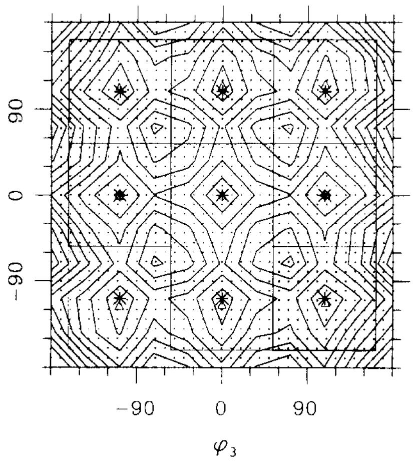


Figure 1 Energy map for the –C3 linkage in PEO sulfonic acid, simulated using the RIS theory. The energy differences between the graph lines are 1 kcal mol^{-1} and all minima are marked with an asterisk

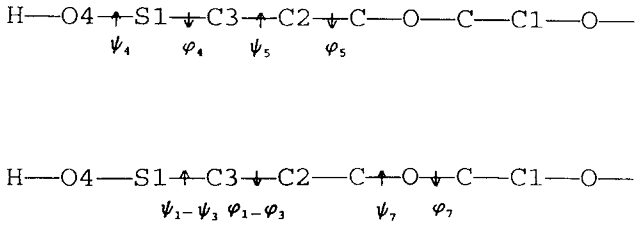


Figure 2 Linkages in the backbone of the PEO sulfonic acid studied in the conformational analysis

$$
\begin{aligned}
E_{\text{pot}} = {} & \sum_{b}\left[K_2(b-b_0)^2+K_3(b-b_0)^3+K_4(b-b_0)^4\right] && \textbf{(1)}\\
& + \sum_{\theta} H_2(\theta-\theta_0)^2+H_3(\theta-\theta_0)^3+H_4(\theta-\theta_0)^4 && \textbf{(2)}\\
& + \sum_{\phi}\left[V_1\left[1-\cos\left(\phi-\phi_1^0\right)\right]+V_2\left[1-\cos\left(2\phi-\phi_2^0\right)\right]+V_3\left[1-\cos\left(3\phi-\phi_3^0\right)\right]\right] && \textbf{(3)}\\
& + \underset{\textbf{(4)}}{\sum_{\chi} K_\chi \chi^2} + \underset{\textbf{(5)}}{\sum_{b}\sum_{b'} F_{bb'}(b-b_0)(b'-b_0')} + \underset{\textbf{(6)}}{\sum_{\theta}\sum_{\theta'} F_{\theta\theta'}(\theta-\theta_0)(\theta'-\theta'_0)}\\
& + \underset{\textbf{(7)}}{\sum_{b}\sum_{\theta} F_{b\theta}(b-b_0)(\theta-\theta_0)} + \underset{\textbf{(8)}}{\sum_{b}\sum_{\phi}(b-b_0)\left[V_1\cos\phi+V_2\cos 2\phi+V_3\cos 3\phi\right]}\\
& + \sum_{b'}\sum_{\phi}(b'-b_0')\left[V_1\cos\phi+V_2\cos 2\phi+V_3\cos 3\phi\right] && \textbf{(9)}\\
& + \sum_{\theta}\sum_{\phi}(\theta-\theta_0)\left[V_1\cos\phi+V_2\cos 2\phi+V_3\cos 3\phi\right] && \textbf{(10)}\\
& + \underset{\textbf{(11)}}{\sum_{\phi}\sum_{\theta}\sum_{\theta'} K_{\phi\theta\theta'}\cos\phi(\theta-\theta_0)(\theta'-\theta_0')} + \underset{\textbf{(12)}}{\sum_{i>j}\frac{q_i q_j}{\varepsilon r_{ij}}} + \underset{\textbf{(13)}}{\sum_{i>j}\left[\frac{A_{ij}}{r_{ij}^9}-\frac{B_{ij}}{r_{ij}^6}\right]}
\end{aligned}
$$

Figure 3 Form of the PCFF forcefield which allows for bond stretching (term 1) and for angle bending (term 2), a quartic polynomial. A three-term Fourier describes torsions (term 3). Term 4 defines the out-of-plane coordinate. Significant cross-terms up to third order (terms 5–11) are also included. The coulombic interactions between the atomic charges are represented by term 12. Term 13 characterizes the van der Waals interactions[12–14]

a chopped segment extracted from the original polymer segment[11]. The net energy corresponding to a value of φ is obtained by subtracting the chopped segment energy from the total energy at the same value of φ[9].

$$E^{\text{net}}(\varphi,\psi) = E^{\text{tot}}(\varphi,\psi) - E^{\text{seg}}(\varphi) \tag{1}$$

The partition function Z_i is calculated using the $E^{\text{net}}(\varphi,\psi)$. The statistical weights are obtained from

$$u_{jk} = Z_i/Z_{\text{ref}} \tag{2}$$

where Z_{ref} is the partition function of the region with minimum average net energy $E^{\text{net}}(\varphi,\psi)$. The statistical weights are stored in the database in form

$$u_{jk} = A_{jk}\exp(-\epsilon_{jk}/RT) \tag{3}$$

where A_{jk} is a dimensionless prefactor including information about the shape of the energy well, and ϵ_{jk} is the depth of the well in kcal mol^{-1}. The letter j denotes the rotational state of the first bond and k that of the second bond. The temperature was 300 K. All RIS calculations were performed using the PCFF forcefield. Terms included in the PCFF forcefield are shown in *Figure 3*[12–14].

The vibrational frequencies were calculated for PEO, PEO sulfonic acids and for two different polymer electrolyte amorphous cells by using the local mode method. In this method the slow inter- and intramolecular relaxations are modelled by using classical simulation techniques (MD), while fast molecular vibrations are solved accurately by using quantum mechanical calculations[9]. This is done in order to calculate those high frequency localized vibrations for which other methods (normal mode, FFT of time correlation, etc.) are not sufficiently accurate. The limitation of the method is that the vibrational mode must be a good local mode, in other words only bond stretches can be calculated. The advantage is that also anharmonic frequencies can be calculated. The local mode calculations can be used for systems containing 95 000 atoms or less. The accuracy of the method is 50–100 cm^{-1}.

All systems under study were first fully optimized by using molecular dynamics (Verlet algorithm) and

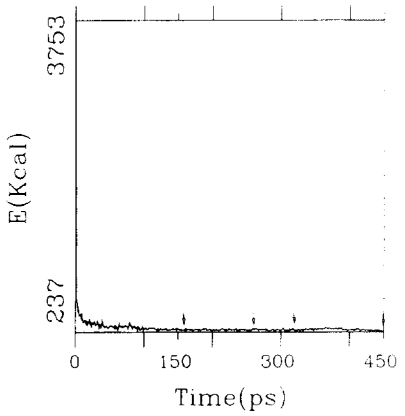


Figure 4 The history file of one dynamic simulation made for a cell containing three PEO molecules, six PEO sulfonic acid molecules and 24 water molecules. Local mode calculations are made for frames marked with an arrow

Table 1 Composition of cells

Cell	Number of EO units	Number of PEO sulfonic acid molecules	Number of water molecules	EO/SO$_3$H
Cell 1	3 × 31	6	24	10
Cell 2	3 × 31	6		10

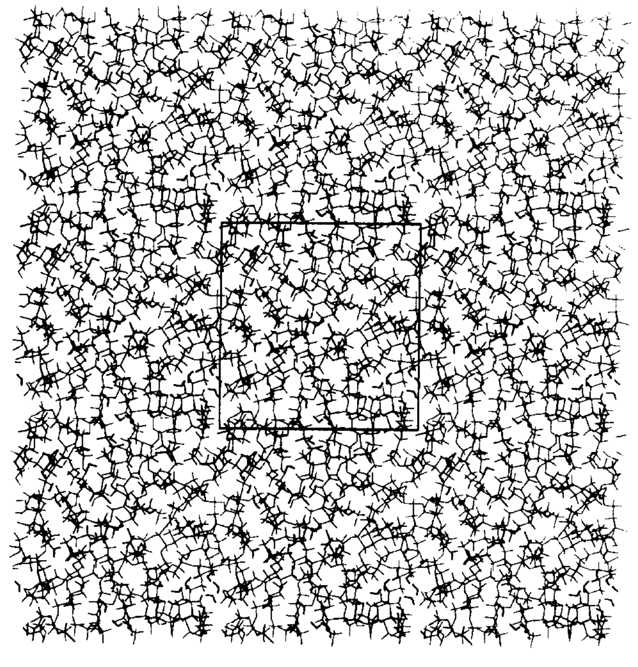


Figure 5 View, with periodic boundaries, of a two-dimensional system simulating one frame of a cell containing three PEO molecules, six PEO sulfonic acid molecules and 24 water molecules. All water molecules are black, and other molecules are grey

molecular mechanics (conjugate gradients), until the maximum derivatives were less than 10^{-5} kcal mol^{-1} Å^{-1}. After that a long (120 ps for single molecules and 450 ps for cells) molecular dynamics simulation was performed, and three to four frames from each trajectory file were selected for further calculations (see *Figure 4*, where the selected frames are marked with arrows). For the cells all selected frames are in the range of 150–450 ps, because the time of 150 ps was needed for the formation of hydrogen bonds in the cells. Due to the fact that polymers change conformation relatively slowly, it was assumed that the conformations taken from one trajectory file were more similar to each other than those taken from another trajectory file calculated for the same system. Thus, each system was constructed three or four times to obtain three or four different trajectory files and different conformations.

The polymer electrolyte material was constructed by packing amorphous minimized PEO and PEO sulfonic acid into an amorphous cell, using periodic boundary conditions for a 2D system. In the case of amorphous cell 1, 6 wt% water was added to the system, while amorphous cell 2 was water-free. The density of the amorphous cells was assumed to be 1.15 g cm^{-3}. The number of the molecules added to each cell is seen in *Table 1*. The size of amorphous cell 1 was 24.7 Å × 24.7 Å × 17.00 Å and the cut distance was 7.95 Å, and the size of amorphous cell 2 was 25.5 Å × 25.5 Å × 15.0 Å and the cut distance was 8.49 Å. A minimum image model was used while the cells were minimized using molecular dynamics at 300 K. One example of a polymer electrolyte corresponding to amorphous cell 1 is shown in *Figure 5*.

All simulations were performed separately in PCFF and CVFF forcefields. The temperature in the calculations was 300 K. Then, for each vibrational mode at a time, a local effective potential energy function represented by a Nth-order polynomial

$$V^{\text{eff}}(Q) = K_0 + K_2Q^2 + K_3Q^3 \ldots \qquad (4)$$

was calculated and the 1-D Schrödinger equation

$$\frac{\hbar}{2M}\left[\frac{\mathrm{d}^2}{\mathrm{d}Q^2} = V^{\text{eff}}(Q)\right]\Psi(Q) = E\Psi(Q) \qquad (5)$$

was solved by using this potential. In equation (5), M is the diagonal term of the G matrix of normal mode analysis in general. The calculated anharmonic frequencies, ($0 \rightarrow 1$), were accumulated to make a histogram, which represents a Boltzmann averaged, inhomogeneously broadened vibrational density of states. The simulated spectra were made by uniting the histograms and the results were calculated for each vibrational mode separately (one example can be seen in *Figure 6*).

RESULTS AND DISCUSSION

Conformational analysis

Energy contour maps for PEO sulfonic acid were calculated for five different linkages, marked in *Figures 2* and *7*. They are the –S1, –C3, –C2, –C1 and –O linkages. The PCFF forcefield was used for all simulations. The –C3 linkage was also calculated using the CVFF forcefield to evaluate the conformational differences in the torsion of the sulfonic acid group in the PCFF and CVFF forcefields. The energy contour maps define the potential energy surface as a function of two rotational angles located respectively on the right side and left side of the linkage atom. The PEO sulfonic acid molecule was first minimized using the steepest descents method to reach the required convergence criteria, the root-mean-square of the energy derivate being less than 0.002 kcal mol^{-1} Å^{-1}. During the generation of the energy contour, the rest of the molecule was minimized using the BFGS (Broyden–Fletcher–Goldfarb–Shanno)

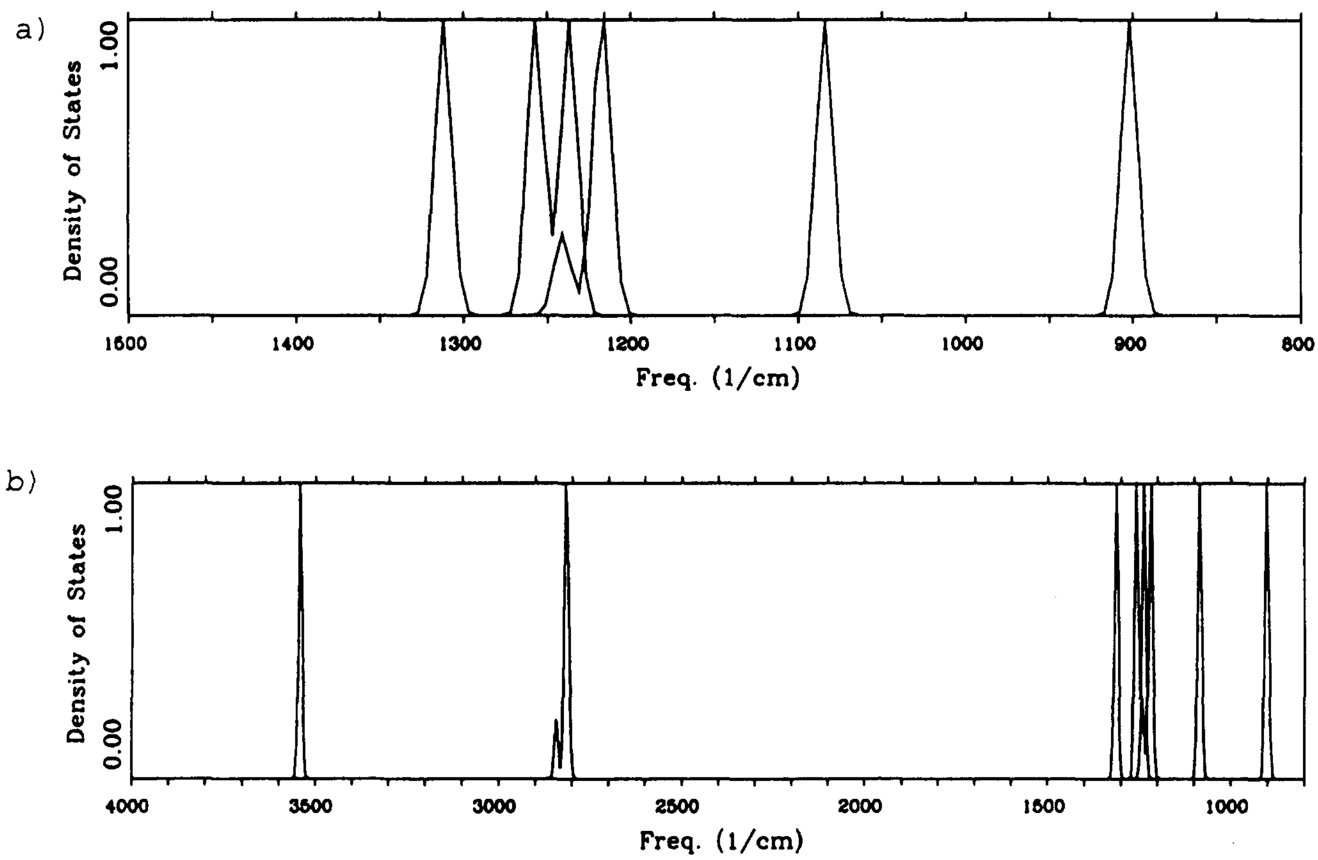
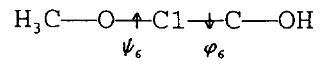


Figure 6 Simulated spectrum of PEO sulfonic acid with $M_w = 438$ (a) for range 800–1500 cm^{-1} and (b) for range 800–4000 cm^{-1}



$$\underset{\psi_6}{\mathrm{H_3C{-}O{-}}}\mathrm{C1}\underset{\varphi_6}{\mathrm{{-}C{-}}}\mathrm{OH}$$

Figure 7 Backbone of 2-methoxy-1-ethanol and the torsion angles for which the conformational analysis was made for the –C1 linkage

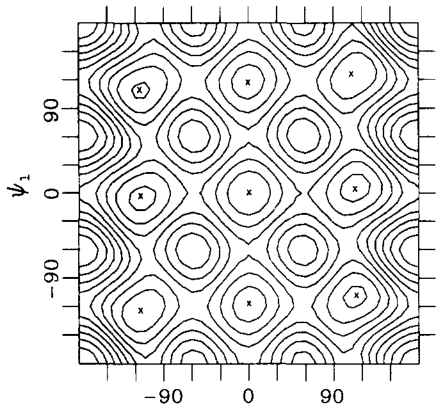


Figure 8 Energy map for the –C3 linkage in PEO sulfonic acid, calculated using the PCFF forcefield. The energy differences between the graph lines are 1 kcal mol^{-1} and all minima are marked with an asterisk

method until the energy derivates were less than 0.005 kcal mol^{-1} Å^{-1}. The torsional angles were calculated at 10° intervals. The energy surface was scanned from −180° to 180° and the all-*trans* conformation was defined as 0°. The energy contours are shown in *Figures 1* and *8–13*. In all figures the energy differences between the graph plots are 1 kcal mol^{-1} and all minima are marked with an asterisk.

Conformational analysis for the –C3 linkage in PEO sulfonic acid was made using both the PCFF and the CVFF forcefields, using molecular mechanics. The results of the energy minimization are seen in *Table 2*. In addition, an RIS calculation in the PCFF forcefield was utilized to obtain configurational statistics of the –C3 linkage; the results are collected in *Tables 3* and *4*. The values of the angles φ from RIS calculations were averaged within 2°, and the angles ψ within 10° for the final calculations. Nine minima separated by relatively low energy barriers were obtained in all the calculations. The results of the conformational analysis of PEO sulfonic acid are collected in the energy contour maps in *Figures 1*, *8* and *9*. *Table 2* shows that the simulations with the two different forcefields gave similar results. The difference in the torsional angles for the nine minima is 20° or less, while the size of the minima is in most cases 30° to 60°. From *Figures 8* and *9* it can be seen that the rotational barriers for the rotation of the sulfonic acid group are about 2 kcal mol^{-1} higher in the map calculated using the PCFF forcefield than in the map simulated using the CVFF forcefield. This is probably by the autoparameters used for the sulfur atom. This matter will be thoroughly discussed in connection with the spectra analyses. In *Table 2* the value of the total energy for the global minimum is set to zero to obtain the relative energies between the minima. The differences between the relative energies calculated with different methods or forcefields for the corresponding minima are observable but not remarkable (see *Table 2*). It seems that both methods are equally good

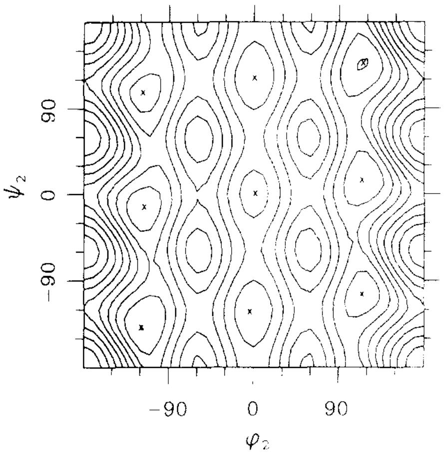


Figure 9 Energy map for the –C3 linkage in PEO sulfonic acid, calculated using the CVFF forcefield. The energy differences between the graph lines are 1 kcal mol^{-1} and all minima are marked with an asterisk

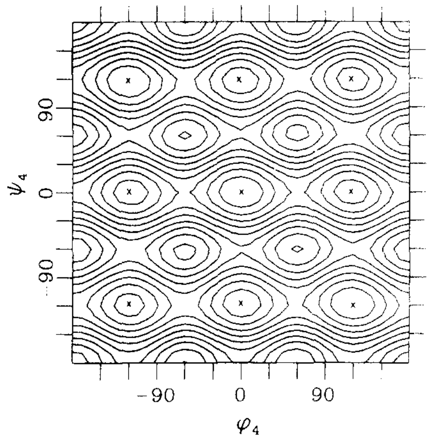


Figure 10 Energy map for the –S1 linkage in PEO sulfonic acid, calculated using the PCFF forcefield. The energy differences between the graph lines are 1 kcal mol^{-1} and all minima are marked with an asterisk

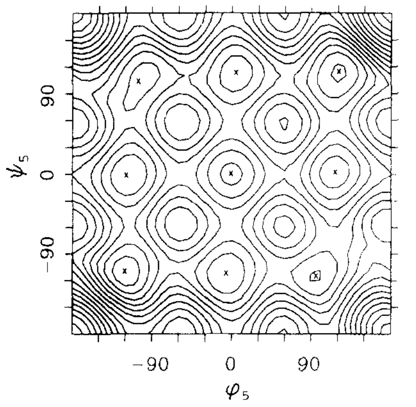


Figure 11 Energy map for the –C2 linkage in PEO sulfonic acid, calculated using the PCFF forcefield. The energy differences between the graph lines are 1 kcal mol^{-1} and all minima are marked with an asterisk

for predicting the minima and the barriers of rotation in PEO sulfonic acid. Since the molecular mechanics method is simpler, it is used for the other linkages.

The –S1 linkage in PEO sulfonic acid has nine minima. The local minima are at $(\varphi_4, \psi_4) = (\pm 120°, \pm 120°)$, $(0°, \pm 120°)$, $(\pm 120°, 0°)$ and the global minimum is at $(0°, 0°)$ (see *Figure 10*). The relative energies between the minima (see *Table 5*) vary by less than 2 kcal mol^{-1}, which means that all minima are nearly equally favourable. When φ_4 reaches any of its minimum values (0° or ±120°), ψ_4 can rotate from one minimum to another through narrow, low energy areas; the barriers are about 3 kcal mol^{-1}. In the case of the S–O bond the barriers are twice as high, about 6 kcal mol^{-1}. This means that the torsion of the OH group is more restricted than the torsion of the SO_3H group.

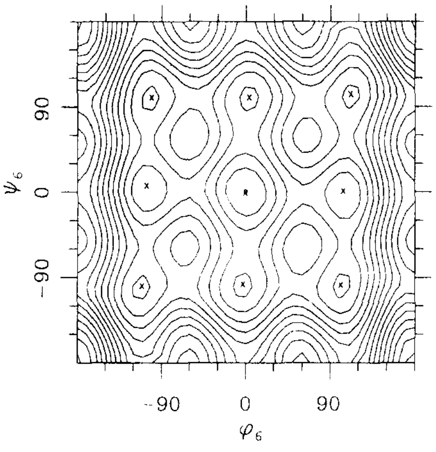


Figure 12 Energy map for the –C1 linkage in 2-methoxy-1-ethanol, calculated using the PCFF forcefield. The energy differences between the graph lines are 1 kcal mol^{-1} and all minima are marked with an asterisk

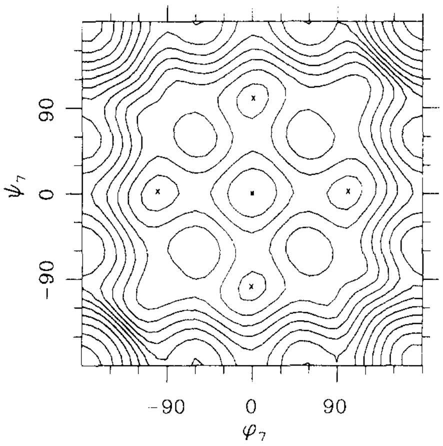


Figure 13 Energy map for the –O linkage in PEO sulfonic acid, calculated using the PCFF forcefield. The energy differences between the graph lines are 1 kcal mol^{-1} and all minima are marked with an asterisk

The –C2 linkage in PEO sulfonic acid also has nine minima with barriers of 2–4 kcal mol^{-1} (see *Figure 11*). The minimum energy conformations occur with $(\varphi_5, \psi_5) = (0°, 0°)$, $(0°, \pm 110°)$, $(90°, -120°)$, $(\pm 120°, 0°)$, $(120°, 110°)$ and $(-100°, 100°)$, respectively. The global minimum is at $(-120°, 0°)$. The relative energies of the minima differ more than they differ for the –C3 or –S1 linkages, the differences being less than 3 kcal mol^{-1}, however (see *Table 5*).

The conformational energy map for the –C1 linkage drawn for the PEO sulfonic acid had a severe disturbance, caused by the tail of the molecule. Thus the

Table 2 Torsional angles and relative energies at minima for –C3 linkage in PEO sulfonic acid in different forcefields using molecular mechanics (MM) and RIS calculations (RIS). The value of φ for the MM calculation in PCFF and in the RIS simulation was within 2° (details in *Table 3*)

PCFF MM RIS $\varphi_{1,3}$ (°)	PCFF MM ψ_1 (°)	PCFF RIS ψ_3 (°)	PCFF MM Relative energy (kcal mol^{-1})	PCFF RIS	CVFF MM	CVFF MM φ_2 (°)	CVFF MM ψ_2 (°)
0	0	0	0.0	0.0	0.5	0	0
0	120	110	0.4	0.3	0.1	0	120
0	−120	−110	0.3	0.3	0.2	0	−120
110	0	0	0.6	0.7	0.1	120	20
110	120	110	1.1	1.2	0.0	120	140
110	−110	−110	0.7	1.1	0.4	120	−100
−110	0	0	0.7	1.4	0.3	−120	−20
−110	110	110	0.8	1.1	0.5	−120	−140
−110	−120	−110	1.2	1.2	0.0	−120	−140

Table 3 For –C3 linkage, averages of angle values for various regions, their partition function Z_i, the corresponding statistical weight u_i for that region and the partition function z_{itot} calculated using the total energy

Average				
φ_3 (°)	ψ_3 (°)	Z_i	u_i	z_{itot}
−108.3	−115.6	1133.62	0.2941	253.58
0.1	−114.1	3854.67	1.0000	945.14
108.9	−111.8	1084.12	0.2812	257.92
−108.0	000.4	1147.39	0.2977	437.49
0.0	000.0	3731.46	0.9680	1456.39
109.0	000.4	1147.15	0.2976	437.51
−108.9	112.0	1084.03	0.2812	257.88
0.1	114.1	3854.99	1.0001	945.02
108.3	115.6	1133.50	0.2941	253.56

Table 4 Resulting statistical weight matrix for –C3 linkage in poly(ethylene oxide) sulfonic acid. A statistical weight for a bond pair consists of a prefactor A_{jk} (dimensionless) and an energy ϵ_{jk} (units kcal mol^{-1})

	$\varphi_3 = -108.8°$		$\varphi_3 = 0°$		$\varphi_3 = 108.8$	
ψ_3 (°)	A_{jk}	ϵ_{jk}	A_{jk}	ϵ_{jk}	A_{jk}	ϵ_{jk}
−114.0	1.016	0.739	1.000	0.000	0.982	0.745
0.0	1.050	0.752	1.014	0.028	1.050	0.751
114.0	0.982	0.745	1.001	0.000	1.016	0.739

calculations for the –C1 linkage were made for 2-methoxy-1-ethanol (see *Figure 7*). From *Figure 12* it can be seen that the conformational energy map for the –C1 linkage has vertical and horizontal symmetry. It seems to have very little effect whether the atom bonded to C1 is carbon or oxygen. There are eight minima separated by very low energy barriers, about 2 kcal mol^{-1} or less. The global minimum is in all-*trans* conformation and the other minima occur at $(\varphi_6, \psi_6) = (0°, \pm100°)$, (±100°, 0°) and (±100°, ±100°), respectively. In the crystalline state of PEO the OCCO dihedral angle has been experimentally found to be in the *gauche* conformation at room temperature[15]. In a simulation the result of conformational analysis mostly depends on the parameters in the terms for torsion, coulombic interactions and van der Waals interactions (*Figure 3*, terms 3, 12 and 13). The distance between the nearest oxygens in the chain in the *gauche* conformation is 2.84 Å, which is the sum of the van der Waals radii of these atoms[15]. This causes an attraction between the oxygen molecules, favouring the *gauche* conformation. However, this attraction is reported to be smaller than the coulombic repulsion of the negatively charged oxygen molecules[15]. Earlier the disagreement between the experimental and simulated results was explained to be due to the inaccuracy of the torsional potential (term 3 in *Figure 3*). However, it has since been reported that the *gauche* effect is caused by the temperature and dielectric constant of the environment[16]. The all-*trans* conformation was found to have the lowest energy for the OCCO dihedral angle in PEO in vacuum ($\epsilon = 1$) and 0 K[16], while the *gauche* conformation has lower energy at higher temperatures and in water ($\epsilon = 80$). These results also have been confirmed experimentally and agree with the results of this work. The relative energies for the minima vary less than 4 kcal mol^{-1} (see *Table 5*).

The energy map for the ether linkage in the PEO sulfonic acid chain shows horizontal and vertical symmetry caused by similar carbon atoms bonded to the oxygen (see *Figure 13*). There are four minima in the energy contour map, namely $(\varphi_7, \psi_7) = (0°, \pm100°)$ and (±100°, 0°), having nearly the same relative energies (see *Table 5*) and energy barriers of about 1 kcal mol^{-1}. The global minimum is at $(\varphi_7, \psi_7) = (0°, 0°)$, with an energy barrier of about 2 kcal mol^{-1}.

Spectral analysis

The vibrational spectrum of PEO is first taken into consideration. The i.r. spectra of pure PEO, $\langle M_w \rangle = 200$,

Table 5 Torsional angles and relative energies in kcal mol^{-1} at energy minima: for –S1 linkage, φ_4, ψ_4 and E_4; for –C2 linkage, φ_5, ψ_5 and E_5; for –C1 linkage, φ_6, ψ_6 and E_6; and for –O linkage, φ_7, ψ_7 and E_7; in PEO sulfonic acid, calculated with molecular mechanics using the PCFF forcefield

φ_4 (°)	ψ_4 (°)	E_4	φ_5 (°)	ψ_5 (°)	E_5	φ_6 (°)	ψ_6 (°)	E_6	φ_7 (°)	ψ_7 (°)	E_7
0	0	0.0	0	110	1.4	0	0	0.0	0	0	0.0
0	120	1.3	0	−110	1.2	0	100	1.8	0	100	1.6
0	−120	1.2	90	−120	2.9	0	−100	1.8	0	−100	1.7
120	0	0.4	120	0	0.3	110	0	2.2	100	0	1.5
120	120	1.4	120	110	0.8	110	100	3.8	−100	0	1.5
120	−120	1.0	−120	0	0.0	100	−100	2.8			
−120	0	0.3	−100	110	2.5	−110	0	2.2			
−120	120	1.0	−120	−110	0.2	−110	100	2.8			
−120	−120	1.5				−110	−100	3.8			

Table 6 Vibrational absorptions for C–O or C–C or C–H stretches of PEO, PEO sulfonic acid (PEOS), membranes and cells[17–20]. Cell 1 consists of 6% water and PEO and PEO sulfonic acid. Cell 2 consists of PEO and PEO sulfonic acid. For simulated values *a* is the harmonic frequency, *b* the anharmonic frequency (0 → 1) and *c* the anharmonic frequency (0 → 2)

	Frequency (cm^{-1})					
	Simulated			Measured	Assignments	
X	CVFF PEO PEOS	PCFF PEO PEOS CELL 2	PCFF CELL 1	PEO PEOS membrane		
a	2950	2940	2970	2925	2925^a	C–H
b	2950	2840	2870	2870	2890^a	
c	5900	5640	5730		2850–3000^b	
a	2950	2970	2980		2960^b	C–H$_3$
b	2950	2860	2980		2870^b	
c	5900	5720	5730			
a	1380	1250	1250	1350	800–1300^b	C–C
b	1380	1250	1250			
c	2760	2500	2500			
a	1380	1270	1250			C–CH$_3$
b	1380	1270	1250			
c	2750	1270	2500			
a	1190	1230	1230	1110	1110^a	C–O
b	1190	1230	1220		1120^a	
c	2380	2450	2440		1070–1150^b	
a	1190	1190^c	1220			C–OH
b	1880	1180^c	1210			
c	2350	2350^c	2240			
a		1230^d				
b		1210^d				
c		4420^d				
				1170	1150^a	CC–COC
					1160^a	
				1070	1060^a	COC + CH$_2$
					1070^a	
				950	950^a	CH$_2$–COC

[a] Values are for PEO
[b] General frequencies
[c] Frequencies for PEO
[d] Frequencies for cell 2

400, 600, 2000 and 4000, were measured. Measured vibrational frequencies and the values taken from the literature are included in *Tables 6* and *7*[17–19]. The calculated values for the corresponding vibrations using forcefields CVFF and PCFF, respectively, are also included in these tables. For PEO the literature values and the measured values for the vibrations corresponded to the calculated values in the accuracy of the local mode method; c.f. *Table 6* and *Table 7*.

The differences between the calculated frequencies of the C–H stretches for the end group of the chain, CH_3–CH_2 (2950 cm^{-1} in the CVFF forcefield and 2970 cm^{-1} in the PCFF forcefield), and for the inner group in the chain, CH_2–CH_2 (2950 cm^{-1} in the CVFF forcefield and 2940 cm^{-1} in the PCFF forcefield), were much smaller than the accuracy of the local mode method. All these frequencies correspond to values in the literature (2960 cm^{-1} for CH_3 and 2925 cm^{-1} for CH_2)[20]. Also, the corresponding calculated values for the C–C bond stretch in the ethyl end group (1380 cm^{-1} in the CVFF forcefield and 1270 cm^{-1} in the PCFF forcefield), and within the chain (1380 cm^{-1} in the CVFF forcefield and 1250 cm^{-1} in the PCFF forcefield), respectively gave values which correspond well to the range from the literature (800–1300 cm^{-1}); see *Table 6*. The differences between the calculated frequency values of the C–O stretches for the end group of the chain, C–OH (1190 cm^{-1} in the CVFF forcefield and 1190 cm^{-1} in the PCFF forcefield), and for the inner group in the chain, C–O–C (1190 cm^{-1} in the CVFF forcefield and 1230 cm^{-1} in the PCFF forcefield), were much smaller than the accuracy of the local mode method. The calculations gave stretching frequencies for the OH end group in PEO at 3670 cm^{-1} in the CVFF forcefield and 3630 cm^{-1} in the PCFF forcefield, respectively. The experimental spectra of PEO show a broad band at 3440 cm^{-1} caused by moisture in the sample (due to the hygroscopic nature of PEO) which cannot be distinguished from peaks caused by the OH end group of the polymers. The differences between the calculations made

Table 7 Vibrational absorptions for the sulphur atom or O–H stretches of PEO, PEO sulfonic acid (PEOS), membranes and cells[20,23,24]. Cell 1 consists of PEO, PEO sulfonic acid and 6% water. Cell 2 consists of PEO and PEO sulfonic acid. For simulated values *a* is the harmonic frequency, *b* the anharmonic frequency (0 → 1), and *c* the anharmonic frequency (0 → 2). The resolution of the experimental spectra is 1 cm^{-1}

	Frequency (cm^{-1})					
	Simulated			Measured	Assignments	
X	CVFF PEO PEOS	PCFF PEO PEOS CELL 2	PCFF CELL 1	PEO PEOS membrane		
a			3640		3400–3600^a	O–H
b			3450			water
c			6890			
a	3670	3630	3550		3400–3600^a	O–H
b	3670	3510	3450			polymers
c	7340	7040	6940			
				3440	3400–3600^a	O–H
						polymers and water
				1600–2800	1650–2800	H_3O^+
				1650	1680	
a	920	1320	1310		1150–1170^b	S=O
b	920	1310	1310		1340–1350^b	
c	1840	2630	2630			
a	880	910	910		890–910^b	S–O
b	880	910	910			
c	1770	1820	1810			
				610	600–700^c	$SO_3^- H_3O^+$
				1040	1010–1080^c	
				1190	1150–1260^c	
a	1060	1090	1090		1070–1100^a	C–S
b	1060	1090	1090			
c	2100	2180	2170			

^{a} General frequencies
^{b} Frequencies for nonhydrated PEOS
^{c} Frequencies for hydrated PEOS

with the PCFF or the CVFF forcefields were only slightly greater than the accuracy of the local mode method. All other PCFF and CVFF forcefields gave similar results. A good agreement was found between calculated and experimental vibrational frequencies. This is because both forcefields gave a similar geometry and charge distribution for the PEO molecule.

PEO sulfonic acids have been thoroughly investigated by Raman and by i.r. spectroscopy[7]. As an example, the i.r. spectrum of the PEO sulfonic acid with $\langle M_w \rangle = 646$ is seen in *Figure 14*, and assignments of the i.r. spectra of the PEO sulfonic acids are collected in *Tables 6* and *7*.

Results from the Raman scattering experiments have been published[7]. With Raman scattering the cationic coordinations in PEO sulfonic acids with $\langle M_w \rangle = 446$, 646, 846, 2246 and 4246 were studied. Spectra were measured in the frequency range 800–1500 cm^{-1}. The preference for the two possible cation coordinations was determined since the number of SO_3^- chain ends exactly matches the number of available cations for the PEO sulfonic acids. The band at 1145 cm^{-1} was assigned to a coupled E_1 C–C stretching and C–O–C antisymmetric stretching mode, $(COC)_a + (CC)$. Previous studies of crystalline PEO showed a band at 1148 cm^{-1} which shifts to higher frequencies, 1160 cm^{-1}, when a salt is dissolved in the polymer[21,22]. The shift was taken as an indication of a change in the environment of the ether oxygens through coordination to cations. No such effect was observed for the PEO sulfonic acids, for which the peak of the band was found at about the same frequency (1145 cm^{-1}) independent of chain length, i.e. independent of the SO_3^- and cation concentrations. The frequencies of the other two C–O–C bands (~1070 cm^{-1} and 860 cm^{-1}) were close to those reported for PEO (~1066 cm^{-1} and ~859 cm^{-1})[17]. From the vibrational behaviour of the C–O–C bands, no indication of any cation–ether oxygen coordinations was found[7].

In the measured spectra for PEO and PEO sulfonic acid the only differences were in frequencies corresponding to the sulfonic acid group. All other spectral components can be attributed to various vibrations using the assignments reported for PEO[17]. Thus we conclude that the observed frequencies of the PEO vibrations are largely unaffected by the introduction of sulfonic acid groups. A similar observation is valid in the calculations; the difference between PEO bond stretches and PEO sulfonic acid bond stretches for C–C, C–O, C–H and O–H is within the accuracy of the local mode method in both forcefields (see *Table 6*). Calculated vibrational frequencies for PEO sulfonic acids are included in *Tables 6* and *7*.

In the simulation, the calculated frequencies correspond

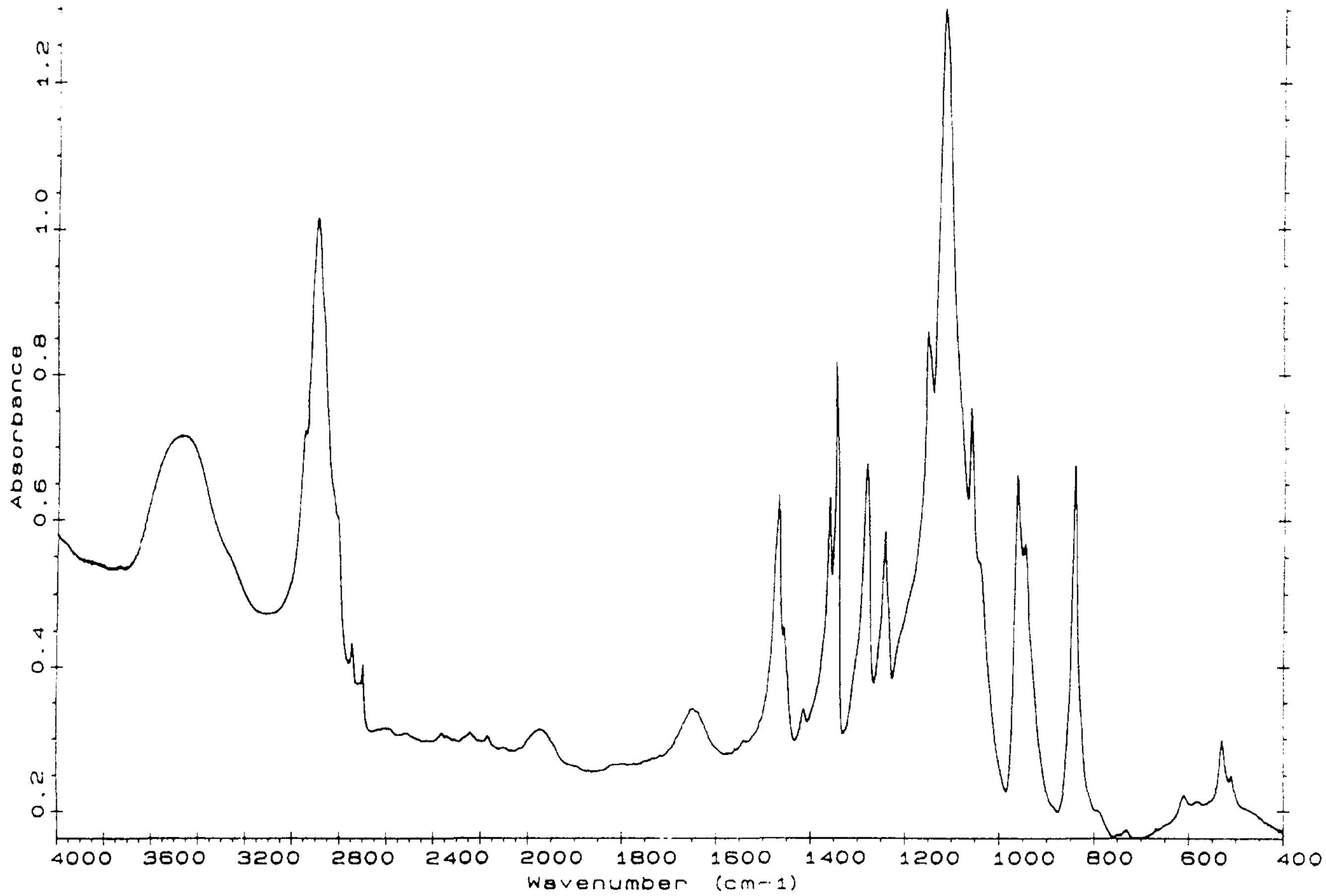


Figure 14 I.r. spectrum of PEO sulfonic acid with $\langle M_w \rangle = 646$

to the measured values in the accuracy of the local mode method, except for S–O and S=O stretches. The simulated values for the harmonic and anharmonic S–O stretches are 880 cm^{-1} in the CVFF forcefield and 910 cm^{-1} in the PCFF forcefield, respectively. For the S=O stretch the calculated values for harmonic and anharmonic stretches are 920 cm^{-1} in the CVFF forcefield. In the PCFF forcefield the corresponding values for S=O stretches are 1320 cm^{-1} for the harmonic and 1310 cm^{-1} for the anharmonic stretch, respectively. Experimentally, the S–O and S=O stretches are indistinguishable and are found at 610 cm^{-1}, 1040 cm^{-1} and 1190 cm^{-1}. The difference between simulated and experimental values is clearly larger than the accuracy of the local mode method.

Vibrational spectra for anhydrous sulfonic acids have been reported[20–23]. The authors conclude that the S=O harmonic stretch occurs between 1170 and 1150 cm^{-1}, and the anharmonic stretch between 1350 and 1340 cm^{-1}. The S–O stretch occurs between 910 and 890 cm^{-1} [20,23]. On the other hand, absorbances for the hydronium sulfonate group ($SO_3^-H_3O^+$) are reported to appear in the 600–700 cm^{-1}, 1010–1080 cm^{-1} and 1150–1260 cm^{-1} regions[20]. Thus, the experimental spectra in this study show the absorbances typical of the hydronium sulfonate group ($SO_3^-H_3O^+$). The calculated values in *Table 7* correspond to vibrational frequencies of S–O and S=O groups in nonhydrated sulfonic acid. The presence of water in the experimental sample is due to the very hygroscopic nature of sulfonic acids. No hydronium sulfonate was able to form during the simulation since the simulation was made for a single molecule.

This study shows that the calculated frequencies for the C–C, C–O, C–H, C–S, S–O and O–H stretches correspond to the literature values, within the accuracy of the local mode method in both forcefields[18,20,23]. However, the calculated values for the S=O stretch clearly differ from the values found in the literature. This indicates that the autoparameters used in the calculation for the sulfur atom are not quite accurate. There was a significant difference for the S=O stretch (400 cm^{-1}) between the values calculated by using the PCFF (920 cm^{-1}) or the CVFF (1320 cm^{-1}) forcefields. Both forcefields gave the same values for the anharmonic and harmonic frequencies, although different values were found in the literature. The anharmonic frequency simulated by using the PCFF forcefield was almost the same as the value of the anharmonic frequency found in the literature (1310 cm^{-1} and 1340–1350 cm^{-1}, respectively). The symmetric frequency calculated with the PCFF forcefield (1320 cm^{-1}) was closer to the literature value[19] (1150–1170 cm^{-1}) than that calculated with the CVFF forcefield (920 cm^{-1}). Also, the value modelled for C–S stretch by using the PCFF forcefield (1090 cm^{-1}) is in the range of the values mentioned in the literature (1070–1100 cm^{-1}), while the value calculated by using the CVFF forcefield (1060 cm^{-1}) is out of the range, although the difference is small. These two results lead to the conclusion that the PCFF forcefield is better suited for calculations for PEO sulfonic acid than the CVFF forcefield.

The forcefields used have a different approach concerning the sulfur atom. To give an example, the calculation of the energy for bond stretching,

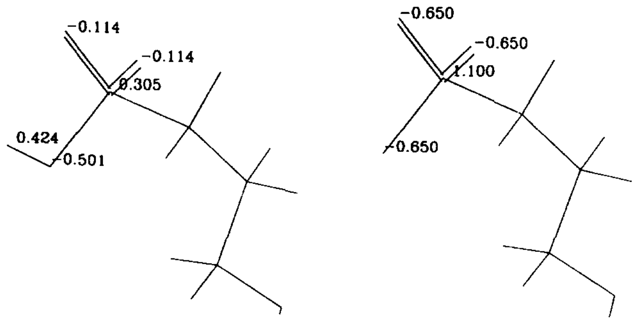


Figure 15 Charge distribution in PEO sulfonic acid (left) and in the PEO sulfonic acid anion (right)

$E = K2(R - R0)^2$, where $K2$ is the force constant and $R0$ is the equilibrium bond length, is examined. Because no parameters for sulfonic acid groups were included in the CVFF database, atom types for similar compounds were used to describe the groups. The sulfur atom type in sulfonic acid was displaced by the atom type originally assigned to the C–S–C group (methione sulfur). The carbon atom bonded to sulfonic acid was treated as an ordinary sp3 carbon. Because no atom types for the S=O group were available, parameters determined for an oxygen in a carbonyl group were used. The oxygen atom singly bonded to hydrogen was explicitly treated as an oxygen bonded to hydrogen. This approach gave the values $K2 = 288.1$ and $R0 = 1.693$ as parameters for the S–O bond and the values $K2 = 360.4$ and $R0 = 1.590$ for the S=O bond. In the same calculation the PCFF forcefield treated the sulfur atom as part of the >S=O group, with which an ordinary sp3 oxygen and an ordinary sp3 carbon are associated. This treatment gave the values $K2 = 286.8$ and $R0 = 1.633$ for parameters concerning the S–O bond, and the nonautomatic values $K2 = 743.76$ and $R0 = 1.4308$ ($K3 = 0$) for the S=O bond. The parameters for the S–O bond calculated with the PCFF forcefield and with the CVFF forcefield have the same values. Also, the frequencies modelled using different forcefields had the same values for the S–O groups. The parameters for the S=O bond clearly have different values in different forcefields. Also, the frequencies for the S=O stretch calculated in different forcefields have different values. Thus the differences between the vibrational spectra can be predicted by comparing the values of the parameters involved in the quartic polynomial for bond stretching. The CVFF forcefield used nine autoparameters for the calculations while the PCFF forcefield used sixteen autoparameters. These autoparameters were different and concerned partly different terms. What they had in common was that they all included some type of sulfur atom.

The Amorphous_cell initial guess generator, which incorporates features of the RIS-based Theodorou–Suter approach and the Meirovitch scanning method, was used to construct amorphous cells of polymer electrolyte material with periodic boundary conditions in a 2D system. One example is shown in *Figure 5*. The picture shows the packing of three PEO molecules ($n = 31$) together with six molecules of PEO sulfonic acid ($M_w = 438$) and 6 wt% of water. This amount of water corresponds to two molecules of water for every sulfonic acid group. The system was minimized first with molecular mechanics and then with molecular dynamics. The water was randomly distributed before the dynamics run. The atomic radial distribution functions for all atom pairs showed that the cell was amorphous. Materials of this type were used for the spectra analysis described below. In amorphous cells containing water the hydrogen in the hydroxyl group in the sulfonic acid molecule seems to be coordinated to at least one water molecule (see discussion concerning hydronium sulfonate in the amorphous cells).

The spectra of cell 1 and cell 2 differed only in the region of the O–H stretch (see *Tables 6* and *7*). The calculated values of frequencies for all amorphous cells corresponded to the literature values for similar stretches (there are no literature data concerning expressly these materials) within the accuracy of the local mode method[17–20,23]. The spectra measured for the dry membranes were similar to the measured spectra of poly(ethylene oxide) sulfonic acid. Also, the calculated spectra of the cells are similar to the calculated spectrum of PEO sulfonic acid, excluding the O–H stretch. This means that the differences reported in the passage concerning the measured and calculated spectra of the pure PEO sulfonic acid molecule apply also to the spectra of simulated and measured polymer electrolyte amorphous cells. There is no noticeable difference between the calculated frequency values for the C–H bond stretch, or for the C–C bond stretch in the end group of the PEO molecule and in the inner group of the PEO molecule (for C–H at the end the values are 2980 cm^{-1} and, for the inner group, 2970 cm^{-1} and, for C–C 1250 cm^{-1}, respectively). The frequencies simulated for the O–H bond stretches concerning polymers for the cells containing water are 3550 cm^{-1}, which is 110 cm^{-1} lower than the value of 3630 cm^{-1} calculated for the water-free cells (see *Table 7*). This difference is slightly larger than the range of the accuracy of the local mode method. This leads to the possibility of hydrogen bonds between the O–H groups in the polymers and the water. The absorption of water was 3640 cm^{-1}, which is near the absorption of 3668 cm^{-1} reported for partially hydrogen bonded water[24]. The simulated frequency for non-hydrogen bonded water is 3780 cm^{-1} [25].

Because the frequencies for S=O for cell 1 (1310 cm^{-1}) and cell 2 (1320 cm^{-1}) are similar, there is no observation of strong hydrogen bond between S=O and water. This can be explained by comparing the charges in the modelled sulfonic acid group. The charge of the hydrogen atom in the S–O–H group (+0.4) is much larger than the charge of the oxygen in the S=O group (−0.1) (*Figure 15*). In the experimental membranes most of the sulfonic acid was dissociated because of the hygroscopic nature of the PEO sulfonic acid. Simulation for the anion gave a large charge of about −0.6[26] for the conjugated oxygen, which supports the possibility of formation of hydronium sulfonates. There was also a detection of a broad band at 1650 cm^{-1} in the experimental measurements, which is thought to be due to the hydronium ion[19]. The frequency measured for the O–H stretch is rather low (3440 cm^{-1}) which indicates the possibility of hydrogen bonds and hydronium ion formation. There was a detection of a shoulder in the range 3200–3400 cm^{-1}, corresponding to the literature values of intermolecular polymeric hydrogen bonds[20]. In the simulations there is no absorption in the range 1230–1120 cm^{-1}, which means that the program did not form any hydronium sulfonate ($SO_3^- H_3O^+$) group to the amorphous cell. This is because the atomistic simulation cannot dissolve the proton and form an anion with a large negative charge, and thus lacks the ability to form hydronium sulfonate. The transference coefficient of water for vapour-equilibrated proton-conducting membranes has been reported to be approximately one, which means that one water molecule is transferred with one proton[27,28]. This agrees with the detection of the hydronium sulfonate ion in the measured spectra.

CONCLUSIONS

Amorphous cells of polymer electrolytes consisting of PEO and PEO sulfonic acid have been constructed. The simulated model proves to be quite good. However, the novel observation of hydronium sulfonate in the measured i.r. spectra and a lack of this compound in the modelled system show that the model should be developed further. It is not appropriate to add hydronium sulfonate molecules to the simulated amorphous cell, since, due to the atomistic nature of the model, the dissociation of the cation cannot take place. In the next model the poly(ethylene oxide) sulfonic acid anion and the cations will be placed separately in the amorphous cell. In order to construct such a cell, the PCFF forcefield is at present modified to be capable of minimizing the ions. In this study the PCFF forcefield was shown to be best suited for modelling PEO sulfonic acid.

The conformational analysis of poly(ethylene oxide) sulfonic acid showed that all rotations are restricted at room temperature. There were several energy minima, the relative energies of which varied very little.

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