Polarizable Continuum Model Study on the Solvent Effect of Polymer Matrix in Poly(ethylene oxide)-Based Solid Electrolyte

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The Polarizable Continuum Model has been used to study the effect of polymer matrix on Li^+ and Mg^{2+} complexation in poly(ethylene oxide)-based solid electrolyte. Structures of complexes, stabilization energies, and vibrational frequencies are compared with corresponding vacuum values. The solvent effect of the polymer decreases with increasing cation coordination number. Optimized complex geometries do not differ significantly compared to vacuum calculations. Calculated shifts in vibrational frequencies depend on the complex structure; for hexacoordinated ion most frequencies are slightly red-shifted. The most important effect is the decrease of differences between relative stabilities of different structures in the solvent.

1. Introduction

Increasing demand for environment-friendly, safe, stable, easy to fabricate, and cheap power sources, power conversion devices, sensors, and electrochromic and electrochemical devices stimulate scientific interest in polymer solid electrolytes. Such electrolyte consists of a salt dissolved in a polymer, a typical example is a lithium salt in poly(ethylene oxide) (PEO) matrix.

Numerous experimental and theoretical studies aim at modification of electrolyte properties to improve its performance in technological applications. As these properties are related to charge carrier transport in the electrolyte, a better insight into processes involved in ion transport and ion complexation becomes a key issue.

Theoretical quantum-chemical calculations were used to study cation−anion pairing[1] and Li^+ interactions with PEO.[2−7] In the latter case electrostatic attraction between cation and negatively charged oxygen atoms from the polymer backbone leads to ion complexation. Preferable structures for complexes of model molecules (usually oligoglymes) with lithium cation[2−5] or $Li^+−ClO_4^-$ pairs[5] were obtained and possible paths for Li^+ migration were suggested.[3,5] Binding energies of such complexes increase with increasing lithium coordination number.[4,5,7] Vibrational spectra of electrolytes and effects of complex formation on vibrational frequencies were also studied by quantum chemical calculations.[4,6,8,9]

Although most electrolytes are based on monovalent salts, several experimental studies using divalent magnesium cation were also reported.[10−12] As expected, increased positive charge on the ion leads to stronger $Mg^{2+}−$polymer interactions and to increased stabilization energies.[13,14]

Most of the reported quantum chemical calculations on the salt−PEO electrolytes were performed in vacuum; therefore, predicted effects of ion complexation correspond to the gas phase. This is in direct opposition to the experimentally studied systems in which all interactions take place in a solution (in a PEO polymer matrix in the case of solid electrolyte). Solvation effects may greatly affect the ion complexation. Of particular importance are the electrostatic interactions of charged species with the surrounding polarizable polymer medium.

Solvent effects on the lithium salt dissociation in nonaequous solvents were recently investigated by standard quantum-chemical methods, and different computational approaches were evaluated.[15,16] These studies were focused on the salt dissociation process and include a large number of salts and a variety of solvents. Such calculations offer general information about average solvation effect for given salt but do not provide details about relative stability of different ion−polymer complexes.

In the present work we want to address a problem complementary to salt dissociation, namely, the process of ion complexation. As the PEO-based systems were extensively studied in vacuum calculations, we restrict ourselves to lithium and magnesium perchlorate dissolved in poly(ethylene oxide). We focus on the effect of the solvent on the complex properties and on the complexation energy in particular.

Among different approaches to solvent effects there are two extreme cases. At one end the solvent is explicitly included in calculations by embedding the solute in a cluster of solvent molecules. Although this method could provide details of solute−solvent interactions, its cost in ab initio calculations is prohibitive. At the opposite side there are continuum models in which the solvent is represented as an effective continuous medium. This approach offers computational speed, but its validity is limited by proper parametrization of the solvent.

It is expected that the major part of the solvent effect on the polymer−cation complexes will be the electrostatic interaction with the polymer. Therefore in this work we use the Polarizable Continuum Model (PCM) to account for the solvation process; i.e., we will embed the system in a solvent chosen to model the poly(ethylene oxide) polymer matrix. This means that part of the solvent is explicitly described (as a model molecule), and the remaining part is implicit (continuous medium) and provides corrections to the energy of the system. In section 2 we describe the structures of complexes obtained in the solvent and compare them to vacuum data. Solvent effects on the complexation energies and vibrational spectra are reported in sections 3 and 4, respectively; we summarize and conclude in section 5.

2. Structures of Model Complexes

Methodology. The process of ion binding to poly(ethylene oxide) has been already extensively studied, and structures of

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complexes formed in vacuum by metal cations and perchlorate anions with model molecules are available in the literature. We used these data to prepare initial complex structures. Oligoglymes from di- to hexaglyme ($CH_3O(CH_2CH_2O)_nCH_3$, where $n = 2-6$) were used to model the PEO chain. Complexes of model molecues with Li^+ were created on the basis of results of refs 3–5. Structures of the $Li^+-ClO_4^-$ ion pair complexed by diglyme molecule were taken from ref 5. It should be noted that our aim was to cover the whole range of lithium coordination number (and thus the range of binding energies) rather than to reproduce all structures reported in previous works.

For all quantum-chemical calculations in this paper the Gaussian 03 program was used.[17] Initial geometries of complexes were optimized in density functional theory (DFT) calculations with B3LYP functional and 6-31G** basis set. This procedure yielded the structures of oligoglyme–ion complexes in vacuum. For selected structures we performed additional calculations with the aug-cc-pVDZ basis to check the effect of diffuse functions and the dependence of the complexation energy on the basis set size.

In the next step vacuum geometries were reoptimized using the PCM to account for the solvent effect of polymer matrix surrounding the complex. From the set of solvents defined in the program, diethyl ether was used as the one best mimicking the polymer. Its dielectric constant was increased from 4.335 to 5.0 to better match the PEO value. The United Atom Topological Model with radii optimized for DFT calculations (UAKS) was used to build the cavity.

In optimized oligoglyme–Li^+ complexes, lithium cation was substituted by Mg^{2+} ion and subsequent geometry optimization in vacuum or within the PCM model resulted in final structures of corresponding magnesium adducts. Additionally, we performed series of optimizations with initial structures of the oligoglyme–Mg^{2+} adducts distorted from the geometries of lithium complexes.

Separate vacuum and PCM calculations were performed for the $Li^+-ClO_4^-$ ion pair and the $Mg^{2+}-2ClO_4^-$ triad to check the solvent effect on the counterion aggregation.

Structures. All but one from the total number of 27 initial structures of oligoglymes complexed with Li^+ or $LiClO_4$ did not change significantly during vacuum optimization and yielded final geometries corresponding to the results reported by other authors.[3–5] Small deviations may be attributed to the difference in applied method and basis set.

Likewise, in most cases the Mg^{2+} complexes do not differ much from their lithium analogues. When the initial geometry was distorted, in most cases the optimization yielded structure analogous to the lithium structure or led to a less stable complex.

It was not clear a priori whether the PCM geometry optimization of the vacuum structure will lead to any significant further change as the solvent effects may favor conformations different than in the gas phase. However, it turned out that except one complex there is no major difference (apart from small distance changes which will be discussed later) between final geometries obtained in vacuum and solvent calculations. This will facilitate direct comparison between complexation energies in gas phase and in the polymer.

Selected PCM geometries for oligoglyme complexes with Li^+ are displayed in Figure 1. For each coordination number the structure with the largest complexation energy in the solvent (cf. next section) is shown. Two structures for hexacoordinated cation are presented, one based on hexaglyme, the other constituting two diglymes. In addition, the Mg^{2+} complexes with hexa- and heptaglyme are displayed. In these cases there are
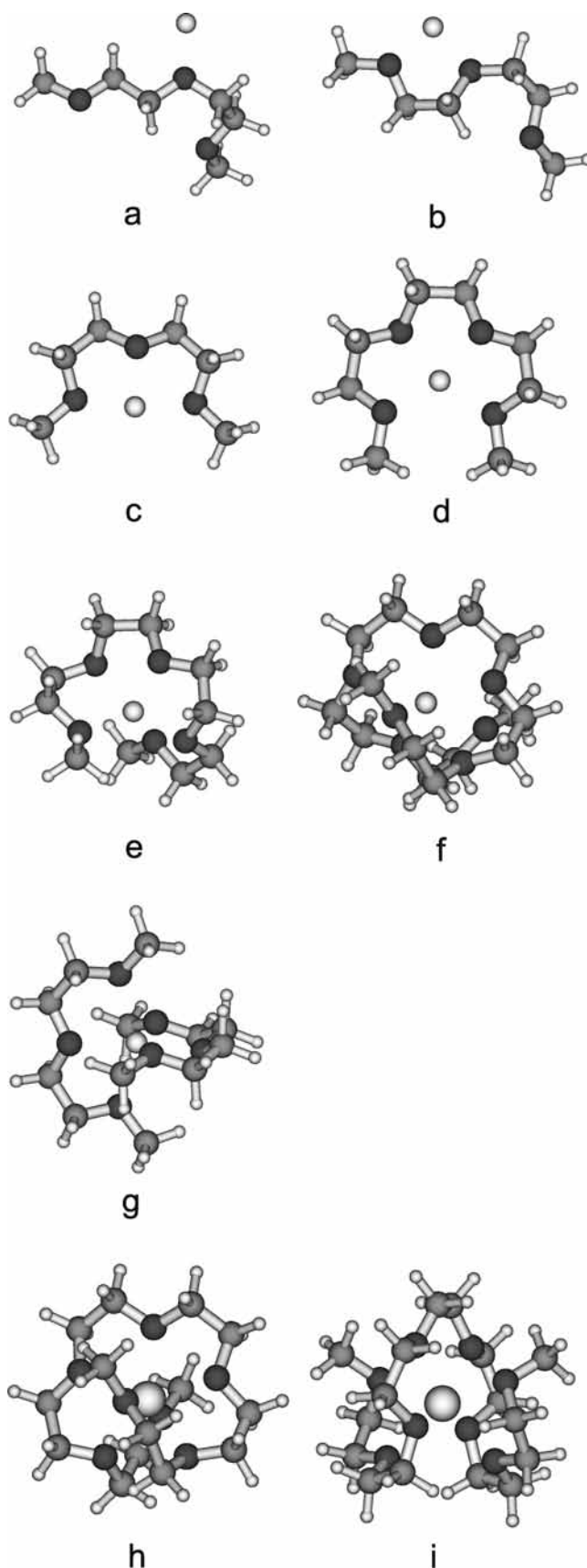

Figure 1. Structures of selected Li^+ (a–g) and Mg^{2+} (h, i) complexes with oligoglymes calculated within the PCM approach at the B3LYP/ 6-31G** level.

larger differences between lithium and magnesium complex—in structures with Mg^{2+} the coordination number of the ion exceeds
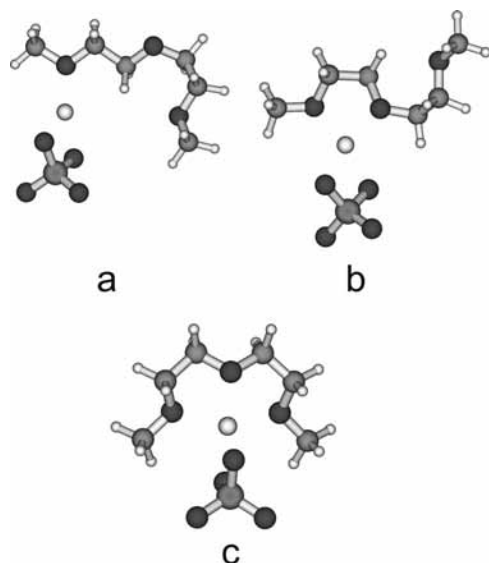
Figure 2. Structures of selected diglyme−LiClO$_4$ complexes calculated within the PCM model at the B3LYP/6-31G** level.

6, apparently due to a strong electric field of the cation. The ion in structure **1h** is clearly heptacoordinated, and in structure **1i** the Mg^{2+} coordination number reaches 8, although the Mg^{2+}−O distances are larger than in other complexes, which results in the binding energy being slightly smaller than that for complex **1h**. The PCM final geometries for all investigated structures are shown in the Supporting Information. Optimized structures found for the diglyme−Li$^+$−ClO$_4^-$ complex are presented in Figure 2. By comparing Figures 1 and 2 to the published vacuum geometries,[3−5] one can see that structures obtained in the polarizable medium are essentially the same.

Ranges of distances from the ion to the nearest oxygen atoms of the glyme molecule and their mean values for Li$^+$ structures shown in Figure 1 and their magnesium analogues are collected in Table 1; a full set of data for all structures is presented in the Supporting Information. In vacuum the average Li$^+$−O distance increases with increasing lithium coordination number, indicating that the strength of an individual ion−oxygen interaction decreases in the same order. This feature agrees well with existing literature data.[3,5] Likewise, cation−oxygen distances for Mg^{2+} are larger than for Li$^+$ (see ref 13) because of the larger magnesium radius.

For low lithium coordination numbers the average Li$^+$−O distance obtained in PCM calculations is up to 0.07−0.08 Å larger than in vacuum. This is expected, as the positively charged ions are attracted by electrostatic interactions to oxygen atoms with partial negative charges. In a polarizable medium (polymer), charged species are stabilized by the polarization of the solvent. The better the charges are separated the larger such stabilization is; when the charges move closer, their electric fields partially cancel and the polarization is smaller. This means that the electrostatic Li$^+$−O attraction effectively weakens in the solvent, which results in larger ion−oxygen distances. When the coordination number increases, the Li$^+$ ion becomes effectively screened from the polarizable medium by the glyme molecule; therefore, the solvent effect is reduced. This is readily visible in Table 1: an increase of the Li$^+$−O distance in polymer matrix gets smaller for bi- and tricoordinated ion, and for large coordination numbers the change is negligible.

Similar dependence was found for diglyme−LiClO$_4$ complexes shown in Figure 2. All structures exhibit bidentate coordination of lithium ion by two oxygens from perchlorate

anion; additionally the cation is coordinated by one, two, or three oxygen atoms from the diglyme molecule. While there is only a minor change in the length of the Li$^+$−O$_{glyme}$ bond between vacuum and PCM results, the Li$^+$−O$_{per}$ distance increases in the solvent. This increase is about 0.06−0.07 Å when the cation is coordinated by three oxygens (one from the glyme and two from the anion) and decreases with increasing coordination to about 0.05 Å for pentacoordinated lithium.

In magnesium complexes such bond lengthening in PCM calculations is less pronounced; the maximum effect of about 0.03 Å is observed for the tricoordinated cation. It should be noted that the change in other structural parameters between vacuum and the solvent is larger than for lithium adducts, which may make the general trend less clear. Moreover, some additional artifacts may result from the cavity generation.

For completeness we performed calculations for Li$^+$−ClO$_4^-$ and Mg^{2+}−2ClO$_4^-$ systems. Both in gas phase and in the solvent the lowest energy structure corresponds to bidentate orientation of perchlorate ions, i.e., Li$^+$ or Mg^{2+} coordinated by two or four oxygen atoms, respectively. The cation−oxygen distances in vacuum are 1.879 Å for Li$^+$ and 2.023 Å for Mg^{2+} and in PCM calculations increase to 1.983 and 2.052 Å, respectively.

Larger changes of the ion−oxygen distances for small coordination numbers may be easily rationalized if one considers partitioning of the system into explicit (oligoglyme) and implicit (polarizable continuum) solvent. In low-coordinated complexes interactions of the ion with the glyme molecule yield only a part of the solvation effect, the other part is missing in vacuum calculations, and when it is accounted for by the PCM corrections, cation−oxygen distances increase. When the coordination number is high, the ion is embedded inside the complex and the oligoglyme models the solvent reasonably well. Therefore the implicit solvent is less needed, and the PCM corrections lead to only slight structural changes.

The geometries obtained at the aug-cc-pVDZ level do not differ significantly from those calculated for smaller basis set. The changes in ion−oxygen distances do not exceed 0.02 Å (cf. Supporting Information). Typically in oligoglyme complexes with Li$^+$ and Mg^{2+} the cation−oxygen distance decreases when the basis set is increased; the changes are larger for magnesium complexes. In LiClO$_4$ complexes with diglyme there is a slight increase in Li$^+$−O distances.

We may conclude that structures of ions bound to oligoglymes do not change significantly between the gas phase and the solvent, although the structural parameters are slightly modified. The most visible difference is the increase of the ion−oxygen distance for low coordination numbers, where a large part of the solvent has to be modeled via the PCM approach unlike the structures with high coordination in which the oligoglyme molecule acting as an explicit solvent is sufficient to account for the solvent effect of the bond length.

3. Complexation Energies

For all investigated structures we calculated the energies at the 6-31G** level. Additionally, single-point calculations in the aug-cc-pVDZ basis at the 6-31G** geometry were performed for all structures listed in Table 1. For selected structures (mainly with low coordination number) the geometry optimization at the aug-cc-pVDZ level was completed and the corresponding binding energies are available. In these cases the difference between single-point value and the energy resulting from full geometry optimization does not exceed 0.35 kcal/mol.

TABLE 1: Cation−Oxygen Distances (Å) for Selected Li$^+$ and Mg^{2+} Complexes with Oligoglymes Calculated in Vacuum and within the PCM Approach at the B3LYP/6-31G** Level^a

			Li$^+$ complexes			
	structure		vacuum		PCM	
CN^b	this work	lit. data^c	range	av	range	av
1	**1a**	Li$^+$−t^{3}g$^+$g$^-$t(center)	1.811	1.811	1.881	1.881
2	**1b**	Li$^+$−tg$^-$tg$^+$g$^-$t	1.858−1.864	1.861	1.912−1.919	1.916
3	**1c**	Li$^+$−tg$^+$t^{2}g$^-$t	1.919−1.922	1.921	1.949-1.962	1.958
4	**1d**	Li$^+$−tg$^+$t^{2}g$^-$t^{2}g$^+$t	1.992−2.016	2.004	2.004−2.022	2.013
5	**1e**	Te9^d	2.003−2.116	2.055	2.004−2.114	2.055
6	**1f**	H3^d	2.102−2.388	2.233	2.096−2.388	2.232
6	**1g**	Min-6^e	2.121−2.232	2.181	2.104−2.246	2.178

		Mg^{2+} Complexes			
		vacuum		PCM	
CN^b	structure^f	range	av	range	av
1	**1a**	1.925	1.925	1.943	1.943
2	**1b**	1.915−1.926	1.921	1.959−1.970	1.965
3	**1c**	1.965−1.972	1.967	2.000−2.000	2.000
4	**1d**	2.005−2.027	2.016	2.016−2.034	2.025
5	**1e**	2.036−2.085	2.060	2.035−2.080	2.057
6	**1g**	2.105−2.144	2.126	2.092−2.130	2.117
7	**1h**	2.151−2.263	2.212	2.140−2.266	2.203
8	**1i**	2.182−2.566	2.344	2.177−2.612	2.334

^{a} Ranges of observed distances and average values are given. ^{b} CN = coordination number ^{c} If not stated otherwise, the label of the corresponding structure from ref.3 is given, although some structures may be found also in refs 2, 5, or. 13. ^{d} Reference 4. ^{e} Reference 5. ^{f} For CN = 1−6, the label of corresponding Li$^+$ complex shown in Figure 1 is given.

Different definitions of the binding energy are used in the literature: the energy of the complex may be calculated relative to free oligoglyme molecule in all-trans geometry (like refs 3 and 5) or relative to the molecule in the complex geometry (see ref 4). Although the all-trans conformation may not be the lowest energy conformer for longer glymes, the advantage of the first method is that it does not require additional single-point calculation for each structure. As the choice of definition does not affect the conclusions regarding the solvent effect (provided that the chosen method is applied for all structures), we used the first approach.

Binding energies in vacuum were therefore calculated relative to the energy of oligoglyme in all-trans conformation; i.e.,

$$\Delta E_{vac} = E_c - (E_{glyme} + E_M) \quad (1a)$$

or

$$\Delta E_{vac} = E_c - (E_{glyme} + E_{Li} + E_{per}) \quad (1b)$$

where E_c stands for the energy of the complex, E_M (M = Li$^+$ or Mg^{2+}) and E_{per} are the energies of free ions, and E_{glyme} is the energy of the model all-trans oligoglyme. To account for the basis set superposition error (BSSE), the BSSE corrections were calculated at the complex geometry using standard counterpoise method. The vacuum binding energies follow the trends observed in the published data.[3−5] Existing differences may be attributed to a different level of theory and basis set used in calculations or a different definition of the complexation energy. As an additional confirmation we performed some test calculations using the same method as described in refs 3−5; resulting energies agree with the literature data with accuracy better than 0.1 kcal/mol, supporting our conclusion that the set of structures used in this paper is essentially the same as reported in previous works.

Before proceeding to the discussion on the energetic effect of complex formation in the solvent, we shall analyze the PCM corrections to the energy of a separated ion or oligoglyme

molecule in a polarizable medium. For charged species the most important is the electrostatic correction resulting from electrostatic interaction of permanent charge of the ion or permanent dipole moment of the molecule with charge distribution induced in the polarizable medium. This polarization contribution is always negative; i.e., stabilizing and its absolute value increases with increasing dielectric permittivity of the solvent. The other corrections in the PCM approach are the cavitation, dispersion, and repulsion energies. While the electrostatic correction results from the self-consistent solution of the problem of induced charges for given cavity and therefore it is essentially nonempirical, the nonelectrostatic terms involve effective parametrization of the solvent to yield the best description of solvation energies. Fortunately they are much smaller than the electrostatic contribution which dominates the overall effect.

In Table 2 we display the PCM corrections to the energy of free ions, free diglyme molecule, and selected complexes (for the complete data set the reader is referred to the Supporting Information). The electrostatic correction varies in a broad range from −3 kcal/mol for diglyme to −270 kcal/mol for Mg^{2+} ion. The largest polarization effect is observed for the ions. In this case it is caused by the electric field induced by the ion, stronger for larger total charge and smaller ion radius (therefore the size of the effect decreases in the order Mg^{2+} > Li$^+$ > ClO$_4^-$). The effect for electrically neutral species is small; therefore, the electrostatic contribution to the energy of LiClO$_4$ and Mg(ClO$_4$)$_2$ complexes is largely reduced compared to individual ions as electric fields of the ions partially cancel in the aggregate.

It is readily seen that the size of the electrostatic contribution decreases with increasing cation coordination number in diglyme complexes with Li$^+$ or Mg^{2+}. This is caused by two factors. First, more oxygen atoms with partial negative charges coordinating the ion lead to more effective cancelation of electric field. In addition, in the case of a high coordination number the ion is surrounded by the glyme molecule (or molecules); therefore, its distance to the cavity surface is larger. Both factors

TABLE 2: Electrostatic and Nonelectrostatic (Cavitation, Dispersion, Repulsion, and Total Nonelectrostatic) PCM Contributions (kcal/mol) to the Energy of Ions and Selected Complexes in the Solvent Calculated at the B3LYP/6-31G Level**

structure	δ_i^{el}	δ_i^{cav}	δ_i^{disp}	δ_i^{rep}	δ_i^{non-el}
diglyme (all-trans)	−2.7	15.9	−21.3	5.1	−0.3
Li$^+$	−83.3	2.3	0.0	0.0	2.3
Mg^{2+}	−270.5	3.0	0.0	0.0	3.0
ClO$_4^-$	−46.4	8.0	−9.8	1.8	0.0
Li$^+$−ClO$_4^-$	−21.2	9.3	−8.7	1.3	1.9
Mg^{2+}−2ClO$_4^-$	−9.9	16.3	−15.9	2.3	2.7
Li$^+$ (CN = 1) (**1a**)	−58.8	17.4	−19.6	4.5	2.3
Li$^+$ (CN = 3) (**1c**)	−38.9	16.3	−20.3	4.9	0.9
Li$^+$ (CN = 6) (**1g**)	−30.0	31.1	−30.6	7.0	7.5
Mg^{2+} (CN = 1) (**1a**)^a	−188.6	17.7	−19.2	4.3	2.7
Mg^{2+} (CN = 3) (**1c**)^a	−151.7	16.6	−20.1	4.8	1.3
Mg^{2+} (CN = 6) (**1g**)^a	−114.1	30.3	−30.5	7.0	6.8

^{a} For Mg^{2+}−oligoglyme complexes, labels of corresponding Li$^+$ structures shown in Figure 1 are given.

result in weakening of electric field acting on the polarizable continuum, therefore, in decrease of the polarization energy.

Our PCM calculations for diglyme−ion complexes may be alternatively viewed as a model of ion solvation with partially explicit (diglyme) and partially implicit solvent (polarizable continuum). Within such an approach part of the polarization contribution is already included in quantum-chemical calculations for the explicit part of the system (in the electronic energy of the ion−glyme complex), the other part (from implicit solvent) comes as electrostatic PCM contribution. When the explicit part of the system is increased from one diglyme in structure **1a** to two diglyme molecules in complex **1g**, contribution from the implicit part (PCM electrostatic correction) decreases, because the surface of the continuous solvent is further away from the charged ion. Therefore the risk of double counting the contributions from the discrete and continuous solvent is generally avoided. In some sense this resembles a formulation of the self-consistent polarization field problem with electrostatic interactions treated explicitly for the discrete part of the system and a correction from the remaining continuous part described by the dielectric constant of the medium.[18] There is a possibility of some errors introduced by the construction of the cavity (the volume by which the implicit part is reduced may not exactly match the volume of molecule introduced as an explicit solvent), but such effects are expected to be small and they are inevitable when the continuous solvation models are used. The "second-order" effect of explicit solvent molecule polarizing the implicit part of the system is negligibly small—as readily seen from Table 2, the PCM correction for a diglyme molecule is about −3 kcal/mol, which is only a tiny fraction of the effect for an ion or charged complex.

The size of non-electrostatic PCM corrections to the energy is related to the size of solvated species—values obtained for Li$^+$ or Mg^{2+} complex with one diglyme molecule are close to the values for free diglyme; the effect approximately doubles upon addition of the second diglyme molecule. Cavitation and repulsion energies destabilize the system, while the effect of dispersion is stabilizing. The contributions of opposite signs partially cancel; therefore, the total non-electrostatic contribution to the solvation energy is small. Values of these three contributions presented in Table 2 should be taken with care, as the non-electrostatic part of parametrization was optimized for

TABLE 3: Binding Energies in Vacuum and ΔE_{PCM}^{el} Values for Selected Complexes^a

			Ion Aggregates		
stucture		ΔE_{vac}	BSSE	ΔE_{PCM}^{el}	Δ^{el}	Δ^{non-el}
Li$^+$−ClO$_4^-$		−153.1	6.9	−41.6	108.6	−0.4
Mg^{2+}−2ClO$_4^-$		−531.8	14.8	−176.9	353.4	−0.3

		Li$^+$−Oligoglyme Complexes				
CN	structure^b		ΔE_{vac}	BSSE	ΔE_{PCM}^{el}	Δ^{el}	Δ^{non-el}
1	**1a**	Li$^+$−t^{3}g$^+$g$^-$t(center)	−46.9	3.2	−15.9	27.2	0.3
2	**1b**	Li$^+$−tg$^-$tg$^+$g$^-$t	−73.4	4.4	−32.5	39.5	−0.4
3	**1c**	Li$^+$−tg$^+$t^{2}g$^-$t	−91.4	5.9	−43.8	47.1	−1.1
4	**1d**	Li$^+$−tg$^+$t^{2}g$^-$t^{2}g$^+$t	−108.2	7.0	−55.4	52.8	−0.4
5	**1e**	Te9	−119.1	7.5	−63.7	55.5	1.3
6	**1f**	H3	−127.0	7.5	−67.9	59.3	4.7
6	**1g**	Min-6	−129.0	14.3	−70.4	58.8	5.8

		Mg^{2+}−Oligoglyme Complexes				
CN	structure	ΔE_{vac}	BSSE	ΔE_{PCM}^{el}	Δ^{el}	Δ^{non-el}
1	**1a**	−143.5	3.6	−45.0	84.6	0.0
2	**1b**	−186.1	4.7	−79.9	100.2	−0.5
3	**1c**	−231.9	6.1	−107.8	121.5	−1.4
4	**1d**	−278.9	7.2	−136.6	141.3	−1.1
5	**1e**	−312.6	8.4	−159.2	153.1	0.3
6	**1g**	−343.0	14.9	−181.1	161.8	4.3
7	**1h**	−347.9	6.0	−184.5	163.4	2.8
8	**1i**	−346.6	5.4	−179.5	167.0	4.3

		LiClO$_4$−Diglyme Cmplexes				
CN	structure^c		ΔE_{vac}	BSSE	ΔE_{PCM}^{el}	Δ^{el}	Δ^{non-el}
3	**3a**	min-8	−180.2	12.5	−57.9	120.1	2.3
4	**3b**	min-10	−193.0	13.3	−71.0	121.0	1.8
5	**3c**	min-12	−199.9	15.9	−77.5	121.0	2.1

^{a} BSSE corrections in vacuum, electrostatic, and total non-electrostatic PCM corrections to the complexation energy in the solvent are listed separately. All values in kilocalories per mole. ^{b} Labels for Li$^+$ structures as in Table 1. ^{c} Labels for LiClO$_4$−diglyme from ref 5.

diethyl ether and not poly(ethylene oxide); nevertheless it is obvious that the total non-electrostatic PCM contribution to the energy is much smaller than the electrostatic term, and therefore it was not accounted for in the calculated complexation energies shown in Table 3.

To calculate the energetic effect of complex formation in a polarizable continuum, we use an analogue of eq 1, with electronic energy of each species E_i replaced by $E_i' + \delta_i$, where E_i' is the electronic energy (we use the prime sign to note that it differs from the vacuum value E_i, because wave functions of the molecule in vacuum and in the solvent differ), and $\delta_i = \delta_i^{el} + \delta_i^{cav} + \delta_i^{disp} + \delta_i^{rep}$ collects the PCM corrections: electrostatic, cavitation, dispersion, and repulsion energy, respectively. Then the equation takes the form

$$\Delta E_{PCM} = \Delta E' + \Delta_{PCM} = \Delta E' + \Delta^{el} + \Delta^{non-el} =$$

$$\Delta E' + \Delta^{el} + \Delta^{cav} + \Delta^{disp} + \Delta^{rep} \quad (2)$$

where $\Delta E' = E_c' - (E_{glyme}' + E_M')$ is the change in the electronic energy and Δ_{PCM} (which may be further separated in electrostatic and non-electrostatic terms) is the net change of the PCM contribution to the energy upon complex formation from the ion and the glyme molecule. As the electrostatic PCM contributions are the most important, we calculated also $\Delta E_{PCM}^{el} = \Delta E' + \Delta^{el}$ values i.e., the effect of complex formation in the

solvent with all non-electrostatic contributions neglected. For ion aggregates or complexes containing perchlorate anions formula 2 is appropriately modified. The physical meaning of ΔE_{PCM} will be discussed later.

Table 3 collects the vacuum complexation energies and the ΔE_{PCM}^{el} values for selected representative structures. BSSE corrections and total non-electrostatic PCM contributions are listed separately. A detailed summary of all PCM energy contributions for all structures may be found in the Supporting Information.

The simplest is the case of $Li^+-ClO_4^-$ and $Mg^{2+}-2ClO_4^-$ ion aggregates. ΔE_{PCM} is then an energetic effect of the formation of the solvated aggregate from individual solvated ions, i.e., complexation energy in the solvent. The complexation energy in the solvent is more than three times reduced compared to the binding energy under vacuum. As readily seen from Table 3, the factors responsible for this reduction are large positive Δ^{el} values, i.e. the change in the polarization energy upon complex formation. This is easily understood if one compares δ^{el} contributions to the energy listed in Table 2. Polarization effect is very strong for separated ions; when they form a complex, their electric field cancels and the polarization is greatly reduced. Therefore, the sum of δ^{el} for ions is more negative (more stabilizing) than the δ^{el} value for the complex which results in large positive net effect Δ^{el}. The non-electrostatic term is close to zero and negligible.

The same effect is observed for Li^+ or Mg^{2+} complexes with oligoglymes. The electric field of positively charged ion cancels partially with negative charges located on oxygen atoms, and solvent polarization for the complex is smaller than for separated ion and molecule, which again leads to positive values of Δ^{el}. Similarly to ion aggregates, the non-electrostatic contributions Δ^{nonel} are small. Closer inspection of the data (cf. Supporting Information) reveals that cavitation and repulsion contributions (always negative) partially cancel with positive dispersion contribution. Signs of different non-electrostatic terms may be easily explained by taking into account that the size of the cavity (and its surface) for the complex is smaller than the total size of the separate cavities for separate ion and molecule. Therefore, upon complex formation there is a gain in cavitation and repulsion energy and corresponding destabilizing effect of dispersion.

Physical interpretation of "complexation energy" in the solvent ΔE_{PCM} for oligoglyme−ion complexes is less straightforward than for ion pairs. It corresponds to the process of formation of a solvated complex from solvated ion and solvated molecule: $(oligoglyme)_{solv} + (ion)_{solv} \rightarrow (oligoglyme-ion)_{solv}$

It may be viewed as a hypothetical process in which part of the dielectric continuum solvating the ion is transformed into an explicit solvent molecule (oligoglyme). This means that the ΔE_{PCM} values are the measures of ion stabilization in a given complex relative to an ion in averaged continuous medium (the latter stabilization is given by the solvation effect shown in Table 2). Therefore, the differences rather than individual values of ΔE_{PCM} can be interpreted, and they provide a measure for relative stabilities of solvated complexes with different ion coordination.

The differences in relative stabilization of different complexes in the solvent are smaller than the differences of binding energies calculated in vacuum as apparently seen from Table 3. This is even more visible in Figure 3, where we plot ΔE_{PCM}^{el} versus ΔE_{vac} for all structures. The dependence is linear, and its slope is 0.644 and 0.685 for oligoglyme complexes with Li^+ and Mg^{2+}, respectively, i.e. significantly smaller than 1. Differences of
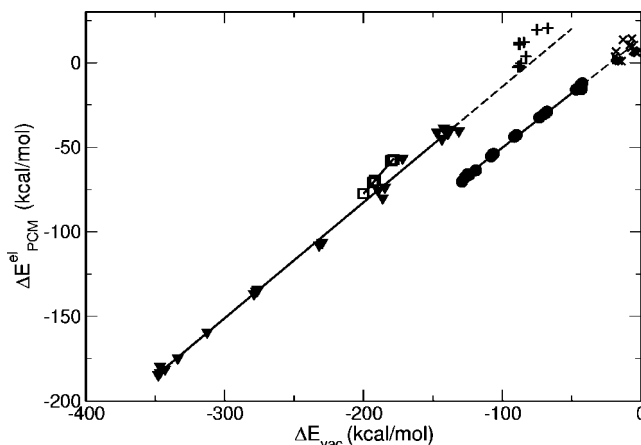

Figure 3. Plot of ΔE_{PCM}^{el} vs binding energy in vacuum ΔE_{vac} for Li^+ (circles), Mg^{2+} (triangles), and $LiClO_4$ (squares) complexes with oligoglymes. Lines are linear fits to the data. Results of additional single point calculations (see text) are marked by crosses and plus signs.

stabilization energies in the solvent are therefore reduced by about 30% compared to vacuum values. An exception is the dependence obtained for oligoglyme−$LiClO_4$ complexes in which case the slope equals 0.965 and is close to 1. This might be expected as the effect is mainly due to solvent polarization, which is small for electrically neutral structures.

Vacuum binding energies obtained at the aug-cc-pVDZ level are reduced to about 86−96% of the 6-31G** values. The slope of the ΔE_{PCM}^{el} vs ΔE_{vac} dependence resulting from the energies calculated at 6-31G** geometry is 0.59 and 0.63 for Li^+ and Mg^{2+} complexes, respectively; the corresponding values for fully optimized structures differ from single-point results by no more than 0.01. With increasing the size of the basis set, the slope decreases slightly; the solvent effect is therefore little more pronounced for larger basis.

All structures investigated so far correspond to minima of energy; therefore, it is not surprising that the ΔE_{PCM}^{el} values are negative, meaning that the ion in such solvated complex is better stabilized than in averaged medium. This gives rise to a question whether an opposite effect may be observed, i.e., whether a structure of the oligoglyme−ion complex can be found in which the ion is less stabilized than in continuous averaged solvent. This is most likely to occur in complexes with small binding energy in vacuum. As a check we performed single-point energy calculations in vacuum and within the PCM solvent model for structures where the ion is located close to the CH_2 or CH_3 group (2−3 Å to the carbon atom). Resulting ΔE_{PCM}^{el} values were in most cases positive; corresponding points are displayed in Figure 3. It may be noted that in the case of Li^+ complexes they fit very well to the extrapolated line; for Mg^{2+} complexes the deviation is larger, but the general trend is still followed. This supports our conclusion that the ΔE_{PCM} for a complex measures stabilization of the ion relative to the energy of an ion in average implicit solvent.

4. Vibrational Frequencies

As infrared or Raman spectroscopy are the tools often used in experimental studies of polymer electrolytes, vibrational frequencies of model oligoglyme molecules and their complexes have been already calculated in vacuum for many systems.[4,6,8,9,14,19] In this section we will try to estimate how large are the gas to solvent frequency shifts for complexes studied in this work.

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TABLE 4: Selected Vibrational Frequencies (cm^{-1}) for All-Trans Diglyme and Oligoglyme Complexes with Li$^+$ Calculated in Vacuum and within the PCM Approach at the B3LYP/6-31G Level**

stretch	all-trans diglyme		CN = 2 (**1b**)		CN = 3 (**1c**)		CN = 5 (**1d**)		CN = 6[a]		CN = 6 (**1g**)	
	vac	PCM	vac	PCM	vac	PCM	vac	PCM	vac	PCM	vac	PCM
Li–O			513	449	491	451	445	434	372	367	403	417
			558	484	594	517	522	506				
C–O	1169	1158	1074	1086	1085	1091	1110	1107	1100	1096	1116	1112
	1184	1170	1163	1159	1109	1113	1139	1132	1110	1106	1116	1113
					1144	1142			1133	1129	1146	1138
									1138	1131		
C(CH$_2$)–H[b]	3033	3027	2978	2970	3100	3081	3091	3077	3055	3046	3070	3060

[a] Structures **1–19** in the Supporting Information. [b] Only one mode with largest IR intensity has been shown for C–H stretches.

The Polarizable Continuum Model may be used in vibrational frequency calculations. However, one should be aware of potential problems related to the dielectric response of the medium. Namely, in the equilibrium approach the static dielectric constant of the solvent is used. Its value comprises effects of electronic and orientational polarization. While the first process may be treated as instantaneous, the other is slower than fast vibrations, meaning that in the reality the response of the cavity cannot follow movements of an oscillating molecule. The solvent effect on frequencies is therefore overestimated. Although a non-equilibrium formulation of the PCM approach exists,[20] an uncertainty about correct parametrization of the dielectric constant remains. Moreover, if, e.g., optical dielectric constant is used, molecule conformation will no longer correspond to the stationary point obtained in equilibrium geometry optimization. On the other hand, overestimation of the frequency shifts should be the larger the more polar the solvent is[20] (i.e., in the case where a major part of the polarizability is due to orientational motions). As PEO has low dielectric constant, such an effect is expected to be limited. Therefore we decided to use the equilibrium PCM approach to perform vibrational frequency calculations. The vacuum–solvent shifts of the frequencies will then give the upper limit of the effect.

Vibrational frequencies were calculated in vacuum and in solution for selected complexes with increasing lithium coordination number. For some structures (e.g., complexes in which Li$^+$ is monocoordinated) despite various attempts we failed to eliminate one imaginary frequency in PCM calculations. These complexes were not used in further analysis.

The gas to solvent frequency shifts differ between different vibrational modes. It is expectable that the effect of polarizable medium will be the strongest for stretches of polar groups. Therefore, we focused on two modes typical for PEO–LiClO$_4$ electrolyte: stretching of the C–O bond and oscillations of the Li$^+$ ion. For comparison we used the stretch of the C–H bond from the CH$_2$ group, i.e., from the part of the molecule not involved directly in ion binding. The vacuum and PCM data are displayed in Table 4; we present only the modes with largest IR intensity.

The C–O and C–H vibrations of the diglyme molecule are red-shifted in the PCM calculations. This behavior is usually expected, as the polarization of the dielectric medium flattens the potential energy curve and facilitates bond stretching. Such effect is observed in most structures for lithium cation oscillations. Presence of the solvent weakens the interactions of the ion with oxygen atoms which results in a red shift of the corresponding mode. It may be easily seen that this red shift decreases with increasing coordination from as much as 70 cm^{-1} for bicoordinated Li$^+$ to 5 cm^{-1} for the pentaglyme complex in which the cation is hexacoordinated. In the case of low coordination numbers the ion is exposed to interact with the dielectric continuum, which leads to large solvent effect. This situation changes with increasing coordination—the ion is encaged inside the complex, and it is screened from the solvent by the oligoglyme molecule; therefore, the solvent effect is minimal. Alternatively, we could imagine that in the first case a large part of the solvent is missing in vacuum calculations; therefore, the effect of implicit solvent introduced via PCM is large. In the other case the oligoglyme molecule acts effectively as explicit solvent and the correction due to continuous medium is small. The Li$^+$ complex with two diglyme molecules is an exception where the frequency of Li$^+$ oscillation increases in the solvent. We think that this effect is related to the change of interatomic distances—as seen from Table 1, average Li–O distance for this structure decreases in PCM calculations.

Small red shift of about 6–16 cm^{-1} is also observed for methylene C–H stretching vibration, but unlike the Li$^+$ oscillations it does not decrease with increasing coordination number and even seems to increase. This results from the fact that CH$_2$ groups are located outside the complex, and their interaction with the solvent does not change significantly between different structures. The solvent effect is therefore approximately the same for all complexes.

The case of C–O vibrations is more complicated. The frequency of this stretch decreases with increasing Li$^+$ concentration in the electrolyte[21] because when the complex is formed and the oxygen atom interacts with the lithium ion, the C–O bond weakens. In the solvent the Li–O interaction is weaker; therefore, the C–O frequency should shift upward, i.e., return toward its value in the free diglyme molecule. On the other hand, a general effect of the solvent is the red shift of vibrational frequencies. The net shift results from these two opposite effects, and therefore its sign may vary.

Such behavior can be seen in the complex with the bicoordinated cation. The frequency of the C–O stretches increase in the solvent for groups involved in complex formation (blue shift of 12 cm^{-1}). In this case the effect of weakening of the Li$^+$–O interaction and corresponding strengthening of C–O bond prevails. The other frequency listed for this structure in Table 4 corresponds to the vibration of the "free" C–O–C group (cf. Figure 1b) and exhibits a typical red shift in the solvent. As already discussed, the effect of the implicit solvent in PCM calculations decreases for larger coordination numbers; therefore, the blue shift becomes smaller for tricoordinated cation (6 and 4 cm^{-1}), and in all other complexes in Table 4 the C–O vibrations are red-shifted. The smallest are the shifts in complexes with hexacoordinated ion (−4 or −3 cm^{-1} for most vibrations).

TABLE 5: Frequencies (cm^{-1}) of the C–O Stretching Vibrations for Perchlorate Anion and Ion Aggregates Calculated at the B3LYP/6-31G Level in Vacuum and in the Solvent**

	vacuum	PCM
ClO_4^-	852	861
	1060	1049
	1060	1049
	1060	1049
Li^+–ClO_4^-	800	824
	896	924
	1080	1059
	1169	1123
Mg^{2+}–$2ClO_4^-$	768	779
	777	785
	849	852
	850	852
	1082	1068
	1093	1075
	1198	1169
	1198	1169

Effects similar to those observed for C–O bonds in Li^+ complex with diglyme are even more clearly pronounced for Cl–O stretches in ClO_4^- and ion aggregates (Table 5). The frequency of the t_2 vibration at 1060 cm^{-1} is red-shifted in the solvent to 1049 cm^{-1} (the a_1 mode is blue-shifted, but it carries no IR intensity). In aggregates with Li^+ and Mg^{2+} two or four oxygen atoms from perchlorate ion (or ions), respectively, are coordinating the cation. Interactions with the cation weaken the Cl–O bonds involved in complexation and vibrational frequencies of corresponding modes (two or four in the case of Li^+ or Mg^{2+} complex, respectively) shift in vacuum to lower wavenumbers compared to free perchlorate ion. Simultaneously two (Li^+) or four (Mg^{2+}) frequencies of Cl–O stretches ("free" bonds) are blue-shifted. As discussed above, the solvent weakens the cation interaction with oxygen atoms, which results in strengthening of Cl–O bonds. Accordingly, the two or four frequencies shifted downward upon complexation move in the solvent to higher wavenumbers; an opposite red shift is observed for the frequencies of "free" Cl–O bonds.

5. Conclusions

We studied the solvent effect on ion complexation in poly(ethylene oxide)-based solid electrolyte. We compared properties of Li^+ and Mg^{2+} complexes with model oligoglyme molecules in vacuum and in the solvent modeled via the Polarizable Continuum Model.

The major changes between vacuum and the solvent are observed for complexes with low lithium coordination number. These differences decrease with an increasing number of oxygen atoms binding to the ion. Such a trend is explained by increasing effect of model oligoglyme molecule effectively acting as an explicit solvent. With increasing size of complexing molecule and lithium coordination number the ion and complexing oxygen atoms (i.e., the part of the complex which is of our interest) are hidden inside the structure and screened from the polarizable medium by the backbone of the oligoglyme molecule. They interact therefore mainly with oligoglyme (explicit solvent) and interactions with continuous implicit solvent are less important and lead only to small correction.

The optimized structures of complexes do not change significantly between vacuum and PCM calculations. The most pronounced change is the increase of Li^+–O distances which is the largest in complexes with low lithium coordination number.

We found that the complexation energies for Li^+ and Mg^{2+} aggregates with perchlorate anions are greatly reduced in the solvent due to the effect of solvent polarization. Differences in relative stabilities of cation–oligoglyme complexes are reduced in the solvent by about 30%. This means that vacuum calculations overestimate the range of complexation energies. Moreover, such reduction seems independent of the binding energy for given structure; therefore, it is expected that also the energy barriers between different minima decrease in the solvent. Such effect should be general for different polymers and ions, which suggests that the energy differences obtained in vacuum calculations need to be scaled down to better describe relative stabilities of complexes in polymer medium.

The vibrational frequency shifts between vacuum and the solvent may be as large as 70 wavenumbers (as obtained for oscillations of bicoordinated Li^+). With increasing lithium coordination number solvent effect becomes smaller, and for structures with penta- or hexacoordinated ion (which are the most abundant in real electrolyte) most frequencies are slightly red-shifted. Such shifts depend on the vibrational mode and on the strength of interactions of oscillating atoms with the solvent. In most cases they do not exceed 10 cm^{-1}.

To conclude, we showed that the effect of polymer matrix in solid electrolyte may be modeled via the PCM approach. While for the most important structures predictions of PCM calculations are not significantly different from the results obtained in vacuum, the solvent effect on relative stabilization energies is non-negligible and should be taken into account.

Supporting Information Available: PCM structures for all studied complexes. Complete data sets of PCM energy contributions and corrections to the complexation energies for all structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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