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Effects of Basis Set Superposition Error on Optimized Geometries and Complexation Energies of Organo-Alkali Metal Cation Complexes

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Theoretical studies were performed to study the binding of alkali metal cations, X^+ (X = Li, Na, K), to poly(ethylene oxide) (PEO, **I**), poly(ethylene amine) (PEA, **II**), and poly(ethylene *N*-methylamine) (PEMA, **III**) by the Hartree−Fock (HF) and B3LYP methods using the 6-31G(d) and 6-311+G(d,p) basis sets. Two types of complex were considered in this study: a singly coordinated system (SCS) and a doubly coordinated system (DCS). Complexation energies were calculated both without and with basis set superposition error (BSSE). Because of the strong charge−dipole interactions, the complexation energies were largely negative and decreased in the order $Li^+ > Na^+ > K^+$. Three possible counterpoise (CP) approaches were examined in detail. In the case of the function CP (fCP) correction, the complexation energies exhibited an unusual trend because of the deformation of the subunits. This problem was solved by including geometry relaxation in the CP-corrected (GCP) interaction energies. The effects on the structures and vibrational frequencies were small when the complexes were reoptimized on the CP-corrected potential energy surface (PES).

Introduction

Polymer-based solid electrolytes have been the subject of intensive study because of their growing importance in solid-state electrochemistry.[1] Polymer electrolytes having ionic conductivity are typically formed when a metal salt is dissolved in a polymer whose backbone contains electron-donor atoms such as O and N. Ionic conductivity generally varies with the concentration of the metal salt, the temperature, and the mobility of the charge carrier, which depends on the degree of interaction between a cation (and/or an anion) of the dissolved metal salt and a polymeric ligand.[2] Therefore, various experimental approaches have been attempted to increase the ionic conductivity,[3] but theoretical works have remained relatively scarce. Nevertheless, the combination of theoretical and experimental studies is likely to be more efficient in explaining the ionic conductivity of polymer electrolytes and designing new polymer electrolytes. The characteristics of complexation between the dissolved metallic salt and polymeric ligand can be predicted theoretically by applying a supermolecular approach.

In calculating the molecular interactions between two or more species, the interaction energy, ΔE_c in eq 1, can be estimated from the energy difference between the whole system (AB) and its subunits (A and B) within the supermolecular approach.[4] In eq 1, $E_Y^Z(X)$ is the electronic energy of molecular system X at geometry Y computed with basis set Z.[5]

$$\Delta E_c = E_{AB}^{AB}(AB) - E_A^A(A) - E_B^B(B) \qquad (1)$$

However, it is well recognized that a difficult problem in the supermolecular approach arises from the basis set superposition error (BSSE), in which the interaction energy in the supermolecular approach is artificially overestimated because the intermolecular descriptions between subunits can be improved by utilizing the basis functions of the partners.[6] Therefore, to obtain accurate results corrected for BSSE, two methodologies have been commonly used: the counterpoise (CP) approach proposed by Boys and Bernardi[7] and the chemical Hamiltonian approach (CHA) developed by Mayer.[8] The latter eliminates the BSSE terms in the CHA of a supermolecule and, hence, provides a rigorous, BSSE-free description, whereas the former determines a correction term to minimize BSSE by using the same basis set for the supermolecule and its subunits. However, Mayer[9] and Paizs et al.[10] have demonstrated that the two methodologies, CHA and CP, tend to give similar results, despite their wide conceptual differences. Therefore, the usefulness of the CP method has also been well-established.

The CP correction function, ΔE_c(fCP) in eq 2 proposed by Boys and Bernardi,[7] has been estimated using fixed geometries of subunits, A and B, at the equilibrium geometry of the supermolecule, AB

$$\Delta E_c(\text{fCP}) = E_{AB}^{AB}(AB) - E_{AB}^{AB}(A) - E_{AB}^{AB}(B) \qquad (2)$$

Therefore, eqs 1 and 2 will not converge to the same result, even if a complete basis set is used, because the electronic energies of A and B are evaluated at different geometries of isolated and supermolecular systems. This problem can be solved by estimating the relaxation energies, as calculated in eq 3, required to distort fragments A and B from their isolated geometries to those in the supermolecule.[5,11,12] When geometry relaxation is considered, the CP-corrected interaction energy, ΔE_c(GCP), can be estimated by eq 4. In practice, use of the CP correction without considering geometrical effects has been reported to commonly lead to physically incorrect terms.[5,12]

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$$E^{\mathrm{A}}_{\mathrm{rel}}(\mathrm{A}) = E^{\mathrm{A}}_{\mathrm{AB}}(\mathrm{A}) - E^{\mathrm{A}}_{\mathrm{A}}(\mathrm{A}) \quad \text{and} \quad E^{\mathrm{B}}_{\mathrm{rel}}(\mathrm{B}) = E^{\mathrm{B}}_{\mathrm{AB}}(\mathrm{B}) - E^{\mathrm{B}}_{\mathrm{B}}(\mathrm{B}) \tag{3}$$

$$\Delta E_{\mathrm{c}}(\mathrm{GCP}) = E^{\mathrm{AB}}_{\mathrm{AB}}(\mathrm{AB}) - E^{\mathrm{AB}}_{\mathrm{AB}}(\mathrm{A}) - E^{\mathrm{AB}}_{\mathrm{AB}}(\mathrm{B}) + E^{\mathrm{A}}_{\mathrm{rel}}(\mathrm{A}) + E^{\mathrm{B}}_{\mathrm{rel}}(\mathrm{B}) \tag{4}$$

On the other hand, the intermolecular interaction with the CP correction might reduce the stability compared to that obtained from the normal supermolecular approach, because BSSE artificially overestimates the intermolecular interaction. This indicates that the intermolecular distances could be lengthened by consideration of the CP correction, despite the small changes in the geometries. Actually, for a weak complex having a flat potential energy surface (PES), some researchers have reported significant differences between the critical geometries of the BSSE-corrected and BSSE-uncorrected PESs.[13]

Therefore, this work examines in detail the effects of the BSSE corrections on the geometries and complexation energies for the organo-alkali metal cation complexes shown in Scheme 1. The model systems selected as the polymer electrolytes were alkali metal salts of poly(ethylene oxide) (PEO, **I**), poly(ethylene amine) (PEA, **II**), and poly(ethylene *N*-methylamine) (PEMA, **III**). Moreover, as shown in Scheme 1, two structures, a singly coordinated system (SCS) and a doubly coordinated system (DCS), were considered in this work, as the type of coordination could be dependent on the concentration of dissolved salts.

Theoretical and Experimental Methods

A. Theoretical Details. The complexation energies (ΔE_{c}) of the SCSs and DCSs were obtained using Hartree–Fock (HF) and density functional theory (DFT) of the B3LYP hybrid exchange functional[14] with the 6-31G(d) and 6-311++G(d,p) basis sets. All stationary species were fully optimized and characterized as minima by frequency calculations with all positive frequencies.

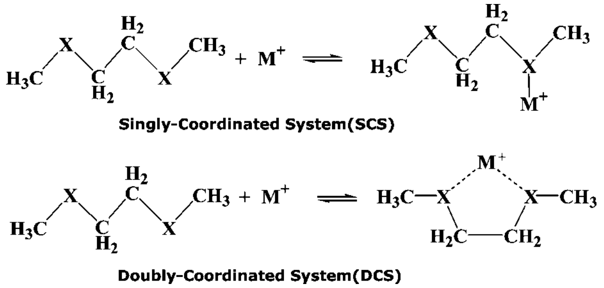
To evaluate the BSSE effects on ΔE_{c}, the CP corrections were performed using three different methodologies: (i) fCP (ii) GCP, and (iii) CP correction with the reoptimized geometries on the BSSE-corrected PES (RCP).[13d] The complexation energies calculated at the HF and B3LYP levels with the 6-31G(d) and 6-311++G(d,p) basis sets for the SCSs are summarized in Tables 1 and 2. Various complexation energies for the DCSs calculated at the B3LYP/6-311++G(d,p) are summarized in Table 3. To examine the effects of BSSE on the equilibrium geometries and vibrational frequencies, all of the complex structures were fully optimized and characterized by frequency calculations in the RCP correction. These calculations were conducted using the Gaussian 98[15] and Gaussian 03[16] packages.

B. Experimental Details. The ionic conductivities of polymer electrolytes composed of PEO [4:6 (wt ratio) PEO ($M_{\mathrm{w}} = 1 \times 10^6$)/PPG ($M_{\mathrm{n}} = 750$) mixed], PEA ($M_{\mathrm{w}} = 22\,000$), and PEMA ($M_{\mathrm{w}} = 29\,000$) with different iodide salts were measured using an impedance analyzer (IM6, Zahner) in the range from 1 Hz to 1 MHz, and the results are presented in Figure 1. All polymer electrolytes were prepared in 10 wt % solution of methanol, acetonitrile, and chloroform.

Results and Discussion

A. Comparisons of the Complexation Energies. The complexation energies (ΔE_{c}) for alkali metal cations Li^+, Na^+, and K^+ with various ethers have been widely reported in experimental and theoretical works.[17−24] To confirm the reliabilities of the methodologies and basis sets employed in this work, the calculated ΔE_{c} values were compared to those reported earlier. In particular, in an earlier work by Smith and co-workers,[20] a new Li basis set of [8s4p3d/5s3p2d] was developed to improve the description of the Li because the standard triple-ζ 6-311G basis set is inadequate for complexes involving Li^+, leading to very large BSSEs (>12.0 kJ mol^{-1}) and poor representations of the binding energies. However, such poor behavior of the 6-311G basis set might be obtained only for highly ionic systems such as alkali halides. Indeed, Smith et al. reported that the calculated ΔE_{c} and BSSE values for a complex between Li^+ and the ttt form of 1,2-dimethoxyethane (corresponding to the **I**•••Li^+ complex of the SCS) were −173.1 and 6.7 kJ mol^{-1}, respectively, at the MP2 level with Li:[5s3p2d]/ether:D-95+** hybrid basis sets. The corresponding binding energy and BSSE(GCP) reported in Table 2 are −169.7 and 2.8 kJ mol^{-1} at the B3LYP/6-311++G(d,p) level. They also reported that the ΔE_{c} and BSSE values for a complex between Li^+ and the tgt form of 1,2-dimethoxyethane (corresponding to the **I**•••Li^+ complex of the DCS) were −277.1 and 11.8 kJ mol^{-1}, respectively, and the corresponding values listed in Table 3 are −273.7 and 5.6 kJ mol^{-1}, respectively. This indicates that the ΔE_{c} and BSSE values at the B3LYP/6-311++G(d,p) level are comparable to those reported by Smith and co-workers. In a recent work by Borodin and Smith,[24] the corresponding values were −258.2 and 6.3 kJ mol^{-1}, respectively, at the MP2(full)/aug-cc-pvDz level, which are also comparable to our results. In addition, it would be interesting to compare our complexation enthalpies (ΔH_{c}) with experimental and other theoretical ΔH_{c} values for the DCS. Armentrout and co-workers measured the experimental bond dissociation enthalpies using collision-induced dissociation, and the results were 245 ± 18,[18] 161 ±

SCHEME 1: Organo-Alkali Metal Cation Complexes, where X = O (I), NH (II), and N($\mathrm{CH_3}$) (III) and M = Li, Na, and K



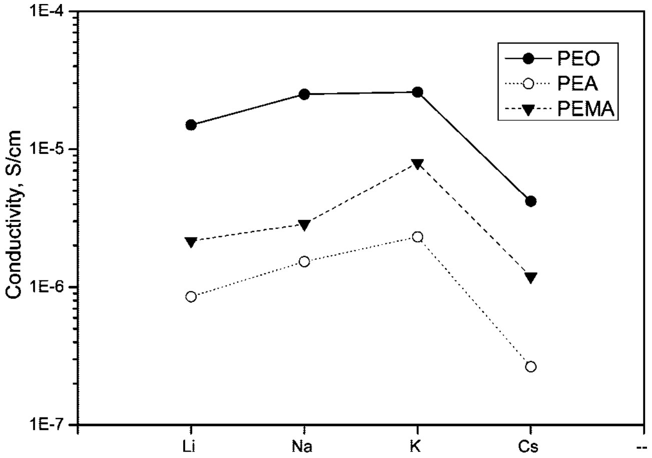


Figure 1. Ionic conductivities of polymer electrolytes composed of PEO, PEA, and PEMA.

TABLE 1: Calculated Complexation Energies (kJ mol^{-1}) for the SCSs at the HF Level of Theory

	HF/6-31G(d)			HF/6-311++G(d,p)		
	ΔE_c	ΔE_c(fCP)	ΔE_c(GCP)	ΔE_c	ΔE_c(fCP)	ΔE_c(GCP)
I···Li$^+$	−168.54	−169.14	−160.47	−164.01	−169.26	−160.99
I···Na$^+$	−112.92	−110.48	−105.77	−106.06	−107.97	−103.48
I···K$^+$	−72.42	−69.89	−66.73	−69.73	−71.76	−68.70
II···Li$^+$	−189.37	−187.24	−180.84	−181.81	−185.52	−179.25
II···Na$^+$	−129.64	−126.69	−122.01	−118.52	−120.65	−116.05
II···K$^+$	−82.58	−80.41	−76.98	−76.37	−78.80	−75.36
III···Li$^+$	−188.21	−186.95	−179.78	−183.10	−187.23	−180.42
III···Na$^+$	−126.97	−124.59	−119.44	−117.81	−120.00	−115.15
III···K$^+$	−79.63	−69.52	−69.98	−75.11	−77.28	−74.09

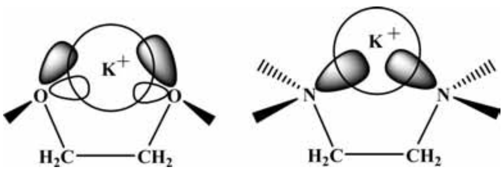
TABLE 2: Calculated Complexation Energies (kJ mol^{-1}) for the SCSs at the B3LYP Level of Theory

	B3LYP /6-31G(d)			B3LYP/6-311++G(d,p)			
	ΔE_c	ΔE_c(fCP)	ΔE_c(GCP)	ΔE_c	ΔE_c(fCP)	ΔE_c(GCP)	ΔE_c(RCP)
I···Li$^+$	−182.89	−180.47	−170.04	−169.71	−175.81	−166.87	−166.88
I···Na$^+$	−125.44	−118.97	−113.26	−112.05	−113.95	−108.99	−109.02
I···K$^+$	−80.94	−74.03	−70.81	−75.12	−77.08	−74.07	−74.07
II···Li$^+$	−207.54	−204.89	−196.34	−191.41	−196.95	−189.04	−189.03
II···Na$^+$	−147.34	−142.11	−136.40	−130.65	−132.68	−127.60	−127.62
II···K$^+$	−94.72	−88.91	−85.10	−85.04	−87.46	−84.02	−84.01
III···Li$^+$	−206.70	−204.79	−195.73	−193.44	−199.11	−191.03	−191.02
III···Na$^+$	−145.00	−140.59	−134.37	−131.22	−132.96	−127.84	−127.84
III···K$^+$	−92.19	−76.89	−75.78	−84.41	−86.77	−83.23	−83.24

TABLE 3: Calculated Complexation Energies (kJ mol^{-1}) for the DCSs at the B3LYP/6-311++G(d,p) Level of Theory

	ΔE_c	ΔE_c(fCP)	ΔE_c(GCP)	ΔE_c(RCP)
I···Li$^+$	−273.76	−288.76	−268.19	−268.24
I···Na$^+$	−188.47	−196.55	−183.25	−183.36
I···K$^+$	−132.84	−141.79	−130.98	−131.06
II···Li$^+$	−286.66	−311.84	−281.90	−281.92
II···Na$^+$	−195.34	−214.95	−189.96	−190.05
II···K$^+$	−129.13	−150.46	−127.22	−127.27
III···Li$^+$	−293.76	−305.38	−289.28	−289.31
III···Na$^+$	−200.44	−206.88	−195.32	−195.41
III···K$^+$	−134.22	−142.00	−132.47	−132.50

SCHEME 2



4,[19] and 120 ± 4[21] kJ mol^{-1} for **I**···Li$^+$, **I**···Na$^+$, and **I**···K$^+$, respectively. Hill and co-workers[22] reported that the BSSE-corrected complexation enthalpies were −257.7, −177.8, and −131.0 kJ mol^{-1} for **I**···Li$^+$, **I**···Na$^+$, and **I**···K$^+$, respectively, at the MP2/6-31+G(d) level. In this work, the GCP-corrected ΔH_c values at the B3LYP/6-311++G(d,p) level were −260.8, −178.3, and −127.0 kJ mol^{-1} for **I**···Li$^+$, **I**···Na$^+$, and **I**···K$^+$, respectively. These results indicate that our values were very similar to those obtained at the MP2 level and agreed reasonably well with the experimental values, although the calculated values were somewhat larger than the experimental results. Therefore, it could be expected that use of the B3LYP/6-311++G(d,p) method employed in this work gives reasonable results. Unlike complexation energies for alkali metal−ether complexes, however, those for the alkali metal cations with oligo-amine-based species are less commonly studied.

B. Energetics in the SCS. Examination of Tables 1 and 2 shows that the ΔE_c values at the HF level of theory were smaller than those at the B3LYP level of theory for the same basis set, whereas the ΔE_c values obtained with the 6-31G(d) basis set were larger than those obtained with 6-311++G(d,p) for the same level of theory. This indicates that the proper choice of both the basis set and the theoretical level is important for the accurate prediction of ΔE_c. Therefore, we mainly focused our discussions on the results obtained at the highest level of theory employed in this work, i.e., B3LYP, unless noted otherwise.

The ΔE_c values became negative in the order K$^+$ < Na$^+$ < Li$^+$, indicating the favorability of complex formation with a smaller cation, as is generally expected in the gas phase.[25] Moreover, the ΔE_c values with the nitrogen ligand (**II** and **III**) were more favorable than those with the oxygen ligand (**I**); for example, ΔE_c(**II**···Li$^+$) was 20.2 kJ mol^{-1} lower than ΔE_c(**I**···Li$^+$). Such trends were well in accord with the results reported by Laidig et al. for complexation of alkali metal cations with water (corresponding to the oxygen ligand) and ammonia (corresponding to the nitrogen ligand).[25]

When BSSE was taken into account, the complexation energies were expected to become less favorable. When the calculations were done using a smaller basis set, 6-31G(d), at both levels of theory, the ΔE_c(fCP) values followed this trend except for one case: **I**···Li$^+$ with the HF method. The BSSE corrections calculated using the fCP method, BSSE(fCP) = ΔE_c(fCP) − ΔE_c, at the B3LYP level were much larger than those obtained at the HF level. For example, BSSE(fCP) for **II**···K$^+$ was +5.9 kJ mol^{-1} at the B3LYP/6-31G(d) level but +2.1 kJ mol^{-1} at the HF/6-31G(d) level, indicating that the BSSE effects could be more important for the correlated B3LYP level than for the uncorrelated HF level, as reported by Bende et al.[26] However, when the calculations were done using a larger basis set, 6-311++G(d,p), at both levels of theory, unexpected results were obtained in that the BSSE(fCP) values were negative in all cases, as calculated from the data in Tables 1 and 2. For example, the BSSE(fCP) values for **I**···Li$^+$ were −5.25 and −6.10 kJ mol^{-1} at the HF and B3LYP levels, respectively. A detailed examination of the terms for **I**···Li$^+$ at the B3LYP level gave results of $E_{A}^{A}(A) = -7.28492$ Hartree, $E_{AB}^{AB}(A) = -7.28505$ Hartree, $E_{B}^{B}(B) = -308.95489$ Hartree, and $E_{AB}^{AB}(B) = -308.95243$ Hartree, where A and B refer to the

TABLE 4: Optimized Bond Lengths (d_{X-M^+}, Å) between X and M^+ at the B3LYP/6-311++G(d,p) Level of Theory

	SCS			DCS[a]		
	d_{X-M^+}[b]	d_{X-M^+}[c]	δd_{X-M^+}[d]	d_{X-M^+}[b]	d_{X-M^+}[c]	δd_{X-M^+}[d]
I$\cdots$Li$^+$	1.811	1.814	0.003	1.863	1.868	0.005
I$\cdots$Na$^+$	2.201	2.211	0.010	2.247	2.259	0.012
I$\cdots$K$^+$	2.584	2.592	0.008	2.625	2.640	0.015
II$\cdots$Li$^+$	1.963	1.964	0.001	1.997	2.000	0.003
II$\cdots$Na$^+$	2.356	2.364	0.008	2.381	2.392	0.011
II$\cdots$K$^+$	2.771	2.776	0.005	2.784	2.795	0.011
III$\cdots$Li$^+$	1.962	1.965	0.003	1.993	1.998	0.005
III$\cdots$Na$^+$	2.361	2.371	0.010	2.384	2.396	0.012
III$\cdots$K$^+$	2.765	2.773	0.008	2.786	2.795	0.009

[a] Average of two d_{X-M^+} bond lengths. [b] Optimized values on the CP-uncorrected potential surfaces. [c] Optimized values on the CP-corrected potential surfaces. [d] Differences in d_{X-M^+} between on the CP-corrected and -uncorrected potential surfaces.

TABLE 5: Harmonic Stretching Frequencies of the X—M$^+$ Bond (ν_{X-M^+}, cm^{-1}) at the B3LYP/6-311++G(d,p) Level of Theory

	SCS			DCS		
	ν_{X-M^+}[a]	ν_{X-M^+}[b]	$\delta\nu_{X-M^+}$[c]	ν_{X-M^+}[a]	ν_{X-M^+}[b]	$\delta\nu_{X-M^+}$[c]
I$\cdots$Li$^+$	581.6	578.1	3.5	526.9	520.2	6.7
I$\cdots$Na$^+$	238.3	234.9	3.4	232.4	229.0	3.4
I$\cdots$K$^+$	165.5	164.6	0.9	170.4	168.6	1.8
II$\cdots$Li$^+$	535.0	531.7	3.3	488.5	484.8	3.7
II$\cdots$Na$^+$	329.5	327.6	1.9	371.4	368.5	2.9
II$\cdots$K$^+$	118.0	117.5	0.5	148.7	147.7	1.0
III$\cdots$Li$^+$	558.9	554.4	4.5	514.7	511.8	2.9
III$\cdots$Na$^+$	216.9	212.0	4.9	201.1	198.3	2.8
III$\cdots$K$^+$	137.3	137.3	0.0	148.9	148.6	0.3

[a] Values on the CP-uncorrected potential surfaces. [b] Values on the CP-corrected potential surfaces. [c] Differences in ν_{X-M^+} between on the CP-corrected and -uncorrected potential surfaces.

TABLE 6: Average Bond Lengths (d_{X-M^+}, Å) between X and M$^+$ at the B3LYP Level of Theory

	6-31G(d)			6-311++G(d,p)		
	Li	Na	K	Li	Na	K
(PEO)$_3\cdots$M$^+$	2.207	2.409	2.812	2.182	2.427	2.816
(PEA)$_3\cdots$M$^+$	2.212[a]	2.577	2.962	2.237[a]	2.599	3.010
(PEMA)$_3\cdots$M$^+$	2.222[a]	2.619[a]	2.997	2.219[a]	2.624[a]	3.002

[a] d_{X-M^+} distances longer than 3.5 Å were excluded, as shown in Figure 2.

metal cation and the ligand, respectively. As expected, the electronic energy of Li$^+$ became more negative when the basis set AB was employed. However, the absolute value of $E_{\mathrm{AB}}^{\mathrm{AB}}(\mathrm{B})$ was 6.5 kJ mol^{-1} smaller than that of $E_{\mathrm{B}}^{\mathrm{B}}(\mathrm{B})$, despite the clear improvement in the number of basis functions. As already mentioned, it has previously been reported that the fCP correction (eq 2) often leads to physically incorrect terms in the absence of any consideration of geometrical effects as in $E_{\mathrm{rel}}^{\mathrm{A}}(\mathrm{A})$ and $E_{\mathrm{rel}}^{\mathrm{B}}(\mathrm{B})$ in eq 3.[5,12]

To circumvent this situation, it was necessary to calculate BSSEs using the GCP method. The ΔE_{c}(GCP) values listed in Tables 1 and 2 improved the BSSE effects. Regardless of the basis set and theoretical method employed, the relationship BSSE(GCP) > 0 held [i.e., $\Delta E_{\mathrm{c}}(\mathrm{GCP}) - \Delta E_{\mathrm{c}} > 0$]. From Tables 1 and 2, it was easy to calculate $E_{\mathrm{rel}}^{\mathrm{B}}(\mathrm{B})$ because the total deformation energy ($E_{\mathrm{rel}}^{\mathrm{A}} + E_{\mathrm{rel}}^{\mathrm{B}}$) could be calculated from the relation $\Delta E_{\mathrm{c}}(\mathrm{GCP}) - \Delta E_{\mathrm{c}}(\mathrm{fCP})$ and because $E_{\mathrm{rel}}^{\mathrm{A}}$ was zero because A was an atomic species. $E_{\mathrm{rel}}^{\mathrm{B}}(\mathrm{B})$ calculated in this way was positive in all cases and increased from 1.1 to 10.4 kJ mol^{-1}, which implied that the ligand fragments became unstable during the transformation from the isolated equilibrium geometry to the geometry in the supermolecule. Moreover, the magnitudes of $E_{\mathrm{rel}}^{\mathrm{B}}(\mathrm{B})$ increased when the complex was formed with smaller alkali metal cations. For example, the $E_{\mathrm{rel}}^{\mathrm{B}}(\mathrm{B})$ values for **I**$\cdots$M$^+$ at the B3LYP/6-311++G(d,p) were +8.94, +4.96, and +3.01 kJ mol^{-1} for Li$^+$, Na$^+$, and K$^+$, respectively. This trend arose because the smaller cation had a stronger interaction with the ligand, which maximized the geometrical distortion of the ligand fragment for complexes with Li$^+$.[22] If the CP corrections were considered using the 6-311++G(d,p) basis set, the CP correction should be performed using ΔE_{c}(GCP).

The $E_{\mathrm{rel}}^{\mathrm{B}}(\mathrm{B})$values calculated with the 6-31G(d) basis set were also positive, and the magnitudes were similar to those calculated with the 6-311++G(d,p) basis set. However, the pure basis set effect [for example, $E_{\mathrm{AB}}^{\mathrm{AB}}(\mathrm{B}) - E_{\mathrm{B}}^{\mathrm{B}}(\mathrm{B})$] calculated with the 6-31G(d) basis set was larger than that calculated with the 6-311++G(d,f) basis set. Moreover, the sum of the pure basis set effects was larger than the deformation energy, indicating that the improvements gained by using the basis set corresponding to the whole system were much larger than the effects of geometrical deformations in the case of 6-31G(d). This was not desirable because the pure basis set effects should, in principle, be minimized as the basis set employed approaches the complete basis set. Therefore, we chose to use the results obtained using B3LYP/6-311++G(d,p) in the following discussion.

C. Energetics in the DCS. The DCS might act as a model corresponding to a polymer electrolyte when the concentration of a dissolved metal salt is relatively low compared to that in the SCS; i.e., the relative ratio of the ligand site to the metal cation is large under these conditions, which allows the metal cation to be bound to multiple sites. The ΔE_{c} values shown in Table 3 were about 1.5 times larger than those for the

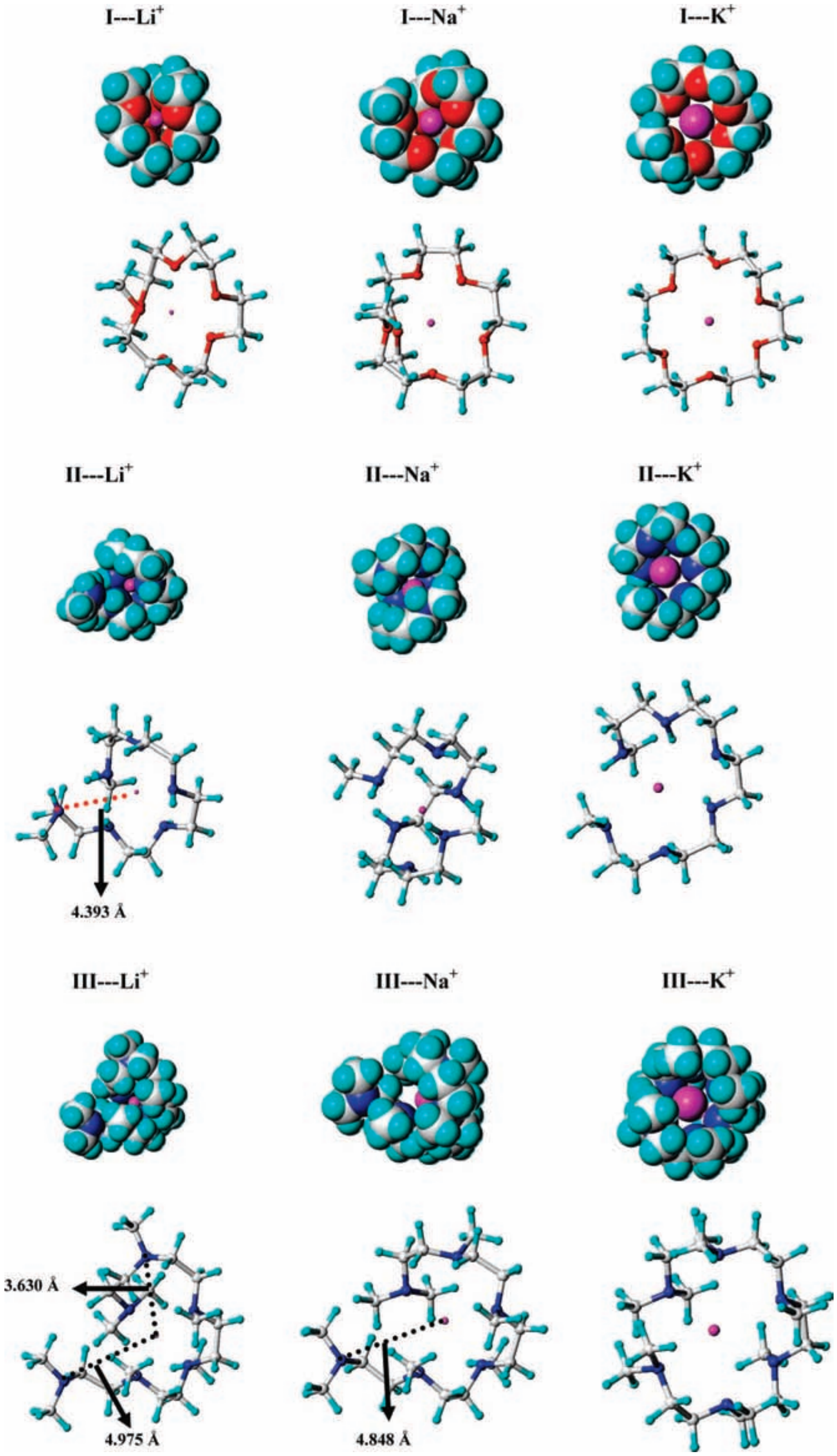


Figure 2. Space-filling and ball-and-stick representations of the complexes of $(PEO)_3$, $(PEA)_3$, and $(PEMA)_3$ with alkali metal ions optimized at the B3LYP/6-311++G(d,p) level.

corresponding SCS, because the alkali metal cation was bound to two ligand sites. For example, the $\Delta E_c(\mathbf{I}\cdots Li^+)$ values were -164.0 and -273.8 kJ mol^{-1} for the SCS and DCS, respectively.

All of the trends in ΔE_c for the DCS were similar to those for the SCS: The ΔE_c values increased negatively in the order $K^+ < Na^+ < Li^+$,[21,22] and the ΔE_c values for **II** and/or **III** were also favorable for complexes containing Li^+ or Na^+ cations compared to those for **I**, as discussed above with respect to the SCS. However, the ΔE_c values for complexes with K^+ cations in the DCS showed a slight fluctuation. In the SCS, $\Delta E_c(\mathbf{I}\cdots K^+)$ was more than 9 kJ mol^{-1} smaller than ΔE_c $(\mathbf{II}\cdots K^+)$ or ΔE_c $(\mathbf{III}\cdots K^+)$. In the DCS, however, $\Delta E_c(\mathbf{I}\cdots K^+)$ was 3.7 kJ mol^{-1} lower than $\Delta E_c(\mathbf{II}\cdots K^+)$ and was comparable to $\Delta E_c(\mathbf{III}\cdots K^+)$, possibly because of the larger size of the K^+ cation, which could interact with two lone pairs of each oxygen in **I**, although such an interaction would not be possible for the nitrogen lone pair in **II** and **III**, as shown in Scheme 2.

When the BSSE was considered using eq 2, the BSSE(fCP) values were also negative, as discussed above in relation to the SCS. Moreover, the BSSE(fCP) values in the DCS were much larger than those in the SCS. For example, BSSE(fCP) for **I**···Li^+ was 6.1 kJ mol^{-1} in the SCS, but 20.6 kJ mol^{-1} in the DCS at the B3LYP/6-311++G(d,p) level. This indicates that the geometrical deformation should be greater in the DCS, because the ligands would have to change their conformations from the free state to the bound state in the DCS, and further that the complexation energies should be evaluated using the ΔE_c(GCP) values in the case of the CP correction.

The magnitudes of the CP corrections to the complexation energies, BSSE(GCP) [$= \Delta E_c(\text{GCP}) - \Delta E_c$], for the DCS were about twice those for the SCS owing to the bidentate nature of the metal coordination in the former. For example, for **I**···M^+, the BSSE(GCP) values were 5.5, 5.2, and 1.8 kJ mol^{-1} in the DCS, but 2.8, 3.0, and 1.1 kJ mol^{-1} in the SCS, for $M^+ = Li^+$, Na^+, and K^+, respectively. Nevertheless, the ratios BSSE(GCP)/$|\Delta E_c|$ (denoted %GCP) were similar (1−3%) for both the SCS and the corresponding DCS, although the magnitude of the CP correction was larger in the DCS. It would be interesting to compare the ratios with those presented in other studies. In previous works, however, the CP correction was considered using eq 2, and thus, the corresponding ratio would be %fCP [$=$ BSSE(fCP)/$|\Delta E_c|$]. The magnitude of %GCP obtained in this work was smaller than %fCP reported for other complexes. For example, Mhin et al.[27] reported that the %fCP value for water dimer was 6.0% and 20.8% at the HF and MP2 levels, respectively, with the DZP basis set. This increased %fCP might have resulted from using a relatively low basis set. In a diacetamide−water dimer study,[28] the %fCP value at the B3LYP level gradually decreased with increasing basis set size, i.e., 25.9%, 5.2%, 2.3%, and 0.8% for the 6-31G(d), 6-31+G(d), 6-311++G(d,p), and 6-311++G(2d,2p) basis sets, respectively. Therefore, the %GCP result of 1−3% obtained in this work could be quite reliable.

D. Effects of the CP Correction on Equilibrium Geometries and Vibrational Frequencies. In general, the intermolecular distances between the ligand and metal cation could be increased by consideration of the CP correction, because of the exclusion of the overestimated intermolecular interaction. Therefore, the effects of the CP correction on the equilibrium geometries were examined using RCP. The optimized bond lengths between X and M^+ (d_{X-M^+}) are summarized in Table 4 and the optimized geometries are provided in the Supporting Information. Table 4 shows that the corrected d_{X-M^+} values are somewhat greater than the uncorrected values and that the lengthening is slightly larger in the DSCs than in the SCSs, reflecting the larger CP correction in the DCSs. However, the differences in the bond length, δd_{X-M^+} [$= d_{X-M^+}(\text{corrected}) - d_{X-M^+}(\text{uncorrected})$], were small in absolute magnitude (less than 0.015 Å). An earlier work on water dimer[29] reported that the O···O distance was sensitive to both the calculation method and the CP correction. Simon and co-workers studied the CP-corrected O···O distances according to the HF, MPn, and DFT methods with the D95++(d,p) basis set.[30] As expected, the optimized O···O distances were longer on the CP-corrected PES, and the differences in the O···O distances between the CP-corrected and -uncorrected surfaces were sensitive to the theoretical method employed. However, they concluded that the B3LYP level provided the best energetic and geometrical results on the CP-corrected PES and that the O···O distance on the CP-corrected surface became 0.032 Å longer at the B3LYP level. This large increase in the O···O distance was made possible by the very flat PES of the water dimer. This result implies that δd_{X-M^+} should be small because the ion−dipole interaction between the metal cation and the ligand is much stronger than the dipole−dipole (or hydrogen-bonding) interaction in water dimer.

In the examination of the effect of the CP methods on vibrational frequencies, as summarized in Table 5, the CP-corrected harmonic stretching frequencies of the X···M^+ bond, ν_{X-M^+}, were little changed from the CP-uncorrected values because of the small geometrical changes. In fact, the variations of ν_{X-M^+}, $\delta\nu_{X-M^+}$, were smaller than 7 cm^{-1}, which suggests that the zero-point vibrational energies were nearly the same for both the CP-corrected and -uncorrected PESs. Moreover, a comparison of the last two columns in Tables 2 and 3 indicates that the complexation energies calculated for the CP-corrected potential surfaces, ΔE_c(RCP), were the same as those calculated including geometry relaxation, ΔE_c(GCP). This confirms the capability of the CP method using eq 4 to give reliable results for organo-alkali metal complexes.

E. Structures of Higher Coordination. The increase in ionic conductivities shown in Figure 1 ($Li^+ < Na^+ < K^+$) was in good agreement with the complexation energies calculated for the DCS at the B3LYP level of theory. Whereas the ion conductivities increased in the order PEA < PEMA < PEO, the complexation energies did not follow this trend: **III**···M^+ had the largest complexation energy regardless of the metal ion. This suggests that the simple models considered in this work might not be sufficient to simulate the conducting phenomena in polymer electrolytes. In general, cation coordination numbers might be higher than the singly and doubly coordinated species discussed above, as was also pointed out by the reviewers.[31,32] To test this possibility, the complexes of $(PEO)_3$, $(PEA)_3$, and $(PEMA)_3$ with alkali metal cations were studied at the B3LYP level with 6-31G(d) and 6-311++G(d,p) basis sets. Optimized structures are shown in Figure 2, and the average X−M^+ distances (d_{X-M^+}) are summarized in Table 6. As represented in Figure 2, in **I**···M^+ complexes, the alkali metal cations were completely surrounded by six X atoms in all cases. However, in **II**···M^+ complexes, the Li^+ cation was bound by five nitrogen atoms, unlike Na^+ and K^+ cations. In **III**···M^+ complexes, coordination numbers decreased further because Li^+ and Na^+ cations were bound by four and five nitrogen atoms, respectively. These results were clearly caused by both the steric repulsion between ligand fragments, similar to the ligand−ligand repulsion found earlier,[18,19,21] and the size effects of the metal cations; i.e., steric repulsion between fragments are the largest in $(PEMA)_3$, and the Li^+ cation is the smallest in size. Studies on the structures and energetics having higher coordination numbers are in progress in our laboratory.

Conclusion

In the organo-alkali metal cation complexes studied in this work, the complexation energies were large and varied in the order $K^+ < Na^+ < Li^+$, and their magnitudes strongly depended on the theoretical levels and basis sets employed. These results confirm the importance of choosing the basis set and theoretical level appropriately. The best method selected in this study was B3LYP/6-311++G(d,p). Moreover, the BSSE effects also varied according to the methodologies of the CP correction. The fCP correction was found to be inadequate because of the geometrical deformation caused by tight binding of the subunits. This result was contrary to the usual cases, which involved weakly bound complexes. The incorporation of geometrical relaxation into the GCP method, as expressed in eq 4, improved the results. Compared to results from the most rigorous method, which reoptimized the structures on the CP-corrected PES, i.e., RCP, the geometrical parameters optimized on the CP-uncorrected PESs showed no appreciable changes, and ΔE_c(GCP) was virtually the same as ΔE_c(RCP). These findings confirm the capability of the GCP method to generate reliable results in the study of the organo-alkali metal complexes.

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Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

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