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Modelling amorphous lithium salt–PEO polymer electrolytes: ab initio calculations of lithium ion–tetra-, penta- and hexaglyme complexes

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Abstract

Several stable structures of the 1:1 complexes of a lithium ion with tetra-, penta- and hexaglyme [$CH_3O(CH_2CH_2O)_nCH_3$, $n = 4–6$] have been obtained with ab initio calculations at the Hartree–Fock level of theory employing the 3-21G* basis set. Twenty-three different stable complexes were found with coordination numbers of lithium ranging from four to six; i.e., no stable heptacoordinated complexes emerged. The total energies and the binding energies were evaluated by using density functional theory (DFT) calculations (B3LYP/6-31G*//HF/3-21G*) and showed the total binding energy to increase with the glyme length. The average binding energy for the different glymes reaches a maximum of ~620 kJ mol^{-1} for the hexaglyme complexes, with an absolute maximum of 631 kJ mol^{-1} obtained for a hexacoordinated Li^+–hexaglyme complex. The average binding energy per bond for a specific coordination number for lithium shows only minor changes when extending the oligomer (<5 kJ mol^{-1} $bond^{-1}$). The large number of complexes obtained with clearly different geometry within a small energy range — six different complexes within 15 kJ mol^{-1} for lithium–tetraglyme — clearly reflects the flexibility of the oligomer chains.

Keywords: Ab initio calculations; Poly(ethylene oxide); Polymer electrolytes

1. Introduction

Solid polymer electrolytes (SPEs) containing poly(ethylene oxide) (PEO) polymers and/or oligomers are of great interest in the context of developing a variety of modern electrochemical applications such as high-energy-density batteries, fuel cells and electrochromic devices [1]. Some examples of recent developments beyond pure PEO or other long-chain polymer-based electrolytes are the polymer gel electrolytes or silica-modified polymer electrolytes [2–4]. In both these cases a polymer network is created in which a low-molecular-weight solvent and a salt are incorporated. Regardless of choice of concept, these new types of SPE to a large extent still rely on the well-documented ability of the repeating ethylene oxide unit to coordinate alkali cations. Hence, both the polymer network and the solvent often contain PEO oligomer segments. In this perspective it is a challenging task to find out how these fragments or solvents of PEO coordinate the alkali cations.

In the context of SPEs, tetraglyme [$CH_3O(CH_2CH_2O)_nCH_3$, $n = 4$], or tetraethylene glycol dimethyl ether, has been one solvent adopted [2,5]; pentaglyme ($n = 5$) has also found use [3]. The salts used in all SPEs preferably have weakly coordinating anions like $CF_3SO_3^-$ (triflate) or $[(CF_3SO_2)_2N]^-$ (imide) to increase the cation mobility. It is, therefore, interesting to investigate how different cations, and especially lithium ions, are coordinated to the solvent molecules and thereby gain information about the glyme–ion complex transport in these systems.

The other and perhaps more intricate aspect of this study is the modelling of the coordination situation around the lithium ion in traditional polymer electrolytes where amorphous long-chain PEO plays a central role. Tetraglyme should be the preferable model for quantum-mechanical studies since lithium has been observed to coordinate five ligands in the first solvation shell in water [6]. Recent calculational results for different ether oxygen containing ligands suggest a coordination number of four to five for lithium [7]. Moreover, the size of the system makes such calculations feasible. Furthermore, to provide the possibility of hexa- or even heptacoordination, the present study also investigates the pentaglyme– and hexaglyme–lithium complexes.

The situation in the amorphous systems clearly differs from the known crystal structures of $(PEO)_3LiCF_3SO_3$ [8] and $(PEO)_3Li[N(CF_3SO_2)_2]$ [9]. In these structures two of the five oxygens coordinating lithium derive from the

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Table 1
Energies and selected geometry parameters for the Li^+–tetraglyme complexes Te1 to Te11

	HF/3-21G*				B3LYP/6-31G*//HF/3-21G*		
	$d(Li^+–O)$ (Å)	CN (Li^+)	E total (au)	ΔE (kJ mol^{-1})	ΔE (kJ mol^{-1})	E_{bond} total (kJ mol^{-1})	E_{bond} (kJ mol^{-1})
Te1	3.887; 1.921; 1.962; 1.964; 1.916	4	−768.90904	54.7	33	543	136
Te2	1.969; 1.942; 2.098; 1.939; 2.014	5	−768.92231	19.8	12.1	586	117
Te3	1.905; 2.031; 1.946; 2.040; 1.941	5	−768.92771	5.6	4.4	585	117
Te4	1.978; 2.074; 2.168; 1.995; 2.095	5	−768.91131	48.7	31.6	569	114
Te5	1.996; 1.971; 2.016; 1.989; 1.984	5	−768.92077	23.8	17.2	587	117
Te6	1.982; 1.976; 2.144; 1.989; 1.984	5	−768.92117	22.8	10.6	586	117
Te7	1.952; 2.027; 2.023; 2.018; 1.924	5	−768.92356	16.5	10.7	581	116
Te8	5.127; 1.867; 1.917; 1.916; 1.869	4	−768.90267	71.4	54.8	525	131
Te9	1.925; 2.049; 1.951; 2.034; 1.915	5	−768.92985	0	0	587	117
Te10	1.911; 2.042; 1.904; 2.043; 1.910	5	−768.92724	6.9	8.1	589	118
Te11	2.028; 1.971; 2.059; 2.054; 1.967	5	−768.91559	37.4	29.4	569	114

anions. In the amorphous systems in general the situation is different; no coordination by the anions can be seen if appropriate concentrations of salt and these types of anions are chosen. Thus pentacoordination by only ether oxygens is suggested. An important exception from pentacoordination by ether oxygens in amorphous systems is observed for amorphous $(PEO)_3LiCF_3SO_3$ [10]. In this material only three consecutive ether oxygens are coordinated by the lithium and the other two needed to make lithium pentacoordinated derive from the anions.

The different source of the oxygens coordinating the lithium is one obvious reason for a careful attitude to conclusions drawn from crystalline structures about the generally more dilute amorphous systems. In addition, one might question the usefulness of the oligomers in models of the conduction behaviour in long-chain amorphous systems due to the effect of exceeding the deGennes entanglement limit for the latter [11]. An excellent discussion on this topic has been made by Latham and Linford [12]. However, in the context of the *local environment* of the lithium ion in the amorphous systems which, generally, have a higher oxygen-to-lithium ratio than the crystalline materials, the available stable or metastable structures of M^{x+}–glyme complexes are of interest as well as the transitions between such structures [13].

Experimental information on the geometry of tetraglyme and the longer PEO oligomers, as well as on short poly(ethylene glycol)s (PEGs), in complexes with metal ions in the solid state has been obtained earlier from a large number of crystal-structure determinations by X-ray diffraction [14–19]. We have recently initiated a series of model calculations on small PEO oligomers coordinated to metal ions [13,20,21]. These calculations are motivated by the need to have additional data, including bonding energies and total energies, on such complexes and on complexes with other equilibrium geometries that may not be possible in a crystal, but still might be of interest in an amorphous system. The present work extends these calculations to include ab initio molecular orbital calculations on 1:1 complexes of tetra-, penta- and hexaethylene glycol dimethyl ether (tetra-, penta- and hexaglyme) with lithium ions.

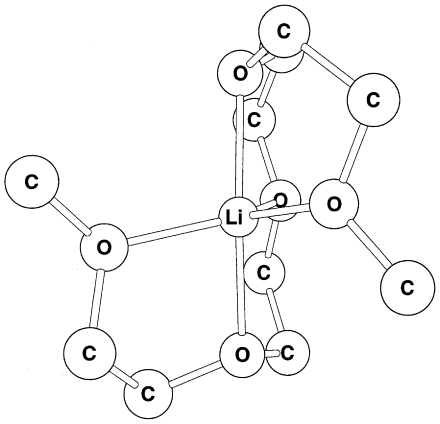

Fig. 1. The pentacoordinated Te9 complex (**aG$^+$a g$^+$G$^+$a aG$^-$a g$^-$G$^-$a**) of Li^+–tetraglyme. Hydrogens omitted for clarity.

2. Calculational method

Semi-empirical PM3 calculations, ab initio Hartree–Fock (HF) self-consistent field molecular orbital calculations and density functional theory (DFT) calculations have been performed with the SPARTAN program [22] and the GAUSSIAN94 program [23].

Initial calculations on the starting geometries were made with the semi-empirical PM3 method. The subsequent final geometry optimizations at HF level used the standard 3-21G* basis set. Vibrational frequency calculations were performed at this level of theory to confirm that the structures obtained were true minima. The optimum usage of computational resources suggests employing DFT methods to finally evaluate the energies and use of a rather small basis set for the geometry optimizations by HF methods [24]. Because of the size of the systems, the energies were finally evaluated using DFT methods at the B3LYP/6-31G* level of theory (B3LYP/6-31G*//HF/321G*) [25,26]. The bonding energies are defined as $E_{bond} = \{E(Li^+\text{–glyme complex}) - [E(\text{glyme(in the complex geometry)}) + E(Li^+)]\}$.

Suitable starting geometries were selected on the basis of discussions by Dale [27] and our own earlier calculations [20,21]. In a previous ab initio molecular orbital calculation for Li^+–diglyme [20], two different stable complexes/structures were found. The diglyme in the two complexes have the conformations **aG$^-$a aG$^+$a** and **aG$^+$a g$^+$G$^+$a**, referred to as structure **1** and **2**, and representing two prototype structures. In both of these prototype structures a sequence of three ether oxygen atoms is suitably arranged for coordination to a metal ion. The present 'shorthand' notation uses g or G (gauche) for dihedral angles of 30–120°, in two different directions, and a (anti) for dihedral angles of 120–180°. Upper-case letters are used to identify O–C–C–O dihedrals. The sequence **g$^+$G$^+$a** found in structure **2** gives rise to a sharp bend referred to as a 'genuine corner' [27]. Structure **1** can be considered as a fragment of a general crown ether which has alternating **aG$^-$a** and **aG$^+$a** conformations.

Many experimentally determined conformers in complexes of a metal ion and tetraglyme or longer glymes [14–19] contain different combinations of structure **1** and structure **2** sequences. However, to our knowledge, some combinations have never been found experimentally, perhaps because of stacking problems in crystals or steric hindrances within the glyme itself caused by the conformation sequence. In the present calculations on lithium cation complexes with various oligomers (tetra- penta- and hexaglyme), we have obtained, respectively, 16, 45 and 126 different possible conformers by combining the prototype structures **1** and **2** in a systematic way. All of these conformers were used as starting geometries in the semi-empirical calculations. Each set of calculations was aimed at reaching as a high coordination number (CN) for lithium as possible. We do not suggest that this study fully covers all the possible complexes of these highly flexible systems — to find all of these would be a truly demanding task. Still, we believe our selection of complexes provides results that are relevant to the complete set of stable complexes.

3. Results and discussion

3.1. Li^+–tetraglyme complexes

Selected geometry parameters and energies of the tetra- and pentacoordinated complexes obtained, Te1 to Te11, are presented in Table 1. The total energies show the Te9 complex (Fig. 1) with a distorted trigonal bipyramidal geometry and the conformational sequence of **aG$^+$a g$^+$G$^+$a aG$^-$a g$^-$G$^-$a** to be the global minimum-energy structure. There are also seven other stable pentadentate structures within 30 kJ mol^{-1} from the global minimum and all structures obtained (including the tetradentate ones) are, in fact, within 55 kJ mol^{-1}. The lowest-energy complexes (apart from Te9) are the Te3 and Te10 ones (not shown) within 8 kJ mol^{-1} from the global minimum. To obtain the Te3 structure from the global minimum structure ($\Delta E = +4.4$ kJ mol^{-1}) requires only one major change in one C–O–C–C dihedral angle from a to g and, accordingly, a sign change for an O–C–C–O angle. This should cause an energy increase of 4.4 kJ mol^{-1} according to earlier potential energy calculations for such a rotation in the diglyme molecule [28]. For the Te10 structure the **1** and **2** scheme is broken, two gauche O–C–C–O angles (dh6 and dh9) with the same sign follow in sequence without a gauche C–O–C–C angle in between. The Te10 structure has approximate C_2 symmetry and all other structures have C_1 symmetry. Similarly to the Te10 structure, Te1, Te4, Te6 and Te8 (not shown) do not follow the **1** and **2** scheme due to steric hindrances and/or less suitable arrangement for cation coordination. The energies of these are on the average ~15 kJ mol^{-1} higher than for the ones following the scheme.

Table 2
Energies and selected geometry parameters for the Li^+–pentaglyme complexes P1 to P7

	HF/3-21G*				B3LYP/6-31G*//HF/3-21G*		
	$d(Li^+–O)$ (Å)	CN (Li^+)	E total (au)	ΔE (kJ mol^{-1})	ΔE (kJ mol^{-1})	E_{bond} total (kJ mol^{-1})	E_{bond} (kJ mol^{-1})
P1	1.918; 3.214; 2.026; 2.062; 2.060; 2.107	5	−920.99291	21.8	28.2	592	118
P2	2.015; 2.228; 2.311; 2.315; 2.228; 2.016	6	−920.99712	10.7	8.8	617	103
P3	2.047; 2.341; 2.213; 1.974; 2.279; 2.027	6	−920.99408	18.7	25.1	608	101
P4	1.989; 2.002; 3.112; 1.987; 2.230; 1.975	5	−920.99535	15.4	25.1	610	122
P5	1.886; 1.921; 1.918; 1.857; 4.200; 4.498	4	−920.98252	49.1	57.7	552	138
P6	3.690; 1.950; 2.042; 1.953; 2.070; 1.929	5	−921.00054	1.7	24.6	590	118
P7	2.001; 2.330; 2.177; 2.177; 2.330; 2.001	6	−921.00121	0	0	612	102

Although it is tempting to assume that tetraglyme should be suitable as solvent for lithium owing to its possibility to adopt a conformation sequence similar to a crown ether, we have been unable to find such a sequence (**aG$^-$a aG$^+$a aG$^-$a aG$^+$a**) to be stable for Li^+ as the coordinating cation. In fact, this sequence is hindered energetically in the case of lithium as the coordinating cation. To obtain such a sequence, all the O–C–C–O dihedral angles of the oligomer would need to be ∼15° larger than generally preferred for lithium coordination, causing higher torsional energy. On the other hand, if the dihedral angles are kept at their preferred values, the terminal $–CH_3$ groups of the tetraglyme would collide.

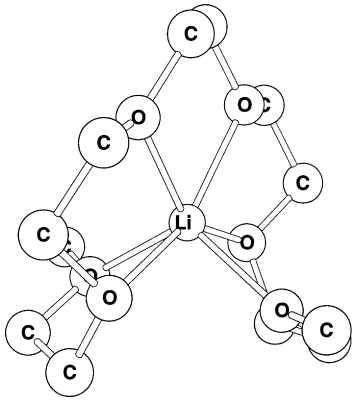

Fig. 2. The Li^+–pentaglyme P7 complex (**aG$^+$g$^+$ aG$^+$a aG$^-$a aG$^+$a g$^+$G$^+$a**). Hydrogens omitted for clarity.

3.2. Li^+–pentaglyme complexes

Selected geometry parameters and energies of the tetra-, penta- and hexacoordinated complexes obtained, P1 to P7, are listed in Table 2. The total energies show the P7 complex (Fig. 2) with distorted trigonal prism geometry and a conformational sequence of **aG$^+$g$^+$ aG$^+$a aG$^-$a aG$^+$a g$^+$G$^+$a** to be the global minimum-energy structure and all penta- or hexacoordinated complexes are within 30 kJ mol^{-1} of this minimum. The second-lowest-energy complex is P2 (not shown) ($\Delta E = +8.8$ kJ mol^{-1}). The conformation sequence of this complex contains two more gauche C–O–C–C angles than the global minimum. According to the potential energy calculations [28] mentioned earlier, it should have an energy increase by 4.4 kJ mol^{-1} for each C–O–C–C angle changed, or a total of 8.8 kJ mol^{-1}, in excellent agreement with our current calculation. Both P2 and P7 have approximate C_2 symmetry and they are also the two structures having the highest bonding energies. The **1** and **2** scheme is broken for P3 and P6 (not shown), but the average energy of these is similar to that of the ones obeying the scheme ($\Delta E < 1$ kJ mol^{-1}).

3.3. Li^+–hexaglyme complexes

In Table 3 selected geometry parameters and energies of the penta- and hexacoordinated lithium complexes obtained with hexaglyme, H1 to H5, are presented. The total energies show the H3 complex (Fig. 3), which has a geometry somewhat resembling a mixture of an octahedron and a trigonal prism and a conformational sequence of **aG$^+$g$^+$ aG$^+$a aG$^-$a aG$^+$a g$^+$G$^+$a g$^+$G$^+$a**, to be the

Table 3
Energies and selected geometry parameters for the Li^+–hexaglyme complexes H1 to H5

	HF/3-21G*				B3LYP/6-31G*//HF/3-21G*		
	$d(Li^+–O)$ (Å)	CN (Li^+)	E total (au)	ΔE (kJ mol^{-1})	ΔE (kJ mol^{-1})	E_{bond} total (kJ mol^{-1})	E_{bond} (kJ mol^{-1})
H1	3.903; 1.885; 2.067; 1.975; 2.009; 1.971; 4.809	5	−1073.05831	53.1	56.8	585	117
H2	1.913; 2.050; 1.961; 2.018; 1.968; 3.756; 5.093	5	−1073.07562	7.6	25.6	617	123
H3	2.011; 2.384; 2.143; 2.127; 2.442; 2.015; 3.593	6	−1073.07556	7.5	0	631	105
H4	3.706; 1.890; 2.039; 1.929; 2.047; 1.925; 3.570	5	−1073.07852	0	13.9	627	125
H5	3.633; 1.970; 2.252; 2.401; 2.134; 2.200; 2.046	6	−1073.07226	16.5	17.2	621	104

global minimum-energy structure; all penta- or hexacoordinated structures are within 60 kJ mol^{-1}.

The second-lowest-energy complex is H4 (ΔE = +13.9 kJ mol^{-1}) (not shown). H4 has approximately the same total bonding energy as H3 (627 and 631 kJ mol^{-1}, respectively), but is a pentacoordinated complex. All structures obey the **1** and **2** scheme except for the non-coordinated oxygen end of the H1 structure. None of the structures has a higher symmetry than C_1.

3.4. Comparison of the different Li^+–glyme complexes

The total bond energies as a function of glyme length (n = 3–6) are shown in Fig. 4, allowing a general statement about the Li–O bonding strength in these systems to be made. Calculations for triglyme have been performed on the previously obtained T1–T4 complexes [21]. The increase in the bond energy is almost linear for the n = 4–6 complexes, but since no calculations for n = 7 have been performed, it is not evident that the increase would continue.

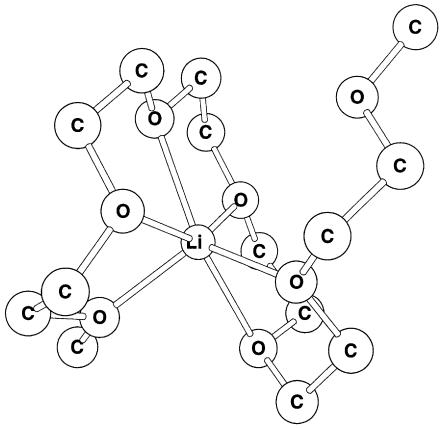

Fig. 3. The Li^+–hexaglyme H3 complex (**aG$^+$g$^+$ aG$^+$a aG$^-$a aG$^+$a g$^+$G$^+$a g$^+$G$^+$a**). Hydrogens omitted for clarity.

More important are the conclusions drawn from a comparison across the different glymes, but for the same coordination number (CN) of lithium. By a curve-fitting procedure to the points given in Fig. 5 and then extrapolating, a value of 626(± 5) kJ mol^{-1} is obtained for CN = 7. Heptacoordination in these systems, therefore, seems less likely since the energy gain per bond would decrease to ~90 kJ mol^{-1} and no gain in total bonding energy would result, in contrast to the situation up to hexacoordination.

This conclusion can also be made from the number of complexes obtained with different coordination numbers across the glymes (n = 3–6), which clearly suggests pentacoordination as most likely: eight complexes for CN = 4, 15 for CN = 5 and five for CN = 6. The energy per bond for the same coordination number shows only small differences when varying the glyme length, as depicted in Fig. 6.

To compare all the Li^+–oxygen distances qualitatively for all complexes obtained, a histogram is shown in Fig. 7. From this we extract a peak value at ~ 2.03 Å — which we compare with the reported preliminary rdf of Annis et al. [29] on LiI dissolved in PEO, from which a crude estimate gives us a peak value of ~ 2.1 Å. Also, molecular dynamics simulations by Müller-Plathe and van Gunsteren [30] on the same system exist, with a peak value in their 'rdf' at ~2.3 Å. Their larger average distance is probably due to the deliberately reduced electrostatic interactions in their simulations (via ϵ).

Furthermore, using the data from our earlier calculations on lithium–diglyme complexes [20] with the 6-31G** basis set, our present lithium–oxygen distances calculated with the 3-21G* basis set should be adjusted by ca. +0.09 Å. The resulting average distance then becomes ~2.12 Å. The peak values for the three different glyme lengths used differ by less than ± 0.02 Å compared with the total in Fig. 7.

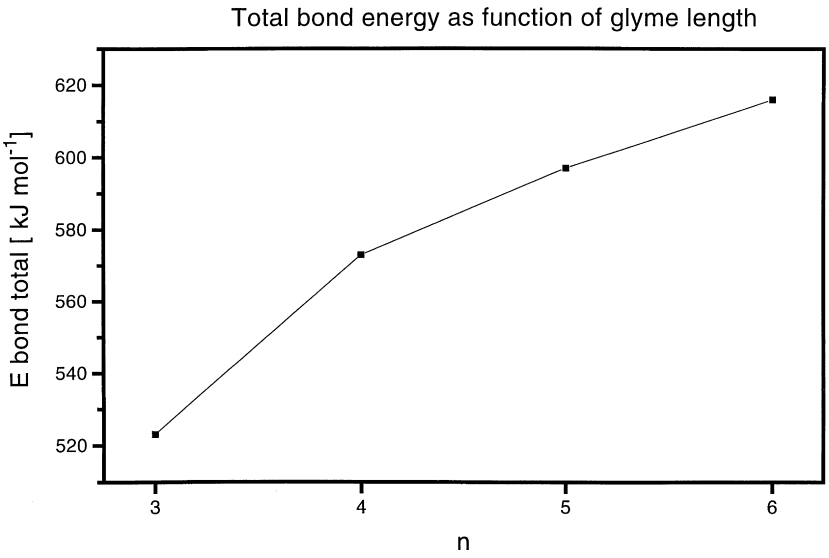

Fig. 4. The total bonding energy as a function of glyme length.

The geometries of the complexes obtained show different coordination figures, but some trends are apparent. Amongst the pentacoordinated complexes the quadratic pyramid (five examples) and the trigonal bipyramid (eight examples) geometries dominate, the latter generally being of lower energy. The trigonal bipyramid was observed earlier by us in a calculation of a lithium–diglyme 1:2 complex [20]. For the hexacoordinated complexes only the trigonal prism geometry can be detected (five examples), although sometimes severely distorted (H3). These complexes altogether account for 18 of the 23 complexes obtained in total. The connection between the conformation of the oligomer chain and the resulting geometries is another intruiging question. All the trigonal prisms, and thus all hexacoordinated complexes, have the structure **2** type of conformation at both ends of the oligomer chain.

3.5. Vibrational frequencies

Vibrational frequency calculations were made mainly to identify the structures obtained as minimum-energy structures but also to provide vibrational information of several interesting regions. We will focus here on two regions often debated in polymer electrolyte studies, regions where the so-called ‘breathing’ and ‘rattling’ modes are situated.

An interesting common feature in the spectra of lithium salt/PEO mixtures is the band obtained at $\sim$860 cm^{-1} [31,32]. This is a strong Raman band and has been assigned

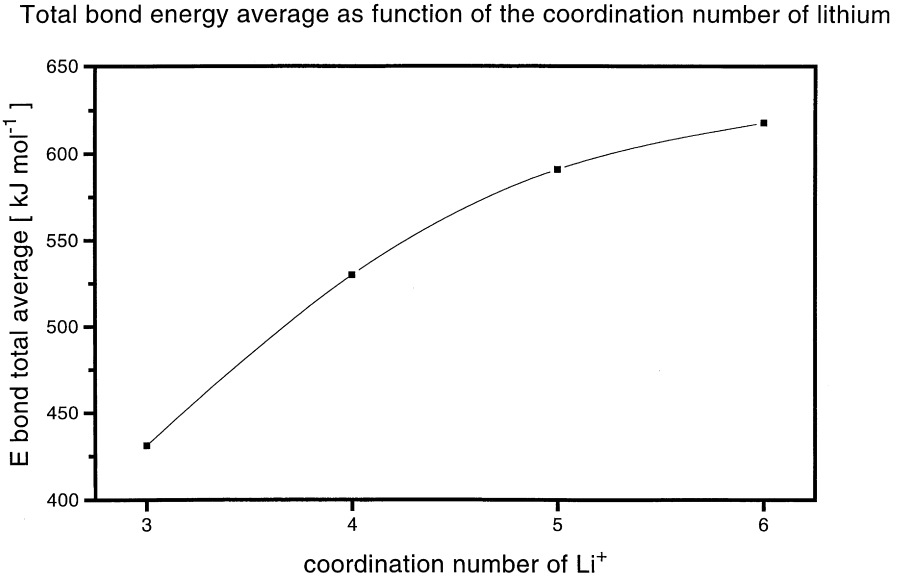

Fig. 5. The total bonding energy as a function of coordination number of lithium.

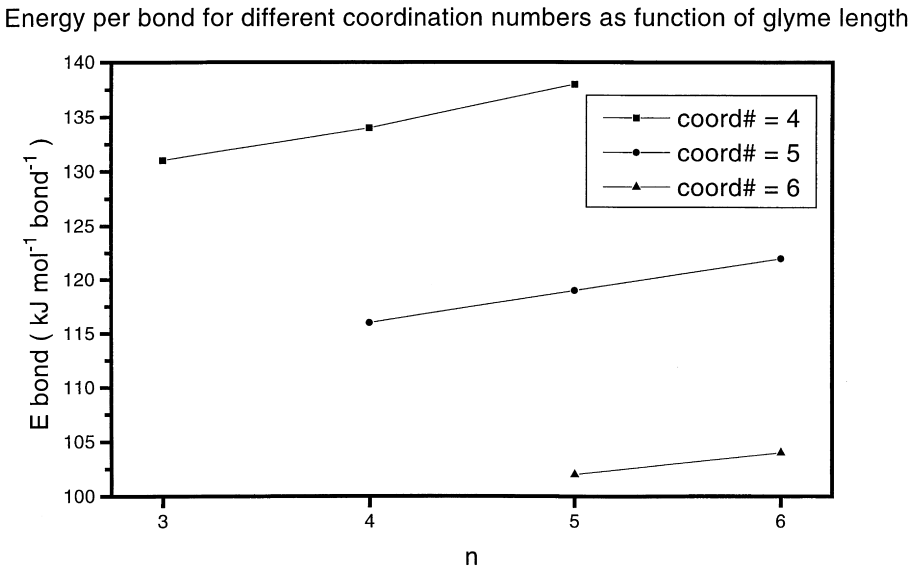

Fig. 6. The energy per bond for different coordination numbers as a function of glyme length.

to a so-called 'breathing' mode of a PEO segment solvating the lithium ion and adopting a kind of 'crown–ether conformation'. The corresponding calculated modes in the present work for the lithium–tetraglyme, and indeed also for the penta- and hexaglyme complexes, reveal that regardless of chain conformation a band calculated at $\sim 830(\pm 9)\ cm^{-1}$ (scaled) with a high Raman intensity exists. Visualization of these modes gives a 'breathing' mode where all coordinated oxygens move towards the metal ion in phase. The vibrations are mainly due to C–O and C–O–C coordinate changes with the lithium ion more or less fixed. The behaviour of the C–O and C–O–C units as independent oscillators with similar force constants may explain the insensitivity of the vibrational band to the chain conformation.

Furthermore, for all complexes, several vibrational bands in the region 340–540 cm^{-1} (scaled) were obtained. Visualizing the calculated modes confirmed that all complexes have several modes often described as 'rattling' modes, meaning the cation rattling inside a 'rigid' solvating cage of ether oxygens. Infrared spectra in this region often consist of broad features [31]. One would in general expect three modes, one for each of the translational degrees of freedom of the lithium ion. The involvement of other internal coordinates implies, however, that more than three modes contain lithium-ion motions. These modes also vary in

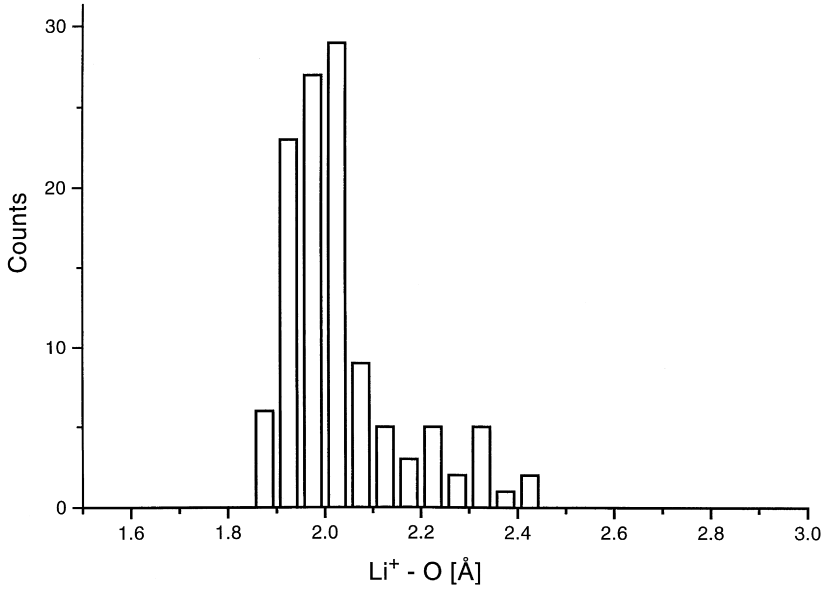

Fig. 7. Histogram of Li^+–oxygen distances.

frequency depending on the complex and, in a situation with possibilities for the formation of different complexes, a broad feature from overlapping bands is predicted in agreement with experimental observations.

4. Conclusions

As proposed in our earlier calculations on diglyme and triglyme [20,21], the large flexibility of the oligomer chain appears to allow numerous stable structures within a narrow energy range with quite different geometrical arrangements of the ether oxygens. Eleven different structures of different geometries have been obtained for the Li^+–tetraglyme systems. Those with the lowest relative energies can basically be described in terms of the prototype structures of the Li^+–diglyme complex (structure **1** and **2**). Using these basic structures, and extending the glyme beyond $n = 4$ does not, in fact, give more possible geometries but fewer. The steric hindrances play a vital role in the coordination procedure. It is remarkable that only a few hexacoordinated complexes have been obtained and no heptacoordinated. The average coordination number for lithium in dilute or even rather concentrated solutions of lithium salts in long-chain PEO, with a non-coordinating anion such as triflate or imide, is therefore suggested to be five.

The coordination figures are dominated by the quadratic pyramid, trigonal bipyramid and the trigonal prism type of geometries. The hexacoordinated complexes are all trigonal prisms and the chain conformation in all of these end with the type **2** structure sequence.

Acknowledgements

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