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Ion Pairs in Polymer Electrolytes Revisited: An Ab Initio Study

Patrik Johansson* and Per Jacobsson

Department of Experimental Physics, Chalmers University of Technology, SE-41296 Göteborg, Sweden

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Several stable structures of 1:1:1 anion−lithium ion−ethylene glycol (EG) complexes have been obtained by ab initio calculations at the Hartree−Fock level of theory (HF/6-31G*). The anions investigated are BF_4^-, ClO_4^-, PF_6^-, AsF_6^-, $CF_3SO_3^-$ (Tf^-), and $[(CF_3SO_2)_2N]^-$ (TFSI). Larger basis sets and electron correlation effects have been accounted for by performing single-point calculations (HF/6-311+G*//HF/6-31G* and MP2/6-311+G*//HF/6-31G*). The advantages of the 1:1:1 complexes as model systems for ion pairing in polymer electrolytes are outlined with emphasis on the coordination geometries and the resulting vibrational spectra. Comparisons are made with calculated data for "free" anions and 1:1 lithium ion−anion ion pairs and experimental spectroscopic data. On average, the 1:1:1 complexes reproduce the experimentally observed vibrational shifts better than the 1:1 ion pairs. The results are discussed in relation to the usually encountered nomenclature; solvent-separated ion pairs, solvent-shared ion pairs, and contact ion pairs.

Introduction

New solid polymer electrolytes (SPEs) are crucial in the development of modern high energy density lithium batteries.[1] New choices of polymers and salts are constantly employed, mainly to enhance the ion conductivity and the cation transference number, which still are limiting factors. However, most new types of SPEs still rely on PEO and/or the repeated ethylene oxide unit, $(CH_2CH_2O)_n$, to coordinate the lithium cations and thereby dissolve the salts in the polymer matrix. This concept has some important implications: the main part of the conductivity is likely to be transferred by the anion and the interactions with the cation are of uttermost importance.

Although the salts used in SPEs preferably have weakly lithium coordinating anions such as ClO_4^- (perchlorate), $CF_3SO_3^-$ (triflate), or $[(CF_3SO_2)_2N]^-$ (TFSI), cation−anion interactions do occur, increasing with elevated temperatures. Ion-pair formation is undesirable because it reduces the number of effective charge carriers momentarily present in the fluxional SPE systems, and analysis of the ion pairs characteristics is therefore crucial to gain more knowledge of the ion conduction mechanism on a molecular level. Various cation−anion interactions have previously been modeled by ab initio calculations with this purpose in mind.[2−6]

In general, when weakly interacting ion pairs have been modeled, only the actual cation−anion pair of interest has been considered. For more strongly interacting anions such as halides, sulfate, and nitrate, there has been many experimental and computational efforts, especially focusing on their behavior in aqueous solution.[7−10] Sometimes not only one single type of ion pair is possible, the lithium ions may for example be mono-, bi-, or tri-dentately coordinated to the anions. However, to merely account for the cation−anion interaction is not enough, at least not for reproducing trends in the vibrational spectra. Although several computational studies of 1:1 cation−anion ion pairs predict vibrational frequencies that in *general* are in good agreement with experimental data, the most crucial parameter, the results for the anion bands used for "fingerprinting" of ion interaction experimentally, often give erroneous results.

As an example, a well-performed ab initio calculational work on the $LiClO_4$ ion pair report vibrational frequencies and their relevance for detecting ion-pairing phenomena in electrolytic systems.[4] However, although in general, in very good agreement with experimental data, the coordination to Li^+ experimentally causes an *upshift* in the spectra for the symmetric stretch mode of ClO_4^- of about 10 wavenumbers and the calculations, even at the highest employed level (HF/6-311+G*), produce a *downshift* ($\sim$16 cm^{-1}). Indeed, the same behavior is true also for the triflate anion and for BF_4^-.[2,11] Gejji et al. noted that downshifts have been reported for the often used υ_sSO_3 mode of the triflate anion, probably because of different coordination geometries depending on the cation size, but this phenomenon has not been observed for lithium as the cation.[2] Furthermore, this cannot, as shown by both Gejji et al. and Nazri et al., be corrected for by using larger basis sets or electron correlation methods. Electron correlation methods such as MP2 do in fact seldom improve on Hartree−Fock calculated vibrational frequencies, unless resulting in a substantial change in electron distribution and/or geometry, (when using appropriate scaling factors in both cases).[12]

Altogether, this suggests that the physical picture of an isolated ionic species in a noninteracting medium is incorrect and thus, in the present cases, that the explicit cation interaction with the PEO matrix cannot be totally neglected in the models. Some computational effort, primarily by the Argonne group,[13] has been done to investigate 1:1:1 anion−cation−polymer models and the effects on static barriers for ion transport in PEO-based systems. Unfortunately, no vibrational frequencies have been reported.

The 1:1:1 approach also considers the different types of ion pairs supposed to occur in polymer electrolytes: solvent-separated ion pairs, solvent-shared ion pairs, and contact ion pairs. Experimental studies (vibrational spectroscopy) have earlier been used to detect these ion pairs and previous discussions are mainly based on data therefrom.[14,15] An excellent discussion on the topic is found in ref 14. By explicitly adding

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* To whom correspondence should be addressed. E-mail: patrikj@fy.chalmers.se.

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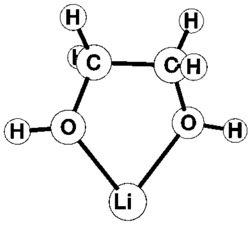

Figure 1. The Li^+−EG unit (approximate C_2 symmetry).

the "polymer mimic" to the cation, we have a model both for contact ion pairs (1:1) and for solvent-shared ion pairs (1:1:1), the former are also treated as a subpart of the latter. The present study does, however, not treat the possible occurrence of solvent-separated ion pairs, more than as "free" anions.

In the present work, 1:1:1 complexes between a lithium cation, ethylene glycol (EG; $HOCH_2CH_2OH$), and several anions often used in SPE studies have been subjected to a systematic study. EG here acts as a model molecule for a PEO segment. Calculations on "free" anions and 1:1 ion pairs have also been performed to serve as unambiguous comparison material. The resulting structures, energies, atomic charges, bond orders, vibrational frequencies, and IR intensities are reported.

Computational Method

Ab initio Hartree−Fock (HF) self-consistent field molecular orbital calculations were performed using the PC GAMESS version[16] of the GAMESS (US) QC package.[17]

Initial calculations on the starting geometries, for the anions and the 1:1 ion pairs based on symmetry and earlier studies,[2−4,6,8,18,19] were made at the HF level with the 3-21G* basis set. The geometries were subsequently optimized at the HF level using the standard 6-31G* basis set. Diffuse functions (+), HF/6-31+G*, were added for all "free" anions, as generally presumed to be needed to get accurate geometries for negatively charged species. Atomic charges were evaluated using the Mulliken partitioning scheme. Vibrational frequency calculations were performed both to confirm that the obtained structures were true minima on the potential energy surfaces and to be able to compare with experimental (spectroscopic) data. The effects of larger basis sets and electron correlation have been accounted for by performing single-point calculations (HF/6-311+G*//HF/6-31G* and MP2/6-311+G*//HF/6-31G*). For the As atom, the 6-311+G* basis is not available, and therefore, no such calculations could be performed for AsF_6^-. The binding energies are defined as $\Delta E_{\mathrm{bind}} = E_{\mathrm{complex/ion-pair}} - \Sigma E_{\mathrm{components}}$.

The present study relies on building 1:1:1 complexes based on knowledge of the stable 1:1 ion pairs' geometries. Our main aim was to perform a comparative study for several anions while keeping the lithium ion−EG unit more or less constant (in approximate local C_2 symmetry; Figure 1). This together with the different anions provides us with approximate tetrahedral and trigonal bipyramidal coordination environments for lithium ion coordination numbers (CN) 4 and 5, respectively. We therefore believe our range of 1:1:1 complexes to provide a solid base for a discussion on ion pairs in SPEs and how to preferably model them.

Results and Discussion

As the main purpose was to investigate the effects of adding a "solvent" molecule to the 1:1 cation−anion ion pairs, only a brief section deals with the "free" anions. The obtained differences between the 1:1 and 1:1:1 models are given special attention, especially with respect to charge distribution and comparison with available experimental data.

"Free" Anions. Initially, the anion geometries and vibrational frequencies are needed. Although in many cases already calculated, they were recalculated for all anions using the same method and basis set, HF/6-31+G*, to ensure that a reliable and straightforward comparison for the entire set of anions with the present calculations on the 1:1 ion pairs and the 1:1:1 complexes could be made. Spectroscopic literature values for the MX_4^- and MX_6^- type of anions were extracted from Nakamoto.[20]

BF_4^- and ClO_4^- were both optimized in T_d restricted geometry. The resulting B−F and Cl−O distances were 1.397 and 1.452 Å, respectively, in agreement with previously reported data.[4,11] The optimizations of PF_6^- and AsF_6^-, both restricted in O_h symmetry, gave M−F distances of 1.609 and 1.715 Å, respectively. Energies and selected geometry parameters are reported in Table 1.

For the triflate and the TFSI anions, the geometries from refs 18 and 19 were used as starting points for the recalculations using HF/6-31+G*. The TFSI conformers studied have C_2 and C_1 symmetries, respectively, and the triflate anion has a staggered C_{3v} symmetry. The addition of a diffuse function did not affect the equilibrium geometries of the TFSI anion significantly, in agreement with the original calculations.[19] The energy difference between the two obtained conformers was only ~1.7 kJ mol^{-1}. For the triflate anion, the most pronounced change upon diffuse function addition was the lengthening of the C−S bond by less than 1% (+0.015 Å). Selected computed vibrational frequencies and experimental literature values for the anions are reported in Table 2.

Li^+−Anion 1:1 Ion Pairs. For both the T_d and the O_h symmetry anions, there are three main possibilities for cation coordination with some preserved symmetry: monodentate (lowers the symmetry to C_{3v} and C_{4v}, respectively), bidentate (C_{2v} and C_{2v}), and tridentate (C_{3v} and C_{3v}). For the triflate anion, the previously reported monodentate and bidentate lithium ion pairs both have C_s symmetry, whereas the tridentate has C_{3v} symmetry.[2,3] The Li^+−TFSI ion-pair study uses both the ion pair where the cation is coordinated by two oxygen atoms from two different sulfonyl groups, thereby maintaining the anion's C_2 symmetry (denoted OO) and a C_1 symmetry ion pair obtained by lithium coordination to one sulfonyl oxygen and the central nitrogen (ON). These are the structures A1a and A1b from ref 6, respectively. Also, Bakker et al. outlined both these coordination possibilities for the cation.[21]

Selected geometry parameters for the most stable 1:1 ion pairs for each choice of anion are listed in Table 1, and in Table 2, selected vibrational frequencies and IR intensities are tabulated. In agreement with previous work, the bidentate structure is the only true minimum for $LiClO_4$, and both the bi- and tridentate structures are minima for $LiBF_4$.[4,11] The bidentate $LiBF_4$ ion pair is only 8−14 kJ mol^{-1} more stable than the tridentate ion pair, depending on the level of calculation. For the $LiMF_6$ ion pairs, only the tridentate structures are minima. The elongation of the M−X bonds because of cation coordination is ~3% (~0.05 Å) for both the MX_4^- and the MX_6^- anions. The shortening of the uncoordinated M−X bonds is of about the same size.

For triflate as the anion, only the bidentate ion pair is a minimum on the potential energy surface, in agreement with earlier calculations.[2] Both the investigated 1:1 Li−TFSI ion pairs are minima and resemble closely, both with respect to geometries and energies, those reported in ref 6. The single S−O

TABLE 1: Energies and Selected Geometry Parameters[a]

			1:1 ion pairs		1:1:1 complexes	
anion		"free"		ΔE_{bind}		ΔE_{bind}
BF_4^-	B−F	1.397	1.462,1.339		1.445,1.349	
(bident)	F−Li		1.761 × 2		1.827 × 2	
	Li−O				1.997 × 2	
	E[b]	−422.761635	−430.206824	679	−659.186283	834
	E2[c]	−422.863088	−430.325071	623	−659.367294	772
	E3[d]	−423.814505	−431.277065	623	−661.005940	786
ClO_4^-	Cl−O	1.452	1.486,1.422		1.477,1.427	
(bident)	O−Li		1.897 × 2		1.97 × 2	
	Li−O				1.987 × 2	
	E	−758.594297	−766.042684	622	−955.023905	785
	E2	−758.686859	−766.142609	600	−995.185358	754
	E3	−759.680330	−767.141445	614	−996.870948	780
PF_6^-	P−F	1.609	1.663, 1.561		1.65, 1.57	
(trident)	F−Li		1.881 × 3		1.96, 1.97, 2.01	
	Li−O				2.00 × 2	
	E	−937.639134	−945.067571	645	−1174.046378	795
	E2	−937.800910	−945.246782	592	−1174.290100	740
	E3	−939.213539	−946.664702	601	−1176.395271	768
AsF_6^-	As−F	1.715	1.759, 1.667		1.75, 1.68	
(trident)	F−Li		1.886 × 3		2.00 × 2,1.944	
	Li−O				2.00 × 2	
	E	−2828.944481	−2836.333021	665	−3065.313641	818
Tf^-	S−O	1.443	1.471 × 2,1.418		1.46 × 2,1.422	
(bident)	C−F	1.324	1.31		1.31	
	C−S	1.832	1.813		1.813	
	O−Li		1.899 × 2		1.98 × 2	
	Li−O				1.993 × 2	
	E	−958.304555	−965.746962	647	−1194.726130	801
	E2	−958.467790	−965.927262	618	−1194.968279	764
	E3	−959.996313	−967.457133	621	−1197.186582	785
TFSI	S−O	1.430, 1.429	1.463, 1.416		1.454, 1.419	
(OO)	C−F	1.31	1.31		1.31	
	C−S	1.831	1.817		1.817	
	S−N	1.573	1.561		1.563	
	O−Li		1.824 × 2		1.904 × 2	
	Li−O				2.011 × 2	
	E	−1821.227056	−1828.654179	632	−2057.630526	782
	E2	−1821.530758	−1828.992579	619	−2058.030998	760
	E3	−1824.354383	−1831.812099	610	−2061.540641	773

[a] E in au, distances in Å, and ΔE_{bind} in kJ mol^{-1}. [b] HF/6-31G*. [c] HF/6-311+G*//HF/6-31G*. [d] MP2/6-311+G*//HF/6-31G*.

TABLE 2: Selected Vibrational Frequencies and IR Intensities[a]

		"free"		1:1 ion pairs		1:1:1 complexes		
anion/	mode	calc. freq. (IR int.)	expt	calc. freq. (IR int.)	$\Delta\nu$calc	calc. freq. (IR int.)	$\Delta\nu$calc	$\Delta\nu$obs
BF_4^-	ν_1	800 (0.0)	777[30]	779 (1.0),[b] 814 (0.2)[c]	−21,[b] 14[c]	794 (0.8),[b] —[c]	−6,[b] —[c]	7[35]
ClO_4^-	ν_1	957 (0.0)	928[31]	947 (1.0)	−10	958 (0.8)	1	11[36]
PF_6^-	ν_1	792 (0.0)	756[32]	768 (1.3)	−24	781 (1.2)	-11	?
AsF_6^-	ν_1	755 (0.0)	689[33]	730 (1.5	−25	745 (1.8)	-10	15[37]
Tf^-	ν(C−F,C-S)	830 (0.5)	753[34]	861 (0.3)	31	857 (0.3)	27	7[34]
	ν_sSO_3	1118 (4.5)	1032[34]	1103 (5.6)	−15	1113 (5.7)	-5	9[34]
TFSI	ν_sSNS	809(0.7),[d] 809(0.7)[e]	740[29]	816(0.1),[d] 835 (1.7)[e]	7,[d] 24[e]	815 (0.1),[d] —[e]	6,[d] —[e]	7[29]
	ν_aSNS	1177(11.5),[d] 1172(6.1)[e]	1060[29]	1157(7.2),[d] 1159 (8.4)[e]	−20,[d] −13[e]	1170 (7.9),[d] —[e]	−7,[d] —[e]	?

[a] Frequencies in cm^{-1}, and IR intensities in km mol^{-1}. [b] Bidentate. [c] Tridentate. [d] OO. [e] ON.

shortening in the Li^+-Tf^- ion pair is ∼0.025 Å (∼1.5%) and, thus, only about half compared to the MX_4^- and the MX_6^- anions, which can be interpreted as reflecting the partly double-bond character of the S−O bonds in the triflate anion, as the E_{bind} values are of comparable sizes. The corresponding elongations are also less pronounced: +0.028 Å. Similarly for $TFSI^-$, the effects are smaller: −0.014 and +0.033 Å. Here also, the two central S−N bonds gain electron density and becomes shorter by 0.012 Å. Interesting is that the ΔE_{bind} value for Li^+-TFSI^- is second lowest of all (highest level of calculation) but the Li^+-O distances are by far the shortest; this anomaly may be due to the highly delocalized electron density in the central region of the anion.

The lowest energy minimum structures on the potential energy surfaces were transferred to construct starting geometries for the 1:1:1 complexes.

Li^+−Anion−EG 1:1:1 Complexes. As the 1:1 ion pairs cannot provide a full coordination shell for the cation and neither reproduces the observed cation-induced vibrational shifts satisfactorily, a changed model system is needed. Specifically, the local environment of the cation needs to be more realistically modeled.

Computationally, this can be done either via immersing the ion pair of interest in a dielectric continuum (SCRF type calculations), or (the present choice) by explicitly adding a "solvent" molecule or molecules to construct "supermolecules".

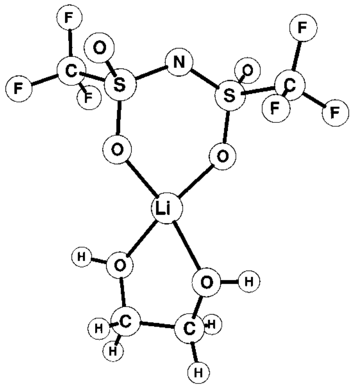

Figure 2. Example of a 1:1:1 complex: Li^+−$TFSI^-$−EG.

This latter approach has the advantage that it also provides spectroscopic data on the cation-"solvent" interactions[22] and completes the solvation shell of the cation. The former approach could be advantageous, e.g., for studying concentration dependences in strong electrolytic solutions.

Experimentally, the lithium ions in PEO-based SPE systems coordinate to the ether oxygen atoms, which arguably should be true also for lithium ions involved in ion pairs. Huang et al. used OH groups coordinated to the lithium cation in an attempt to model the local environment in LiTf based polymer electrolytes[3]. Thereby, the resulting vibrational shift for the $\upsilon_s(SO_3)$ mode of Tf^- upon lithium coordination was obtained in the right direction even for the most stable ion pair (mono-dentate). However, for this "1:1:1 complex", the CN for lithium was only 2. Furthermore, the addition of an OH group caused the most stable 1:1 ion pair, the bidentate (CN = 3), to become a transition state. We now try to avoid these problems and strengthen the approach with our current 1:1:1 models.

In the present 1:1:1 complexes, we model the effects of the cation being coordinated to the polymer, as in a real polymer electrolyte system, by adding an ethylene glycol molecule (EG; $HOCH_2CH_2OH$) to the most stable 1:1 ion pairs for each choice of anion. For all 1:1:1 complexes, the resulting bidentate lithium coordination to EG has Li−O distances in the range 1.99−2.01 Å, which is within 0.1 Å of earlier calculations on Li^+−glyme systems[23−26] and experimental studies on LiI/PEO systems.[27] An example of a 1:1:1 complex is given in Figure 2.

For BF_4^-, ClO_4^-, Tf^-, and TFSI the 1:1:1 complexes have C_2 symmetry (for Tf^- only approximate). The PF_6^- and AsF_6^- complexes have C_1 symmetry.

1:1:1 Complexes vs 1:1 Ion Pairs. The structural and energetic effects of adding an EG molecule to the different 1:1 ion pairs can be found in Table 1. The induced changes in the M−X bond lengths due to cation coordination are reduced by ∼23% on average for all anions. As was the case for the ion pairs, Tf^- also here shows a rather different behavior: the elongations are reduced by 39%, which is 1.5 times the second largest reduction, whereas the shortening of 16% is on par with the other anions. No similar divergent behavior is seen for TFSI. In contrast, for TFSI, a minor lengthening of the S−N bonds is observed compared to the ion pair, which is not found for the C−S bond in Tf^-. A tentative and tempting explanation is that the three S−O bonds in triflate accommodate the change in electron density almost totally, whereas for TFSI, the two SO_2 groups are interconnected via the two central S−N bonds, and thus the change is delocalized over a larger number of bonds. Thus, the behavior is essentially identical to the one observed for the 1:1 ion pairs. The trends in charge redistribution are discussed in the next section.

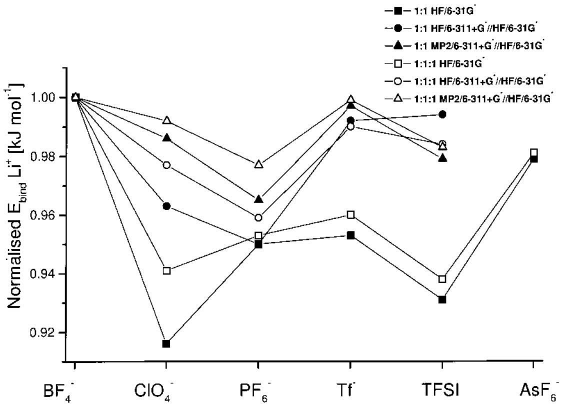

Figure 3. Binding energies for the lithium ion as a function of different anions.

The trends for the total binding energy of Li^+ are shown in Figure 3, normalized to the BF_4^- case (highest E_{bind} values), to make a comparison across the computational levels easier. If we only consider the ordering of the relative binding strengths, it is not changed when going from 1:1 ion pairs to 1:1:1 complexes. However, the relative percentages clearly change with the basis set chosen and if electron correlation is included or not.

The largest relative effects, for both the 1:1 and the 1:1:1 system, are seen for the perchlorate anion. The triflate and TFSI anions show a similar behavior: large dependence on the basis set size, less dependence on electron correlation. This latter might be because the perturbation caused by the lithium ion becomes significantly better accommodated and represented with a larger basis set for these diffuse anions, a problem not observed for the anions when isolated and unperturbed. In absolute numbers, however, the use of MP2 (Table 1, E3 values) recovers more energy than does the larger basis set (E2). Similarly sized changes are observed for both 1:1 ion pairs and 1:1:1 complexes.

In general, the binding energy differences become less pronounced with increasing the level of calculation, not surprising since HF calculations often exaggerate the interactions. For the two higher levels of calculation, the binding energies (E2 and E3) of all systems are within 4% of BF_4^-. Also, the PF_6^- and the TFSI anions result in the lowest binding energies, which is what would be expected from conductivity studies on liquid electrolytes.[28] In a previous study, it was shown that the anion binding energies to the lithium ion and the Li^+−EG unit, respectively, follow about the same trends.[22]

Atomic Charges and Bond Orders. As the anions gets perturbed by Li^+ or Li^+−EG addition, charge redistribution occurs throughout the entire "supermolecular" entities. For simplicity, we here focus on the differences between the 1:1 and 1:1:1 models and on the atom of most interest: the lithium ion.

When a lithium ion is added to an anion in a 1:1 ion pair, the Mulliken charge of the lithium ion becomes less than the nominal +1 value. The average values for the current choices of anions are +0.69 (HF/6-31G*) and +0.67 (MP2/6-311+G*). Similarly, coordination by the ether oxygen of EG leads to charge transfer to the cation, and the lithium ion gets less positive, +0.81/+0.80. The consistency in absolute values between the two levels of computation must be regarded as more or less coincidential, as Mulliken charges are highly basis set dependent. For the small basis HF level calculations, the combination of the two effects in the 1:1:1 complexes leads to reduced charge transfer from both species, nonadditive, and a resulting average lithium charge of +0.58. On the other hand, if the larger basis set and electron correlation is included, the charge transfer is slightly larger than for the two separate cases combined and almost additative (+0.43).

Arguably, the charge transferred to the cation in part determines the strength of the interaction. Thus, qualitatively, the sequence of lithium charge should complement the calculated lithium ion binding energies. For HF/6-31G*, the sequence is

$$\text{TFSI} > \text{ClO}_4^- > \text{BF}_4^- > \text{PF}_6^- > \text{Tf}^-$$

for both the 1:1 and the 1:1:1 systems, whereas for MP2/6-311+G*, the obtained sequences are

$$\text{BF}_4^- > \text{TFSI} > \text{ClO}_4^- > \text{PF}_6^- > \text{Tf}^- \text{ and}$$
$$\text{TFSI} > \text{ClO}_4^- > \text{BF}_4^- > \text{Tf}^- \gg \text{PF}_6^-$$

respectively. No coherent trend can be detected for the latter, and furthermore, the correlation with the obtained lithium binding energies is poor for both computation levels. For PF_6^- the effect of going from the 1:1 to the 1:1:1 system is particularly large (MP2/6-311+G*), $\Delta \sim -0.41$, whereas for TFSI, only a negligible difference is obtained, $\Delta \sim -0.01$. The approach of using only the crude estimate of Mulliken charges seems inadequate, as they do not give information on the balance between the ionic/covalent contributions.

Perhaps a better choice is to look at the bond orders in the different ion pairs and complexes. By studying the bond orders for Li^+-O_{ether}(EG) and Li^+-An^- separately, and the total bond orders for the different choices of anions, the following picture emerges: (i) TFSI and ClO_4^- provide the lowest cation−anion bond orders, with the exception of BF_4^-. (ii) BF_4^- is the only case where the cation−anion bond order decreases with the MP2 treatment. (iii) For all but PF_6^-, the Li^+−EG bond orders decrease upon electron correlation treatment, and the largest change is observed for TFSI. These two different behaviors reflect what was already observed with the atomic charge. (iv) TFSI provides the 1:1:1 complex with the lowest Li^+−EG bond order (MP2 level). (v) As expected, AsF_6^- and PF_6^- behave almost identically.

The comparably high total bond orders for the MX_6^- anion based complexes should however be carefully viewed because the total CN's (5) for these are higher than for the other complexes (CN = 4). Also, the comparison across the Li−F and Li−O interactions is not completely fair as the results depend not only on the type of anion but also on the different basis set functions and how these respond to the MP2 treatment. To summarize: from both approaches, the TFSI and ClO_4^- anions based complexes provide the least charge transfer to the cation and among the lowest bond orders.

Vibrational Frequencies. The interaction of the cation with the anion is a suitable task both for molecular spectroscopy and ab initio calculations. However, to compare the results, it is often necessary to scale the ab initio obtained frequencies because of the incompletenesses of the computational methods. Here, we choose not to; the bands in question are already identified, and any scaling would not contribute to a better understanding.

We do, however, need to meet another criterion: the small difference in recommended scaling factors for the two methods used, HF/6-31+G* (anions) and HF/6-31G* (ion pairs and complexes), 0.8970 and 0.8953,[12] respectively, is a prerequisite for a fair analysis of the calculated shifts. The used theories should treat both cases with an average relative systematic error smaller than 2 cm^{-1} for bands below 1000 wavenumbers (1000·(0.8970 − 0.8953) = 1.7). Thus, the *calculated shifts* in the anions' vibrations caused by the cation can be directly compared with the *observed shifts*, even if the absolute frequency values are not correctly computed. In Table 2, all frequencies are unscaled.

On average, the calculated downshift for the symmetric stretching M−F and Cl−O bands upon cation coordination in the present study is ~20 cm^{-1} for the 1:1 ion pairs (Table 2). For Tf^-, the two here chosen bands are poorly reproduced in the calculations. On the other hand, the shift for the often used ~740 cm^{-1} band (ν_sSNS[29]) of TFSI is reproduced perfectly, whereas for the asymmetric counterpart, we have no experimental value to quote. On the basis of the 1:1 ion-pair calculations, one should easily be able to distinguish between the bi- and tridentately coordinated BF_4^- as well as the two conformers of TFSI. As a quantitative measure the average difference between calculated and observed shifts is ~23 cm^{-1}.

Can the 1:1:1 complexes perform better? Quantitatively the average difference between observed and calculated shifts decreases to ~14 cm^{-1}, which is an improvement clearly beyond the error margins. Furthermore, we find that not only the average but also the correlation for each anion with the experiments becomes better. About 40% of the observed deviation can this way be accounted for. Common for all anions is that the sizes of the shifts become smaller and that the IR intensities are almost insensitive to the addition of the EG molecule.

Furthermore, the OH-ended EG molecule makes a study of the sensitivity of the OH-stretching vibrations to the presence of contact ion pairs possible, which is presented elsewhere.[22]

Concluding Remarks

The 1:1 ion pairs as ab initio models for calculating the vibrational shifts upon cation coordination in SPEs may be improved by adding a molecule that mimics the local environment and provides a more realistic coordination number for the cation. This approach can easily be used also for non-ether-based polymers. Possible routes to improve even further the current models of ion pairs in polymer electrolytes would be to additionally make use of dielectric continuum methods (SCRF) to more generally model the environment of the ion pairs in a nonlocal way, use higher levels of electron correlation to calculate the vibrational spectra (MP2 or even MP4), increase the flexibility of the basis sets used, and/or using even larger molecules to the mimic the polymer chain.

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