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Pb(II) Extraction with Benzo-18-Crown-6 Ether into Benzene under the Co-Presence of Cd(II) Nitrate in Water

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Abstract: Extraction of Pb(II) with picrate ion [Pic^-] and 0, 0.58, 15, 48, or 97 mmol dm^{-3} $Cd(NO_3)_2$ by benzo-18-crown-6 ether (B18C6; L as its symbol) into benzene (Bz) was studied. Three kinds of extraction constants, K_{ex}, $K_{ex\pm}$, and $K_{Pb/PbL}$ (or $K_{ex2\pm}$), were determined at 298 K: these constants were defined as $[PbLPic_2]_{Bz}/P$, $[PbLPic^+]_{Bz}[Pic^-]_{Bz}/P$, and $[PbL^{2+}]_{Bz}/[Pb^{2+}][L]_{Bz}$ (or $[PbL^{2+}]_{Bz}([Pic^-]_{Bz})^2/P$), respectively. The symbol P shows $[Pb^{2+}][L]_{Bz}[Pic^-]^2$ and the subscript "Bz" denotes the Bz phase, Bz saturated with water. Simultaneously, conditional distribution constants, $K_{D,Pic}$ (=$[Pic^-]_{Bz}/[Pic^-]$), of Pic^- with distribution equilibrium-potential differences (dep) were determined. Then, based on the above four constants and others, the component equilibrium constants of $K_{1,Bz}$ (=$[PbLPic^+]_{Bz}/[PbL^{2+}]_{Bz}[Pic^-]_{Bz}$), $K_{2,Bz}$ (=$[PbLPic_2]_{Bz}/[PbLPic^+]_{Bz}[Pic^-]_{Bz}$), and $K_{D,PbL}$ (=$[PbL^{2+}]_{Bz}/[PbL^{2+}]$) were obtained. Using these constants, the Pb(II) extraction with B18C6 under the co-presence of Cd(II) in the water phase was characterized. In such a characterization, I and I_{Bz} dependences on the constants were mainly discussed, where their symbols denote the ionic strength of the water phase and that of the Bz one, respectively.

Keywords: extraction constants; conditional distribution constants; distribution equilibrium potential; ion-pair formation constants; ionic strength; lead picrate; cadmium nitrate; benzo-18-crown-6 ether; benzene

1. Introduction

In extraction systems with crown compounds (L), some extraction constants, such as K_{ex} and $K_{ex\pm}$, have been employed for evaluating their extraction-abilities and -selectivities [1–6]. Here, the constants K_{ex} and $K_{ex\pm}$ have been generally defined as $[MLA_z]_{org}/P$ and $[MLA_{z-1}{}^+]_{org}[A^-]_{org}/P$, respectively, with $P = [M^{z+}][L]_{org}[A^-]^z$ at z = 1 and 2 [1,7–9]. The symbols M^{z+}, A^-, and the subscript "org" denote a metal ion with the formal charge of z+, a univalent pairing anion, and an organic phase, respectively. For evaluating the ability and selectivity of L for its extraction, many studies have been present [1–9], but those for clarifying ionic strength (I) dependences of the equilibrium constants seemed to be few [10,11]. Recently, one of the authors reported the I and I_{DCE} (with HNO_3 as an I conditioner) dependences of the K_{ex} and $K_{ex\pm}$ values in the silver picrate (AgPic) extraction with benzo-18-crown-6 ether (B18C6) into 1,2-dichloroethane (DCE), where I_{DCE} refers to the I value for the DCE phase [12]. At the same time, conditional distribution constants ($K_{D,A}$ = $[A^-]_{org}/[A^-]$) of the picrate ion Pic^- (=A^-) into the DCE (=org) phases have been determined [12] and thereby distribution equilibrium potential-differences (dep; $\Delta\varphi_{eq}$ as a symbol in an equation) have been evaluated [7,8,12].

In the present paper, to expand such characterization [12] for the AgPic extraction system to that for an $M^{II}Pic_2$ extraction one, we determined at 298 K the K_{ex}, $K_{ex\pm}$, and $K_{D,Pic}$ values for $PbPic_2$

extraction with B18C6 into benzene (Bz) under a co-presence of $Cd(NO_3)_2$ in a water phase. Then, I and I_{Bz} dependences of these equilibrium constants were mainly examined [12]. Similar examinations were performed for other overall or component equilibrium-constants, such as $K_{Pb/PbL}$, $K_{ex,ip}$, and $K_{1,Bz}$ (see Equations (6)–(8) for their definitions), derived from the above equilibrium constants. This study is expected to be useful for comparisons between the K_{ex} and $K_{ex\pm}$ values, because magnitudes of their comparable values depend on I [10,11] or I_{Bz} in general. Consequently, such data relevant to I and I_{Bz} can make more precise comparisons between the values possible.

In addition, it had been pointed out that the presence of alkali metal and transition metal ions by high concentrations may cause significant interferences in the removal of Pb in acidic waste streams [13]. Similarly, the M^{z+} separation with solvent extraction [13] and membrane transport experiments has been studied [14,15]. However, these quantitative considerations based on any equilibrium constants have not been reported. This situation reveals the importance of these fundamental studies [10–12] and this work as well, which can make a prediction for their separation more precise.

As well as the previous paper [12], the dep values which were fundamentally based on the ion transfer of Pic^- at the water/Bz interfaces were evaluated from the determined $K_{D,Pic}$ values [16]. Moreover, the relationship between log $K_{ex\pm}$ and dep was quantitatively discussed [7,16].

The both M(II) ions are well-known as toxic metals to living things in nature [17], but were employed here as simply model metal ones. Additionally, Bz was selected because a lot of data for the extraction of these M(II) ions with B18C6 or 18-crown-6 ether (18C6) is available [1,3,6,8,18–20].

A competitive extraction between Pb(II) and Cd(II) with B18C6 into Bz had been assumed with the addition of Cd(II) in the water phase in the beginning of this study, compared with the log ($K_{ex,Pb}/K_{ex,Cd}$) value of 9.73 for the Pb(II) and Cd(II) extraction with 18C6 [9]. However, against our plan, such an extraction behavior was not observed here.

2. Results and Discussion

2.1. Determination of Composition of Extracted Species with Pb(II) at Some $[Cd]_t/[Pb]_t$ Values

Determination of an M(II):L composition is based on the following K_{ex} or $K_{ex\pm}$ definition [1,8,19,21]: $K_{ex} = [MLA_2]_{org}/P$ and $K_{ex\pm} = [MLA^+]_{org}[A^-]_{org}/P$ with $P = [M^{2+}][L]_{org}[A^-]^2$ at $z = 2$. Taking common logarithms of both sides of these definitions and then rearranging them, we can easily obtain

$$\log (D_0/[A^-]^2) = \log K_{ex} + \log [L]_{org} \quad (1)$$

$$\text{and } \log (D_+/[A^-]) = \log K_{ex+} + \log [L]_{org} \quad (2)$$

with $D_0 = [MLA_2{}^0]_{org}/[M^{2+}]$, $D_+ = [MLA^+]_{org}/[M^{2+}]$ (see the Section 2.9), and K_{ex+} ($=K_{ex\pm}/K_{D,A}$) = $[MLA^+]_{org}/[M^{2+}][L]_{org}[A^-]$ [1,8,19]. From applying the approximate that D_0 and D_+ nearly equal D for Equations (1) and (2), respectively, the following equations were derived:

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

$$\text{and } \log (D/[A^-]) \approx \log K_{ex+} + \log [L]_{org} \quad (2a)$$

where D is an experimental distribution ratio and defined as $[Pb(II)]_{(\text{species analyzed by AAS measurement})}/([Pb(II)]_t - [Pb(II)]_{(\text{species analyzed by AAS measurement})})_{org}$. In addition, $[Pb(II)]_t$ refers to a total concentration of $Pb(NO_3)_2$ employed. Therefore, in terms of a plot of log $(D/[A^-]^2)$ versus log $[L]_{Bz}$ come from Equation (1a) or that of log $(D/[A^-])$ from Equation (2a), we can determine the Pb(II):L compositions in the extraction systems from their slopes [9]. Figure 1 shows such plots based on Equation (1a).

Experimentally-obtained slopes were 0.98 for the Pb(II)–B18C6 extraction system with 0 mmol·dm^{-3} of Cd(II) (or $[Cd]_t/[Pb]_t = 0$), 1.0 for that with 0.58 of Cd(II) (or 1.06), 0.97 for that with 14 of Cd(II) (or 26.6), 0.98 for that with 48 of Cd(II) (or 88.4), and 1.0 for that with 97 of Cd(II) (or 178). From these results, we can see easily that the compositions of Pb(II):B18C6 are 1:1 for all the systems. In the present study, there was no need of employing Equation (2a). The compositions of Pb(II):Pic(−I) were speculated to be 1:2 from similarity to the systems [3] reported before for M(II) extraction with 18C6 into Bz and from a charge balance in the Bz phases [1,8,19,21]: approximately $[PbLPic^{+}]_{Bz} \approx [Pic^{-}]_{Bz}$ from more-precisely $2[Pb^{2+}]_{Bz} + 2[PbL^{2+}]_{Bz} + [PbLPic^{+}]_{Bz} + [PbPic^{+}]_{Bz} \approx [Pic^{-}]_{Bz} + [NO_3^{-}]_{Bz}$, because it was expected that $[PbLPic^{+}]_{Bz} >> 2[Pb^{2+}]_{Bz} + 2[PbL^{2+}]_{Bz} + [PbPic^{+}]_{Bz}$ and $[Pic^{-}]_{Bz} >> [NO_3^{-}]_{Bz}$ [9,21].

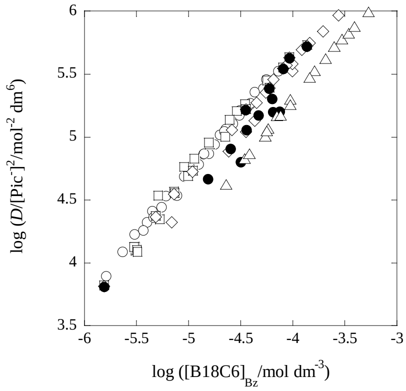

Figure 1. Plots for composition determination based on Equation (1a) under the conditions of $[Cd]_t/[Pb]_t$ = 0 (open circle), 1.06 (square), 26.6 (diamond), 88.5 (full circle), and 178 (triangle).

2.2. Determination of K_{ex}, $K_{ex\pm}$, and $K_{D,Pic}$

According to previous papers [1,8,9,22], the extraction-constant parameter ($K_{ex}{}^{mix}$) has been proposed:

$$\begin{aligned} \log K_{ex}{}^{mix} &= \log \{([MLA_2]_{org} + [MLA^{+}]_{org} + [ML^{2+}]_{org} + \ldots)/P\} \\ &\approx \log \{K_{ex} + (K_{D,A}/[M^{2+}][L]_{org}[A^{-}])\} \end{aligned} \tag{3}$$

with $K_{D,A} \approx [MLA^{+}]_{org}/[A^{-}]$. Using this equation, we can immediately obtain the K_{ex} and $K_{D,A}$ values from a plot of $\log K_{ex}{}^{mix}$ versus $-\log([M^{2+}][L]_{org}[A^{-}])$. In addition, Equation (3) can be rewritten as:

$$\log K_{ex^{mix}} \approx \log\left(K_{ex} + \sqrt{K_{ex\pm}/P}\right) \tag{4}$$

Similarly, the $K_{ex\pm}$ value (with the K_{ex} one; see Table 1) can be obtained from a plot of $\log K_{ex}{}^{mix}$ versus $-\log P^{1/2}$. Figures 2 and 3 show examples of such plots.

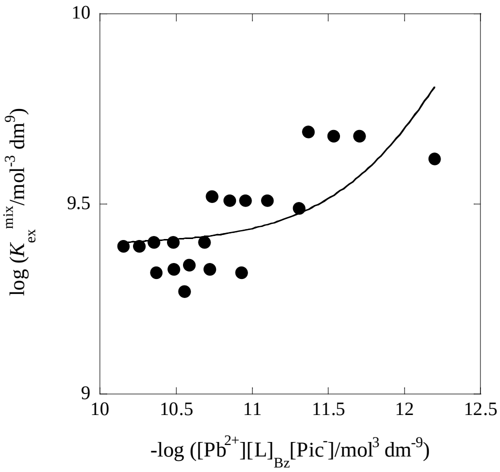

Figure 2. Plot of $\log K_{ex}{}^{mix}$ versus $-\log([Pb^{2+}][L]_{Bz}[Pic^{-}])$ with L = B18C6 at $[Cd]_t/[Pb]_t$ = 88.5. The line is based on Equation (3).

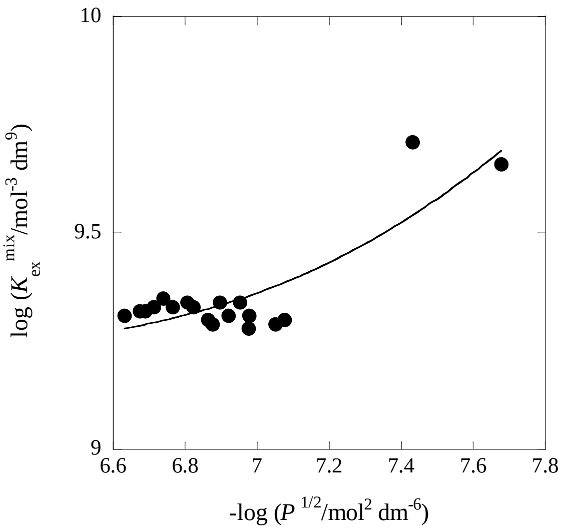

Figure 3. Plot of log K_{ex}^{mix} versus $-$log $P^{1/2}$ with B18C6 at $[Cd]_t/[Pb]_t$ = 88.5. The line is based on Equation (4).

From these plots, the $K_{D,Pic}$, $K_{ex\pm}$, and K_{ex} values were determined at 298 K. Table 1 lists these extraction constants, K_{ex} and $K_{ex\pm}$, and the conditional distribution constants, $K_{D,Pic}$, with averaged ionic strength-values (I) for the water phase in the five $[Cd]_t/[Pb]_t$ conditions. The K_{ex} values determined with Equation (4) were equal or close to those with Equation (3). This fact raises the credibility of the values themselves and also shows the effects of Equations (3) and (4) on evaluation. The K_{ex} and $K_{ex\pm}$ values at $[Cd]_t/[Pb]_t$ = 0 were smaller than those ($10^{11.712}$ mol^{-3} dm^{9} and $10^{4.1}$ mol^{-2}·dm^{6} [9]) reported before at I = 0.0059 mol·dm^{-3} for the $PbPic_2$ extraction with 18C6 into Bz.

Table 1. Basic data for the Pb(II) extraction by B18C6 from the water phase with co-presence of $Cd(NO_3)_2$ into Bz at 298 K.

$[Cd]_t/[Pb]_t$ [1]	I [2]/mol dm^{-3}	log K_{ex} [] [3]	log $K_{ex\pm}$ [3] (log y_{Pic} [4])	log $K_{D,Pic}$ ($\Delta\varphi_{eq}$ [5]/V)
0	0.0074	9.715 ± 0.006 (9.70 ± 0.01)	$2.6_6 \pm 0.2_5$ (-0.04)	$-3.2_1 \pm 0.1_4$ (-0.3_0)
1.06	0.0060	9.68 ± 0.02 (9.61 ± 0.04)	$3.9_0 \pm 0.2_3$ (-0.03)	$-2.4_4 \pm 0.1_3$ (-0.3_4)
26.6	0.048	9.58 ± 0.02 (9.51 ± 0.03)	$3.9_7 \pm 0.2_5$ (-0.07)	$-2.3_7 \pm 0.1_6$ (-0.3_5)
88.5	0.15	9.39 ± 0.03 (9.24 ± 0.05)	$3.9_5 \pm 0.1_9$ (-0.10)	$-2.6_0 \pm 0.1_5$ (-0.3_3)
178	0.29	9.31 ± 0.02 (9.21 ± 0.03)	$3.6_8 \pm 0.1_6$ (-0.12)	-2.65 ± 0.09 (-0.33)

[1] $[Pb(NO_3)_2]_t$ = 5.48 × 10^{-4} mol·dm^{-3}. [2] Averaged ionic strength for the water phase. [3] Values determined from Equation (4). [4] Logarithmic activity coefficient of Pic^- in water, calculated from the I value. [5] Dep values calculated from Equation (5).

2.3. Dep Determination from $K_{D,Pic}$

From the log $K_{D,Pic}$ values listed in Table 1, using the following equation and a standardized distribution constant ($K_{D,Pic}^{S}$), we can easily obtain the dep (or $\Delta\varphi_{eq}$) values for the five $[Cd]_t/[Pb]_t$ conditions at 298 K:

$$\Delta\varphi_{eq} = -0.05916(\log K_{D,Pic} - \log K_{D,Pic}^{S}) = \Delta\varphi_{Pic}^{0'} - 0.05916\log K_{D,Pic} \quad (5)$$

Here, the $K_{D,Pic}{}^{S}$ value is defined as the $K_{D,Pic}$ one at $\Delta\varphi_{eq}$ = 0 V, equals antilog ($\Delta\varphi_{Pic}{}^{0'}/0.05916$) (=exp ($\Delta\varphi_{Pic}{}^{0'}/0.02569$) [23]), and, as its common logarithmic value, −8.208 or −7.4473 is available from references [24,25]. In addition, the minus sign of −0.05916 (=−2.303RT/F) and the symbol $\Delta\varphi_{Pic}{}^{0'}$ denote the formal charge of Pic^{-} and the standard formal potential for the Pic^{-} transfer across the water/Bz interface, respectively. We mainly employed the former value for the evaluation described below. Table 1 lists the dep/V values evaluated from log $K_{D,Pic}{}^{S}$ = −8.208 [24].

2.4. Determination of $K_{Pb/PbL}$, $K_{ex,ip}$, $K_{1,Bz}$, $K_{2,Bz}$, and $K_{D,PbL}$

These constants can be evaluated from the following relations [1,18,26–28].

$$\log K_{Pb/PbL} = \log ([PbL^{2+}]_{Bz}/[Pb^{2+}][L]_{Bz}) \approx \log (D/[L]_{Bz}), \quad (6)$$

$$\log K_{ex,ip} = \log ([PbLPic_2]_{Bz}/[PbL^{2+}][Pic^{-}]^2) = \log (K_{ex}K_{D,L}/K_{PbL}), \quad (7)$$

$$\log K_{1.Bz} = \log ([PbLPic^{+}]_{Bz}/[PbL^{2+}]_{Bz}[Pic^{-}]_{Bz}) \approx \log \{K_{ex\pm}/K_{Pb/PbL}(K_{D,Pic})^2\} \quad (8)$$

$$= \log (K_{ex\pm}/K_{ex2\pm}), \quad (8a)$$

$$\log K_{2,Bz} = \log ([PbLPic_2]_{Bz}/[PbLPic^{+}]_{Bz}[Pic^{-}]_{Bz}) = \log (K_{ex}/K_{ex\pm}), \quad (9)$$

$$\text{and } \log K_{D,PbL} = \log ([PbL^{2+}]_{Bz}/[PbL^{2+}]) \approx \log (K_{Pb/PbL}K_{D,L}/K_{PbL}). \quad (10)$$

Only for the $K_{Pb/PbL}$ values, they were obtained as the averages of $D/[B18C6]_{Bz}$ at every $[Cd]_t/[Pb]_t$ value [27]. For the above evaluation at 298 K, 0.943 [2] and 3.19 [29] were used as the logarithmic values of $K_{D,B18C6}$ (=$[B18C6]_{Bz}/[B18C6]$) and $K_{PbB18C6}$ (=$[PbB18C6^{2+}]/[Pb^{2+}][B18C6]$), respectively. These five logarithmic K-values are summarized in Table 2, together with the ionic strength-values (I_{Bz}) for the Bz phase.

Table 2. Some equilibrium constants obtained from the Pb(II) extraction experiments by L = B18C6 from the water phase with co-presence of $Cd(NO_3)_2$ into Bz at 298 K.

$[Cd]_t/[Pb]_t$	log $K_{Pb/PbL}$ (log y_{Pb} [1])	log $K_{ex,ip}$	log $K_{1,Bz}$ (I_{Bz} [2]/10^{-6})	log $K_{2,Bz}$	log $K_{D,PbL}$
0	3.42 ± 0.05 (−0.16)	7.47	5.7 ± 0.3 (0.4$_4$)	7.1 ± 0.2	1.18
1.06	3.42 ± 0.08 (−0.14)	7.143	5.4 ± 0.3 (2.$_6$)	5.8 ± 0.2	1.17
26.6	3.2$_3$ ± 0.1$_2$ (−0.34)	7.34	5.5 ± 0.4 (2.$_7$)	5.6 ± 0.2	0.9$_8$
88.5	3.1$_3$ ± 0.2$_1$ (−0.50)	7.15	6.0 ± 0.4 (1.$_7$)	5.4 ± 0.2	0.8$_8$
178	2.9$_5$ ± 0.2$_8$ (−0.62)	7.06	6.0 ± 0.3 (7.$_8$)	5.6 ± 0.2	0.7$_1$

[1] Logarithmic activity coefficient of Pb^{2+} in water, calculated from the averaged I value. [2] Averaged ionic strength for the Bz phase.

2.5. Correlation between log $K_{ex\pm}$ and Dep

We can obtain the following relation from the thermodynamic cycle of the $PbLPic^{+}$ extraction with Pic^{-}.

$$\begin{aligned}\log K_{ex\pm} &= 2\log K_{D,Pic} + \log K_{Pb/PbL} + \log K_{1,Bz} \\ &= 2\log K_{D,Pic}{}^{S} - 2(F/2.303RT)\Delta\varphi_{eq} + \log K_{Pb/PbL}\cdot K_{1,Bz}\end{aligned} \quad (11)$$

Here, the log $K_{Pb/PbL}\cdot K_{1,Bz}$ term was in the range of 8.7 to 9.1 (see the data in Table 2) and log $K_{D,Pic}{}^{S}$ (=−8.208 [24] or −7.4473 [25]) equals log $K_{D,Pic}$ at $\Delta\varphi_{eq}$ = 0 V. Hence, we obtained to be −7.7 to

-7.3 for the former $K_{D,Pic}{}^{S}$ value or the -6.2 to -5.8 for the latter one as the term of 2log $K_{D,Pic}{}^{S}$ + log $K_{Pb/PbL} \cdot K_{1,Bz}$ (see Tables 1 and 2). In addition, $2F/2.303RT$ becomes 33.80 V^{-1} at T = 298.15 K. Rearranging Equation (11), we can immediately derive

$$\log K_{ex\pm} \approx (-7.7 \text{ to } -7.3) - 33.80\Delta\varphi_{\text{Equation}} \tag{11a}$$

From the regression analysis of an experimental plot in Figure 4, the following line was obtained: log $K_{ex\pm}$ = ($-5._3 \pm 1._4$) $-$ ($27._3 \pm 4._2$)$\Delta\varphi_{eq}$ at $|R|$ = 0.967, where the symbol R denotes a correlation coefficient. This regression line is close to Equation (11a) which was estimated from the experimental K values. This fact indicates the presence of dep, as similar to the results reported previously [7,8,12,16,21,22].

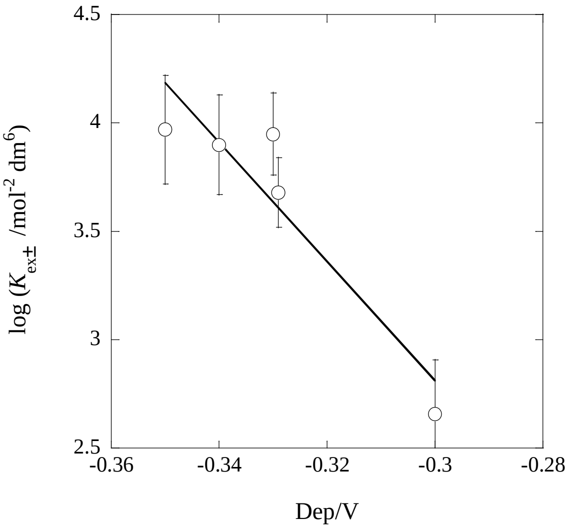

Figure 4. Plot of log $K_{ex\pm}$ versus dep for the Pb(II) extraction with $Cd(NO_3)_2$ and B18C6 into Bz. The line corresponds to Equation (11a).

2.6. I Dependences of log K_{ex} and log $K_{ex,ip}$

The thermodynamic extraction constant of K_{ex} is $K_{ex}{}^{0}$ = $[PbLPic_2]_{Bz}/a_{Pb}[L]_{Bz}(a_{Pic})^2$, where a_{Pb} and a_{Pic} refer to activities of Pb^{2+} and Pic^{-} in the water phase, respectively, and it was assumed that $[PbLPic_2]_{Bz}$ is equal to the activity in the Bz phase, because $PbL^{2+}(Pic^{-})_2$ is charge-less. The same is true of $[B18C6]_{Bz}$ too. Taking the common logarithms of both sides of the $K_{ex}{}^{0}$ definition, we can obtain

$$\log K_{ex}{}^{0} = \log K_{ex} - \log \{y_{Pb}(y_{Pic})^2\} \tag{12}$$

with $y_{Pb} = a_{Pb}/[Pb^{2+}]$ and $y_{Pic} = a_{Pic}/[Pic^{-}]$. Introducing the extended Debye–Hückel (DH) equation [30,31] in Equation (12) and arranging it, the following equation was obtained:

$$\log\ K_{ex} = \log K_{ex^0} - 6A\sqrt{I}/(1 + Ba_{\pm}\sqrt{I}) \tag{12a}$$

Here, the DH equation was based on the mean activity coefficient and the symbol $a_{\pm}$ denote the ion-size parameter [30] in Å unit. Although the extended DH equation holds in the I range of $\leq$0.1 mol$\cdot$dm^{-3} [30] as you know, we approximately employed it for the condition of I = 0.29 (see Table 1). Figure 5 shows curve-fittings of the plots for Equation (12a).

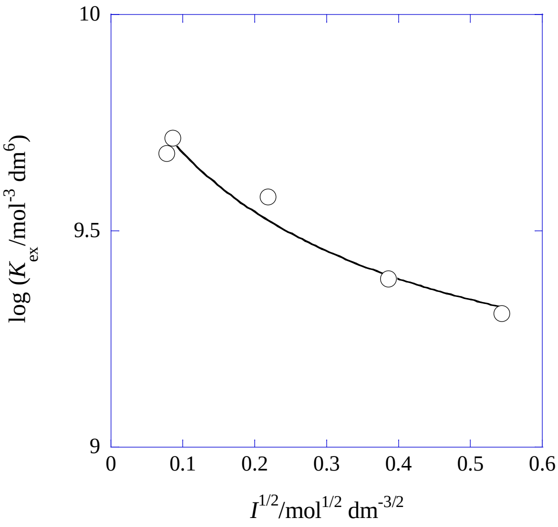

Figure 5. Plot of log K_{ex} versus $I^{1/2}$ for the Pb(II) extraction with $Cd(NO_3)_2$ and B18C6 into Bz. The line is based on Equation (12a).

Its regression line was log K_{ex} = (9.91 ± 0.03) − 6 × (0.5114)$\sqrt{I}$/(1 + (3.4$_0$ ± 0.4$_6$)$\sqrt{I}$) at R = 0.980, where the coefficient A was fixed to 0.5114 $mol^{-1/2}·dm^{3/2}$ [30] and the $a_{\pm}$ value in water was evaluated to be 10 Å (=3.4$_0$/0.3291) at 298 K.

Similarly, the log $K_{ex,ip}$ values were analyzed. Their constants were expressed as

$$\log\ K_{ex,ip} = \log K_{ex,ip^0} - 6A\sqrt{I}/\left(1 + Ba_{\pm}\sqrt{I}\right) \tag{13}$$

$$\text{with } K_{ex,ip}{}^0 = [PbLPic_2]_{Bz}/a_{PbL}(a_{Pic})^2 = K_{ex,ip}/y_{PbL}(y_{Pic})^2 \tag{13a}$$

The regression analysis of the plots yielded log $K_{ex,ip}$ = (7.66 ± 0.03) − 6 × (0.5114)$\sqrt{I}$/(1 + (3.4$_1$ ± 0.5$_1$)$\sqrt{I}$) at R = 0.975 and then the $a_{\pm}$ value was evaluated to be 10 Å. The accordance between Pb^{2+}–Pic^- distance and $PbB18C6^{2+}$–Pic^- one suggests that the former interaction between the Pb^{2+} and Pic^- ions in water saturated with Bz is equivalent with the latter one between $PbB18C6^{2+}$ and Pic^-.

It is interesting that the evaluated $a_{\pm}$ values are close to the sum (=11.$_5$ Å) of the ion-size parameters [32] between Pb^{2+} (4.5 Å) and Pic^- (7 Å) for water. This $K_{ex,ip}{}^0$ value was well in accord with that (=$10^{7.66}$ $mol^{-1}·dm^3$) calculated from the thermodynamic cycle of $K_{ex,ip}{}^0 \approx K_{ex}{}^0 K_{D,L}/K_{PbL}$ (=$10^{9.91} \times 10^{0.943}/10^{3.19}$).

Considering that the K_{ex} values are most precise ones of the some extraction constants determined here (see their errors in Table 1), the fair dependences of log K_{ex} on I indicate a simple role of $Cd(NO_3)_2$ only as the ionic strength conditioner in the present extraction systems. In other words, the authors were not be able to clearly find out positive or negative effects of $Cd(NO_3)_2$ on the present Pb(II) extraction with B18C6 into Bz.

2.7. *I_{Bz} Dependences of log $K_{1,Bz}$ and log $K_{2,Bz}$*

Using I_{Bz} and the DH limiting law [30], both log $K_{1,Bz}{}^0$ and log $K_{2,Bz}{}^0$ can be expressed as

$$\log K_{1,Bz^0} \approx \log K_{1,Bz} - \log y_{PbL,Bz} = \log K_{1,Bz} + 4A_{Bz}\sqrt{I_{Bz}} \tag{14}$$

with $y_{PbLPic,Bz} \approx y_{Pic,Bz}$ and

$$\log K_{2,Bz^0} = \log K_{2,Bz} - \log(y_{PbLPic,Bz} \cdot y_{Pic,Bz}) = \log K_{2,Bz} + 2A_{Bz}\sqrt{I_{Bz}}. \tag{15}$$

Rearranging Equations (14) and (15), we can obtain

$$\log K_{1,\mathrm{Bz}} \approx \log K_{1,\mathrm{Bz}^0} - 4A_{Bz}\sqrt{I_{\mathrm{Bz}}} \tag{14a}$$

$$\text{and } \log K_{2,\mathrm{Bz}} = \log K_{2,\mathrm{Bz}^0} - 2A_{Bz}\sqrt{I_{\mathrm{Bz}}} \tag{15a}$$

Based on Equations (14a) and (15a), we prepared Figure 6 from the data in Table 2.

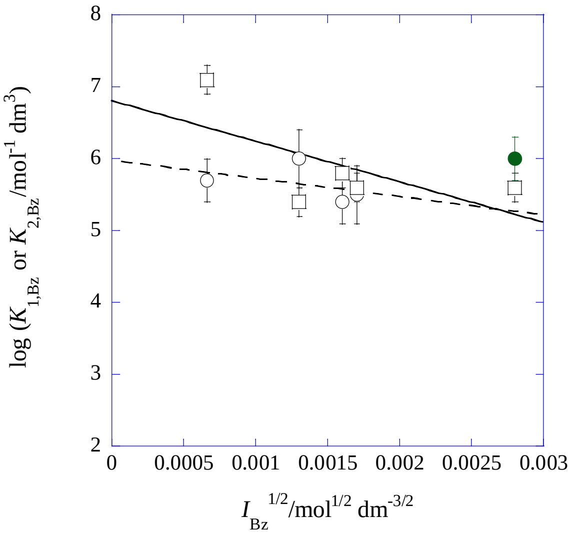

Figure 6. Plots of log $K_{1,\mathrm{Bz}}$ (circle) and log $K_{2,\mathrm{Bz}}$ (square) versus $I_{\mathrm{Bz}}{}^{1/2}$ for the Pb(II) extraction with $\mathrm{Cd(NO_3)_2}$ and B18C6 into Bz. The regression lines were based on Equations (14a) and (15a). The full circle was omitted from the regression analysis of log $K_{1,\mathrm{Bz}}$.

At the same time, these plots were analyzed by using the both equations. Their regression lines were log $K_{1,\mathrm{Bz}}$ = ($5.9_8 \pm 0.4_9$) − 4 × (63 ± 89)$\sqrt{I_{\mathrm{Bz}}}$ at R = 0.449 except for the point of $[\mathrm{Cd}]_t/[\mathrm{Pb}]_t$ = 178 and log $K_{2,\mathrm{Bz}}$ = ($6.8_1 \pm 0.6_8$) − 2 × (282 ± 195)$\sqrt{I_{\mathrm{Bz}}}$ at R = 0.641. These lines intersected with each other at $I_{\mathrm{Bz}}{}^{1/2}$ = $2._7 \times 10^{-3}$ $\mathrm{mol^{1/2}{\cdot}dm^{-3/2}}$, yielding log $K_{1,\mathrm{Bz}}$ = log $K_{2,\mathrm{Bz}}$ = 5.3_1. This fact indicates that, in the lower I_{Bz} range less than $7._1 \times 10^{-6}$ $\mathrm{mol{\cdot}dm^{-3}}$, the $K_{2,\mathrm{Bz}}$ values are larger than the $K_{1,\mathrm{Bz}}$ ones. The latter values may be estimated to actually be the smaller values because of the approximation [33] for the $K_{1,\mathrm{Bz}}$ determination (see Equation (8)). Unlike the case of the $\mathrm{CdPic_2}$–B18C6 extraction system [33], unfortunately, we do not have the procedure which corrects such deviations for the present extraction systems, because of a lack of adequate data used for the correction.

In addition, we tried curve-fittings to the two plots using the following equations:

$$\log K_{1,\mathrm{Bz}} \approx \log K_{1,\mathrm{Bz}^0} - 4A_{\mathrm{Bz}}\sqrt{I_{\mathrm{Bz}}} + b_1 I_{\mathrm{Bz}} \tag{14b}$$

$$\text{and } \log K_{2,\mathrm{Bz}} = \log K_{2,\mathrm{Bz}^0} - 2A_{\mathrm{Bz}}\sqrt{I_{\mathrm{Bz}}} + b_2 I_{\mathrm{Bz}}. \tag{15b}$$

with the approximation of 1 >> $\sqrt{I_{\mathrm{Bz}}}$ (see Table 2). Here, the symbols b_1 and b_2 denote empirical curve-fitting parameters [30,31] which were simply predicted in this study from the plot shapes (see Figure 6). The regression analyses of the plots at 298 K gave log $K_{1,\mathrm{Bz}}$ = ($6.1_6 \pm 0.8_0$) − 4 × (179 ± 247)$\sqrt{I_{\mathrm{Bz}}}$ + ($2._3 \pm 2._7$) × $10^5 I_{\mathrm{Bz}}$ at R = 0.569 and log $K_{2,\mathrm{Bz}}$ = ($8.8_0 \pm 0.9_8$) − 2 × (1625 ± 603)$\sqrt{I_{\mathrm{Bz}}}$ + ($7._6 \pm 3._3$) × $10^5 I_{\mathrm{Bz}}$ at 0.914 (see Figure 7). Modifying these equations like the Davies one [30,31], their 2nd and 3rd terms became −4 × (179 ± 247)($\sqrt{I_{\mathrm{Bz}}}$ − ($3._2 \pm 5._9$) × $10^2 I_{\mathrm{Bz}}$) and − 2 × (1625 ± 603)($\sqrt{I_{\mathrm{Bz}}}$ − ($2._3 \pm 1._3$) × $10^2 I_{\mathrm{Bz}}$), respectively. These $b_1/4A_{\mathrm{Bz}}$ and $b_2/2A_{\mathrm{Bz}}$ values of about 320 and 230 $\mathrm{mol^{-1/2}{\cdot}dm^{3/2}}$ for the Bz phases are much larger than 0.3 [31] for the aqueous solution at 298 K. Equation (14b) intersects

Equation (15b) around $I_{Bz}^{1/2}$ = 3.$_3$ × 10^{-3} $mol^{1/2}·dm^{-3/2}$, yielding log $K_{1,Bz}$ = log $K_{2,Bz}$ = 6.3$_0$, and then their two lines equal with each other within the experimental errors (see the plots in Figure 7).

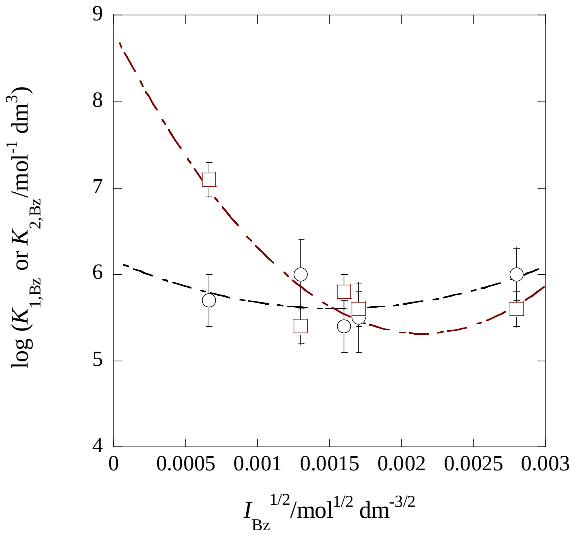

Figure 7. Plots of log $K_{1,Bz}$ (circle) and log $K_{2,Bz}$ (square) versus $I_{Bz}^{1/2}$ for the Pb(II) extraction with $Cd(NO_3)_2$ and B18C6 into Bz. The regression lines were based on Equations (14b) and (15b).

In comparison of Equations (14a) and (15a) with Equations (14b) and (15b), the point of intersection changed from $I_{Bz}^{1/2}/mol^{1/2}·dm^{-3/2}$ = 0.002$_7$ to 0.003$_3$, while their corresponding log $K_{1,Bz}$ (=log $K_{2.Bz}$) value changed from 5.3 to 6.3.

At least in the lower I_{Bz} range less than 1.$_1$ × 10^{-5} $mol·dm^{-3}$, the $K_{2,Bz}$ values are larger than the $K_{1,Bz}$ ones. From the results of the calculation based on Equations (14a,b) and (15a,b), the relation of $K_{1.Bz}$ < $K_{2,Bz}$ holds in the range less than (0.7$_1$–1.$_1$) × 10^{-5} $mol·dm^{-3}$ (see above). According to the paper [8], such a fact suggests a structural change around Pb(II) in the reaction of $Pb(B18C6)Pic^{+}_{Bz}$ + Pic^{-}_{Bz} ⇌ $Pb(B18C6)Pic_{2,Bz}$, such as $Cd(18C6)Pic_{2,Bz}$ of the Cd(II) extraction systems [33]. Trends similar to $K_{1,Bz}$ < $K_{2,Bz}$ are observed in the reactions of $Cd18C6^{2+}$ with Pic^-, Cl^-, and Br^- in the Bz phases for fixed I_{Bz} values [1,8]. The higher I_{Bz} range may lead to the formation of ion-pair complexes with other coordination structures around Pb(II), although their structures are not clear.

Table 3 shows results for the both estimated values from Equations (14a) and (15a) and those from Equations (14b) and (15b). In comparison with differences, |dif.|, in $K_{1,Bz}$ and $K_{2,Bz}$ between the experimental and estimated values, the |dif.| values estimated from Equations (14b) and (15b) were essentially smaller than those done from Equations (14a) and (15a). Especially, the former equations seem to be superior to the latter ones in the I_{Bz} range, namely the present experimental $[Cd]_t/[Pb]_t$ range, of 4 × 10^{-7} to 8 × 10^{-6} $mol·dm^{-3}$ in the cases of the prediction of $K_{2,Bz}$. Unfortunately, chemical and physical meanings of b_1 and b_2 are not clear still now.

Table 3. Comparison between Equations (14a) and (15a) and Equations (14b) and (15b) in the re-production of the experimental $K_{1,Bz}$ and $K_{2,Bz}$ values [1] at 298 K.

$[Cd]_t/[Pb]_t$	log $K_{1,Bz}$				log $K_{2,Bz}$			
	Equation (14a)	|Dif.| [2]	Equation (14b)	|Dif.| [2]	Equation (15a)	|Dif.| [2]	Equation (15b)	|Dif.| [2]
0	5.8$_1$	0.2	6.1$_6$	0.2	6.4$_4$	0.6	6.9$_8$	0.1
1.06	5.5$_8$	0.2	5.6$_1$	0.2	5.9$_1$	0.1	5.5$_4$	0.2
26.6	5.5$_6$	0.1	5.6$_1$	0.1	5.8$_7$	0.3	5.5$_0$	0.1
88.5	5.6$_6$	0.4	5.6$_2$	0.4	6.0$_8$	0.6	5.8$_7$	0.4
178	5.2$_8$	0.8	5.9$_6$	0.1	5.2$_4$	0.4	5.6$_2$	0.0

[1] See Table 2 for these values. [2] Absolute value for the difference between the experimental $K_{1,Bz}$ or $K_{2,Bz}$ value and their estimated one.

2.8. I_{Bz} Dependences of log $K_{ex\pm}{}^{0'}$, log $K_{D,Pic}{}^{0'}$, and log $K_{Pb/PbL}{}^{0}$

The thermodynamic equilibrium constant $K_{ex\pm}{}^{0}$ is equal to $(y_{\pm,Bz})^2 K_{ex\pm}{}^{0'}$, with $y_{\pm,Bz}$ = $(y_{PbLPic,Bz} \cdot y_{Pic,Bz})^{1/2}$ and $K_{ex\pm}{}^{0'}$ = $[PbLPic^+]_{Bz}[Pic^-]_{Bz}/(a_{Pb}[L]_{Bz}(a_{Pic})^2)$. Taking the common logarithms of the both sides in this equation and rearranging it with the DH limiting law, we can easily obtain

$$\log K_{ex\pm^{0'}} = \log(K_{ex\pm}/y_{Pb}(y_{Pic})^2) = \log K_{ex\pm^0} + 2A_{Bz}\sqrt{I_{Bz}} \quad (16)$$

Figure 8 shows the plot of log $K_{ex\pm}{}^{0'}$ versus $I_{Bz}{}^{1/2}$ based on Equation (16). The regression analysis of this plot gave the equation of log $K_{ex\pm}{}^{0'}$ = $(3.1_1 \pm 0.6_9) + 2 \times (315 \pm 196)\sqrt{I_{Bz}}$ at R = 0.680. From this $K_{ex,\pm}{}^{0}$ value and the $K_{ex}{}^{0}$ one, we calculated log $K_{2,Bz}{}^{0}$ to be $6.8_0 \pm 0.6_9$, being in good agreement with that (=6.8) evaluated from Equation (15a).

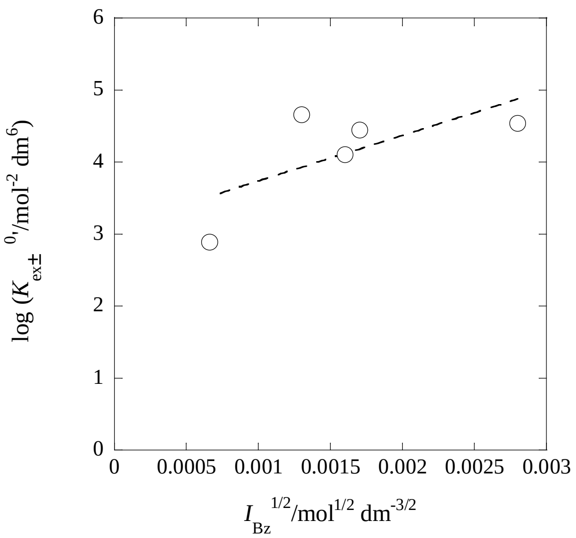

Figure 8. Plot of log $K_{ex\pm}{}^{0'}$ versus $I_{Bz}{}^{1/2}$ based on Equation (16) for the Pb(II) extraction with $Cd(NO_3)_2$ and B18C6 into Bz. The symbol $K_{ex\pm}{}^{0'}$ was defined as $K_{ex\pm}/y_{Pb}(y_{Pic})^2$.

Similarly, the plot of log $K_{D,Pic}{}^{0'}$ versus $I_{Bz}{}^{1/2}$ was performed in Figure 9, where $K_{D,Pic}{}^{0'}$ is defined as $[Pic^-]_{Bz}/a_{Pic}$. This plot is based on the equation

$$\log K_{D,Pic^{0'}} = \log(K_{D,Pic}/y_{Pic}) = \log K_{D,Pic^0} + A_{Bz}\sqrt{I_{Bz}} \quad (17)$$

The regression analysis yielded log $K_{D,Pic}{}^{0'}$ = $(-3.0_0 \pm 0.3_6) + (258 \pm 210)\sqrt{I_{Bz}}$ at R = 0.578.

In addition, the analysis was tried by using an equation similar to Equations (14b) and (15b) with $1 >> \sqrt{I_{Bz}}$ Its regression line was

$$\log K_{D,Pic^{0'}} = (-4.2_5 \pm 0.1_2) + (1949 \pm 154)\sqrt{I_{Bz}} + (-4.7_6 \pm 0.4_2) \times 10^5 I_{Bz} \quad (17a)$$

at R = 0.995. Here, the latter two terms are rearranged into $(1949 \pm 154)(\sqrt{I_{Bz}} - (245 \pm 29)I_{Bz})$. This value, 245 mol$^{-1/2}\cdot$dm$^{3/2}$, is comparable to the $b_1/4A_{Bz}$ (=~320) and $b_2/2A_{Bz}$ (=~230) values estimated above.

Lastly, the log $K_{Pb/PbL}{}^{0'}$ (=log $([PbL^{2+}]_{Bz}/a_{Pb}[L]_{Bz})$) values were analyzed. This constant was related with the log $K_{Pb/PbL}{}^{0}$ (=log $(a_{PbL,Bz}/a_{Pb}[L]_{Bz})$) value by the following equation:

$$\log\ K_{Pb/PbL^{0'}} = \log(K_{Pb/PbL}/y_{Pb}) = \log\ K_{Pb/PbL^0} +\ 4A_{Bz}\sqrt{I_{Bz}} \quad (18)$$

The log $K_{Pb/PbL}{}^{0'}$ values were plotted against the $I_{Bz}{}^{1/2}$ ones. The regression line based on Equation (18) was log $K_{Pb/PbL}{}^{0'}$ = (3.546 ± 0.001) + 4 × (2.1_6 ± 0.1_6)$\sqrt{I_{Bz}}$ at R = 0.997, except for the two points of $I_{Bz} = 4._4 \times 10^{-7}$ and $1._7 \times 10^{-6}$ mol·dm^{-3} (see Table 2). These two log $K_{Pb/PbL}{}^{0'}$ values excluded from the regression analysis are included in the regression line within experimental errors. However, the A_{Bz} value is much smaller than the others. In addition, the analysis was tried by using an equation similar to Equations (14b) and (15b). However, its regression line showed the result of $A_{Bz} < 0$.

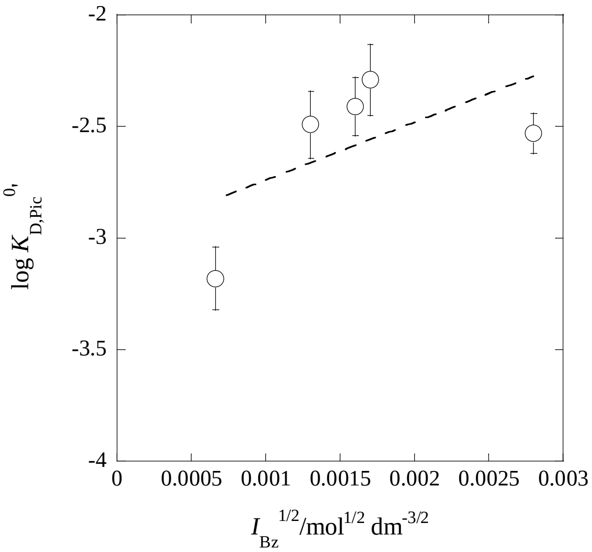

Figure 9. Plot of log $K_{D,Pic}{}^{0'}$ versus $I_{Bz}{}^{1/2}$ based on Equation (17) for the Pb(II) extraction with $Cd(NO_3)_2$ and B18C6 into Bz. The symbol $K_{D,Pic}{}^{0'}$ was defined as $K_{D,Pic}/y_{Pic}$. The error bars in the figure are those of the log $K_{D,Pic}$ values.

By a combination with log $K_{D,Pic}{}^0$, the log $K_{Pb/PbL}{}^0$ can be changed into log $K_{ex2\pm}{}^0$ (=log ($a_{PbL,Bz}(a_{Pic,Bz})^2/a_{Pb}[L]_{Bz}(a_{Pic,Bz})^2$)) = log $K_{Pb/PbL}{}^0$ + 2log $K_{D,Pic}{}^0$. Thus, the log $K_{ex2\pm}{}^0$ value was estimated to be $-2.4_5 \pm 0.3_7$ from Equation (17) (the linear type) or $-4.9_6 \pm 0.1_3$ from Equation (17a) (the $f(p) = a + bp + cp^2$ type). Using log $K_{ex\pm}{}^0 = 3.1_1$ obtained from Equation (16) and log $K_{1,Bz}{}^0 = 5.9_8$ from Equation (14a) (the linear type), the log $K_{ex2\pm}{}^0$ value was calculated to be $-2.8_7 \pm 0.8_5$. On the other hand, the log $K_{ex2\pm}{}^0$ value became $-3._1 \pm 1._1$ in the calculation with log $K_{1,Bz}{}^0 = 6.1_6$ from Equation (14b) (the $f(p) = a + bp + cp^2$ type). Except for −4.9 from Equation (17a), the values calculated from the three equations agreed with each other within their calculation errors. According to the thermodynamic cycle, the relation of $K_{ex\pm} = K_{Pb/PbL}K_{1,Bz}(K_{D,Pic})^2$ holds. From this relation, we obtained log $K_{ex\pm}{}^0 = 3.5_4 \pm 0.7_2$ (=log $K_{Pb/PbL}{}^0$ + log $K_{1,Bz}{}^0$ + 2log $K_{D,Pic}{}^0$). This value is in agreement with that (=3.1) calculated from Equation (16) within the calculation error of ±0.7. In addition, the same calculation was performed with the values obtained from the polynomial Equations (14b) and (17a). Its value was $1.2_0 \pm 0.8_3$, being much smaller than 3.1. These results suggest that the linear-type equation is the more reliable than the polynomial-type one, from the thermodynamic points of view.

From the four experimental A_{Bz}/mol$^{-1/2}$·dm$^{3/2}$ values based on Equations (14a), (15a), (16), and (17), except for the value obtained from Equation (18), their average value was estimated to be 230. Consequently, this A_{Bz} value for Bz saturated with water was about 2-times larger than that (=103.3 mol$^{-1/2}$·dm$^{3/2}$) calculated for pure Bz with ε_r = 2.275 [2] at 298.15 K. To agree with this conclusion, however, a reasonable reason will be required for the omission of the result of Equation (18).

2.9. A Try for Estimation of Detailed Separation Factor

According to the previous papers [8,33], the following relations hold for given Pic^- and L.

$$\log (K_{ex,Pb}/K_{ex,Cd}) = \log (D_{0,Pb}/D_{0,Cd}), \tag{19}$$

$$\log (K_{ex\pm,Pb}/K_{ex\pm,Cd}) = \log (D_{+,Pb}/D_{+,Cd}), \tag{20}$$

$$\text{and } \log (K_{Pb/PbL}/K_{Cd/CdL}) = \log (D_{2+,Pb}/D_{2+,Cd}) \tag{21}$$

with

$$D_{0,Pb} = [PbLPic_2]_{Bz}/[Pb^{2+}] = K_{ex}[L]_{Bz}[Pic^-]^2, \tag{22}$$

$$D_{+,Pb} = [PbLPic^+]_{Bz}/[Pb^{2+}] = K_{ex\pm}[L]_{Bz}[Pic^-]/K_{D,Pic}, \tag{23}$$

$$\text{and } D_{2+,Pb} = [PbL^{2+}]_{Bz}/[Pb^{2+}] = K_{Pb/PbL}[L]_{Bz}. \tag{24}$$

Here, $D_{0,Pb}$, $D_{+,Pb}$, and $D_{2+,Pb}$ show the values of M = Pb at z = 0, 1, and 2, respectively. The same is true of the definitions for the Cd(II) (=M(II)) extraction system with B18C6.

For example, Equation (19) can be expressed as:

$$\log (D_{0,Pb}/D_{0,Cd}) = \log ([PbLPic_2]_{Bz}/[CdLPic_2]_{Bz}) + \log ([Cd^{2+}]/[Pb^{2+}]) \tag{25}$$

Assuming that $[Cd^{2+}]/[Pb^{2+}]$ approximately equals $[Cd^{2+}]_t/[Pb^{2+}]_t$, then we can estimate the more detailed value than the separation factor. In the Pb(II) extraction with Cd(II) by B18C6 into Bz, the $\log (D_{0,Pb}/D_{0,Cd})$ value was 7.09 in which the $\log K_{ex}$ value (=9.44$_8$) was estimated at I = 0.095 [33] from the regression line of Figure 5. From Equation (25) and $[Cd^{2+}]_t/[Pb^{2+}]_t$ = 55.$_5$ estimated from a correlation between $[Cd]_t/[Pb]_t$ and I in Table 1, the $\log ([PbLPic_2]_{Bz}/[CdLPic_2]_{Bz})$ value became 5.35. At least this result shows that the actual separation of Pb(II) from a test solution with an 56 excess amount of Cd(II) is possible. The same can be true of an application based on the handling for $D_{+,Pb}/D_{+,Cd}$ and $D_{2+,Pb}/D_{2+,Cd}$, if the $K_{ex\pm,Cd}$ and $K_{Cd/CdL}$ values are determined about the $CdPic_2$ extraction with B18C6 (=L) into Bz.

2.10. Relative Concentrations of the Three Species Extracted into Bz

We can immediately calculate relative concentrations of $PbLPic_2$, $PbLPic^+$, and PbL^{2+} in the Bz phases from the $D_{0,Pb}$, $D_{+,Pb}$, and $D_{2+,Pb}$ values, respectively [8,24,30]. For example, the percentage of the relative concentration of $PbLPic_2$ can be obtained from $100D_{0,Pb}/(D_{0,Pb} + D_{+,Pb} + D_{2+,Pb})$. In addition, the concentrations of $PbLPic^+$ and PbL^{2+} were evaluated from similar equations. The thus-calculated values were: 46% for $PbLPic_2$, 10% for $PbLPic^+$, and 44% for PbL^{2+} at I = 0.0074 mol·dm^{-3} (or $[Cd]_t/[Pb]_t$ = 0); 38%, 25%, and 37% at 0.0060 (or 1.06$_1$), respectively; 35%, 32%, and 34% at 0.048 (or 26.6$_3$), respectively; 24%, 53%, and 23% at 0.15 (or 88.4$_8$), respectively; and 26%, 49%, and 25% at 0.29 (or 177.$_5$), respectively.

One can see easily that the distribution of $PbLPic_2$ and PbL^{2+} into Bz is dominant in the lower I or $[Cd]_t/[Pb]_t$ values, while that of $CdLPic^+$ is dominant in the higher I ones. That is, in the I range more than 0.15 mol·dm^{-3}, the distribution of $PbLPic^+$ with Pic^- may be dominant, compared with those of both $PbLPic_2{}^0$ and PbL^{2+} with $2Pic^-$. Now, the authors cannot clearly explain this result; namely, in the higher I range, why is the univalent cationic complex more extractable to the Bz phase than the other complexes are? Conversely, can they call this phenomenon "salting out effect"? However, these data can be useful for the discussion of membrane transport phenomena with L [34]. That is, what species mainly transfer through the membrane?

3. Materials and Methods

3.1. Materials

Purities of the reagents $Pb(NO_3)_2$ (Wako, 99.9%) and $Cd(NO_3)_2\cdot 4H_2O$ (Kanto, Guaranteed pure reagent (GR), >98.0%) were determined by an EDTA titration with $Na_2EDTA\cdot 2H_2O$ (Dojin, Kumamoto in Japan, >99.5%): their purities obtained were 98.3% for Pb(II) and 96.6–98.7% for Cd(II). A basic aqueous solution (pH > 10) of picric acid, $HPic\cdot mH_2O$, (Wako, GR, >99.5%: added water 15–25%) was analyzed at 355 or 356 nm by using a Hitachi UV–Visible spectrophotometer (type U-2001) (Hitachi High-Technologies Corporation, Tokyo, Japan) and then its concentration was determined with the calibration curve ($\varepsilon_{356} = 1.45 \times 10^4$ $cm^{-1}\cdot mol^{-1}\cdot dm^3$ [35]) for Pic^-. Using a calibration curve ($\varepsilon_{273} = 2.50 \times 10^3$ cm^{-1} $mol^{-1}\cdot dm^3$ [6]) of B18C6 at 273 nm, a concentration of an aqueous solution with its ether (Tokyo Chemical Industry, Co. Ltd., Tokyo, Japan, >98.0% and others) was determined spectrophotometrically. The diluent Bz (Wako Pure Chemical Industries, Ltd., Osaka, Japan, or Kanto Chemical Co., Ltd., Tokyo, Japan) was washed three times with pure water and then saturated with water. Other chemicals were of the GR grades. Pure water was prepared as follows: a tap water was distilled once with a stainless-steel still and then passed through the Autopure system (Yamato/Millipore, type WT 101 UV) (Tokyo, Japan).

3.2. Extraction Procedures

Aqueous solution containing $5.47_8 \times 10^{-4}$ $mol\cdot dm^{-3}$ $Pb(NO_3)_2$, $1.27_2 \times 10^{-3}$ HPic, x $Cd(NO_3)_2$, 0.019_8 HNO_3, and y B18C6 was prepared and mixed with the equal volume (10 or 12 cm^3) of Bz saturated with water in a stoppered glass tube of about 30 cm^3. Here, x was fixed at 0 $mol\cdot dm^{-3}$, $5.81_0 \times 10^{-4}$, 0.0145_9, 0.0484_7, or 0.0972_6 and, at a fixed x, y was changed in the ranges of 6.5×10^{-6} to 1.6×10^{-4} $mol\cdot dm^{-3}$ (see circle in Figure 1), 3.9×10^{-6} to 1.9×10^{-4} (square), 1.3×10^{-5} to 4.4×10^{-4} (diamond), 3.9×10^{-6} to 2.6×10^{-4} (full circle), or 3.7×10^{-5} to 7.4×10^{-4} (triangle), respectively. The glass tubes with some kinds of the L concentrations were agitated for 2 min. by hands and then mechanically shaken for 2 h in a water bath thermostated at 25 ± 0.3 °C. After it, the mixtures were centrifuged. The Bz phases were separated at 25 °C, transferred into the other tubes, and some cubic centimeters of 0.1 $mol\cdot dm^{-3}$ HNO_3 were added to them. These mixtures in the tubes were handled with the same manner as that described above. The Pb(II) amounts of the acidic water phases, into which the Pb(II) species normally-extracted into Bz was back-extracted, were determined at 283.3 nm by the atomic absorption spectrophotometer (Hitachi, type Z-6100) (Hitachi High-Technologies Corporation, Tokyo, Japan) with an air–C_2H_2 flame. At the same time, the amounts of Cd(II) in all the acidic phases were atomic-absorption-spectrophotometrically measured at 228.8 nm, but its element was not detected.

3.3. Extraction Model Employed for the Analysis of the System

Since significant amounts of Cd(II) in the Bz phases were not detected with the AAS measurements, the following extraction model was employed for the analysis of the present system: (1) $Pb^{2+} + L \rightleftharpoons PbL^{2+}$ [29] ($K_{CdL} = 0.89$ $mol^{-1}\cdot dm^3$ [18] was omitted; (2) $Pb^{2+} + Pic^- \rightleftharpoons PbPic^+$ [21]; (3) $Cd^{2+} + Pic^- \rightleftharpoons CdPic^+$ [1]; and (4) $H^+ + Pic^- \rightleftharpoons HPic$ [33] in the water phase; (5) $Pic^- \rightleftharpoons Pic^-{}_{Bz}$; (6) $HPic \rightleftharpoons HPic_{Bz}$ [36]; (7) $L \rightleftharpoons L_{Bz}$ [2]; and (8) $PbL^{2+} \rightleftharpoons PbL^{2+}{}_{Bz}$ between the water and Bz phases; and (9) $PbL^{2+}{}_{Bz} + Pic^-{}_{Bz} \rightleftharpoons PbLPic^+{}_{Bz}$; and (10) $PbLPic^+{}_{Bz} + Pic^-{}_{Bz} \rightleftharpoons PbLPic_{2,Bz}$ in the Bz phase. Except for the Processes (5), (8)–(10), the equilibrium constants of the above processes at 298 K were available from References [1,2,18,21,29,36,37]. Analytic method of the extraction system based on this model was essentially the same as that reported before [1,9] (see Section 2.2).

4. Conclusions

The thermodynamic values for K_{ex}, $K_{ex\pm}$, $K_{Pb/PbL}$, $K_{ex,ip}$, and $K_{D,Pic}$ were determined at 298 K. The same is also true of the $K_{1,Bz}{}^0$ and $K_{2,Bz}{}^0$ values at $I_{Bz} \rightarrow 0$ for the simple Bz phases. It was demonstrated that the thermodynamic relations, $K_{ex}{}^0 \approx K_{ex,ip}{}^0 K_{PbL}/K_{D,L}$, $K_{2,Bz}{}^0 = K_{ex}{}^0/K_{ex\pm}{}^0$, $K_{ex2\pm}{}^0 = K_{Pb/PbL}{}^0(K_{D,Pic}{}^0)^2$, $K_{ex2\pm}{}^0 = K_{ex\pm}{}^0/K_{1,Bz}{}^0$, and $K_{ex\pm}{}^0 = K_{Pb/PbL}{}^0 K_{1,Bz}{}^0(K_{D,Pic}{}^0)^2$, hold in the system. It seems that the linear equation is superior to the polynomial-type one for the I_{Bz} dependences of the above equilibrium constants, although the R values with the former were less than those with the latter. Consequently, these results make comparisons between the K_{ex}, $K_{ex\pm}$, or $K_{1,Bz}$ values reported in different I or I_{org} conditions possible. However, there may be a fact that this study must be applied to the more practical extraction and separation systems. Moreover, it was clarified experimentally that log $K_{ex\pm}$ is proportional to dep.

At least, the separation of Pb(II) by B18C6 into the Bz phase from the mixtures at $[Cd]_t/[Pb]_t \approx 60$ was confirmed experimentally and theoretically. This condition exceeds $[PbLPic_2]_{Bz}/[CdLPic_2]_{Bz} = 2.2 \times 10^5$ at B18C6 (=L) and satisfies a measure (=10^4) of the separation factor. The $K_{ex,Pb}/K_{ex,Cd}$ ratio at the fixed I condition can promise more precise evaluation of Pb(II) selectivity of L against Cd(II), compared with the ratio calculated at different I conditions. While, the co-presence of $Cd(NO_3)_2$ less than 180 of $[Cd]_t/[Pb]_t$ has no clear effect to the experimental Pb(II) extraction with B18C6 into Bz. This Cd(II) salt in the present system acted only as the ionic strength conditioner in the water phases.

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Abbreviations

K_{ex}	Extraction constant for MLA_2
$K_{ex\pm}$	Extraction constant for MLA^+ with A^-
I	Ionic strength for the water phase
$K_{D,A}$	Conditional distribution constant of A^- into the org phase
$K_{M/ML}$	Incorporative constant of M^{2+} with L into the org phase
$K_{ex,ip}$	Ion-pair extraction constant for MLA_2
$K_{1,org}$	Ion-pair formation constant for ML^{2+} with A^- in the org phase
D_0, D_+, D	Distribution ratio for MLA_2, that for MLA^+, that for mixture
K_{ex+}	Extraction constant for MLA^+
$K_{ex}{}^{mix}$	Extraction-constant parameter
Dep, $\Delta\phi_{eq}$	Distribution equilibrium potential between the bulk water and org phases
$K_{D,Pic}{}^S$	Standard distribution constant of Pic^- into the org phase
$\Delta\phi_{Pic}{}^{0'}$	Standard formal potential for the Pic^- transfer across the water/org interface
$K_{2,org}$	Ion-pair formation constant for MLA^+ with A^- in the org phase
$K_{D,PbL}$	Conditional distribution constant of PbL^{2+} into the org phase
$K_{ex2\pm}$	Extraction constant for ML^{2+} with $2A^-$
$K_{D,L}$	Distribution constant of L into the org phase
K_{PbL}	Complex formation constant of Pb^{2+} with L in water
$K_{ex}{}^0$	Thermodynamic extraction constant of K_{ex}
$å_\pm$	Ion-size parameter, a mean value
$K_{ex,ip}{}^0$	Thermodynamic ion-pair extraction constant of $K_{ex,ip}$
$K_{1,Bz}{}^0$	Thermodynamic ion-pair formation constant for ML^{2+} with A^- in the Bz phase
$K_{2,Bz}{}^0$	Thermodynamic ion-pair formation constant for MLA^+ with A^- in the Bz phase
$K_{ex\pm}{}^0$	Thermodynamic extraction constant of $K_{ex\pm}$
$K_{Pb/PbL}{}^0$	Thermodynamic incorporative constant of Pb^{2+} with L into the org phase
$K_{ex2\pm}{}^0$	Thermodynamic extraction constant of $K_{ex2\pm}$
$D_{2+,Pb}$	Distribution ratio for PbL^{2+}

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