

CdI₂ Extraction with 18-Crown-6 Ether into Various Diluents: Classification of Extracted Cd(II) Complex Ions Based on the HSAB Principle

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Abstract

CdI₂ in water was extracted with 18-crown-6 ether (L) into 10 diluents at 298 K. The following equilibrium constants were determined or evaluated: some extraction constants ($K_{\text{ex}}/\text{mol}^{-3}\cdot\text{dm}^9$ & $K_{\text{ex,ip}}/\text{mol}^{-2}\cdot\text{dm}^6$ for CdLI₂, $K_{\text{ex}\pm}/\text{mol}^{-2}\cdot\text{dm}^6$ for CdLI⁺ with I[−], & $K_{\text{ex}2\pm}/\text{mol}^{-1}\cdot\text{dm}^3$ for CdL²⁺ with 2I[−]), conditional distribution constants ($K_{\text{D,I}}$ for I[−], $K_{\text{D,CdLI}}$ for CdLI⁺, & $K_{\text{D,CdL}}$ for CdL²⁺) between the two phases, and an ion-pair formation constant ($K_{\text{1,org}}/\text{mol}^{-1}\cdot\text{dm}^3$) for CdLI⁺ and that ($K_{\text{2,org}}/\text{mol}^{-1}\cdot\text{dm}^3$) for CdLI₂ in the organic (org) phases. Using the $K_{\text{1,org}}$ and $K_{\text{2,org}}$ values, acidities of the complex ions, CdL²⁺ and CdLA⁺ ($\text{A}^{-} = \text{I}^{-}, \text{Br}^{-}, \text{Cl}^{-}$), in the 11 diluents were classified by applying the HSAB rule. Especially, the CdLA⁺ ions were classified as the soft acids in 9 diluents. Also, molar volumes ($V_j/\text{cm}^3\cdot\text{mol}^{-1}$) of $j = \text{CdLI}_2$ and CdL²⁺ were determined with the regular-solution-theory plot of $\log K_{\text{ex,ip}}$ vs. $\log K_{\text{D,I}}$ and its pseudo-plot of $\log K_{\text{D,CdL}}$, respectively. Here, $K_{\text{D,L}}$ denotes the distribution constant of L between the two phases. So, sizes among CdLA₂ and CdL²⁺ were compared by using the V_j values. Additionally, some distribution equilibrium potentials (dep/V) between the water and org bulk phases were topically calculated from an equation of $K_{\text{D,I}}$ with $K_{\text{D,I}}^{\text{S}}$, where the symbol $K_{\text{D,I}}^{\text{S}}$ shows a standard distribution constant of I[−] at dep = 0 V for a given diluent.

Keywords

Ion-Pair Formation Constants, HSAB Acidity, Molar Volume, Conditional Distribution Constants, Distribution Equilibrium Potentials, Cadmium Iodide, 18-Crown-6 Ether

1. Introduction

It is well known that crown ethers (L) extract Cd(II) and Pb(II) salts, such as metal picrates (MPic₂) [1] [2] [3] [4] [5], the former chloride [6], and bromides [1] [6], into various diluents. Similar extraction behaviors into benzene (Bz) and nitrobenzene (NB) have been reported for Ca(II), Sr(II), and Ba(II) picrates with L [7] [8]. In these studies, the distribution equilibrium potentials (dep or $\Delta\phi_{eq}$) for monovalent anions (A⁻) between the water and diluent bulk phases and the ion-pair formation for ML²⁺ and MLA⁺ in the diluent phases saturated with water have been examined and clarified, respectively [1]-[6] [8]. For the latter [1] [2] [4] [6] [8], the reactivities of CdL²⁺ and CdLA⁺ with A⁻ = Cl⁻, Br⁻, and picrate ion Pic⁻ in various organic (org) phases have been quantitatively discussed at L = 18-crown-6 ether (18C6). The complex ions composed of a soft Cd²⁺ and hard L, Cd18C6²⁺ and CdB18C6²⁺, have been classified in terms of the HSAB rule [9] as the hard acids in water [10], where B18C6 refers to benzo-18C6. This classification would make the studies on reactivity of the Cd(II) complexes and properties of the diluent molecules in the extraction interesting. However, there were few comprehensive studies for the M(II) extraction systems with L and various diluents [11].

In the present paper, by doing extraction experiments of CdI₂ with 18C6 into ten diluents, we determined extraction constants, K_{ex} and $K_{ex\pm}$, and their related equilibrium constants, $K_{D,I}$ and $K_{Cd/CdL}$, [4] [5] at 298 K. Here, K_{ex} , $K_{ex\pm}$, $K_{D,I}$, and $K_{Cd/CdL}$ were defined as $[CdLI_2]_{org}/P$, $[CdLI^+]_{org}[I^-]_{org}/P$ with $P = [Cd^{2+}][L]_{org}[I^-]^2$, $[I^-]_{org}/[I^-]$, and $[CdL^{2+}]_{org}/[Cd^{2+}][L]_{org}$ [1]-[6], respectively. From these values and the thermodynamic relations, $K_{1,org}$ and $K_{2,org}$ values were evaluated:

$K_{1,org} = K_{ex\pm} / (K_{Cd/CdL} K_{D,I}^2)$ and $K_{2,org} = K_{ex} / K_{ex\pm}$ [4] [5] (see the Section 2.4). Using these evaluated $K_{1,org}$ and $K_{2,org}$ values, reaction properties of CdLA⁺ and CdL²⁺ with mainly A⁻ = I⁻, Br⁻, and Cl⁻ in the org or diluent phases were also classified based on the HSAB principle [9] [10] [11]. Moreover, molar volumes ($V/\text{cm}^3\cdot\text{mol}^{-1}$) of the ion-pair complex CdLI₂ and complex ion CdL²⁺ were determined at 298 K with the plots based on the regular solution theory (RST) [1] [2] [3] [4] [6] and then their comparable sizes were estimated from these V . On the basis of these data, the HSAB acidic and structural properties of the Cd(II) complexes with 18C6 were discussed independently.

2. Results and Discussion

2.1. Composition Determination of Cd(II) Species Extracted into Various Diluents

According to previous papers [1]-[6], the following equation was employed for the determination of the composition of Cd(II) species extracted into the org phases.

$$\log\left(D/[A^-]^{-2}\right) \approx \log[L]_{org} + \log K_{ex} \quad (1)$$

with D defined as $[Cd(II)]_{org}/([Cd(II)]_t - [Cd(II)]_{org})$ at A⁻ = I⁻ and L = 18C6.

This equation was derived approximately from the definition of K_{ex} [7] described in the introduction. Here, the symbols D , $[\text{Cd(II)}]_{\text{org}}$, and $[\text{Cd(II)}]_{\text{t}}$ denote an experimental distribution ratio for Cd(II), a measurement concentration of all the Cd(II) species extracted into the org phase determined by AAS, and a total concentration of CdI_2 included in the water phase at the beginning of the extraction experiment, respectively. When slopes obtained from the plots of $\log(D/[A^-]^2)$ vs. $\log[L]_{\text{org}}$ are unity, they would mean that the extracted species have the composition of Cd(II): L = 1:1 [1]-[7].

The experimental slopes were 0.95 at correlation coefficient (R) = 0.813 for the NB system, 1.03 at 0.989 for 1,2-dichloroethane (DCE), 0.97 at 0.939 for *o*-dichlorobenzene (*o*DCBz), 1.03 at 0.940 and 0.96 at 0.754 for dichloromethane (DCM), 1.07 at 0.883 for chlorobenzene (CBz), 1.08 at 0.959 for bromobenzene (BBz), 1.02 at 0.769 for chloroform (CF), 1.01 at 0.871 for Bz, 0.90 at 0.827 for toluene (TE), and 1.05 at 0.924 for *m*-xylene (*m*X). Here, the R values were obtained from the regression lines determined with the $\log(D/[I^-]^2)$ vs. $\log[18\text{C6}]_{\text{org}}$ plots. Also, the composition of I(-I) was speculated from the formal charge of Cd(II). This speculation was based on the experimental data plots of the $\log(D/[L]_{\text{Bz}})$ vs. $\log[\text{Pic}^-]$ with the slope of two [7]. These results indicated that the complexes composed of Cd(II):18C6:I(-I) = 1:1:2 were extracted into the employed ten diluents.

2.2. Determination of $K_{\text{D,L}}$, $K_{\text{ex}\pm}$, and K_{ex} by Using the Parameter

$$K_{\text{ex}}^{\text{mix}}$$

For the determination of $K_{\text{D,L}}$, $K_{\text{ex}\pm}$, and K_{ex} , we employed the parameter

$$K_{\text{ex}}^{\text{mix}} = [\text{Cd(II)}]_{\text{org}} / P \quad (2)$$

as similar to the previous papers [1]-[6]. Therefore, we can determine the $K_{\text{D,L}}$ and K_{ex} values from the plot of $\log K_{\text{ex}}^{\text{mix}}$ vs. $-\log([\text{Cd}^{2+}][\text{L}]_{\text{org}}[\text{I}^-])$ based on

$$K_{\text{ex}}^{\text{mix}} \approx K_{\text{ex}} + K_{\text{D,L}} / ([\text{Cd}^{2+}][\text{L}]_{\text{org}}[\text{I}^-]) \quad (2a)$$

while can do the $K_{\text{ex}\pm}$ and K_{ex} ones from that of $\log K_{\text{ex}}^{\text{mix}}$ vs. $-\log P^{1/2}$ on

$$K_{\text{ex}}^{\text{mix}} \approx K_{\text{ex}} + ([\text{CdLI}^+]_{\text{org}}[\text{I}^-]_{\text{org}} / P^2)^{1/2} = K_{\text{ex}} + (K_{\text{ex}\pm} / P)^{1/2} \quad (2b)$$

at L = 18C6; see the Section 3.3 for the detailed derivation of Equations (2)-(2b).

Figure 1 and **Figure 2** show examples of these plots for the present Cd(II) extraction systems and logarithmic values of these equilibrium constants were listed in **Table 1**. The K_{ex} values determined with Equation (2a) in the 5 diluent systems (**Table 1**) were in accordance with those with Equation (2b) within their experimental errors.

From the thermodynamic relation of $K_{\text{ex}} = K_{\text{CdL}}K_{\text{ex,ip}}/K_{\text{D,L}}$ [1]-[7], the $K_{\text{ex,ip}}$ values were evaluated at the same time (see **Table 1**). Here, the symbols K_{CdL} , $K_{\text{ex,ip}}$, and $K_{\text{D,L}}$ denote a complex formation constant ($=[\text{CdL}^{2+}]/[\text{Cd}^{2+}][\text{L}]$) [12] for CdL^{2+} in water, an ion-pair extraction constant ($=[\text{CdLI}_2]_{\text{org}}/[\text{CdL}^{2+}][\text{I}^-]^2$) of

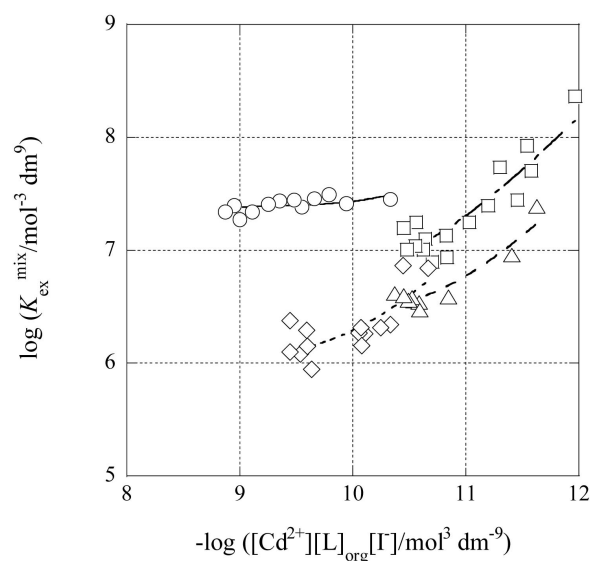


Figure 1. Plots of $\log K_{\text{ex}}^{\text{mix}}$ vs. $-\log([Cd^{2+}][L]_{\text{org}}/[I^-])$ based on Equation (2a) at $L = 18C6$. CdI_2 was extracted with L into NB (square), DCE (circle), BBz (triangle), and CF (diamond).

Table 1. Logarithmic values of $K_{D,I}$, $K_{\text{ex}\pm}$, K_{ex} , and $K_{\text{ex,ip}}$ for the CdI_2 extraction with 18C6 into various diluents at 298 K.

Diluent ^a	$I/\text{mol dm}^{-3}$	$\log K_{D,I}$	$\log K_{\text{ex}\pm}$	$\log K_{\text{ex}} ()^c$	$\log K_{\text{ex,ip}}^d$
NB	0.013	-3.83 ± 0.09	$1.4_8 \pm 0.1_7$	$6.7_5 \pm 0.1_6$ (--- ^e)	5.8_0
DCE	0.0063	$-3.4_7 \pm 0.2_7$	$1.3_5 \pm 0.3_7$	7.38 ± 0.02 (7.33 ± 0.04)	7.46
<i>o</i> DCBz	0.013	$-3.8_8 \pm 0.1_8$	$1.6_1 \pm 0.2_7$	$7.2_2 \pm 0.1_9$ (--- ^e)	6.1_4
DCM	0.013	$-4.2_0 \pm 0.2_1$	$0.8_5 \pm 0.4_8$	6.86 ± 0.06 ($6.7_2 \pm 0.1_8$)	7.51
	0.013	$-4.1_4 \pm 0.2_9$	$0.2_2 \pm 0.5_7$	$6.0_0 \pm 0.1_2$ ($5.8_7 \pm 0.3_8$)	6.7_4
CBz	0.013	$-4.6_9 \pm 0.1_3$	$-0.2_4 \pm 0.2_0$	$6.2_3 \pm 0.1_4$ (--- ^e)	5.2_1
BBz	0.013	-4.45 ± 0.09	$0.2_0 \pm 0.2_7$	6.38 ± 0.07 ($6.1_5 \pm 0.2_4$)	5.31
CF	0.013	$-4.0_3 \pm 0.1_3$	$0.5_5 \pm 0.2_9$	$6.0_1 \pm 0.1_1$ ($5.4_5 \pm 0.7_9$)	6.8_5
Bz	0.013	$-3.86_3 \pm 0.09_7$	$2.0_4 \pm 0.3_0$	7.68 ± 0.07 (--- ^e)	6.46
TE	0.013	$-4.4_6 \pm 0.2_8$	$0.9_2 \pm 0.6_5$	$7.3_1 \pm 0.1_5$ ($7.2_2 \pm 0.2_7$)	5.7_7
<i>m</i> X	0.013	$-4.0_9 \pm 0.2_6$	$1.0_6 \pm 0.2_0$	$7.3_6 \pm 0.1_4$ (--- ^e)	5.4_6

a. Abbreviations of the diluents were NB: nitrobenzene; DCE: 1,2-dichloroethane; *o*DCBz: *o*-dichlorobenzene; DCM: dichloromethane; CBu: 1-chlorobutane; CBz: chlorobenzene; BBz: bromobenzene; CF: chloroform; Bz: benzene; TE: toluene; *m*X: *m*-xylene; b. Ionic strength for the water phases; c. Values determined with Equation (2b); d. Calculated from $\log K_{\text{ex,ip}} = \log K_{\text{ex}} - \log K_{D,18C6} - \log K_{Cd18C6} = \log K_{\text{ex}} - \log K_{D,18C6} + 0.05$. See ref. [12]; e. Not determined with Equation (2b).

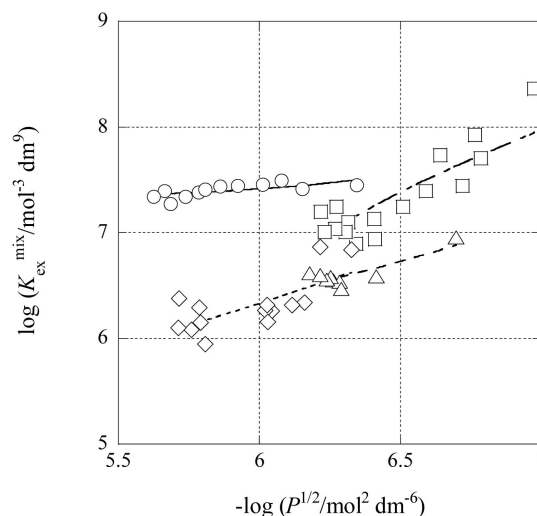


Figure 2. Plots of $\log K_{\text{ex}}^{\text{mix}}$ vs. $-\log P^{1/2}$ based on Equation (2b). CdI_2 was extracted with 18C6 into NB (square), DCE (circle), BBz (triangle), and CF (diamond).

CdLi_2 into the org phase, and a distribution constant ($=[\text{L}]_{\text{org}}/[\text{L}]$) [13] [14] of L into the org phase, respectively. As described below, the $K_{\text{ex,ip}}$ and $K_{\text{D,L}}$ values are employed for the RST plot [1]-[6] [13].

2.3. Estimation of Dep for Some Diluent Systems

The relation between dep or $\Delta\phi_{\text{eq}}$ and $K_{\text{D,A}}$ has been reported for these extraction systems [1]-[6] [8].

$$\Delta\phi_{\text{eq}} = (2.303RT/z_A F) (\log K_{\text{D,A}} - \log K_{\text{D,A}}^{\text{S}}) \quad (3)$$

$$= (0.05916/z_A) (\log K_{\text{D,A}} - \log K_{\text{D,A}}^{\text{S}}) \quad (3a)$$

at $T = 298$ K, where the symbols z_A and $K_{\text{D,A}}^{\text{S}}$ denote the formal charge of A^- with its sign and a standard distribution constant at dep = 0 V for an A^- transfer across the interface between the water and org bulk phases, respectively. The value of $K_{\text{D,A}}$ called a conditional distribution constant of A^- into the org phase changed in depending on species of M(II), L, and diluent molecule [1]-[6] [8].

Estimated dep values at $z_1 = -1$ were -0.01_0 V for the NB system, -0.06_4 for DCE, and 0.02_4 and 0.02_1 for DCM. Here, the following $\log K_{\text{D,L}}^{\text{S}}$ values at 298 K were used for these calculations: -4.0 [15] for NB, -4.56 [15] for DCE, and -3.790 [16] for DCM. The dep presences were clarified at least for these diluents systems, as similar to the results [1]-[6] [8] reported previously.

2.4. Determination of $K_{1,\text{org}}$ and $K_{2,\text{org}}$

Referring to the previous papers [1]-[6] [8] [17], the $K_{1,\text{org}}$ and $K_{2,\text{org}}$ values were obtained from

$$\begin{aligned} K_{1,\text{org}} &= [\text{CdLA}^+]_{\text{org}} / [\text{CdL}^{2+}]_{\text{org}} [\text{A}^-]_{\text{org}} \\ &= K_{\text{ex}\pm} / K_{\text{ex}2\pm} \approx K_{\text{ex}\pm} / (K_{\text{Cd/CdL}} K_{\text{D,A}}^2) \end{aligned} \quad (4)$$

and

$$K_{2,\text{org}} = [\text{CdLA}_2]_{\text{org}} / [\text{CdLA}^+]_{\text{org}} [\text{A}^-]_{\text{org}} = K_{\text{ex}} / K_{\text{ex}\pm} \quad (5)$$

for a given ionic strength (I_{org}) in the org phase. Here, the equilibrium constant $K_{\text{Cd/CdL}}$ has been assumed to be equal to $D/[L]_{\text{org}}$ [3] [5] [6] [17]. The thus-calculated values are listed in **Table 2**, together with the $K_{\text{Cd/CdL}}$ and their corresponding I_{org} values.

Figure 3 shows the $K_{1,\text{org}}$ and $K_{2,\text{org}}$ values with ten kinds of the diluents described in **Table 2**. The x -axis indicates the decrease of the diluent's polarities from No. 1 (NB) to 10 (mX). Except for the DCE and mX systems, there was the relation [3] [5] [6] [17] of $K_{1,\text{org}} \geq K_{2,\text{org}}$. This trend seems to be similar to that [18] [19] of the complex formation for CdA_2 in water with $\text{A}^- = \text{Cl}^-$, Br^- , and I^- . For the two systems, some structural changes around Cd(II) in the second-step reaction, $\text{CdLI}_{\text{org}}^+ + \text{I}_{\text{org}}^- \rightleftharpoons \text{I-CdLI}_{\text{org}}$ at $L = 18\text{C6}$, could be suggested [3] [5] [6].

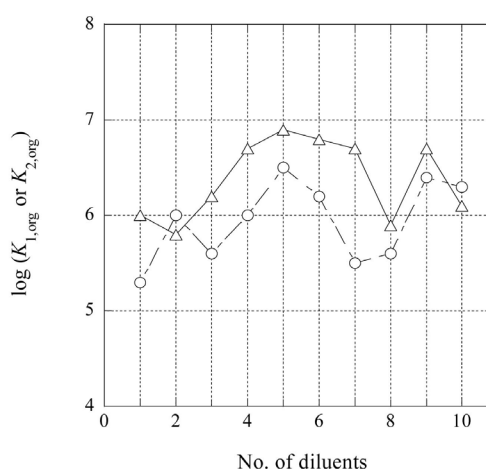


Figure 3. $\log K_{1,\text{org}}$ (triangle) and $\log K_{2,\text{org}}$ (circle) values with ten kinds of diluents described in **Table 2**.

Table 2. Logarithmic values of $K_{\text{Cd/CdL}}$, $K_{1,\text{org}}$, and $K_{2,\text{org}}$ for the CdI_2 extraction with $L = 18\text{C6}$ into various diluents at 298 K.

No. Diluent ^a	$I_{\text{org}}/10^{-7} \text{ mol}\cdot\text{dm}^{-3}$	$\log K_{\text{Cd/CdL}}^{\text{b}}$	$\log K_{1,\text{org}}^{\text{c}}$	$\log K_{2,\text{org}}^{\text{d}}$
1 NB	15	$3.1_3 \pm 0.6_3$	6.0 ± 0.7	5.3 ± 0.2
2 DCE	18	$2.4_6 \pm 0.2_3$	5.8 ± 0.6	6.0 ± 0.4
3 <i>o</i> DCBz	14	$3.1_5 \pm 0.3_6$	6.2 ± 0.5	5.6 ± 0.3
4 DCM	6.8	$2.5_8 \pm 0.2_1$	$6.7 \pm 0.6^{\text{e}}$	$6.0 \pm 0.5^{\text{e}}$
	7.4	$1.8_6 \pm 0.1_9$	6.7 ± 0.7	5.9 ± 0.6
5 CBz	2.1	$2.2_2 \pm 0.2_6$	6.9 ± 0.4	6.5 ± 0.2
6 BBz	3.7	$2.3_5 \pm 0.4_3$	6.8 ± 0.5	6.2 ± 0.3
7 CF	9.8	$1.9_5 \pm 0.3_4$	6.7 ± 0.5	5.5 ± 0.3
8 Bz	14	$3.8_5 \pm 0.8_2$	5.9 ± 0.9	5.6 ± 0.3
9 TE	3.6	$3.1_3 \pm 0.2_9$	6.7 ± 0.8	6.4 ± 0.7
10 <i>mX</i>	8.5	$3.1_1 \pm 0.1_0$	6.1 ± 0.4	6.3 ± 0.2

a: See the footnote a in **Table 1**; b. Average values calculated from experimental $D/[L]_{\text{org}}$ ones; c. Calculated from Equation (4); d. Calculated from Equation (5); e. The values were employed for the plots of **Figure 3**.

2.5. Determination of $K_{\text{ex}2\pm}$, $K_{\text{D,CdLI}}$, and $K_{\text{D,CdL}}$ and Their Characterization

The extraction constant $K_{\text{ex}2\pm}$ {see Equation (4)} and the two conditional distribution constants, $K_{\text{D,CdLI}}$ and $K_{\text{D,CdL}}$, were calculated from the following thermodynamic relations [1] [3] [6].

$$K_{\text{ex}2\pm} = [\text{CdL}^{2+}]_{\text{org}} [\Gamma^-]_{\text{org}}^2 / P \approx K_{\text{Cd/CdL}} K_{\text{D,I}}^2 \quad (6)$$

$$K_{\text{D,CdLA}} = [\text{CdLI}^+]_{\text{org}} / [\text{CdLI}^+] \approx K_{\text{ex,ip}} / (K_1 K_{2,\text{org}} K_{\text{D,I}}) \quad (7)$$

and

$$K_{\text{D,CdL}} = [\text{CdL}^{2+}]_{\text{org}} / [\text{CdL}^{2+}] = K_{\text{ex,ip}} / (\beta_{2,\text{org}} K_{\text{D,I}}^2) \quad (8)$$

with $K_1 = [\text{CdLI}^+]/[\text{CdL}^{2+}][\Gamma^-]$, called the ion-pair formation constant for water, and $\beta_{2,\text{org}} = K_{1,\text{org}} K_{2,\text{org}}$, which is an overall ion-pair formation constant for the org phase. As described in Equation (3a), $K_{\text{D,CdLI}}$ and $K_{\text{D,CdL}}$ are expressed as functions of $\Delta\phi_{\text{eq}}$ and called the conditional distribution constants:

$\log K_{\text{D,CdLI}} = \log K_{\text{D,CdLI}}^{\text{S}} + (\Delta\phi_{\text{eq}}/0.05916)$ {(standard distribution constant at $\Delta\phi_{\text{eq}} = 0$ V) + ($\Delta\phi_{\text{eq}}$ term)} at $z_{\text{CdLI}} = +1$ and

$\log K_{\text{D,CdL}} = \log K_{\text{D,CdL}}^{\text{S}} + (2\Delta\phi_{\text{eq}}/0.05916)$ at $z_{\text{CdL}} = +2$ and 298 K.

Assuming that the relation of $K_1^0 = K_{\text{CdI}}^0 K_{\text{CdLBr}}^0 / K_{\text{CdBr}}^0$ ($=308 \times 10^{-0.25}/118 = 10^{0.17} \text{ mol}^{-1} \cdot \text{dm}^3$ [1] [6] [10] [19] at $I \rightarrow 0$ & 298 K) holds, the K_1 values in Equation (7) were estimated approximately from the experimental I (Table 1) and K_1^0 ($\approx y_{\text{II}+} K_1$) values. Here, the K_{CdA}^0 and K_{CdLBr}^0 refer to an ion-pair (or a complex) formation constant [19] of Cd^{2+} with A^- ($=\Gamma^-$ & Br^-) and that [10] of Cd18C6^{2+} with Br^- in water at $I \rightarrow 0$, respectively. The activity coefficient ($y_{\text{II}+}$) of CdL^{2+} in water was evaluated from the Davies equation [20]. These calculated values, with the $K_{\text{D,18C6}}$ values available from references [13] [14] were listed in Table 3. The $\log K_{\text{ex}2\pm}$ values were energetically ($-\Delta G^\circ/2.303RT = \log K$) the

Table 3. Logarithmic values of $K_{\text{ex}2\pm}$, $K_{\text{D,CdLI}}$, $K_{\text{D,CdL}}$, and $K_{\text{D,L}}$ for the CdI_2 extraction with L = 18C6 into various diluents at 298 K.

No. Diluent ^a	$\log K_{\text{ex}2\pm}$ ^b	$\log K_{\text{D,CdLI}}$ ^c	$\log K_{\text{D,CdL}}$ ^d	$\log K_{\text{D,L}}$ ^e
1 NB	-4.5	4.4	2.2	-1.00
2 DCE	-4.5	4.9	2.5	0.03
3 oDCBz	-4.6	4.4	2.1	-1.13
4 DCM	-5.8	5.7 ^f	3.2 ^f	0.60
	-6.4	5.0	2.5	
5 CBz	-7.2	3.5	1.2	-1.07
6 BBz	-6.6	3.6	1.3	-1.12
7 CF	-6.1	5.4	2.8	0.786
8 Bz	-3.9	4.7	2.6	-1.27
9 TE	-5.8	3.9	1.6	-1.59
10 mX	-5.1	3.3	1.2	-1.95

a. See the footnote a in Table 1; b. Calculated from Equation (6); c. Calculated from Equation (7); d. Calculated from Equation (8); e. Refs. [13] & [14]; f. The values were employed for the plots of Figure 4.

smallest in the three extraction constants determined: $\log K_{\text{ex}2\pm} < \log K_{\text{ex}\pm} < \log K_{\text{ex}}$ (see **Table 2** for K_{ex} & $K_{\text{ex}\pm}$). Equations (7) and (8) are related with pseudo-RST plots described in the Section 2.8.

As shown in **Figure 4**, the $K_{D,j}$ values were in the order $j = \Gamma^- (<18\text{C6}) < \text{Cd}18\text{C6}^{2+} < \text{Cd}(18\text{C6})\text{I}^+$. This order is basically different from that [3] for the CdPic_2 -B18C6 extraction system: $j = \text{Pic}^- \{<\text{Cd}(\text{B18C6})\text{Pic}_2^0\} < \text{Cd}(\text{B18C6})\text{Pic}^+ < \text{CdB18C6}^{2+}$. Equations (7) and (8) predict that a difference between $K_{D,\text{CdLA}}$ and $K_{D,\text{CdL}}$ is proportional to that between K_1^{-1} and $(K_{1,\text{org}}K_{D,A})^{-1}$. The relation of $K_1^{-1} > (K_{1,\text{org}}K_{D,I})^{-1}$ can cause the $K_{D,j}$ order of $j = \text{Cd}18\text{C6}^{2+} < \text{Cd}(18\text{C6})\text{I}^+$, while that of $K_1^{-1} < (K_{1,\text{org}}K_{D,\text{Pic}})^{-1}$ can do that of $\text{CdB18C6}^{2+} > \text{Cd}(\text{B18C6})\text{Pic}^+$. These experimental results of the CdI_2 -18C6 extraction systems were in the $-\log K_1$ range of -0.0_3 to 0.0_3 and in the $-\log(K_{1,\text{org}}K_{D,I})$ one of -2.6_3 to -2.0_4 . On the other hand, the values of the CdPic_2 -B18C6 systems were evaluated to be in the $-\log K_1$ range of -4.60 to -4.39 (see **Appendix** for the calculation of $\log K_1$ averaged in the Bz system) and in the $-\log(K_{1,\text{org}}K_{D,\text{Pic}})$ one of -2.7 to -0.1 [3]. These experimental orders are in good agreement with the orders predicted above.

2.6. For Relative Concentrations of CdLI_2 , CdLI^+ , and CdL^{2+} Extracted into the Diluents

We have defined distribution ratios D_0 , D_+ , and D_{2+} as described below [3] [5] [6] [17]. Using the experimental data sets of $[\text{L}]_{\text{org}}$ and $[\text{I}^-]$, these values were calculated from

$$D_0 = [\text{CdLI}_2]_{\text{org}} / [\text{Cd}^{2+}] = K_{\text{ex}} [\text{L}]_{\text{org}} [\text{I}^-]^2 \quad (9)$$

$$D_+ = [\text{CdLI}^+]_{\text{org}} / [\text{Cd}^{2+}] = K_{\text{ex}\pm} [\text{L}]_{\text{org}} [\text{I}^-] / K_{D,I} \quad (10)$$

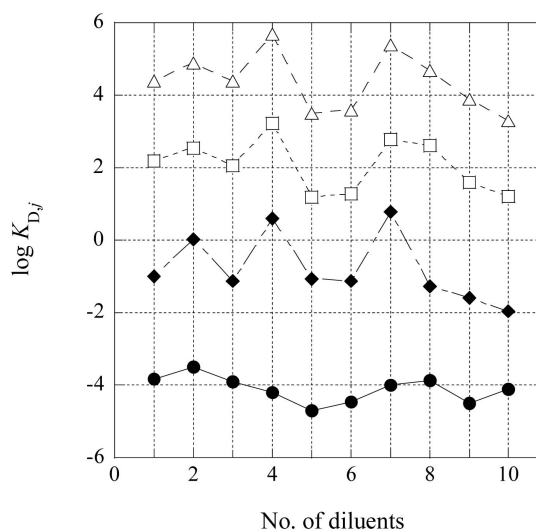


Figure 4. Variation of $\log K_{D,j}$ with kinds of diluents. Here, $j = \text{I}^-$ (full circle), L (full diamond), CdL^{2+} (square), and CdLI^+ (triangle) at $\text{L} = 18\text{C6}$. For the DCM system, the $\log K_{D,I}$ value of -4.2 in **Table 1** was used for this plot.

and

$$D_{2+} = [\text{CdL}^{2+}]_{\text{org}} / [\text{Cd}^{2+}] \approx K_{\text{Cd/CdL}} [\text{L}]_{\text{org}} \quad (11)$$

at each experimental point. Here, the K_{ex} , $K_{\text{ex}\pm}$, $K_{\text{D,L}}$ and $K_{\text{Cd/CdL}}$ values at $\text{L} = 18\text{C6}$ in **Table 1** and **Table 2** were used for the calculations. From the three equations, we can calculate relative concentrations (or molar fractions), such as $f_0/\% = 100D_0/D_t$ and $f_+ = 100D_+/D_t$ with $D_t = D_0 + D_+ + D_{2+}$ [5]. The mean values of f_0 , f_+ , and f_{2+} were listed in **Table A1** of the **Appendix**, where the symbols f_0 , f_+ , and f_{2+} ($=100D_{2+}/D_t$) denote the relative concentrations of CdLI_2 , CdLI^+ , and CdL^{2+} , respectively.

As can be seen from **Figure 5** and **Table A1**, the f_+ values were the largest in the extraction into the many diluents, except for the values of the DCE and $m\text{X}$ systems. Especially, the f_+ values exceeded 50% in the NB, $o\text{DCBz}$, DCM, BBz, CF, and Bz systems. These behaviors in **Figure 5** can be explained as follows. Considering a homogeneous reaction defined as $K_{1,\text{org}}/K_{2,\text{org}}$.

$\left(= [\text{CdLI}^+]_{\text{org}}^2 / [\text{CdL}^{2+}]_{\text{org}} [\text{CdLI}_2]_{\text{org}} \right)$, we can evaluate the formation of CdLI^+ or CdLI_2 which is dominant about the reaction of $\text{CdL}_{\text{org}}^{2+} + \text{CdLI}_{2,\text{org}} \rightleftharpoons 2\text{CdLI}_{\text{org}}^+$.

From the $K_{1,\text{org}}$ and $K_{2,\text{org}}$ values in **Table 2**, the $\log (K_{1,\text{org}}/K_{2,\text{org}})$ values were calculated to be negative (namely $K_{1,\text{org}} < K_{2,\text{org}}$) for the $\text{org} = \text{DCE}$ and $m\text{X}$ systems, while their values to be positive (namely $K_{1,\text{org}} > K_{2,\text{org}}$) for the other systems. Therefore, we can easily see that the formation of CdLI_2 is dominant,

$\text{CdL}_{\text{org}}^{2+} + \text{CdLI}_{2,\text{org}}$, in the DCE and $m\text{X}$ phases, while that of CdLI^+ is dominant, $2\text{CdLI}_{\text{org}}^+$, in the other diluents. The diluent dependence of the f values in **Figure 5** reflects mainly the difference between $K_{1,\text{org}}$ and $K_{2,\text{org}}$ (see the Section 2.4). Considering these phenomena from ion-pair-formation point of view [3] [6], the systems dominant for the distribution of CdLI^+ can be a major case in the present extraction systems.

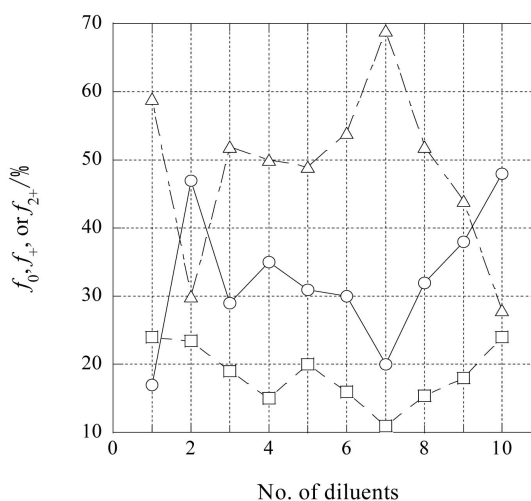


Figure 5. Variation of the relative concentrations of CdLI_2 (circle), CdLI^+ (tri-angle), and CdL^{2+} (square) with kinds of diluents at $\text{L} = 18\text{C6}$. Their concentrations are expressed by f_0 , f_+ , and f_{2+} , respectively.

2.7. Classification of the Acidity of CdL^{2+} and CdLA^+ in the Org Phases Based on the HSAB Rule

According to our previous paper [10], the complex ions Cd18C6^{2+} and CdB18C6^{2+} in water have been classified as the hard acids in their reactions with $\text{A}^- = \text{Cl}^-$, Br^- , (I^-) or Pic^- . As standards of the HSAB classification, we assumed that 1) trends in the hardness and softness of the anions A^- in the org phases are the same as those [9] [10] in water. That is, I^- and Br^- are soft bases [9], while Cl^- and Pic^- are hard bases [9] [10]. 2) The reactions with the halogen ions are primarily employed for the classification. Only when one of the reactions with the three halogen ions lack, the reaction of Pic^- was used for it. In the classification, 3) we neglected effects of the I_{org} values on $K_{1,\text{org}}$, $K_{2,\text{org}}$, and $\beta_{2,\text{org}}$, because the I_{org} values were in the lower ranges [1] [2] [3] [6]: see Table 2 as an example.

For example, the $K_{1,\text{NB}}$ and $\beta_{2,\text{NB}} (=K_{1,\text{NB}}K_{2,\text{NB}})$ values were in the order $\text{Pic}^- < \text{I}^- < \text{Cl}^-$ (see Table A2 in Appendix). These orders suggested that the Cd18C6^{2+} is a borderline acid in the NB phase, because the order between the hard and soft bases is random. The $K_{1,\text{oDCBz}}$ values were in the order $\text{Br}^- < \text{I}^- < \text{Cl}^-$, while the $\beta_{2,\text{oDCBz}}$ ones were $\text{Cl}^- < \text{I}^- < \text{Br}^-$ (see Table A2). The former order suggested that Cd18C6^{2+} in the oDCBz phase is a hard acid. On the other hand, the latter one indicated that Cd18C6^{2+} is a soft acid. This discrepancy in the classification between $K_{1,\text{org}}$ and $\beta_{2,\text{org}}$ can reflect the soft acidity of the intermediate ion-pair complex ion, Cd(18C6)A^+ ; namely the effect of $K_{2,\text{org}}$. A similar trend was observed in the Bz systems: they were classified as the hard acid from $K_{1,\text{Bz}}$ ($\text{Br}^- < \text{I}^- < \text{Cl}^-$) and as the borderline acid from $\beta_{2,\text{Bz}}$ ($\text{I}^- < \text{Cl}^- < \text{Br}^-$). The Cd18C6^{2+} ions in the other diluents were classified as the soft acids for the DCE, DCM, CBz, BBz, and CF systems, the borderline acid for CBu, and the hard acid for *m*X and TE: see Table A2 in Appendix. In these systems, the HSAB classifications by $K_{1,\text{org}}$ were in accordance with those by $\beta_{2,\text{org}}$.

On the basis of the above results, it could be considered that Cd18C6^{2+} in water almost changes from the hard acid to the soft or borderline acids in the extraction into the org phases. This indicated that the hardness and softness of Cd18C6^{2+} might be changed with species of the diluents, according to the criteria of the A^- basicity.

The following measure can be also considered for the HSAB classification of Cd(18C6)A^+ in the each phase, because there were no data for the reactions, such as $\text{CdLCl}^+_{\text{org}} + \text{Br}^-_{\text{org}} \rightarrow \text{Br-CdLCl}_{\text{org}}$ and $\text{CdLCl}^+_{\text{org}} + \text{I}^-_{\text{org}} \rightarrow \text{I-CdLCl}_{\text{org}}$. The ratio of

$$K_{2,\text{org}}(\text{A})/K_{2,\text{org}}(\text{Cl}) = [\text{CdLA}_2]_{\text{org}}[\text{CdLCl}^+]_{\text{org}}[\text{Cl}^-]_{\text{org}}/([\text{CdLCl}_2]_{\text{org}}[\text{CdLA}^+]_{\text{org}}[\text{A}^-]_{\text{org}})$$

at $\text{L} = 18\text{C6}$ was proposed and simply expressed as $K_{2,\text{org}}(\text{A}/\text{Cl})$. Fixing the $([\text{CdLCl}^+]_{\text{org}}[\text{Cl}^-]_{\text{org}}/[\text{CdLA}^+]_{\text{org}}[\text{A}^-]_{\text{org}})$ term or both $[\text{CdLCl}^+]_{\text{org}}[\text{Cl}^-]_{\text{org}}$ and $[\text{CdLA}^+]_{\text{org}}[\text{A}^-]_{\text{org}}$ terms at unity, the ratio virtually can become the $[\text{CdLA}_2]_{\text{org}}/[\text{CdLCl}_2]_{\text{org}}$ ratio. Hence, we considered that if the $\log K_{2,\text{org}}(\text{A}/\text{Cl})$ value is positive, the formation of CdLA_2 in the org phase becomes dominant and if it is negative, that of CdLCl_2 does dominant. The former case means the

softer complex ion, while the latter one does the harder ion. So, this $K_{2,\text{org}}(\text{A/Cl})$ value gives us a criteria for evaluating the HSAB acidity of Cd(18C6)A^+ in the org phases (water). Consequently, the order of $K_{2,\text{org}}$ among A^- yields the magnitude in the formation of CdLA_2 in the org phase under the assumption for the above ratio.

As an example, the $\log K_{2,\text{oDCBz}}(\text{A/Cl})$ values were in the order $\text{A}^- = \text{Cl}^- = 1.0 < \text{I}^- < \text{Br}^-$ (see **Table A2**), suggesting that Cd(18C6)A^+ in the oDCBz phase is the soft acid. Similarly, the Cd(18C6)A^+ in the other diluents were classified as the soft acid for the org = NB, DCE, DCM, CBz, BBz, CF, TE, and *m*X systems, the borderline acid for CBu $\{\log K_{2,\text{CBu}}(\text{A/Cl}): 1.0 = \text{Cl} < \text{Br} < \text{Pic}\}$ and Bz ($\text{I} < 1.0 = \text{Cl} < \text{Br}$), and not the hard acid, except for water $\{\log K_2(\text{A/Cl}): \text{Br} < 1.0 = \text{Cl} < \text{Pic}\}$. From the above, all Cd(18C6)A^+ change from the hard acids in water to the soft and borderline ones in the org phases.

Thus, the changes of the diluents (or the org phases) are reflected into the HSAB acidities of these complex ions in the extraction of Cd18C6^{2+} and Cd(18C6)A^+ . In other words, this means that the HSAB acidity of the complex ion or the ion-pair cation varies with the kinds of the diluents, if the HSAB basicity of the A^- can be considered to be the standard. It can be seen that it is easier for the monovalent CdLA^+ to become the soft acid than for the divalent CdL^{2+} to do it with the extraction into the diluents. This can be supported by the fact that Cd(18C6)A^+ in the 9 diluents among the 11 ones is classified as the soft acids, compared with Cd18C6^{2+} in the 4 diluents done as the hard acids (**Table A2**). We can see it particularly from this comparison that the six diluents, DCE, oDCBz, DCM, CBz, BBz, and CF, are the higher effect than the others in softening the acidity of the complex ions. It is interesting that these diluents contain the Cl- or Br-group(s) in their molecules, though CBu, $\text{Cl-CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, does not clearly show its effect.

2.8. Comparisons of Molar Volumes among the Ion-Pair Complexes

We obtained the regression line from the RST plot [1] [2] [3] [6] [13] of $\log K_{\text{ex,ip}}$ vs. $\log K_{\text{D,18C6}}$ for the present Cd(II) extraction systems, except for the points of the NB and CF ones [3] [13]: $\log K_{\text{ex,ip}} = (0.7_5 \pm 0.2_1) \log K_{\text{D,18C6}} + (6.8_0 \pm 0.2_5)$ at $R = 0.800$. Also, using $V_{18\text{C6}} = 214 \pm 47 \text{ cm}^3 \text{ mol}^{-1}$ [13] reported by Takeda, the V_{CdLI2} value was calculated to be 160 ± 57 from the slope of the RST plot. Adding the data of previous papers, the V_j values became in order $V_{\text{CdLI2}} \leq V_{\text{CdLPic2}}$ ($=171 \text{ cm}^3 \text{ mol}^{-1}$ [2]) $\leq V_{\text{L}}$ [13] $\leq V_{\text{CdLBr2}}$ ($=248$ [1]) $< V_{\text{CdLCl2}}$ ($=398$ [6]) at $\text{L} = 18\text{C6}$. At least, there is a tendency in the order of V_{CdLA2} among $\text{A} = \text{Cl}, \text{Br}, \text{and I}$.

In general, the RST plot for the M(II) extraction system is expressed as $\log K_{\text{ex,ip}} = (V_{\text{MLA2}}/V_{\text{L}}) \log K_{\text{D,L}} + C + \log \beta_2$ in the form of a linear equation, where the constant C shows solute-solvent (or non-electrostatic) interactions term with cohesive energy densities [1] [2] [3] [6] [13]. From the thermodynamic relation of Equation (8), we can derive the following equation:

$$\begin{aligned}\log K_{D,CdL} &= (V_{MLA2}/V_L) \log K_{D,L} + C + \log \beta_2 - \log(\beta_{2,org} K_{D,A}^2) \\ &= (V_{MLA2}/V_L) \log K_{D,L} + C'\end{aligned}\quad (12)$$

with $C' = C + \log(\beta_2/\beta_{2,org} K_{D,A}^2)$. Hence, one can see that the C' term includes the $\beta_2/\beta_{2,org}$ term corresponding to the ion-ion interactions in addition to the solute-solvent interactions term C . The plot of $\log K_{D,CdL}$ vs. $\log K_{D,L}$ for the CdI_2 -18C6 extraction systems is shown in **Figure 6**. Its regression line was $\log K_{D,CdL} = (0.56 \pm 0.15) \log K_{D,L} + (2.47 \pm 0.17)$ at $R = 0.774$, where the data of the NB and CF systems were added in the estimation, because of the plot for the ionic species. This slope was somewhat smaller than that (≈ 0.8) of the RST plot. If this difference reflects a difference in V_j between $j = CdLI_2$ and CdL^{2+} , then the ratio between the slopes can directly express that between V_j . So, the ratio of $\text{slope}(CdLI_2)/\text{slope}(CdL^{2+})$ ($=1.3$) is equivalent to V_{CdLI_2}/V_{CdL} at a fixed V_L . Therefore, the V_{CdL} value was estimated to be $120 \pm 64 \text{ cm}^3 \cdot \text{mol}^{-1}$ from the V_{CdLI_2} one ($=160$). This value was smallest in the V_j with $j = CdLCl_2$, $CdLBr_2$, $CdLI_2$, and $CdLPic_2$. This is in good agreement with the image that the size of CdL^{2+} is smaller than those of $CdLA_2$.

The same trend as above can be seen in a plot of $\log K_{D,CdLI}$ vs. $\log K_{D,L}$ (see **Table 3** for their data): the V_{CdLI} value was $155 \pm 46 \text{ cm}^3 \cdot \text{mol}^{-1}$ at $L = 18C6$. Similarly, $V_{CdLBr}/\text{cm}^3 \cdot \text{mol}^{-1}$ was estimated to be 225 ± 55 from the slope ($=1.05 \pm 0.11$) of the $\log K_{D,CdLBr}$ vs. $\log K_{D,L}$ plot reported previously. These values satisfy the following relations: $V_{CdLI_2} \geq V_{CdLI} \geq V_{CdL}$ and $V_{CdLBr_2} \geq V_{CdLBr} \geq V_{CdL}$.

2.9. Estimation of Apparent Sizes for the Cd(II) Complexes

From the V_j data, we can evaluate apparent sizes of $Cd(18C6)_2$ or $Cd18C6^{2+}$. Assuming $V_j = 4\pi R_j^3/3$, namely that shapes of the ion pairs and complex ion are close to spheres, we can easily calculate apparent radii (R_j) from the V_j . Their

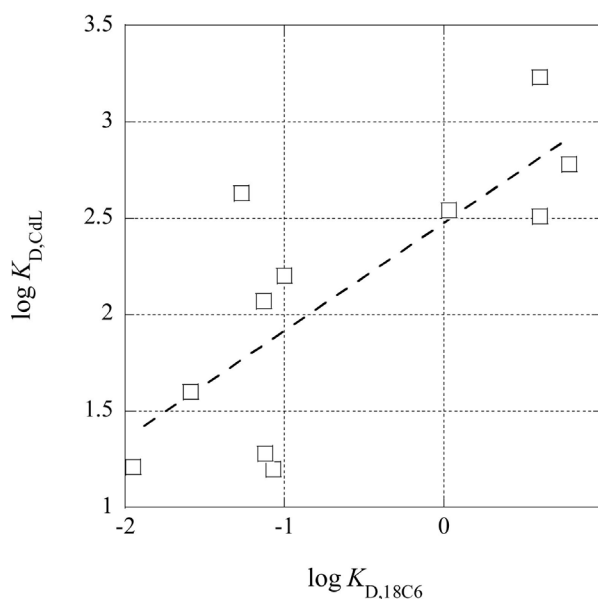


Figure 6. Pseudo-RST plot of $\log K_{D,CdL}$ vs. $\log K_{D,L}$ at $L = 18C6$.

R_j values were 5.4 Å for $j = \text{CdLCl}_2$, 4.6 for CdLBr_2 , 4.0 for CdLI_2 , 4.1 for CdLPic_2 , and 3.6 for CdL^{2+} at $L = 18\text{C6}$. As similar to the results of V_{CdL} (see the Section 2.8), the R_{CdL} value was smallest of the R_j ones.

The $R_{\text{Cd}18\text{C6}}$ value ($=3.6$ Å) was larger than the following data of bond lengths [21]; the DFT study of $[\text{Cd}(18\text{C6})(\text{OH}_2)_2]^{2+}$, in which 18C6 acts as a tridentate ligand, has reported that the Cd-O and Cd-OH₂ bond lengths were 2.40 Å and 2.34, respectively. This fact suggested that the $R_{\text{Cd}18\text{C6}}$ value expresses the hydration structure around $\text{Cd}18\text{C6}^{2+}$. Regarding this, it is demonstrated from the Karl-Fischer titration that $\text{Ca}18\text{C6}^{2+}$ is present in the NB phase as $\text{Ca}18\text{C6}^{2+} \cdot 4.7\text{H}_2\text{O}$ [22], where the ion size ($=0.95$ Å) of the six coordinated Cd^{2+} is close to that ($=1.00$) of the Ca^{2+} [23]. Besides, the suggestion is supported by the facts that Cd-A bond lengths ($d_{\text{Cd-A}}$, see below for its values) in CdLA_2 crystals [24] [25] with $L = 18\text{C6}$ are in the order $d_{\text{Cd-Cl}} < d_{\text{Cd-Br}} < d_{\text{Cd-I}}$, while the R_j values are in that $j = \text{CdLCl}_2 > \text{CdLBr}_2 > \text{CdLI}_2$. Additionally, it was shown that $d_{\text{Cd-Pic}}$ is apparently close to $d_{\text{Cd-I}}$.

Also, the bond lengths $d_{\text{Cd-Cl}}$ and $d_{\text{Cd-O}}$ in a $\text{Cd}(18\text{C6})\text{Cl}_2$ crystal have been reported to be 2.364 Å and 2.752, respectively [24]. The same trend is also observed in $\text{Cd}(18\text{C6})\text{Br}_2$ and $\text{Cd}(18\text{C6})\text{I}_2$ crystals [25]: $d_{\text{Cd-Br}} = 2.506$ Å and $d_{\text{Cd-O}} = 2.752$ for CdLBr_2 and $d_{\text{Cd-I}} = 2.692$ and $d_{\text{Cd-O}} = 2.768$ for CdLI_2 . Interestingly, the three $d_{\text{Cd-O}}$ values have been almost constant among the crystals. These results suggested that CdLCl_2 , CdLBr_2 , and CdLI_2 with $L = 18\text{C6}$ are close to solvent-separated or -shared ion pairs, such as $\text{CdL}(\text{OH}_2)_x\text{A}_2$, in phases. If this suggestion is correct, then both the R_j and V_j values can strongly reflect the structural properties of the complexes “in the water phase”. On the basis of the above results, the V_j values obtained in the section 2.8 and those reported before seem to be self-consistent.

3. Experimental

3.1. Chemicals

Commercial CdI_2 {guaranteed pure reagent (GR): $>99.0\%$, Kanto Chemical, Japan} and $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (GR: $>98.0\%$, Kanto Chemical) were used: their purities were determined by the chelatometric titration with di-Na(I) salt of EDTA [1] [6]. Here, this nitrate was employed for the preparation of calibration curves in the AAS measurement. The crown ether, 18C6 (GR: 98.0%), was purchased from Tokyo Chemical Industry (Japan) and its solutions were prepared by weighed amounts. The ten commercial diluents were of GR grades: NB ($>99.5\%$), *o*DCBz ($>99.0\%$), DCE ($>99.5\%$), DCM ($>99.5\%$), BBz ($>98.0\%$), CF ($>99.0\%$), Bz ($>99.5\%$) and *m*X ($>98.0\%$) were purchased from Kanto Chemical and CBz ($>99\%$) and TE ($>99.5\%$) done from Wako Pure Chemical Industries, Japan [1] [2] [3] [4] [6]. These diluents were washed three times with pure water and stored in the state saturated with water [1] [2] [4] [6]. Other chemicals were of GR grades. A tap water was distilled once and then deionized by passing through Autopure System (Yamato/Millipore, type WT 101 UV).

3.2. Extraction Procedure

Basic operations and equipment were the same as those described before [1]-[6]. That is, the operations were constructed of original Cd(II) extraction, its back one, and Cd(II) analyses with the AAS measurements at 228.8 nm. The calibration curves of $\text{Cd}(\text{NO}_3)_2$ in the aqueous $0.1 \text{ mol}\cdot\text{dm}^{-3}$ HNO_3 solutions were employed for the AAS determination of Cd(II). Here, differences in the calibration curve between pure water and the aqueous HNO_3 solution were experimentally negligible. So, the back extraction was operated with pure water instead of $0.1 \text{ mol}\cdot\text{dm}^{-3}$ HNO_3 [1]-[6] as the back extraction phase, because the Cd(II) amounts in the latter acidic solutions analyzed by the AAS deviated largely.

In the extraction experiments, the $[\text{CdI}_2]_i$ values were in the range of $0.0029 - 0.0081 \text{ mol}\cdot\text{dm}^{-3}$ and total concentrations of 18C6 in the water phases were in the ranges of $(0.5_6 - 2.1) \times 10^{-5} \text{ mol}\cdot\text{dm}^{-3}$ for the NB system, $(0.1_1 - 5.5) \times 10^{-4}$ for DCE, $(0.2_5 - 2.5) \times 10^{-5}$ for *o*DCBz, $(0.01_3 - 1.1) \times 10^{-4}$ and $(0.2_5 - 4.1) \times 10^{-5}$ for DCM, $(0.2_5 - 4.1) \times 10^{-5}$ for CBz, $(0.8_2 - 2.5) \times 10^{-5}$ for BBz, $(0.2_5 - 2.5) \times 10^{-5}$ for CF and Bz, $(0.2_5 - 7.4) \times 10^{-5}$ for TE, and $(1.4 - 7.4) \times 10^{-5}$ for *m*X. The water phases containing these CdI_2 and 18C6 were mixed with equal volumes of the diluents or org phases.

3.3. Extraction Equilibrium Model and Its Data Handlings

The following extraction model [4] was employed for the analysis of the present extraction system with $L = 18\text{C6}$: 1) $\text{Cd}^{2+} + L \rightleftharpoons \text{CdL}^{2+}$ [12] and 2) $\text{Cd}^{2+} + \text{I}^- \rightleftharpoons \text{CdI}^+$ [19] in the water phase; 3) $\text{I}^- \rightleftharpoons \text{I}_{\text{org}}^-$, 4) $\text{CdLI}^+ \rightleftharpoons \text{CdLI}_{\text{org}}^+$, 5) $\text{CdL}^{2+} \rightleftharpoons \text{CdL}_{\text{org}}^{2+}$, and 6) $L \rightleftharpoons L_{\text{org}}$ [13] [14] between the water and org phases; 7) $\text{CdL}_{\text{org}}^{2+} + \text{I}_{\text{org}}^- \rightleftharpoons \text{CdLI}_{\text{org}}^+$ and 8) $\text{CdLI}_{\text{org}}^+ + \text{I}_{\text{org}}^- \rightleftharpoons \text{CdLI}_{2,\text{org}}$ in the org phase. Except for the processes 3)-5), 7), and 8), the equilibrium constants of the above processes at 298 K were available from the references [12] [13] [14] [19].

Data analyses of the extraction equilibria based on this model were essentially the same as those reported before [1] [2] [4]. The parameter $K_{\text{ex}}^{\text{mix}}$ has been defined as

$$K_{\text{ex}}^{\text{mix}} = \frac{[\text{Cd}(\text{II})]_{\text{org}}}{P} = \frac{([\text{CdLI}_2]_{\text{org}} + [\text{CdLI}^+]_{\text{org}} + [\text{CdL}^{2+}]_{\text{org}} + [\text{CdI}^+]_{\text{org}} + [\text{CdI}_2]_{\text{org}} + \dots)}{P} \quad (13)$$

Assuming that

$$[\text{CdLI}_2]_{\text{org}} + [\text{CdLI}^+]_{\text{org}} \gg [\text{CdL}^{2+}]_{\text{org}} + [\text{CdI}^+]_{\text{org}} + [\text{CdI}_2]_{\text{org}} + \dots$$

this equation can be rearranged into

$$K_{\text{ex}}^{\text{mix}} \approx K_{\text{ex}} + K_{\text{D,L}} / ([\text{Cd}^{2+}][L]_{\text{org}}[\text{I}^-]) \quad (2a)$$

in the case of $[\text{CdLI}^+]_{\text{org}} \approx [\text{I}^-]_{\text{org}}$ which was approximately derived from the charge balance equation for the org phase [1]-[6]. At least, the conditions of $[\text{CdLI}_2]_{\text{org}} + [\text{CdLI}^+]_{\text{org}} + [\text{CdL}^{2+}]_{\text{org}} \gg [\text{CdI}^+]_{\text{org}} + [\text{CdI}_2]_{\text{org}} + \dots$ were checked by blank experiments of the CdI_2 extraction without $L = 18\text{C6}$. On the other hand, in the case of $[\text{CdLI}^+]_{\text{org}}/P \approx K_{\text{ex}\pm}/[\text{I}^-]_{\text{org}}$, we can immediately obtain

$$K_{\text{ex}}^{\text{mix}} \approx K_{\text{ex}} + \left(\frac{[\text{CdLI}^+]_{\text{org}} [\text{I}^-]_{\text{org}}}{P^2} \right)^{1/2} = K_{\text{ex}} + (K_{\text{ex}\pm}/P)^{1/2} \quad (2b)$$

The parameter $K_{\text{ex}}^{\text{mix}}$ was calculated from the experimental $[\text{Cd(II)}]_{\text{org}}$, $[\text{Cd}^{2+}]$, $[\text{18C6}]_{\text{org}}$, and $[\text{I}^-]$, where the latter three concentrations were determined with a successive approximation procedure, using the equilibrium constants of the processes 1), 2), and 6) [2] [4]. When a negative value for K_{ex} had been obtained from the analysis with Equation (2b), its analysis was performed again by fixing the K_{ex} value to that determined by the analysis with Equation (2a) [1]-[6] (see the footnotes c & e in Table 1).

4. Conclusions

The ion-pair formation in the 11 diluents saturated with water was classified in terms of the HSAB principle, although the hardness and softness of the simple A^- in the diluents were assumed to be the same as those in water. This classification mainly showed us the two results. 1) CdL^{2+} and CdLA^+ with $\text{L} = \text{18C6}$ and $\text{A}^- = \text{Cl}^-$, Br^- , and I^- change from the hard acids in water to almost the soft or borderline acids in the extraction into the org phases at least. 2) The charge effects on CdLA^+ and CdL^{2+} in the org phases are remarkable. Namely, CdLA^+ softens more its acidity than CdL^{2+} does in the extraction. Especially, DCE, oDCBz, DCM, CBz, BBz, and CF have the higher ability to soften the HSAB acidity of the complex ions.

The presence of dep was also observed in the CdI_2 -18C6 extraction into NB, DCE, and DCM. The relation of $f_+ < f_0$ simply reflects that of $K_{1,\text{org}} < K_{2,\text{org}}$, about which the structural changes around Cd(II) were suggested, while the relation of $f_+ > f_0$ does that of $K_{1,\text{org}} > K_{2,\text{org}}$.

The molar volumes V_j obtained from the RST plots indicated the size-dependence on the Cd(18C6)A_2 ($=j$) ion pairs. Additionally, the V_{Cd18C6} value was evaluated from the pseudo-RST plots and then was the smallest of the V_j ones of all the Cd(18C6)A_2 examined. At the same time, it was demonstrated that the apparent radii R_j , estimated from the V_j values, reflects inversely the bond lengths of Cd-A with $\text{A}^- = \text{Cl}^-$, Br^- , and I^- in the crystallographic and DFT studies. These V_j and R_j results proved validities for the analyses of the RST and pseudo-RST plots about such extraction systems and thereby indicated a possibility that the two plots give the structural information about some complexes, although it is unclear which of org or water phase is the corresponding phase.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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Appendix

The following **Table A1** is supplementary data for the discussion in the Section 2.6. The numbers of **Table A1** express the diluents in **Figure 5**.

In the following **Table A2** are listed basic data for the HSAB classification. The data were used for consideration in the Section 2.7. The Pic with parenthesis in **Table A2** was not employed for it.

Table A1. Relative concentrations^a, f_0 for CdLI_2 , f_+ for CdLI^+ , and f_{2+} for CdL^{2+} , in the CdI_2 extraction with L = 18C6 into various diluents at 298 K.

No. Diluent ^b	$f_0/\%$: CdLI_2	$f_+/\%$: CdLI^+	$f_{2+}/\%$: CdL^{2+}
1 NB	17	59	24
2 DCE	47	30	23
3 oDCBz	29	52	19
4 DCM	35 ^c	50 ^c	15 ^c
	30	55	15
5 CBz	31	49	20
6 BBz	30	54	16
7 CF	20	69	11
8 Bz	32	52	16
9 TE	38	44	18
10 mX	48	28	24

a. Definition: $f_0 = 100D_0/D_i$; $f_+ = 100D_+/D_i$; $f_{2+} = 100D_{2+}/D_i$ with $D_i = D_0 + D_+ + D_{2+}$. All the values were mean ones; b. See the footnote a in **Table 1**; c. The values were employed for the plots of **Figure 5**.

Table A2. Orders of the $K_{1,\text{org}}$, $K_{2,\text{org}}$ (A/Cl), and $\beta_{2,\text{org}}$ values^a at 298 K for the HSAB classification.

Diluents ^b or water	Water ^c	org = NB	DCE
$\log(K_{1,\text{org}} \text{ or } K_1^{\text{d}})$	A = I < Br (<Pic) < Cl	Pic < I < Cl	Cl < Br < I (<Pic)
$\log\{K_{2,\text{org}}(\text{A/Cl}) \text{ or } K_2(\text{A/Cl})^{\text{e}}\}$	Br < Cl < Pic	Pic < Cl < I	Cl < Br \approx I (\approx Pic)
$\log(\beta_{2,\text{org}} \text{ or } \beta_2^{\text{f}})$	Br < Cl < Pic	Pic < I < Cl	Cl < Br < I (<Pic)
Diluents ^b	oDCBz	DCM	CBu
$\log K_{1,\text{org}}$	Br < I < Cl (<Pic)	Cl < Br < I (<Pic)	Cl < Br < Pic
$\log K_{2,\text{org}}(\text{A/Cl})$	Cl < I < Br (<Pic)	(Pic<) Cl < I < Br	Cl < Br < Pic
$\log \beta_{2,\text{org}}$	Cl < I < Br (<Pic)	Cl < Br < I (<Pic)	Cl < Br < Pic
Diluents ^b	CBz	BBz	CF
$\log K_{1,\text{org}}$	Cl < Br < I (<Pic)	Cl < Br < I (<Pic)	Cl < Br \approx I (<Pic)
$\log K_{2,\text{org}}(\text{A/Cl})$	Cl (<Pic) < I < Br	Cl < I (<Pic) < Br	Cl < I (<Pic) < Br
$\log \beta_{2,\text{org}}$	Cl (<Pic) < I < Br	Cl < I < Br (<Pic)	Cl < I (<Pic) < Br
Diluents ^b	Bz	TE	mX
$\log K_{1,\text{org}}$	Br < I < Cl (<Pic)	I < Br < Pic	I < Br < Pic
$\log K_{2,\text{org}}(\text{A/Cl})$	I < Cl < Br (<Pic)	Cl (<Pic) < I < Br	Cl < Br < I (<Pic)
$\log \beta_{2,\text{org}}$	I < Cl (<Pic) < Br	I < Br < Pic	I < Br < Pic

a. See Refs. [1] [2] & [6] for the numerical data; b. See the footnote a in **Table 1**; c. Refs. [10] & [26]; d. See the Section 2.5 for its definition; e. Ratio between the ion-pair formation constant for A^- in water, defined as $[\text{CdLA}_2]/[\text{CdLA}^+][\text{A}^-]$, & that for Cl^- ; f. Overall ion-pair formation constant for water defined as $[\text{CdLA}_2]/[\text{CdL}^{2+}][\text{A}^-]^2$.

The evaluation of $\log\{K_1(\text{average})\}$ for the CdPic₂ extraction with B18C6 into Bz was as follows. Using $K_1^0 = 6.4 \times 10^4 \text{ mol}^{-1} \cdot \text{dm}^3$ [26] at 298 K and the Davies equation [20], we calculated its value from the thermodynamic relation of

$$\log K_1^0 \{ = \log K_1 + \log(y_{\text{CdLA}}/y_{\text{II+}}y_{\text{A}}) \} \approx \log K_1 - \log y_{\text{II+}}$$

where the activity coefficient ratio $y_{\text{CdLA}}/y_{\text{A}} \approx 1$. Rearranging this equation and then introducing the Davies equation in it, the following equation can be easily obtained at 298 K:

$$\log K_1 \approx \log K_1^0 - 0.511_4 \times 2^2 \times \left\{ I^{1/2} / (1 + I^{1/2}) - 0.3I \right\} \quad (\text{A1})$$

So, introducing K_1^0 and $I = 0.095 \text{ mol} \cdot \text{dm}^{-3}$ [3] in this equation without the ion-size parameter of CdL²⁺, we obtained immediately $\log K_1 \approx 4.39$. Here the I value was an average one for the Bz extraction system [3]. Similarly, the $\log\{K_1(\text{average})\}$ values calculated from Equation (A1) with the I data [3] at 298 K were 4.57 for the NB system with B18C6 and CdPic₂, 4.60 for DCE, 4.56 for *o*DCBz, DCM, CF, and *m*X, 4.55 for CBu and dibutylether, 4.49 for CBz and TE, and 4.53 for BBz.