Basis Set Superposition Error on Structures and Complexation Energies of Organo-Alkali Metal Iodides

Chang Kon Kim, Hui Zhang, Sung Hoon Yoon, Jongok Won,[†] and Chan Kyung Kim*

Department of Chemistry, Inha University, Incheon 402-751, Korea. *E-mail: kckyung@inha.ac.kr

[†]Department of Chemistry, Sejong University, Seoul 134-747, Korea

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Theoretical studies have been performed to study the binding characteristics of the alkali metal iodides, $\mathbf{M}-\mathbf{I}$ ($\mathbf{M} = \text{Li, Na, K}$), to poly(ethylene oxide) (PEO, **I**), poly(ethylene amine) (PEA, **II**) and poly(ethylene *N*-methylamine) (PEMA, **III**) via the B3LYP method. In this study, two types of complexes, singly-coordinated systems (SCS) and doubly-coordinated systems (DCS), were considered, and dissociation energies (ΔE_D) were calculated both with and without basis set superposition error (BSSE). Two types of counterpoise (CP) approach were investigated in this work, but the ΔE_D values corrected by using the function CP (fCP) correction exhibited an unusual trend in some cases due to deformation of the sub-units. This problem was solved by including geometry relaxation in the CP-corrected (GCP) interaction energy. On the other hand, the effects of the BSSE on the structures were very small when the complexes were re-optimized on the CP-corrected (RCP) potential energy surface (PES), even if the bond lengths between X and $\mathbf{M}^+$ ($d_{\text{X-M}^+}$) and between $\mathbf{M}^+$ and Γ^- ($d_{\text{M}^+-\Gamma^-}$) were slightly lengthened. Therefore, neither the GCP nor RCP corrections made much difference to the dissociation energies.

Key Words: Alkali metal iodides, Basis set superposition error, Dissociation energy, Density functional theory

Introduction

Polymer-based solid electrolytes with ionic conductivity have been targets of extensive studies because of their potential application as solid electrolytes in rechargeable batteries, fuel cells, etc.¹ Polymer electrolytes typically consist of a metal salt and a polymer that functions as a solvent. Ionic conductivities in polymer electrolytes could therefore depend upon the interactions between ionic species of dissolved metal salts and polymeric ligands. The interaction between ionic species and polymeric ligands is thus an important factor in determining ionic conductivity, although this property also varies with the concentration of the dissolved metal salt and the mobility of the charge carriers.²

The interaction between ionic species and polymeric ligands corresponds to a complexation (or dissociation, in the inverse direction) process. Hence, related information such as complexation energy and/or structure can be predicted theoretically using the supermolecular approach.³ In this approach, the dissociation energy, ΔE_D in eq. (1), is simply estimated as the energy difference between the whole system and its subunits. In eq. (1), we follow the notation $E_r^Z(\text{X})$ to indicate the electronic energy of a molecular system X at geometry Y computed with basis set Z.⁴ However, it has been well known that one of the difficult problems in the simple supermolecular approach arises from the basis set superposition error (BSSE). That is, in the supermolecular approach, the interaction energy is artificially overestimated, because in this approach the intermolecular descriptions between subunits does not incorporate the basis functions of the partners.⁵ Therefore, in order to obtain accurate results corrected for BSSE, two methodologies, the counterpoise (CP) approach proposed by Boys and Bernardi⁶ and the Che-

mical Hamiltonian Approach (CHA) developed by Mayer,⁷ have been commonly used. Moreover, even though the CHA and CP methodologies are conceptually very different, it has been well demonstrated that they tend to give similar results.⁸

$$\Delta E_D = E_A^A(\text{A}) + E_B^B(\text{B}) - E_{AB}^{AB}(\text{AB}) \quad (1)$$

In this work, the effects of the BSSE on dissociation processes in polymer electrolytes with alkali-metal iodides have been examined using the CP method. The function CP correction proposed by Boys and Bernardi⁶, $\Delta E_D(\text{fCP})$ in eq. (2), determines a correction term that BSSE is minimized by using the same basis set for the equilibrium geometry as for the supermolecule and its subunits with fixed geometries of molecular systems, A and B, at the supermolecule.

$$\Delta E_D(\text{fCP}) = E_{AB}^{AB}(\text{A}) + E_{AB}^{AB}(\text{B}) - E_{AB}^{AB}(\text{AB}) \quad (2)$$

Unfortunately, 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 for different geometries of isolated and supermolecular systems, this problem can be solved by estimating the relaxation energies, eq. (3), required for distorting fragments A and B from their isolated geometries to the ones in the supermolecule.^{4,9} If the effects of geometry relaxation are considered, then the CP-corrected interaction energy, $\Delta E_D(\text{GCP})$, can be estimated by eq. (4).

$$\begin{aligned} E_{rel}^A(\text{A}) &= E_{AB}^A(\text{A}) - E_A^A(\text{A}) \quad \text{and} \\ E_{rel}^B(\text{B}) &= E_{AB}^B(\text{B}) - E_B^B(\text{B}) \end{aligned} \quad (3)$$

$$\Delta E_D(GCP) = E_{AB}^{AB}(A) + E_{AB}^{AB}(B) - E_{AB}^{AB}(AB) - E_{rel}^A(A) - E_{rel}^B(B) \quad (4)$$

However, it has been reported that the CP correction without considering geometrical effects often leads to physically incorrect terms.^{4,9b} Therefore, in this work, the effects of CP corrections, $\Delta E_D(fCP)$ and $\Delta E_D(GCP)$, on uncorrected ΔE_D have been examined for the dissociation processes of complexes in polymer electrolytes. In polymer electrolytes, two types of dissociation processes, eqs. (5) and (6), are considered in the first step, where **P**, **M**⁺, and **I**[−] denote a polymeric ligand, a metal cation, and an iodide ion, respectively, and the resulting **P**—**M**⁺ or **M**⁺—**I**[−] may be dissociated in the next stage.

However, the dissociation of **M**⁺—**I**[−] to **M**⁺ and **I**[−] corresponds to the simple heterolytic bond cleavages of molecular metal salts in a polymeric solvent, and the dissociations of **P**—**M**⁺ for alkali metal cations have been reported in a previous work.¹⁰ Therefore, in this work, the first steps in the dissociation processes shown in eqs. (5) and (6) were studied for complexes consisting of a polymeric ligand and an alkali-metal iodide, **P**—**M**—**I**, where **P** = CH₃—X—CH₂—CH₂—X—CH₃ (X = O, NH and N—CH₃). These complexes have been selected as model systems for poly(ethylene oxide) (PEO, X = O), poly(ethylene amine) (PEA, X = NH) and poly(ethylene N-methylamine) (PEMA, X = N—CH₃), because these systems, having an iodide anion, could be potentially applied for polymer electrolytes in a solar cell, since, as is well known, the key function in the conventional dye-sensitized solar cell (DSSE) is the electron transfer to an oxidized dye molecule by the iodide/triiodide electrolytes; thus, the concentration of free iodide anion could influence the efficiency of the DSSC.¹¹ However, the studies on dissociation (or complexation) of iodide have been few, even though numerous works have been reported the iodide/triiodide redox potential in various materials.¹² Therefore, in this work, the dissociation processes were considered in two structures, singly-coordinated (SCS) and doubly-coordinated structures (DCS), as represented in Scheme 1, since the type of coordination could be dependent on the concentration of dissolved salts. This study could provide useful information for the BSSE of the dissociation process of

Scheme 1

metal salts in polymer electrolytes.

Computational Methods

To examine the effects of the BSSE on optimized geometries, vibrational frequencies, and dissociation energies, the CP-corrected and uncorrected structures of organo-alkali metal iodides were fully optimized and characterized by frequency calculations by using the Gaussian-03 program.¹³ All calculations were carried out at the B3LYP level of theory with the 6-311++G(d,p) basis set, except for iodine. For iodine, a standard all-electron TZ-quality basis set¹⁴ augmented by a 2-D polarization function with exponents of 0.30 and 0.08, and one SP diffuse function with an exponent of 0.025, were used.¹⁵ In this basis set, we used a split valence (SV) of 433321/43321/43, which we named the SV4PPD basis set, where PP stands for two polarization functions with exponents of 0.105 and 0.334.¹⁶ In our previous work on alkali-metal iodides,¹⁷ the combination of 6-311+G(d) for alkali metals and a SV4PPD basis set for iodine at the B3LYP level gave reliable results for energetics and geometries compared to the experimental results.

Results and Discussion

The dissociation processes of iodide ion, eq. (5). The calculated dissociation energies (ΔE_D) of molecular alkali-metal iodides, **M**—**I**→**M**⁺ and **I**[−], are 139.0, 121.6, and 105.0 kcal mol^{−1} for **M** = Li, Na, and K, respectively, indicating that the dissociation is in the order of difficulty **K**—**I** < **Na**—**I** < **Li**—**I**.¹⁸ Therefore, one may expect the dissociation processes of the iodide ion in the complexes formed from polymer alkali-metal iodides shown in eq. (5) to have a similar trend. The complexation energies (ΔE_D) of the SCSs and DCSs are shown in Table 1. The ΔE_D values shown in Table 1 revealed the same trend as those of molecular alkali-metal iodides in all cases, as expected. For example, the ΔE_D values increased in the order **I**—**K**—**I** < **I**—**Na**—**I** < **I**—**Li**—**I**. However, the ΔE_D values in the SCSs were much smaller, by about 20 (Li⁺) ~ 8 (K⁺), than those in the corresponding molecular alkali-metal iodides, since the polymer ligands stabilized the dissolved alkali-metal cations by electrostatic interaction. Moreover, the ΔE_D values in the DCSs were

Table 1. The calculated dissociation energies (in kcal mol^{−1}) for eq. (5) in the SCS and DCS complexes

	SCS			DCS		
	ΔE_D	ΔE_D (fCP)	ΔE_D (GCP)	ΔE_D	ΔE_D (fCP)	ΔE_D (GCP)
I — Li — I	121.4	119.7	118.7	108.4	107.9	105.9
I — Na — I	109.9	109.4	108.2	101.6	100.9	99.8
I — K — I	97.9	97.4	96.5	91.0	90.7	89.5
II — Li — I	119.2	118.0	116.5	106.3	107.7	103.8
II — Na — I	109.0	110.0	106.9	100.4	102.2	98.4
II — K — I	98.0	99.2	96.2	93.3	94.4	91.3
III — Li — I	117.9	116.8	115.0	106.8	105.7	104.0
III — Na — I	107.2	106.0	105.1	100.5	99.3	98.3
III — K — I	96.4	96.0	94.8	91.0	90.3	89.1

further decreased by about $10 (\text{Li}^+) \sim 5 \text{ kcal mol}^{-1} (\text{K}^+)$ as compared to the SCSs, due to stronger electrostatic interaction. Such effects could be one of the reasons why the metal salts were easily dissolved in polymer electrolytes.

The CP-corrected ΔE_D values, $\Delta E_D(\text{fCP})$, could be expected to be smaller than the uncorrected ΔE_D values, because the artificially overestimated interactions in the supermolecular approaches were minimized by the CP corrections. In many cases, the $\Delta E_D(\text{fCP})$ values seemed to decrease compared to the ΔE_D values, and the differences between two dissociation energies were small, within *ca.* 2 kcal mol^{-1} . However, the $\Delta E_D(\text{fCP})$ values were unexpectedly larger than those of the corresponding ΔE_D values in some complexes formed with **II**. For example, in **II**—K—I, the $\Delta E_D(\text{fCP})$ values were larger by 1.2 (in the SCS) and 1.1 (in the DCS) kcal mol^{-1} than the corresponding ΔE_D values. This result might be due to neglect of the effects of geometry relaxation, as shown in eq. (3). In general, when a larger basis set is employed, the calculated electronic energies are improved up to the Hartree-Fock limit. To explain this phenomenon, we can discuss the effects on the two fragments, **P**—**M**⁺ (labeled A) and Γ (labeled B), separately. The calculated electronic energies for molecular units of **P**—**M**⁺ worsened going from $E_A^A(\text{A})$ to $E_{AB}^{AB}(\text{A})$ in all cases studied in this work, although the number of basis functions employed to calculate the $E_{AB}^{AB}(\text{A})$ was obviously larger than that employed to calculate the $E_A^A(\text{A})$. The changes in electronic energies going from $E_A^A(\text{A})$ to $E_{AB}^{AB}(\text{A})$ actually included both the unfavorable geometrical deformation ($\Delta E_{\text{def}} > 0$) and the favorable increase in the number of basis functions ($\Delta E_{\text{basis}} < 0$), i.e., $E_A^A(\text{A}) \xrightarrow{\Delta E_{\text{def}} > 0} E_{AB}^{AB}(\text{A}) \xrightarrow{\Delta E_{\text{basis}} < 0} E_{AB}^{AB}(\text{A})$. The ΔE_{def} and ΔE_{basis} are summarized in Table 2. The calculated electronic energies therefore changed for the worse going from $E_A^A(\text{A})$ to $E_{AB}^{AB}(\text{A})$, since the ΔE_{def} values were larger than the $|\Delta E_{\text{basis}}|$ ($\leq 0.2 \text{ kcal/mol}$ in all cases). In the case of the counterion Γ , there was no geometrical deformation ($\Delta E_{\text{def}} = 0$), which meant that the calculated electronic energy improved on going from $E_B^B(\text{B})$ to $E_{AB}^{AB}(\text{B})$ due to the favorable ΔE_{basis} ($-1.3 \sim -2.8 \text{ kcal/mol}$). In any case, the $\Delta E_D(\text{fCP})$ values included both effects of $E_A^A(\text{A}) \rightarrow E_{AB}^{AB}(\text{A})$ and $E_B^B(\text{B}) \rightarrow E_{AB}^{AB}(\text{B})$, and the favorable ΔE_{basis} were (fully or partially) cancelled out by the unfavorable ΔE_{def} . In other words, fCP corrections may be inadequate when the molecular unit(s) experience relatively large deformation.

In order to examine the CP corrections after removing the effects of deformation, the $\Delta E_D(\text{GCP})$ values obtained from eq. (4) are also summarized in Table 1. All the $\Delta E_D(\text{GCP})$ values shown in Table 1 were smaller than the corresponding uncorrected ΔE_D values. This agrees well with the expectation that the CP correction minimizes the artificially overestimated molecular interaction in the supermolecular approach. Moreover, the differences between the $\Delta E_D(\text{GCP})$ and ΔE_D values, $\delta \Delta E_D(\text{GCP}) [= \Delta E_D - \Delta E_D(\text{GCP})]$, for the SCSs were very similar to those for the corresponding DCSs, indicating that the CP corrections without geometrical deformation were similar for both cases. These results could be easily understandable - The $\delta \Delta E_D(\text{GCP})$ value was actually applicable to the pure basis set effect, ΔE_{basis} , i.e., the $\delta \Delta E_D(\text{GCP})$ could be represented as eq. (7) by subtracting eq. (1) from eq. (4). Therefore, the $\delta \Delta E_D(\text{GCP})$ value

Table 2. The ΔE_{def} and ΔE_{basis} (in kcal mol^{-1}) for eq. (5) in the SCS and DCS complexes

	SCS		DCS	
	ΔE_{def}	ΔE_{basis}	ΔE_{def}	ΔE_{basis}
I —Li—I	1.0	-2.7	1.9	-2.5
I —Na—I	1.2	-1.7	1.1	-1.9
I —K—I	0.9	-1.4	1.2	-1.6
II —Li—I	1.5	-2.7	3.8	-2.5
II —Na—I	3.1	-2.1	3.8	-2.1
II —K—I	3.0	-1.9	3.1	-2.0
III —Li—I	1.9	-2.9	1.7	-2.8
III —Na—I	0.9	-2.1	1.0	-2.2
III —K—I	1.2	-1.6	1.2	-1.8

could be similar for the SCSs and the corresponding DCSs with the same basis set effects on the same subunits, $\text{A} = \text{P—M}^+$ and $\text{B} = \Gamma$, even if the structures are very different in the supermolecule, $\text{AB} = \text{P—M—I}$. On the other hand, the $\delta \Delta E_D(\text{GCP})$ value decreased in the order $\text{P—Li—I} > \text{P—Na—I} > \text{P—K—I}$ in both the SCSs and DCSs. This indicates that ΔE_{basis} values decreased as the number of basis functions increased in the **P**—**M**⁺ fragments, since contributions by the Γ fragment were the same in all cases.

$$\begin{aligned} \delta \Delta E_D(\text{GCP}) &= \{E_{AB}^{AB}(\text{A}) - E_A^A(\text{A})\} + \{E_{AB}^{AB}(\text{B}) - E_B^B(\text{B})\} \\ &= \Delta E_{\text{basis}}(\text{A}) + \Delta E_{\text{basis}}(\text{B}) \end{aligned} \quad (7)$$

The dissociation processes of molecular alkali-metal iodides, eq. (6). The dissociation process shown in eq. (5) is a typical electrolytic bond fission requiring high energy, but the process shown in eq. (6) is a simple dissociation to neutral molecules, **P** and **M—I** from **P—M—I**. Therefore, the ΔE_D values for eq. (6) should be much smaller than those for eq. (5). The ΔE_D , $\Delta E_D(\text{fCP})$ and $\Delta E_D(\text{GCP})$ values of the SCSs and DCSs are shown in Table 3. The ΔE_D values shown in Table 3 were in the range of $10.9 \sim 25.9$ and $17.8 \sim 38.0 \text{ kcal mol}^{-1}$ for the SCSs and DCSs, respectively, and smaller by *ca.* 80 kcal mol^{-1} than those for eq. (5), as expected. Nevertheless, the general trends were nearly the same as those found in eq. (5), i.e., the ΔE_D values decreased in the order $\text{P—Li—I} > \text{P—Na—I} > \text{P—K—I}$, and the ΔE_D values for the DCSs were much larger than those for the corresponding SCSs.

On the other hand, as can be seen in Table 3, the $\Delta E_D(\text{fCP})$ values in the SCSs were slightly smaller than the corresponding CP-uncorrected ΔE_D values, indicating that the $|\Delta E_{\text{basis}}|$ terms overweighed the unfavorable ΔE_{def} terms. However, in most cases of the DCSs, the $\Delta E_D(\text{fCP})$ values were larger than the corresponding ΔE_D values, because the ΔE_{def} term was much larger than the $|\Delta E_{\text{basis}}|$ term, as shown in Table 4. These results can easily be explained. In the DCSs, the **M—I** fragment interacted concurrently with two X sites of the ligand, and thus its structural deformation should be larger since the twisted bonds in the $\text{X—CH}_2\text{—CH}_2\text{—X}$ fragment were released during the decomposi-

Table 3. The calculated dissociation energies (in kcal mol⁻¹) for eq. (6) in the SCS and DCS complexes

	SCS			DCS		
	ΔE_D	ΔE_D (fCP)	ΔE_D (GCP)	ΔE_D	ΔE_D (fCP)	ΔE_D (GCP)
I—Li—I	22.9	21.4	20.8	34.8	35.8	32.2
I—Na—I	15.1	14.1	13.7	25.1	24.9	22.9
I—K—I	10.9	10.4	9.9	17.8	18.3	16.5
II—Li—I	25.9	24.5	23.8	35.8	40.2	33.3
II—Na—I	18.7	18.0	16.8	25.5	28.8	23.2
II—K—I	13.4	12.5	11.9	19.2	22.9	17.3
III—Li—I	25.1	23.4	22.7	38.0	38.6	35.2
III—Na—I	17.0	15.4	14.9	26.9	26.3	24.3
III—K—I	11.7	10.8	10.3	18.1	18.4	16.4

Table 4. The ΔE_{def} and ΔE_{basis} (in kcal mol⁻¹) for eq. (6) in the SCS and DCS complexes

	SCS		DCS	
	ΔE_{def}	ΔE_{basis}	ΔE_{def}	ΔE_{basis}
I—Li—I	0.6	-2.1	3.7	-2.7
I—Na—I	0.4	-1.4	2.0	-2.2
I—K—I	0.4	-1.0	1.8	-1.3
II—Li—I	0.7	-2.1	6.8	-2.4
II—Na—I	1.2	-1.9	5.6	-2.3
II—K—I	0.6	-1.5	5.6	-1.9
III—Li—I	0.8	-2.4	3.4	-2.9
III—Na—I	0.5	-2.1	2.1	-2.6
III—K—I	0.4	-1.3	2.0	-1.7

tion processes (see Scheme 1). In the SCSs, however, there was no need to twist the bonds, since the **M—I** fragment interacted with only one X site of the ligand. As a result, the structural deformation during the decomposition processes was smaller in the SCSs than that in the DCSs.

Table 3 shows that the $\Delta E_D(GCP)$ values for the SCSs were smaller by 1.0 ~ 2.4 kcal mol⁻¹ than the corresponding ΔE_D values. The differences, $\delta\Delta E_D(GCP)$, were very similar to those (1.4 ~ 2.9 kcal mol⁻¹) obtained from eq. (5), even if the ΔE_D values for eq. (5) were much larger than those for eq. (6). In the DCSs, the $\delta\Delta E_D(GCP)$ values obtained from eq. (6) (1.3 ~ 2.8 kcal mol⁻¹) were also similar to those obtained from eq. (5) (1.6 ~ 2.8 kcal mol⁻¹). Moreover, the $\delta\Delta E_D(GCP)$ values decreased in the same order, **P—Li—I** > **P—Na—I** > **P—K—I**, in both cases. This indicated that the ΔE_{basis} values were similar for the dissociation processes described in eqs. (5) and (6). These results were somewhat confusing, since the dissociation modes were different, and the ΔE_D values were also very different from each other. Nevertheless, this could be easily understandable: the dissociation processes of eqs. (5) and (6) produced two different sub-units in the product side, A and B, i.e., A = **P—M⁺** and B = **I⁻** for eq. (5) and A' = **P** and B' = **M—I** for eq. (6). However, the supermolecule was the same for both eqs., i.e., AB = A'B' =

P—M—I. Therefore, the $\delta\Delta E_D(GCP)$ values for eqs. (5) and (6) could be represented as eqs. (8) and (9), respectively, by modifying eq. (7). In eqs. (8) and (9), the number of basis sets for fragment A was obviously larger than that for the fragment A', since the fragment A (= **P—M⁺**) was larger in size than A' (= **P**). This indicated that the basis set effect for A' was larger than that for A since the same basis set AB was employed, i.e., $\Delta E_{basis}(A') > \Delta E_{basis}(A)$. On the contrary, for the fragments B (= **I⁻**) and B' (= **M—I**), the basis set effect was reversed, i.e., $\Delta E_{basis}(B) > \Delta E_{basis}(B')$. For example, in the dissociation process for the DCS complex of **I—Li—I**, the ΔE_{basis} (A = **I—Li⁺**) and ΔE_{basis} (A' = **I**) values were -0.1 and -1.2 kcal mol⁻¹, indicating that the basis set effect was larger by 1.1 kcal mol⁻¹ for A'. However, the ΔE_{basis} (B = **I⁻**) and ΔE_{basis} (B' = **LiI**) values were -2.4 and -1.5 kcal mol⁻¹, indicating that the basis set effect of B was 0.9 kcal mol⁻¹ larger than that of B'. Since these two effects were cancelled out, the $\delta\Delta E_D(GCP)$ values in eqs. (8) and (9) became similar. Therefore, the $\Delta E_D(GCP)$ could be more reliable than the $\Delta E_D(fCP)$ in correcting the pure basis set effects if the decomposition (or complexation) process produces different fragments from the same initial complex.

$$\begin{aligned} \delta\Delta E(GCP, eq(5)) \\ = \{E_{AB}^{AB}(A) - E_{AB}^A(A)\} + \{E_{AB}^{AB}(B) - E_{AB}^B(B)\} \\ = \Delta E_{basis}(A) + \Delta E_{basis}(B) \end{aligned} \quad (8)$$

$$\begin{aligned} \delta\Delta E(GCP, eq(6)) \\ = \{E_{AB}^{AB}(A') - E_{AB}^{A'}(A')\} + \{E_{AB}^{AB}(B') - E_{AB}^{B'}(B')\} \\ = \Delta E_{basis}(A') + \Delta E_{basis}(B') \end{aligned} \quad (9)$$

Effects of CP-corrections on the optimized geometries. The intermolecular distances between the ligands and alkali-metal iodides in the complexes could be lengthened when the CP correction is considered, since the overestimation in the intermolecular interaction is minimized. Therefore, in this work, the effects of the CP correction on the equilibrium geometries were examined by using the three cases of CP corrections; the complexes formed from (i) the two sub-units, **P** and **M—I**, (ii) the two sub-units, **P—M⁺** and **I⁻**, and (iii) the three sub-units, **P**, **M⁺** and **I⁻**. These calculations were performed using the counterpoise = n option in Gaussian 03 (where n refers to the number of fragments comprising the complex). The optimized bond lengths between X and **M⁺** (d_{X-M^+}) and between **M⁺** and **I⁻** ($d_{M^+-I^-}$) are summarized in Figures 1 and 2. As expected, in the case of (iii) both the corrected d_{X-M^+} and $d_{M^+-I^-}$ were lengthened compared to the uncorrected ones. Likewise, the corrected d_{X-M^+} in the case of (i) and $d_{M^+-I^-}$ in the case of (ii) were also lengthened as compared to the corresponding uncorrected ones.

However, interestingly, the corrected $d_{M^+-I^-}$ in the case of (i) was also lengthened slightly, except for $d_{K^+-I^-}$, even though we only considered the CP correction between X and **M⁺** (d_{X-M^+}). Similarly, the corrected d_{X-M^+} in the case of (ii) was also lengthened in all cases, although we only considered the CP corrections between **M⁺** and **I⁻** ($d_{M^+-I^-}$). In general, the d_{X-M^+} ($d_{M^+-I^-}$) would be expected to be shortened when the $d_{M^+-I^-}$ (d_{X-M^+}) was

Figure 1. Optimized bond lengths (in Å) using the three cases of CP corrections in the SCS. The values shown on the left and right sides of each structure are d_{X-M^+} and $d_{M^+-I^-}$, respectively. From top to bottom, the bond lengths are shown in the order: CP-uncorrected, case (i), case (ii), and case (iii).

Figure 2. Optimized bond lengths (in Å) using the three cases of CP corrections in the DCS. The values shown on the left and right sides of each structure are d_{X-M^+} (average of two d_{X-M^+} values) and $d_{M^+-I^-}$, respectively. From top to bottom, the bond lengths are shown in the order: CP-uncorrected, case (i), case (ii), and case (iii).

Table 5. The calculated dissociation energies (in kcal mol⁻¹) for the dissociation process of $\mathbf{P}-\mathbf{M}-\mathbf{I} \rightarrow \mathbf{P} + \mathbf{M}^+ + \mathbf{I}^-$ in the SCS and DCS complexes.

	SCS			DCS		
	ΔE_D	ΔE_D (GCP)	ΔE_D (RCP)	ΔE_D	ΔE_D (GCP)	ΔE_D (RCP)
I —Li—I	161.9	158.6	158.7	173.9	170.1	170.2
I —Na—I	136.7	134.4	134.4	146.7	143.7	143.8
I —K—I	115.8	114.3	114.3	122.8	120.9	120.9
II —Li—I	165.0	161.7	161.9	174.8	171.4	171.4
II —Na—I	140.3	137.5	137.5	147.1	144.0	144.1
II —K—I	118.4	116.3	116.5	124.1	121.8	121.9
III —Li—I	164.1	160.7	160.8	177.1	173.2	173.4
III —Na—I	138.5	135.7	135.8	148.4	145.1	145.2
III —K—I	116.6	114.8	114.8	123.0	120.8	120.9

lengthened by the CP correction, because the bonding interaction between **P** and $\mathbf{M}^+$ ($\mathbf{M}^+$ and $\mathbf{I}^-$) in the complex was reinforced as the bonding interaction between $\mathbf{M}^+$ and $\mathbf{I}^-$ (**P** and $\mathbf{M}^+$) was weakened by the CP correction. Therefore, these results seemed to be strange at first sight: When the CP corrections between dimer and monomer units were considered for the hydrogen-bonded water trimer, (H₂O)₃, and ammonia trimer, (NH₃)₃, the interacting bond lengths in the dimers were shortened and the bond lengths between the dimers and monomers were lengthened, as would be expected.¹⁹ Similarly, in trimer complexes consisting of two neutral species and a cation, such as C₂H₄---M⁺---C₂H₄, the same results were obtained.¹⁹ However, in the various trimers formed from the strong ionic-interactions such as (CH₃)₂O---M⁺---Y⁻ and C₂H₄---M⁺---Y⁻, where M⁺ is a metal cation and Y⁻ is a halide anion, the variations in the bond lengths as a result of the CP corrections were the same as those found in this work, i.e., when the CP corrections between M⁺ and Y⁻ (or between neutral ligands and M⁺) were considered, both the bond lengths between neutral ligands and M⁺, and between M⁺ and Y⁻ were elongated simultaneously.¹⁹ These mysterious results may be due to the strong electrostatic interactions between cation and anion ligands in complexes containing an ionic species. Characterizing the effect of the CP corrections on the optimized geometries for a variety of trimer complexes is in progress in our lab.

For weak complexes having a flat potential energy surface (PES), some researchers have reported significant differences between the critical geometries of the BSSE-corrected and -uncorrected PESs.²⁰ However, despite the changes in the bond lengths discussed above, the differences in the bond lengths between the corrected and the uncorrected, $\delta d [= d(\text{corrected}) - d(\text{uncorrected})]$, were small (less than 0.02 Å in most cases). Such small changes suggested that the effect of the CP correction on the optimized geometries of the supermolecule was also negligibly small. In other words, the dissociation energies calculated at the CP corrected PES, known as $\Delta E_D(\text{RCP})$, were very similar to the $\Delta E_D(\text{GCP})$ values obtained at the CP uncorrected PES due to small changes in molecular geometries. To confirm this, we examined the ΔE_D , $\Delta E_D(\text{GCP})$ and $\Delta E_D(\text{RCP})$ values for the dissociation process of $\mathbf{P}-\mathbf{M}-\mathbf{I} \rightarrow \mathbf{P} + \mathbf{M}^+ + \mathbf{I}^-$ in Table 5.

This dissociation process could have the largest CP corrections, since the dissociation produced three subunits. As expected, the differences between the uncorrected ΔE_D and the corrected $\Delta E_D(\text{GCP})$ —i.e., the effects of the CP correction—were as large as about 1.5 ~ 4 kcal mol⁻¹, but the differences between the $\Delta E_D(\text{GCP})$ and the $\Delta E_D(\text{RCP})$ were negligibly small (ca. 0.1 kcal mol⁻¹). This implied that the CP method calculated from eq. 4 could be reliable for organo-alkali metal iodide complexes.

Conclusions

In the dissociation of organo-alkali metal iodides, the ΔE_D values increased in the order **I**—K—I < **I**—Na—I < **I**—Li—I for both the dissociation processes of eqs. (5) and (6). For the dissociation process of eq. (5), the ΔE_D values for the SCSs were much smaller than those for the corresponding molecular alkali-metal iodides, since the polymer ligands stabilized the dissolved alkali-metal cations by electrostatic interaction. The ΔE_D values for the DCSs were decreased further by about 10 (Li⁺) ~ 5 kcal mol⁻¹ (K⁺) compared to the corresponding values for the SCSs due to a stronger electrostatic interaction. This stabilization effect could be one of the reasons why the metal salts dissolved easily in polymer electrolytes. On the other hand, when BSSE effects were considered, the fCP correction was found to be inadequate in some cases because of the large geometrical deformation caused by tight binding of the subunits, thus making the fCP corrections possibly inadequate when the molecular unit(s) experienced relatively large deformation. The incorporation of geometrical relaxation *via* the GCP method, as expressed in eq. (4), improved the results. When the molecular structures were re-optimized on the CP-corrected PES (the RCP method), the geometrical parameters showed no appreciable changes from the CP-uncorrected PES, and $\Delta E_D(\text{GCP})$ was virtually the same as $\Delta E_D(\text{RCP})$. This work again confirmed the capacity of the GCP method to generate reliable results in the study of the organo-alkali metal complexes.

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