# Determination of Ion-Pair Formation Constants for MA$^+$ Ions (M = Ca, Sr, Ba, Cu, Cd) with A$^-$ = Picrate Ion in Water by Picric Acid Extraction into Benzene

Yoshihiro Kudo[1,*], Shinichi Nakajima[2] and Naoki Horiuchi[1]

[1]*Graduate School of Science, Chiba University, 1-33 Yayoi-cho, Inage-ku, Chiba 263-8522, Japan*

[2]*Department of Chemistry, Faculty of Science, Chiba University, 1-33 Yayoi-cho, Inage-ku, Chiba 263-8522, Japan*

**Abstracts:** Ion-pair formation constants ($K_{MA}{}^0$) for MA$^+$ = MPic$^+$ and MCl$^+$ in water were determined at 298 K and ionic strength → 0 by extraction experiments of picric acid (HPic) in the presence of M(II) in the water phase into benzene (Bz) and by potentiometry with a commercial Cl$^-$-selective electrode, respectively. Here, M denotes Ca(II), Sr(II), Ba(II), Cu(II), and Cd(II). In adding Pb(II) data, a relation between $K_{MA}{}^0$ values was $K_{MCl}{}^0 < K_{MPic}{}^0$ for a given M(II).For CdPic$^+$, the $K_{MA}{}^0$ value (= 136 mol$^{-1}$ dm$^3$) determined by the HPic extraction was somewhat larger than that (= 108) potentiometrically-determined before with a Cd$^{2+}$-selective electrode, while for CaPic$^+$ the former value (= 89) equaled the latter one (= 88) determined before with a Ca$^{2+}$-selective electrode.

**Keywords:** Ion-pair formation constants, extraction, potentiometry, divalent metal ions, picrates, chlorides.

## 1. INTRODUCTION

It is well known that picrates are employed for extraction experiments [1-4], because they have essentially the higher extraction-ability into various diluents, while chlorides are well employed for electrochemical experiments [5-7], because they show the higher conductivity in aqueous solutions. There are systematic studies on ion-pair formation or association in the aqueous solutions with sulfates [8-11]. However, especially for the systems with divalent metal ions (M$^{2+}$), the studies which determine ion-pair formation constants for the above picrates containing metal ions in water have been a few [12,13] unexpectedly. It seems to be obvious that the determination of the corresponding equilibrium constants promotes precise equilibria-analyses of various solvent extraction systems with picrates, such as the extraction of picrate of Cd(II) [14] or Pb(II) [15] (CdPic$_2$ or PbPic$_2$) by neutral ligands, such as crown ethers.

In the present paper, we determined the ion-pair formation constants ($K_{MA}{}^0$) for MA$^+$ in water by the extraction experiments [12] of picric acid (HPic) in the presence of M$^{2+}$ in the water phase into benzene (Bz) at 298 K and ionic strength ($I$) of aqueous solution →0. Here, M is divalent alkaline-earth metal, Cu(II), and Cd(II) and A$^-$ shows Pic$^-$. For comparisons with the Pic$^-$ systems, the $K_{MA}{}^0$ values at A$^-$ = Cl$^-$ were determined potentiometrically with a commercial Cl$^-$-selective electrode (Cl$^-$-se) [16], except for M = Ba(II). The diluent Bz was selected from both its lower extraction-ability to MA$^+$ and MA$_2$ and its lower solubility into water [17].

## 2. EXPERIMENTAL METHODS

### 2.1. Materials

Purities of the chlorides{guaranteed pure reagent (GR) for Ca(II), Wako; > 99.2% for Sr(II), Kanto; > 99.2% for Ba(II), Kanto; > 98.0% for Cd(II), Kanto} and nitrates {> 98.5% for Ca(II), Kanto; > 98.0% for Sr(II), Kanto; 99.9% for Ba(II), Wako; 99-104% for Cu(II), Wako; > 98.0% for Cd(II), Kanto} of M(II) were determined by the precipitation titration with K$_2$CrO$_4$ and the EDTA titration [18], respectively; that of HPic·$x$H$_2$O(> 99.5%, Wako) were determined by the acid-base titration [18] with NaOH(> 97.0%, Wako) and phenolphthalein. Similarly, the purity of NaCl (>99.9%, Kanto), of which the aqueous solutions were used for preparing potentiometric calibration curves, was determined by the precipitation titration [18]. The commercial Bz(GR, Kanto) was saturated with water by washing three-times with pure water [12] and then employed as an organic phase for the extraction experiments. Other chemicals were of GR grades unless otherwise described. Water employed here were purified by the same method as that reported previously [8, 14, 15].

### 2.2. Methods

The experimental procedures for the HPic extraction and potentiometry with the Cl$^-$-se and a reference

*Correspondence Address to this author at the Graduate School of Science, Chiba University, 1-33 Yayoi-cho, Inage-ku, Chiba 263-8522, Japan; Tel: +81 43 290 2786; Fax: +81 43 290 2874; E-mail: iakudo@faculty.chiba-u.jp

electrode of Ag/AgCl/0.1 mol dm$^{-3}$KCl/1.0 mol dm$^{-3}$ KNO$_3$ were the same as those [12,16] reported previously. Also, the apparatuses, such as spectrophotometer, pH/Ion meter, mechanical shaker, and centrifuge, used for the measurements and etc. were the same as those [12,15] employed before.

## 3. RESULTS AND DISCUSSION

### 3.1. Determination of $K_{MA}^0$ for MA$^+$ in Water

The determination methods of $K_{MA}^0$ were the same as those [12,16] reported before. Hence, we describe here the essence of the both methods, namely the HPic extraction [12] and potentiometry with the Cl$^-$-se [16].

For the HPic extraction into Bz, the following component equilibria were initially considered: H$^+$ + Pic$^-$ $\rightleftharpoons$ HPic and HPic $\rightleftharpoons$ HPic$_{Bz}$, where the subscript "Bz" refers to the Bz phase. When a strong electrolyte MX$_2$ is added in this system, the formation of MPic$^+$ occurs in the water (w) phase [12]:

$$M^{2+} + Pic^- + 2X^- \rightleftharpoons MPic^+ + 2X^-, \tag{1}$$
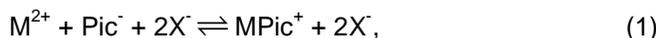
where the formation of MPic$_2$ in the w phase was neglected as a result of the present experiments (see below). Similarly, the MX$^+$ or MX$_2$ formation was neglected at X$^-$ = NO$_3^-$. The MPic$^+$ formation should cause a decrease in the distribution amount of HPic into Bz. Therefore, we can evaluate [MPic$^+$] from the following equation [12].

$$[MPic^+] \approx (^M[HPic]_{Bz}/^M[H^+])\{\Delta D_{Pic}^{-1} - (^M[H^+] - [H^+])/K_{D,HPic}\} \tag{2}$$

with $\Delta D_{Pic}^{-1} = (^M[H^+]/^M D_{Pic}) - ([H^+]/D_{Pic})$. Here, the symbols, $^M[HPic]_{Bz}$, $^M[H^+]$, and $^M D_{Pic}$, denote quantities in the presence of M(II) in the w phase and others do those in the absence of M(II). The symbols, $K_{D,HPic}$ and $D_{Pic}$, refer to the distribution constant of HPic and a distribution ratio for the extracted Pic(-I), respectively, into Bz under the condition that M(II) is absent in the system. Basically, all the values in the right hand side (rhs) of Eq. (2) were experimentally determined [12]. So we obtained the $K_{MPic}$ (= [MPic$^+$]/[M$^{2+}$]$^M$[Pic$^-$]) values at $^M I$ values from [MPic$^+$], [M$^{2+}$] (= [M]$_t$− [MPic$^+$]), and $^M$[Pic$^-$] {= ([Pic]$_t$−$^M$[HPic]$_{Bz}$− [MPic$^+$])/(1 + $K_{HPic}$$^M$[H$^+$])}, where $^M I$ is expressed as $^M$[Pic$^-$] + 2[M]$_t$ + [M$^{2+}$] [12].

Also, we can determine the $K_{MPic}^0$ value with a plot of log $K_{MPic}$ *versus* $^M I$ [12] based on the extended Debye-Hückel (DH) equation:

$$\log K_{MPic} \approx \log K_{MPic}^0 - 4A(^M I)^{1/2}/\{1 + B\mathring{a}(^M I)^{1/2}\} \tag{3}$$

with the assumption that the activity coefficient of MPic$^+$ equals that of Pic$^-$. Here, [M]$_t$, [Pic]$_t$, and $K_{HPic}^{-1}$, and $^M I$ denote a total concentration of MX$_2$, that of HPic in the initial w phase, the acid dissociation constant of HPic in water, and the ionic strength for the w phase with M(II) at equilibrium, respectively. The other symbols $A$, $B$, and $\mathring{a}$ have the meanings which are usually employed for the extended DH equation at 298 K. Figure **1** shows an example for the plot of the BaPic$_2$ system. The dotted line was based on a non-linear regression analysis of the plot using Eq. (3) with $\mathring{a}$= 5 Å [19] for Ba$^{2+}$. The correlation coefficient ($R$) values of the other systems were 0.195 at MA$^+$ = CaPic$^+$, 0.536 at SrPic$^+$, 0.337 at CuPic$^+$, and 0.272 at CdPic$^+$. Strictly speaking, the $K_{MPic}^0$ values determined by the extraction experiments are those at $^M I \to$ 0 for MPic$^+$ in water saturated with Bz [12], as readers know.
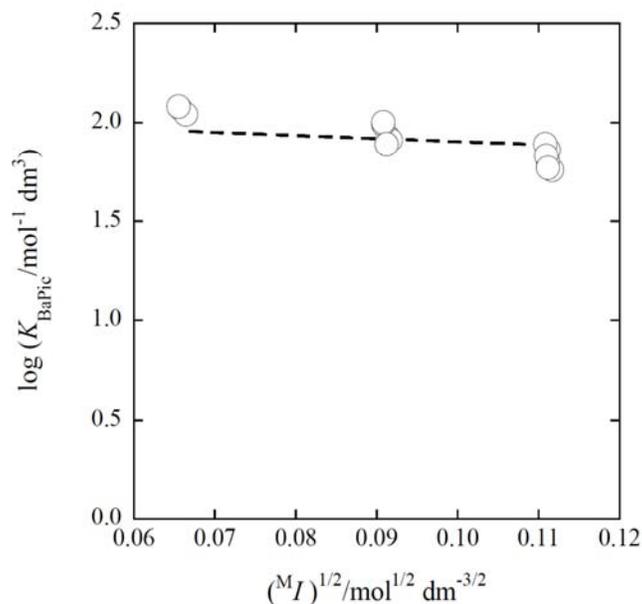


**Figure 1:** Plot of log $K_{BaPic}$ *vs.* $(^M I)^{1/2}$ for the BaPic$_2$ system by the extraction method. The broken line was a regression one at $R$ = 0.637 based on Eq. (3).

Next, potentiometric measurements with the Cl$^-$-se [16] were performed for the aqueous CaCl$_2$, SrCl$_2$, BaCl$_2$, and CdCl$_2$ solutions. Unfortunately, we were not able to obtain an adequate result for the $K_{BaCl}^0$ determination. For the $K_{MCl}^0$ determination by the Cl$^-$ analysis, the following equations were used: [M$^{2+}$] = [Cl$^-$]/(2 + $K_{MCl}$[Cl$^-$]) and [MCl$^+$] = 2$K_{MCl}$[M$^{2+}$]$^2$/(1 −$K_{MCl}$[M$^{2+}$]) [16]. Using the analyzed [Cl$^-$] values, the initial $K_{MCl}$ values were evaluated by a successive approximation. Then, the thermodynamic $K_{MCl}^0$ and $K_2^0$ (= [MCl$_2$]/$a_{MCl}a_{Cl}$) values were determined by another
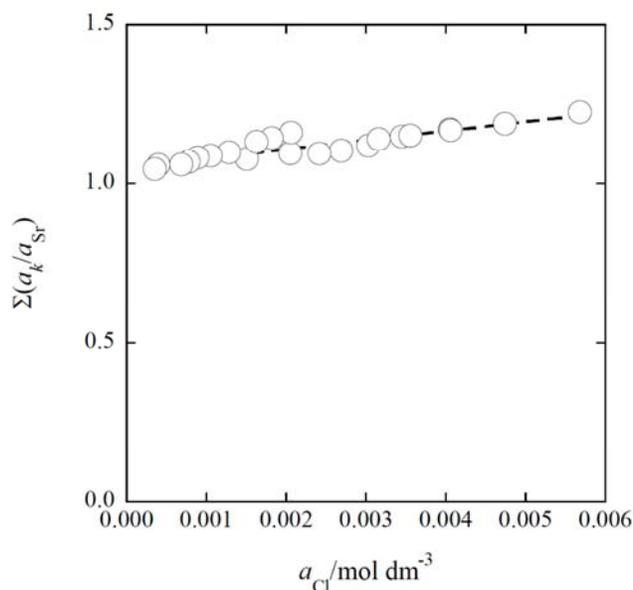
**Figure 2:** Plot of $(\Sigma a_k)/a_{Sr}$ *vs.* $a_{Cl}$ for the SrCl$_2$ system with $k =$ Sr$^{2+}$, SrCl$^+$, and SrCl$_2$ by the potentiometry with the Cl$^-$-se. The broken lone was $(1.050 \pm 0.008) + (29._1 \pm 2._9)a_{Cl}$ of a regression one at $R = 0.909$ based on a modified form of Eq. (4).

successive approximation, using the following equation [16]:

$$(\Sigma a_k)/a_M = 1 + K_{MCl}^0 \cdot a_{Cl} + K_{MCl}^0 K_2^0 \cdot (a_{Cl})^2, \tag{4}$$

where $a_j$ means an activity of the species $j$ {= M(II), MCl(+I), &Cl(-I)}. Figure **2** shows the plot of $(\Sigma a_k)/a_{Sr}$ *versus* $a_{Cl}$ for the SrCl$_2$ system with $k =$ Sr$^{2+}$, SrCl$^+$, and SrCl$_2$; namely, $\Sigma a_k = a_{Sr} + a_{SrCl} + [SrCl_2]$, where $a_{SrCl2} = [SrCl_2]$ was assumed. The intercepts and the $R$ values of the other regression lines were $1.071 \pm 0.007$ and $0.961$ for the CaCl$^+$ system and $1.090 \pm 0.005$ and

0.998 for CdCl$^+$, respectively. The $K_2^0$ value obtained for the CdCl$_2$ system in Table **1** coincided with those (= 8.7 & 13 mol$^{-1}$ dm$^3$ [16]) reported before within experimental errors. Except for the CdCl$_2$ system, since a non-linear regression analysis with Eq. (4) [16] did not give the meaningful 2nd term in the rhs of Eq. (4), accordingly we employed the linear equation of $(\Sigma a_k)/a_M \approx 1 + K_{MCl}^0 a_{Cl}$ for the regression analysis. Results for the $K_{MPic}^0$ and $K_{MCl}^0$ values determined are summarized in Table **1**.

The $K_{MPic}^0$ order was M = Cu(II) < Ca(II) <Pb(II) < Cd(II) ≤Ba(II) <Sr(II), while the $K_{MCl}^0$ one was Cu(II) ≤ Mg(II) <Pb(II) <Sr(II) < Ca(II) < Cd(II). Only the order of Cu(II) <Pb(II) < Cd(II) is in common for these orders. Against these two orders, the ionic radii ($r_c$) [20] of M(II) were in the order Mg(II) <Cu(II) < Cd(II) < Ca(II) <Sr(II) ≤Pb(II) <Ba(II) (see Table **1**). Also, ion size parameters (*å*) were in the order Pb(II) (4.5 Å) <Sr(II) = Cd(II) = Ba(II) (5) < Ca(II) = Cu(II) (6) < Mg(II) (8) [19]. There was no correlation between $K_{MA}^0$ and $r_c$ or *å*.

### 3.2. On the Reproducibility of the $K_{MA}^0$ Values by the Determination Methods

The $K_{CdPic}^0$ value (= 108 mol$^{-1}$ dm$^3$ [13,16]) potentiometrically-determined previously with a Cd$^{2+}$-selective electrode was somewhat smaller than that (= 136) determined by the present HPic extraction. On the other hand, the $K_{CaPic}^0$ value obtained from the HPic extraction equaled that [13,16] determined previously with a Ca$^{2+}$-selective electrode (Table **1**). These results may be dependent on types (or materials) of the electrodes employed; according to their catalogs [21],

**Table 1:   Ion-Pair or Complex Formation Constants for MA+ in Water at 298K**

| M(II) | $r_c{}^a$/Å | $K_{MA}^0$/mol$^{-1}$ dm$^3$ | |
|---|---|---|---|
| | | MA$^+$ = MPic$^{+ b}$ | MCl$^{+ c}$ |
| Mg | 0.720 | ---$^d$ | 4.55$^e$ [11], 0.77$^f$ [23] |
| Ca | 1.00 | 89±10, 88$^g$ | 41 ± 2, 40$^g$, 0.68$^f$ [23] |
| Sr | 1.18 | 152 ±13 | 29± 3, 0.54$^f$ [23] |
| Ba | 1.35 | 120 ± 6 | ---$^d$, 0.34$^f$ [23] |
| Cu | 0.73 | 72 ±10 | 2.49$^h$, 4.0[25] |
| Cd | 0.95 | 136 ±15, 108$^g$, 107$^g$ | 91 ± 4, 86$^g$, 89$^g$ (13 ± 5)$^i$ |
| Pb | 1.19 | 93 [14], 100 [14] | 10$^j$, 9.5 [26], 37$^k$[27] |

$^a$Ionic radii of the coordination number of six. See [20]. $^b$Values determined with the HPic extraction experiments. $^c$Values determined potentiometrically with the Cl$^-$-se. $^d$Not be determined. $^e$Value at $I \to 0$ calculated from the experimental $I$ range of about 0.00032-0.15mol dm$^{-3}$. See [11]. $^f$Value at $I \approx 1$ mol dm$^{-3}$ (NaNO$_3$). See [23]. $^g$Values determined potentiometrically with commercial M$^{2+}$-selective electrodes at M = Ca(II) & Cd(II). See [8,13,16]. $^h$Valuein the [Cl$^-$] range of about 9.8×10$^{-5}$-4.9×10$^{-3}$mol dm$^{-3}$. See [25]. $^i$K$_2^0$ (= [CdCl$_2$]/$a_{CdCi}a_{Cl}$) value obtained here. $^j$Valuein the [Cl$^-$] range of0.0148-3.97mol dm$^{-3}$.See [26]. $^k$Value averaged in the $I$ range of 0.02-0.12 mol dm$^{-3}$. See [27].

the former electrode was of a solid-state membrane, while the latter one was of a liquid membrane. Now, we cannot clearly explain the above results. Also, the $K_{CdCl}^0$ and $K_{CaCl}^0$ values determined with the Cl$^-$-se were in good agreement with those [16,8] determined previously with M$^{2+}$-selective electrodes (Table **1**). The above results indicate that essentially the both methods give good reproducible values.

For the potentiometric measurements with Cl$^-$-se, the $K_{MCl}^0$ values were dependent on the dissociation of NaCl in water, because the calibration curves had been made from the aqueous NaCl solutions. That is, it means that the equilibrium constants are determined comparatively by using the dissociation of NaCl in water as a standard. The results for $K_{MCl}^0$ can be kept at constant by the use of NaNO$_3$ and NaClO$_4$, according to the fact [22] that the $K_{LiL}$ values at L = 19-crown-6 ether have been constant in conductometric titrations with LiCl, LiNO$_3$, and LiClO$_4$ in water.

The $K_{MCl}$ values at $I = 1$ mol dm$^{-3}$ were estimated from Eq. (3). Their values were 1.24 mol$^{-1}$ dm$^3$ for M = Mg, 8 for Ca, and 5 for Sr. The $K_{MgCl}$ value estimated from that at $I \rightarrow 0$ reported by Fischer and Fox [11] is close to that [23] reported by Majer and Štulík, while the $K_{MCl}$ values determined here at Ca and Sr are about 10-times larger than those [23] by them (see Table **1**).

## 4. CONCLUSION

The $K_{MPic}^0$ values were determined at 298 K by the HPic extraction into Bz at M = Ca(II), Sr(II), Ba(II), Cu(II), and Cd(II). The $K_{CaPic}^0$ value determined by the extraction method well agreed with that done by the Ca$^{2+}$-se. Also, the $K_{MCl}^0$ values determined by the Cl$^-$-se were essentially in agreement with those by the Ca$^{2+}$- and Cd$^{2+}$-ses, although there may be positive errors in the values.

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