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Molecular interactions and vibrations in $CH_3(OCH_2CH_2)_2OCH_3–M^+–X^-$ (M = Li, Na, K and X = PF_6, AsF_6, SbF_6): An *ab initio* study

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ABSTRACT

Molecular interactions are one important factor governing the ionic conductivity of solid polymer electrolytes (SPE). In order to understand the role of interactions in SPE, *ab initio* Hartree–Fock calculations have been carried out on diglyme–M^+–X^- (diglyme = $CH_3(OCH_2CH_2)2OCH_3$, M = Li, Na, K and X = PF_6, AsF_6, SbF_6) electrolytes. These calculations predict stronger binding for the lithium ion towards the ether oxygens of diglyme in these electrolytes. Consequences of diglyme–MX interactions to the infrared spectra are presented. Theoretically predicted results are in good agreement with experimental observations. Molecular electron density topology has been used to study the molecular interactions present in the 1:1:1 electrolytes.

1. Introduction

Poly(ethylene oxide) (PEO) oligomers complexed with organic and inorganic salts in solutions or solids have been of considerable interest in recent literature because of their use as solid electrolytes or high ionic conductors [1–3]. Wright [4] first observed the crystalline and amorphous PEO complexes of alkali metal salts capable of acting as high ionic conductors [2,3]. It was determined that this conductivity is likely due to the transfer of charge from the anion and its interaction with the cation in these electrolytes [5]. Anions, such as $CF_3SO_3^-$ (triflate or Tf^-), PF_6^-, $(CF_3SO_2)_2N^-$ (TFSI) used in solid polymer electrolytes (SPE), prefer weak coordination with the cation lithium [6]. These lithium salts are economical, stable and able to provide the large number of fast moving charge carriers to meet the requirement for ion conductivity. The interaction of cation with polymer is especially important in solid polymer electrolytes because ion transport in the amorphous phase of PEO-based electrolytes appears to be coupled to the segmental motion of the host polymer. This motion is highly dependent on the nature of interaction between the cation and the polymer backbone [7]. Thus ionic conductivity is governed by both ion–ion interactions (ionic association) and ion–polymer interactions (polymer conformations and segmental motion) [8].

Analysis of the ion pairs characteristics in polymer electrolytes is crucial to our study of the ion conduction mechanism at the molecular level. In other words interactions between the anion–metal ion as well as between PEO oligomer–metal ion are important in ion transport phenomenon in these electrolytes [5]. Cation–polymer and cation–anion interactions are critical to understanding the microscopic mechanism of ionic transport. With this in mind, a number of theoretical studies aiming to characterize these ion–polymer and ion–ion interactions in PEO have appeared in the literature. Gejji et al. [8–10] have studied 1:1 lithium–diglyme ion pairs where the Li^+ is coordinated by two or three ether oxygens employing *ab initio* molecular orbital calculations. This work has also been *extended* to 1:1 complexes of $CH_3(OCH_2CH_2)_{2-7}OCH_3$–M (M = Li^+, Na^+, K^+, Ca^{2+} and Mg^{2+}) systems in order to understand the role of cation–oxygen interactions in SPE [11–13].

Frech and co-workers observed that the frequencies and intensities of vibrational bands are sensitive to cation–oxygens interactions in PEO. Therefore these modes have been utilized to study cation–polymer interactions in ethylene oxide-based systems [7]. A spectroscopic comparison of $P(EO)_6$:Li–AsF_6, P(EO)6:Li–PF_6 and P(EO)6:Li–SbF_6 compounds reveals that the band frequencies in the former compound are consistently higher by a few wave numbers than those of the latter two systems. This large band frequency is due to cation–ether oxygen interaction. Lassègues [14] observed very similar infrared and Raman spectra for P(EO)6:Li–X (X = PF_6, AsF_6, SbF_6) electrolytes, even though the conformational sequences of the PEO backbone differ. Only very small frequency and intensity differences have been observed between the Raman spectra of these anions. Recently Frech [15] has concluded that ionic association in solution is strongly affected by the dielectric constants of the solvents. As the dielectric constant of the solvent increases, the IR intensity of the band decreases because ion pairing is not favored in high dielectric constants.

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Ab initio HF calculations have predicted the bonds of anion in SPE are contracted relative to the free state of constituents. This implies cation–PEO interactions are stronger interactions in 1:1:1 ethylene glycol M^+–X^- complexes [5]. These results have also been predicted for $CH_3(OCH_2CH_2)_2OCH_3$–M^+–X^- (M = Li, Na and K) (X = CF_3SO_3, PF_6, $(CF_3SO_2)_2N$, ClO_4, BF_4 and SCN) and $CH_3(OCH_2CH_2)_{2\text{-}4}OCH_3$–$M^+$– CF_3SO_3 (M = Li, Na and K) 1:1:1 electrolytes [16–18]. Thus it is interesting to study molecular interactions and consequent vibrations in diglyme–M^+–X^- (M = Li, Na, K and X = PF_6, AsF_6, SbF_6) electrolytes at the molecular level.

In the present work we derive the electronic structure and the normal vibrations of diglyme–M^+–X^- (M = Li, Na, K and X = PF_6, AsF_6, SbF_6) electrolytes using *ab initio* molecular orbital calculations. Manifestation of molecular interactions, such as cation–oxygen and cation–anion interactions to the vibrational spectra of 1:1:1 electrolytes are discussed. The strength of the molecular interactions is studied by calculating molecular electron density (MED) topology. Here we also compare theoretically predicted normal vibrations with experimentally observed vibrations. The computational method is outlined next.

2. Computational method

Hartree–Fock calculations were carried out on $CH_3(OCH_2CH_2)_2OCH_3$–M^+–X^- (M = Li, Na, K) (PF_6, AsF_6, SbF_6) systems using the GAUSSIAN03 program [19] by employing LANL2DZ basis set which has the effective core potential (ECP) on P, As, Sb atoms [20–22]. The geometries thus obtained were subjected to subsequent optimizations using the hybrid density functional theory incorporating Becke's three-parameter exchange with Lee, Yang and Parr's (B3LYP) correlation functional [23,24]. Stationary point geometries obtained were characterized as the local minima or saddle points on the potential energy surface by examining the number of imaginary frequencies and the eigenvalues of the Hessian matrix. Normal vibrations were assigned by visualizing displacements of atoms around their equilibrium (mean) positions [25]. Vibrational frequencies of diglyme and Li–D1–X (X = PF_6, AsF_6 and SbF_6) from the measured spectra [14] were compared with those derived from the HF/LANL2DZ (scaled 0.88) and B3LYP/LANL2DZ (scaled by 0.97) calculations (*cf.* Table 1). As seen from Table 1, that the normal vibrations derived from HF/LANL2DZ method are in good agreement with the experimental vibrations relative to B3LYP/LANL2DZ method justifies the use of low level HF/LANL2DZ calculation in the present work. The molecular electron density (MED) topology and identification of the critical points are calculated using the GAUSSIAN 03 program [19]. Molecular electron density (MED) topology [26] and four types of non-degenerate critical points (CPs) of rank 3 have been identified in the three dimensional space, including (3, −3) maxima (e.g. nuclear position); (3, +3), minima generally known as cage critical points (ccp); and saddle points, denoted by (3, −1) and (3, +1), referred as the bond critical point (bcp) and ring critical point (rcp), respectively.

Table 1a
Comparison of HF, B3LYP and experimental vibrational frequencies of diglyme

Assignments	Expt.	HF/LANL2DZ	B3LYP/LANL2DZ
CH_2 scissor	1453	1451 (20)	
		1449 (24)	1434 (23)
			1430 (22)
CH_2 rock		1407 (9)	
	1370	1368 (28)	
	1354	1345 (66)	1345 (13)
			1319 (39)
CH_2 twist		1253 (26)	1231 (15)
		1214 (26)	1188 (12)
		1203 (15)	1178 (17)
CH_2 wag		1169 (63)	1141 (12)
CO stretch		1126 (82)	1102 (32)
		1120 (21)	
CH_2 wag		1114 (11)	1086 (24)
		1108 (40)	
CO stretch		1086 (238)	1053 (174)
		1071 (92)	1050 (78)
CH_2 wag			
CO stretch		1038 (14)	
CH_2 wag			
CC + CO stretch		998 (16)	1019 (14)
		988 (41)	984 (15)
CH_2 wag		922 (19)	970 (36)
			912 (21)
CH_2 wag		818 (45)	796 (27)
		797 (8)	
		793 (21)	

3. Results and discussion

3.1. Electronic structure

3.1.1. PEO–cation interactions

Optimized geometries of diglyme–M^+–X^- (M = Li, Na and K) (X = PF_6, AsF_6, SbF_6) derived from the HF/LANL2DZ calculations are displayed in Fig. 1 along with their atomic labels. In the crystalline phase diglyme with all trans conformation around the C–O and C–C bonds is of minor importance [27]. In this work, therefore, we considered the diglyme possessing the gauche conformation around the C–C bonds of central CH_2–CH_2–O fragment as a reference. Selected HF/LANL2DZ optimized geometrical parameters are reported in Table 2. As expected, the weakening of the C—O bonds engenders elongation of the C_1–O_2 and C_8–O_9 bonds relative to bond length in the gas phase free diglyme (D_1) conformer. Bond angles generally are less sensitive to metal ion interactions, with the largest deviation within 3° being noted for the COC bond angle. The interaction of a metal ion with the ether oxygen, however, leads to a change around the backbone of the diglyme. The stronger interactions of Li^+ with oxygen atoms engenders a large change in the dihedral angle around C—C and C—O bonds of the diglyme (within 30°) relative to the sodium (24°) and potassium (20°) cations.

3.1.2. Cation–anion interactions

This section describes the mechanism of anion–cation interactions in the polymer electrolytes. For electrolytes containing the PF_6 anion the shortest $Li\cdots F$ distance is predicted to be 2.034 Å compared to sodium (2.272 Å) and potassium (2.741 Å). On the other hand the PF bonds (F^* denotes fluorine which binds to metal ion) of the free Li–PF_6 ion pair have been predicted to be 1.741 Å. These bond distances in the 1:1:1 electrolytes containing metal–PF_6 are shortened due to the weakening of cation–anion interactions in the 1:1:1 electrolyte relative to those in the 1:1 ion pair. Thus contraction of these bonds participating in the interactions can be qualitatively correlated to the strength of metal–anion interactions. The maximum shortening of the PF bonds in the Li–PF_6–diglyme is predicted to be 0.013 Å compared to 0.005 Å for Na–PF_6–diglyme and 0.006 Å for K–PF_6-diglyme. It may, therefore, be inferred that neutral Li^+—PF_6^- ion pairs are facilitated over $Na^+PF_6^-$ or $K^+PF_6^-$ containing electrolytes. Similar inferences can be drawn for electrolytes containing AsF_6^- or SbF_6^- anions.

For 1:1:1 SPE, the Li^+ and Na^+ metal shows pentadentate coordination with the metal ion binding to three ether oxygens of diglyme and two fluorine atoms of the anion. This has also been observed in the crystal structure [7]. The potassium cation, however, shows hexadentate coordination where the cation binds with