

Application of Molar Volumes Obtained From a Solvent Extraction Method for Estimation of Sizes of Metal Complexes With Crown Ethers in Phases

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Abstract

Molar volumes (V_j) of ion-pair complexes ($MLA_z = j$; $z = 1, 2$) and simple complex ions (CdL^{2+}) without a pairing anion A^- obtained at 298 K from the plots of the regular solution theory and the geometrical relation $V_j = (4\pi/3)R_j^3$ were used for an estimation of their apparent radii (R_j) in liquid phases. Here, the cases for $M^{z+} = Li^+-Cs^+$, Cd^{2+} , and Pb^{2+} and $L = 18$ -crown-6 ether (18C6) and benzo-18C6 (B18C6) with $A^- = Cl^-I^-$ and picrate ion (Pic^-) were examined. The thus-estimated R_j values were related to $h(ML^+)$, λ_{max} , and $(r_+ + r_-)$ values, where these symbols refer to the number of water molecules attached to the univalent complex ions, ML^+ , extracted into water-saturated nitrobenzene, absorption maxima of Pic^- with ML^+ in water-saturated chloroform, and the sum in an effective ionic radius, r_+ or r_- , between the central M^{z+} and the pairing A^- , respectively. The data points of $j = Li(18C6)Pic$, $Na(18C6)Pic$, $M(B18C6)Pic$ with $M = Na-Rb(I)$, $Cd(18C6)^{2+}$, $Cd(18C6)Cl_2$, $Cd(18C6)Br_2$, and $Cd(18C6)I_2$ showed larger deviations from the line of $R_j = (r_+ + r_-)$. While $j = M(18C6)Pic$ with $M = K-Cs(I)$ and $M(18C6)Pic_2$ with $Cd(II)$ and $Pb(II)$ were on the line. It was demonstrated that essentially the former groups are present as water-separated and -shared ion pairs in the phases, while the latter ones as contact pairs.

Keywords: molar volume, apparent radii, crown ether complexes, regular solution theory plot, ion pair extraction

1. Introduction

Crown compounds (L) extract alkali and alkaline-earth metal ions (M^{z+} ; $z = 1, 2$) from water into various diluents (Yajima et al., 2000; Takeda, 2002; Levitskaia et al., 2007; Makri k et al., 2008; Kudo et al., 1990; Kudo et al., 2017a; Kudo et al., 2017b; Zakurdaeva et al., 2018), such as nitrobenzene (NB) and chloroform (CF). Particularly, the extraction behaviors of alkali metal picrates ($LiPic-CsPic$) have been reported so far for $L = 18$ -crown-6 ether (18C6) and its benzo-derivatives, benzo-18C6 (B18C6) and dibenzo-18C6 (DB18C6) (Takeda, 2002; Yajima et al., 2000). In course of such studies, Takeda and coworkers have analyzed their extraction systems by applying the regular solution theory (RST) for the systems and then determined the solubility parameters and molar volumes ($V_j/cm^3 mol^{-1}$) of $L (= j)$ and its ion pair complexes, ML^+Pic^- (Takeda, 2002). On the other hand, our groups have systematically studied the $Cd(II)$ and $Pb(II)$ extraction with 18C6 (Kudo et al., 2018; Kudo & Tomokata, 2018; Kudo et al., 2014; Kudo et al., 2015; Kudo et al., 2013a; Kudo et al., 2013b) or B18C6 (Kudo et al., 2017a) into various diluents and applied the same RST analyses for their systems (Kudo et al., 2018; Kudo & Tomokata, 2018; Kudo et al., 2014; Kudo et al., 2015; Kudo et al., 2013a). Here the analyses are based on the plots of $\log K_{ex,ip}$ vs. $\log K_{D,L}$; the symbols $K_{ex,ip}$ and $K_{D,L}$ denote an ion-pair extraction constant of complex ions, ML^{z+} , with A^- into an organic (org) phase and a distribution constant of the free L into the org one, respectively. In such studies, we developed a procedure which estimates apparent radii (R_j) of the complex ion CdL^{2+} at $L = 18C6$ and those of its ion pair complexes $CdLA_2$ ($A^- = Cl^-I^-$, Pic^-) in phases from the experimental V_j values (Kudo et al., 2018). Consequently, it has been clarified that the R_j values depend on the Cd-A bond lengths in the crystals, such as $Cd(18C6)A_2$ with $A(-I) = Cl-I$ (Kudo et al., 2018).

In the present work, we tried to extend such a procedure to the MPic extraction systems with 18C6 and B18C6 and made discussion for the R_j in the $Cd(II)$ extraction systems (Kudo et al., 2018) more quantitative. In particular, it was demonstrated that the ion pair complexes, $M(18C6)Pic_z$ with $M = K-Cs$ at $z = 1$ and with $M = Cd$ and Pb at $z = 2$, were present as contact ion pairs.

2. Results and Discussion

2.1 Basic Procedure for an R_j Estimation

According to Takeda's study (Takeda, 2002) in which the RST has been applied for extraction systems with MA and L, the relation of $\log K_{\text{ex,ip}}$ with $\log K_{\text{D,L}}$ has been derived as

$$\log K_{\text{ex,ip}} = (V_{\text{MLA}}/V_{\text{L}})\log K_{\text{D,L}} + f(C) + \log K_1, \quad (1)$$

where V_j , $f(C)$, and K_1 denote the molar volume of $j = \text{MLA}$ and L , a function with cohesive energy densities (C/J cm^{-3}), and an ion-pair formation constant ($\text{mol}^{-1} \text{dm}^3$) for MLA in water (phase), respectively. Using the relation of $\log K_{\text{ex,ip}} = \log K_{\text{ex}} + \log K_{\text{D,L}} - \log K_{\text{ML}}$ (Takeda & Gotō, 1979; Takeda & Katō, 1979), one can easily obtain the $K_{\text{ex,ip}}$ values from the extraction experiments and the $K_{\text{D,L}}$ values from the reference (Takeda, 2002). Here, the symbols, K_{ex} and K_{ML} , denote an overall extraction constant ($= [\text{MLA}]_{\text{org}}/[\text{M}^+][\text{L}]_{\text{org}}[\text{A}^-]$) and a complex formation constant ($= [\text{ML}^+]/[\text{M}^+][\text{L}]$) for ML^+ in water, respectively. So if the V_{L} values are determined with some methods (Takeda, 2002; Bernal, 2001), then we can immediately obtain the V_{MLA} ones from the slopes of the $\log K_{\text{ex,ip}}$ -vs.- $\log K_{\text{D,L}}$ plots, called the RST plots (Takeda, 2002; Yajima et al., 2000). Table 1 summarizes the thus-obtained V_j values reported previously in the reference (Takeda, 2002) for the alkali metal picrate (MPic) extraction systems with $\text{L} = \text{18C6}$ and B18C6 .

Table 1. Fundamental data for the MLPic extraction systems at 298 K

M ($r_+/ \text{Å}$) ^a	V_j^b ($^{\circ}$)/ $\text{cm}^3 \text{mol}^{-1}$		$R_j/\text{Å}$		$(r_+ + r_-^a)/\text{Å}$
	L = 18C6	B18C6	18C6	B18C6	
Li (0.76)	326 (47)	--- ^f	5.1 ± 0.2	--- ^f	4.11
Na (1.02)	294 (48)	366 (34)	4.9 ± 0.3	5.3 ± 0.2	4.37
K (1.38)	248 (29)	354 (32)	4.6 ± 0.2	5.2 ± 0.2	4.73
Rb (1.52)	267 (43)	393 (35)	4.7 ± 0.3	5.4 ± 0.2	4.87
Cs (1.67)	336 (45)	--- ^f	5.1 ± 0.2	--- ^f	5.02

Table 1 (continued)

M	$h(\text{ML}^+)^d$ for NB		$\lambda_{\text{max}}^e/\text{nm}$ for CF	
	L = 18C6	B18C6	18C6	B18C6
Li	2.5	2.6	352	--- ^f
Na	1.2	1.1	360	362
K	0.3	0.4	364	363
Rb	0.3	0.2	364	363
Cs	0.1	0.2	363	364

^a Effective ionic radii of 6-coordinated ions. See Refs. Shannon, 1976; Katsuta et al., 2007. ^b Molar volumes determined by the RST plots. See Ref. Takeda, 2002. ^c Standard errors. ^d See the text and Ref. Iwachido et al., 1980. ^e See the text and Ref. Kudo et al., 1990. ^f Not determined or reported.

After the V_j determination with the plots, we calculated the R_j values from the following procedure (Kudo et al., 2018). First, we thought the shape of $j = \text{MLPic}$ or ML^+ to be approximately a globe with the radius R_j and then the V_j values in a $\text{cm}^3 \text{mol}^{-1}$ unit divided by $(6.0221 \times 10^{23} \text{mol}^{-1})(10^{-24} \text{cm}^3 \text{Å}^{-3}) (= 0.60221 \text{cm}^3 \text{Å}^{-3} \text{mol}^{-1})$ were converted to those in a $\text{Å}^3 \text{molecule}^{-1}$ unit. Lastly, we calculated these values from the geometrical relation, $V_j = (4\pi/3)R_j^3$, and these converted V_j values. The results are listed in Table 1, together with the $h(\text{ML}^+)$ and λ_{max} values reported before. Here the symbols $h(\text{ML}^+)$ and λ_{max} refer to the number of water molecules attached to ML^+ extracted into water-saturated NB (Iwachido et al, 1980) and absorption maxima (nm) of species with Pic^- in water-saturated CF (Kudo et al., 1990), respectively.

The same is essentially true of the MLA_2 extraction systems. As similar to Eq. (1), the following equation (Kudo & Tomokata, 2018) for the MA_2 extraction with L was applied.

$$\log K_{\text{ex,ip}} = (V_{\text{MLA}_2}/V_{\text{L}})\log K_{\text{D,L}} + g(C) + \log \beta_2, \quad (2)$$

where the symbols $K_{\text{ex,ip}}$ and β_2 are defined as $[\text{MLA}_2]_{\text{org}}/[\text{ML}^{2+}][\text{A}^-]^2$ and $[\text{MLA}_2]/[\text{ML}^{2+}][\text{A}^-]^2$, respectively. Also, the function of $g(C)$ corresponds to that of $f(C)$ in Eq. (1).

2.2 For Correlations of the Parameters $h(ML^+)$ and λ_{\max}^{-1} With Effective Ionic Radii r_+

In order to examine meanings of these parameters, we plotted $h(ML^+)$ for the NB system and λ_{\max}^{-1} for the CF system against r_+^{-1} for $M = \text{Li-Cs(I)}$ and $L = 18\text{C6}$ (see Table 1 for their data). Both the plots showed positive correlation: their correlation coefficients were 0.98₈ for the former and 0.959 for the latter (Figs. 1 & 2, respectively). These findings indicate that the both parameters are essentially proportional to the coulombic forces.

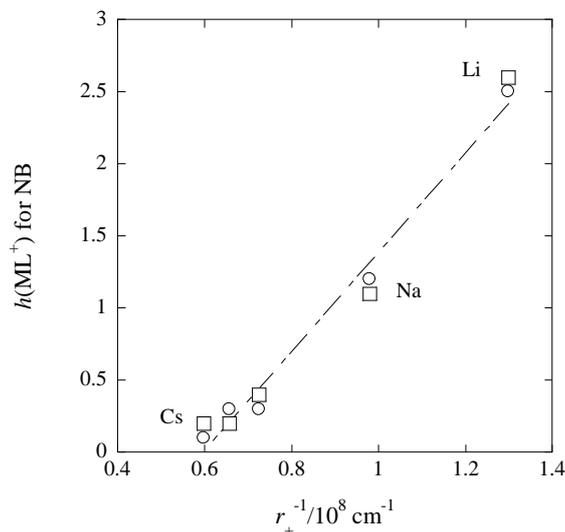


Figure 1. Plots of $h(ML^+)$ vs. r_+^{-1} for the NB extraction systems with $L = 18\text{C6}$ (circle) and $\text{B}18\text{C6}$ (square). The regression line is due to the 18C6 system: $h(\text{M}18\text{C6}^+) = 3.4_0/r_+ - 2.0_1$

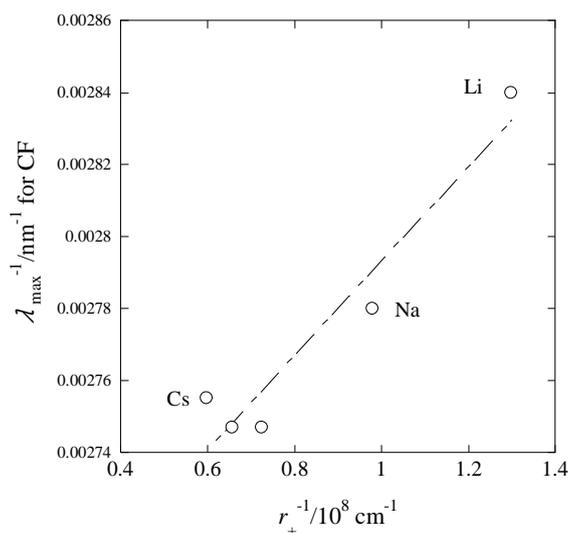


Figure 2. Plot of λ_{\max}^{-1} vs. r_+^{-1} for the CF extraction system with $\text{M}(18\text{C6})\text{Pic}$

The $h(\text{M}18\text{C6}^+)$ values directly reflect the strength of the ion-dipole interaction between M^+ and H_2O , namely the strength of the $M^+\text{-OH}_2$ bond. The $h(\text{NaL}^+)$ values were in the order $L = \text{benzo-15-crown-5 ether}\{\text{B}15\text{C}5; h(\text{NaL}^+) = 0.8\} < 15\text{C}5 (0.9) < \text{B}18\text{C}6 (1.1) < 18\text{C}6 (1.2)$ (Iwachido et al., 1980). This order was the same as that of the logarithms of the average $K_{1,\text{NB}}$ values (Kudo et al., 2017a), where $K_{1,\text{NB}}$ was defined as $[\text{NaLPic}]_{\text{NB}}/[\text{NaL}^+]_{\text{NB}}[\text{Pic}^-]_{\text{NB}}$. Therefore, we assumed that the $h(ML^+)$ values reflect the comparable number of water molecules attached to the $ML^+\text{Pic}^-$ extracted into the NB phase. Similarly, the λ_{\max}^{-1} values reflect a change of the electronic state on Pic^- due to the ion-ion interaction and are indirect parameters for the interaction between M^+ and Pic^- .

Consequently, the both parameters mainly depend on the strength of the electrostatic interaction between M^+ in/on 18C6 and H_2O or Pic^- , not scarcely that between “ $\text{M}18\text{C6}^+$ ” and H_2O or Pic^- , in the NB or CF phase. That is, Pic^- and H_2O do not recognize the size of the $\text{M}18\text{C6}^+$, but mainly do that of M^+ . Seeing from another point of view, $h(ML^+)$ is the direct

parameter for the interaction between M^+ and H_2O (schematically LM^+-OH_2), but becomes the indirect one in the present application for MLPic. On the other hand, λ_{\max}^{-1} is the indirect parameter for the interaction with M^+ and Pic^- (LM^+-Pic^-), but becomes the direct one for its application.

Obviously, the $h(ML^+)$ plot showed the higher sensitivity than the λ_{\max}^{-1} one at $L = 18C6$, owing to the magnitudes of the plot's slopes. The slope $\Delta h(ML^+)/\Delta(r_+^{-1})$ was 3.4 \AA^{-1} (see Fig. 1) and $\Delta(\lambda_{\max}^{-1})/\Delta(r_+^{-1})$ was $0.00013 \text{ nm}^{-1} \text{ \AA}^{-1}$.

On the basis of the above results, we can see that, in MLPic, the smaller the sizes of the central M^+ , the larger the amounts of H_2O which interacts with its M^+ become. Also, the smaller their sizes, the larger the energetic change of the electronic state on Pic^- become. It is highly important that the two parameters fundamentally express the interaction with the central M^+ in/on L.

2.3 For the Plots of R_j vs. r_+ , $(r_+ + r_-)$, $h(ML^+)$, and λ_{\max}^{-1} for the MLPic System

These plots were of all V-shaped curves as shown in Fig. 3. They were the plots with the inflection points at $M = K(I)$. Especially, the plot (Fig. 3) of R_j vs. r_+ is important, because the line produced for $M(I) = K\text{-Cs}$ has a positive slope ($\approx +1.7$): the R_{MLPic} order was $M(I) = Li > Na > K < Rb < Cs$ at $L = 18C6$ with an increase in r_+ . This fact that their R_j values are proportional to the r_+ ones in the $M = K\text{-Cs}(I)$ range suggests the direct interaction between the M^+ in/on L and Pic^- {see the $(r_+ + r_-)$ values in Table 1 for comparison}. On the other hand, the same plot showed us an abnormality of the R_j values at $j = Li(18C6)Pic$ and $Na(18C6)Pic$. This suggests an indirect interaction between M^+ in $18C6$ and Pic^- , for example the interaction between them via hydrated H_2O .

In contrast with the R_j vs. r_+ plot in Fig. 3, the R_j values were proportional to the $h(M18C6^+)$ in the M range of Li-K(I): the $R_{M(18C6)Pic}$ order was $M(I) = Cs > Rb > K < Na < Li$ with an increase in $h(M18C6^+)$. This order for Li-K(I) shows the hydration of these $M(18C6)Pic$ {and accordingly reflects the relation of $h(M18C6^+) \approx a/r_+ + b$ as shown in Fig. 1}. The same was also observed in the R_j vs. λ_{\max}^{-1} plot.

From the above results, we can see that $Li(18C6)^+Pic^-$ and $Na(18C6)^+Pic^-$ in the phases have a hydrated structure of M^+ in $18C6$, a wrapped one of M^+ by the flexible $18C6$, or do the mixture of their structures, since the ionic sizes of Li^+ and Na^+ (see Table 1) are smaller than the cavity size $\{= 1.34\text{-}1.43 \text{ \AA}$ (Takeda, 1991)} of $18C6$. That is, these complexes are suggested to be a water-separated, L-separated, or water-shared ion pairs.

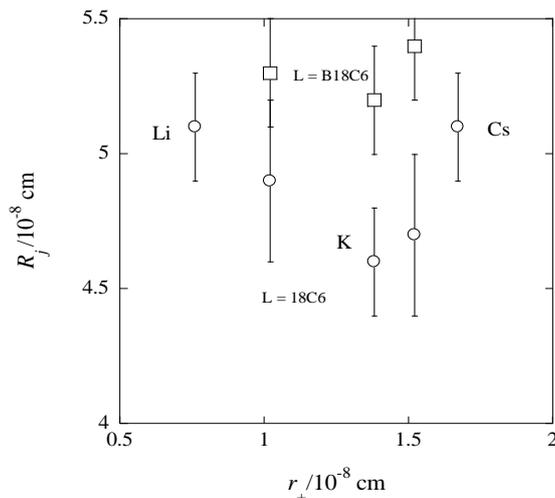


Figure 3. Plots of R_j vs. r_+ for the MLPic systems with $M = Li\text{-Cs}(I)$ and $L = 18C6$ (circle) and $B18C6$ (square)

The above structures were self-consistently supported by Fig. 4. The plots of $j = K(18C6)Pic$ to $Cs(18C6)Pic$ were on the hypothetical straight line of $R_j = (r_+ + r_A)$ at $A = Pic^-$ within the calculation errors, while those of $j = Li(18C6)Pic$ and $Na(18C6)Pic$ deviated largely from its line. Here the symbol r_A is equivalent with r_- in Table 1. These results indicate that the three formers are contact ion pairs. Also, these structures are not conflict with the fact that the $K_1^0(K)$ value $\{= [KLPic]/[KL^+][Pic^-] = 738 \text{ mol}^{-1} \text{ dm}^3$ at $I \rightarrow 0 \text{ mol dm}^{-3}$ (Kudo, 2013)} is larger than the $K_1^0(Li)$ and $K_1^0(Na)$ ones $\{= 52 \text{ \& } 62$ at $I \rightarrow 0$ (Kudo, 2013)} at $L = 18C6$. Here K_1 {see Eq. (1)} expresses the equilibrium in water, $ML(OH_2)_x^+ + Pic^- \rightleftharpoons ML(OH_2)_yPic + (x - y)H_2O$ at $x \geq y$. In such a reaction, $x > 0$ should be predicted for $M = Li(I)$ and $Na(I)$, while $x > y \approx 0$ for $K(I)$. For the structure of such $M18C6(OH_2)_x^+$ in water, it has been proposed with an X-ray diffraction study that one molecule of water interacts with $Na18C6^+$ and two ones of water do with $K18C6^+$ and $Cs18C6^+$ (Ozutsumi et al., 1989).

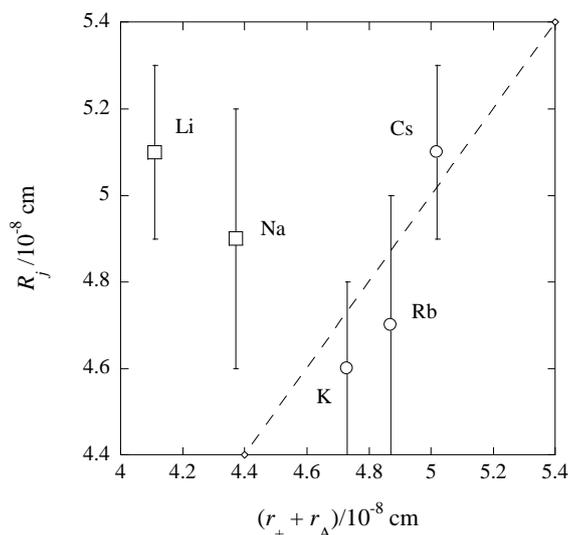


Figure 4. Plot of R_j vs. $(r_+ + r_-)$ for the M(18C6)Pic systems with M = Li, Na (square), and K-Cs (circle). The broken line is of $R_j = (r_+ + r_A)$ with A = Pic(-I)

The same is true of the MPic-B18C6 extraction system, although there were less data, compared with those of the 18C6 system (see Table 1). Additionally, a size effect of the benzo group seems to appear in the difference ($= 0.5\text{-}0.9 \text{ \AA}$) between the R_j and $(r_+ + r_-)$ values. Also, taking the hydrophobicity of the benzo group, the less-flexibility of the B18C6 skeleton, compared with the 18C6 one (Kudo et al., 2017a), and the finding of the $h(\text{MB18C6}^+)$ vs. r_+ plot (see Fig. 1) into account, we can imagine that the K(B18C6)Pic and Rb(B18C6)Pic are the contact ion pairs. The same analysis can be effective for the MPic-DB18C6 extraction system (Takeda, 2002; Yajima et al., 2000); see Ebata & Inokuchi 2012 in reference to the structure of MDB18C6⁺ in the gas phase.

2.4 For the Plots of R_j vs. $(r_+ + r_-)$ for the MLA_2 System

Table 2 lists the V_j and R_j values for the MLA_2 extraction systems with M = Cd(II) and Pb(II), L = 18C6 and B18C6, A = Cl(-I) and Pic(-I), and without A(-I) (Kudo et al., 2018), together with the $(r_+ + r_-)$ values. The V_{Cd18C6} values were obtained from pseudo-RST plots for the Cl(-I), Br(-I), and I(-I) extraction systems (Kudo & Tomokata, 2018; Kudo et al., 2013a; Kudo et al., 2018). These three values agreed with each other within calculation errors ($= \pm 0.4\text{-}0.6 \text{ \AA}$) listed in Table 2. This larger deviation may be caused by defects of conditions applied for the pseudo-plots. However, we cannot discuss this matter in more detail.

Table 2. V_j and R_j values for the MLA_2 extraction systems at 298 K

$\text{MLA}_2 (r_+/\text{\AA})^a$	$V_j^b (\text{cm}^3/\text{mol})^{-1}$		$R_j/\text{\AA}$		$(r_+^a + r_-)/\text{\AA}$
	L = 18C6	B18C6	18C6	B18C6	
CdLCl ₂ (1.81)	398 (96)	--- ^d	5.4 ± 0.4	--- ^d	2.76, 2.364 ^e , 2.3645 ^e
CdLBr ₂ (1.96)	248 (56)	--- ^d	4.6 ± 0.3	--- ^d	2.91, 2.506 ^e
CdLI ₂ (2.20)	160 (57)	--- ^d	4.0 ± 0.5	--- ^d	3.15, 2.692 ^e
CdLPic ₂ (3.35)	171 (47)	249 (49)	4.1 ± 0.4	4.6 ± 0.3	4.30
CdL ²⁺ (without A ⁻)	120 (64) ^f ,	--- ^d	3.6 ± 0.6^e ,	--- ^d	2.34 ⁱ , 2.31 ^j
	244 ± 61^g ,		4.6 ± 0.4^f ,		
	234 ± 75^h		4.5 ± 0.5^g		
PbLPic ₂ (3.35)	205 ± 57	--- ^d	4.3 ± 0.4	--- ^d	4.54, 2.68 ^k

^a Effective ionic radii of ions. For the 6-coordinated M(II), $r_+(\text{Cd}) = 0.95 \text{ \AA}$ & $r_+(\text{Pb}) = 1.19$. See Refs. Shannon, 1976; Katsuta et al., 2007. ^b Molar volumes determined by the RST & pseudo-RST plots. See Refs. Kudo & Tomokata, 2018; Kudo et al., 2013a; Kudo et al., 2018; Kudo et al., 2014. ^c Standard errors. ^d Not determined. ^e The $d_{\text{Cd-A}}$ values by X-ray diffraction measurements of crystals. See Refs. Paige & Richardson, 1983; Hazell, 1988; Kennedy, 1990. ^f Value for the I(-I) system. See Ref. Kudo et al., 2018. ^g Value for the Br(-I) system. See Ref. Kudo et al., 2013a. ^h Value for the Cl(-I)

system. See Ref. Kudo & Tomokata, 2018. ⁱ $r_{\text{Cd-OH}_2}$ value of $[\text{Cd}(\text{18C6})(\text{OH}_2)_2]^{2+}$ by DFT study. See Ref. Harrinton et al., 2009. ^j $r_{\text{Cd-OH}_2}$ value of $[\text{Cd}(\text{OH}_2)_6]^{2+}$ in water by X-ray diffraction measurements. See Ref. Ohtaki et al., 1974. ^k $r_{\text{Pb-ONO}_2}$ value of $[\text{Pb}(\text{NO}_3)_2(\text{18C6})]^{0}$ in crystal by X-ray diffraction measurements. See Ref. Rogers & Bond, 1992.

As similar to Fig. 4, Fig. 5 shows the plot of R_j vs. $(r_+ + r_-)$. As can be seen from this figure, the R_j values for $j = \text{Cd}(\text{18C6})\text{Pic}_2$ and $\text{Pb}(\text{18C6})\text{Pic}_2$ were comparably on the straight line of $R_j = (r_+ + r_-)$. Comparing these results with those for the $\text{M}(\text{18C6})\text{Pic}$ system, we can easily suppose that these two complexes with $\text{M}(\text{II})$ are of contact ion pairs in the phases. Since the $(r_+ + r_-)$ values were larger than the Cd-A bond lengths ($d_{\text{Cd-A}}$) in their crystals, Cl-Cd18C6-Cl, Br-Cd18C6-Br, and I-Cd18C6-I (Table 2), we thought here the former values to become a measure of their species “in solutions” for the comparison. In other words, this means that the line of $R_j = (r_+ + r_-)$ in Fig. 5 expresses an ionic bond character of the Cd-A bond appeared in the solutions (also refer to Fig. 4). Comparing R_j with $(r_+ + r_-)$ at $j = \text{Cd}(\text{B18C6})\text{Pic}_2$ in Table 2, this ion pair seems to be simply the contact form.

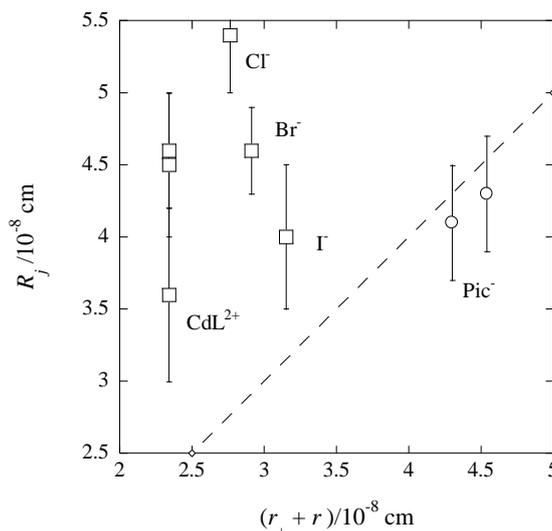


Figure 5. Plots of R_j vs. $(r_+ + r_-)$ for the $\text{M}(\text{18C6})\text{A}_2$ and Cd18C6^{2+} systems. The symbols were $\text{Cd}(\text{18C6})\text{A}_2$ (square) with $\text{A}^- = \text{Cl}^- - \text{I}^-$, Cd18C6^{2+} (square), and $\text{M}(\text{18C6})\text{Pic}_2$ (circle) with $\text{M}^{2+} = \text{Cd}^{2+}$ and Pb^{2+}

On the other hand, the other ion pairs and the complex ion can take the hydrated forms, such as $\text{A-Cd}(\text{18C6})(\text{OH}_2)_x\text{-A}$ and $\text{Cd}(\text{18C6})(\text{OH}_2)_x^{2+}$, in the phases, respectively. Such ion pairs are speculated to be the water-separated or water-shared form, because the donor numbers (DN) of the representative diluents, such as benzene ($DN = 0.1$), 1,2-dichloroethane (0), and NB (4.4), used in the extraction experiments are much smaller than that (33) of water (Izutsu, 2002; Gutmann, 1978). It is interesting that Cd18C6^{2+} shows the higher water affinity, as similar to $\text{Ca}(\text{18C6})(\text{OH}_2)_{4.7}^{2+}$ (Iwachido et al., 1980; Kudo et al., 2018).

3. Conclusion

It was proved that the R_j values are estimated from the V_j ones for the water/diluent systems determined with the RST and pseudo-RST plots and then reflect the sizes of MLA_z with $z = 1$ and 2 and CdL^{2+} in the corresponding phases. Although extraction experiments are needed for the about ten diluents, the proposed procedure can be convenient one, compared with some spectroscopic methods, such as X-ray diffraction analysis of solution samples. Unfortunately, it is now difficult to establish a liquid phase in which the objective species are present. However, its procedure can have the higher cost performance in such solution-chemical studies.

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