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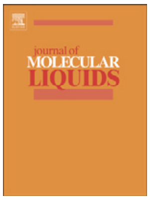

Extraction of lead picrate by 18-crown-6 ether into various diluents: Examples of sub-analysis of overall extraction equilibrium based on component equilibria

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ABSTRACT

Extraction constants for lead picrate, $PbPic_2$, with 18-crown-6 ether (L) from aqueous solutions at a narrow range of ionic strength (I) into eleven diluents were determined at 298 K by AAS measurements. These constants were defined as $K_{ex} = [PbLPic_2]_o/([Pb^{2+}][L]_o[Pic^-]^2)$ and $K_{ex\pm} = [PbLPic^+]_o[Pic^-]_o/([Pb^{2+}][L]_o[Pic^-]^2)$, where the subscript "o" denotes the organic phase (or diluent). The ratio, $K_{ex}/K_{ex\pm}$, gave an ion-pair formation constant for $PbLPic^+{}_o + Pic^-{}_o \rightleftharpoons PbLPic_{2,o}$ at the averaged value of ionic strength (I_o) of the organic phase. A plot of log $K_{ex\pm}$ versus log $K_{D,Pic}$ yielded a straight line with the slope of 2.1 in a series of the diluents employed; $K_{D,Pic}$ refers to an apparent distribution constant of Pic^- between the aqueous and organic phases and its values were experimentally determined. The slope indicated that $K_{ex\pm}$ is mainly controlled by the square of $K_{D,Pic}$ when a thermodynamic cycle is assumed. The extraction constant based on the cycle was expressed as $K_{ex\pm} = (K_{D,Pic})^2K_{D,M}K_{ML,org}K_{1,org}$, where $K_{D,M}K_{ML,org}K_{1,org}$ denotes the product of other component equilibrium-constants. Moreover, the relation of $\log K_{D,Pic} = a\log(I_o/I) + b$ was experimentally found at $a \approx 1$ and then an example of b was expressed theoretically. It was shown that Pb(II) can be separated from mixtures with Cd(II) in unit operation.

1. Introduction

It is known that crown compounds (L) extract divalent metal ions (M^{2+}), such as alkaline-earth metal ions, Pb^{2+}, Cd^{2+}, and Hg^{2+}, with picrate ion (Pic^-), SCN^-, or NO_3^- into various diluents [1–11]. Recently, the authors have reported in this journal an extraction of $CdBr_2$ and $CdPic_2$ by 18-crown-6 ether (18C6) into various diluents, such as 1,2-dichloroethane (DCE), dichloromethane (DCM), chlorobenzene (CBz), and *m*-xylene (mX) [6]. In this study, the following component equilibria, (i)–(v), were introduced in analysis of an overall extraction equilibrium: (i) a first-step ion-pair formation of $Cd(18C6)^{2+}$ with Br^- or an overall ion-pair formation of $Cd(18C6)^{2+}$ with Pic^- in water, (ii) a distribution of A^- between water and the diluent at $A^- = Br^-$ and Pic^-, (iii) that of $Cd(18C6)Br^+$ or the distribution of $Cd(18C6)Pic_2$ between them, (iv) a second-step ion-pair formation of $Cd(18C6)A^+$ with A^- in the diluent phases, and (v) the first-step ion-pair formation of a free Cd^{2+} with A^- in water.

By the determination of equilibrium constants corresponding to these component equilibria, more detailed analysis of the overall extraction equilibrium has been performed [5,6]. For example, the second-step ion-pair formation constant ($K_{2,org}$) for the benzene (Bz) saturated with water was largest of those for the other diluents employed [6] {see process (iv) above}. Also, it was demonstrated that extraction-abilities, expressed as $K_{ex\pm}$ (see below), for $Cd(18C6)Br^+$ are actually controlled by the distribution-abilities, expressed as $K_{D,A}$, for Br^- among the diluents [6] {see process (ii)}. However, such studies have not been major for the extraction of M^{2+} by L into the diluents; the extraction of $CdPic_2$ by benzo-18C6 into benzene (Bz) has been reported in ref. [5].

In the present paper, in order to expand this kind of extraction study to other M(II) system, we determined overall extraction constants, such as K_{ex} and $K_{ex\pm}$, for the $PbPic_2$–18C6 system and the apparent distribution ones, $K_{D,Pic}$, of Pic^- into various diluents which contain nitrobenzene (NB) with a high polarity. Here, these constants have been defined as $K_{ex} = [PbLPic_2]_o/([Pb^{2+}][L]_o[Pic^-]^2)$, $K_{ex\pm} = [PbLPic^+]_o[Pic^-]_o/([Pb^{2+}][L]_o[Pic^-]^2)$ [6,12] at L = 18C6, and $K_{D,Pic} = [Pic^-]_o/[Pic^-]$ [6,12] and the subscript "o" denotes an organic phase composed of a diluent saturated with water. By using the equilibrium constants thus determined, characteristics of the Pb(II) extraction systems with 18C6 were discussed, compared to those [6] of the Cd(II) systems. Unfortunately, the equilibrium constants for the component equilibria, (i) and (iii), were not experimentally determined here.

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2. Theory

2.1. Model for sub-analysis of overall extraction equilibrium

We employed here the following model for analyzing overall extraction equilibrium which is fundamentally expressed by the two extraction constants, K_{ex} and $K_{ex\pm}$ [6,12]:

$$L \rightleftharpoons L_o : K_{D,L} \text{ is defined as a corresponding equilibrium constant,} \tag{1}$$

$$M^{2+} + L \rightleftharpoons ML^{2+} : K_{ML}, \tag{2}$$

$$ML^{2+} + 2A^- \rightleftharpoons MLA_2 : K_1K_2, \tag{3}$$

$$MLA_2 \rightleftharpoons MLA_{2,o} : K_{D,MLA2}, \tag{4}$$

$$MLA_{2,o} \rightleftharpoons MLA^+{}_o + A^-{}_o : \left(K_{2,org}\right)^{-1} \tag{5}$$

$$MLA^+ \rightleftharpoons MLA^+{}_o : K_{D,MLA}, \tag{6}$$

$$A^- \rightleftharpoons A^-{}_o : K_{D,A}, \tag{7}$$

$$H^+ + A^- \rightleftharpoons HA : K_{HA}\left(\text{means } K_a{}^{-1} \text{ of HA}\right), \tag{8}$$

$$HA \rightleftharpoons HA_o : K_{D,HA}, \tag{9}$$

and

$$M^{2+} + A^- \rightleftharpoons MA^+ : K_{MA}. \tag{10}$$

However, we could not determine in this study the equilibrium constants of Processes (3) and (4) and, instead of them, used $K_{ex,ip} = [MLA_2]_o/[ML^{2+}][A^-]^2$ $(= K_1K_2K_{D,MLA2})$ for discussion, where $K_{ex,ip}$ is ordinarily called an ion-pair extraction constant [2–4] and K_1K_2 equals $[MLA_2]/[ML^{2+}][A^-]^2$ [6,12]. This means lack of processes (i) and (iii) in the Introduction. Also, the $K_{D,MLA}$ value of Process (6) was not determined. Because of such lack, we expressed here the analysis of the present overall extraction equilibria as "the sub-analysis", compared with that of the Cd(II) system [6].

For the extraction into nitrobenzene, NB, besides, the following component equilibria [8,13,14] were added in the above model:

$$H^+{}_{NB} + A^-{}_{NB} \rightleftharpoons HA_{NB} : K_{HA,NB} \tag{11}$$

$$H^+ \rightleftharpoons H^+{}_{NB} : K_{D,H}, \tag{12}$$

$$X^- \rightleftharpoons X^-{}_{NB} : K_{D,X}, \tag{7a}$$

and

$$H^+{}_{NB} + X^-{}_{NB} \rightleftharpoons HX_{NB} : K_{HX,NB}. \tag{13}$$

Here, HX denotes a strong acid, such as HNO_3 and HCl, and $K_{D,HPic}$ was estimated from the relation $K_{D,H}K_{D,Pic}K_{HPic,NB} = K_{HPic}K_{D,HPic}$.

Details of the derivation of $[M^{2+}]$, $[L]_o$, and $[A^-]$, which are expressed as functions [6,12] of the component equilibrium constants corresponding to Processes (1) to (13), are described in Appendix A.

2.2. For determination of the extraction constants for mixture with M(II)

According to our previous papers [6,12], the extraction constant for mixture of MLA_2 and MLA^+ in the diluent has been actually defined as

$$K_{ex}{}^{mix} = \left([MLA_2]_o + \left[MLA^+\right]_o\right)/\left(\left[M^{2+}\right][L]_o[A^-]^2\right), \tag{14}$$

where the presence of ML^{2+} and ML_2A_2 in the organic phase was neglected: that is, $[MLA_2]_o + [MLA^+]_o \gg [ML^{2+}]_o + [ML_2A_2]_o$. This equation is rearranged into the two forms:

$$K_{ex}{}^{mix} = K_{ex} + K_{D,A}/\left(\left[M^{2+}\right][L]_o[A^-]\right) \tag{14a}$$

$$= K_{ex} + \sqrt{K_{ex\pm}}/\left([A^-]\sqrt{[M^{2+}][L]_o}\right). \tag{14b}$$

Since the $[M^{2+}]$, $[L]_o$, $[A^-]$, and K_{ex}^{mix} values are calculated from experimental data by a successive approximation, one can determine the K_{ex} and $K_{D,A}$ or $K_{ex\pm}$ values in terms of a regression analysis of the plots of log K_{ex}^{mix} versus − log $([M^{2+}][L]_o[A^-])$ or − log $\{[A^-]([M^{2+}][L]_o)^{1/2}\}$, respectively [6,12].

3. Results and discussion

3.1. For the composition-determination of species extracted into the diluents

Compositions of the species extracted into the diluents were determined in terms of plots of log $(D/[A^-]^2)$ versus log $[L]_o$, as described previously [2–6,10,12]. Here, D was experimentally obtained from [analyzed total-concentration of Pb(II)]$_o$/{[initial concentration of Pb(II)] − [analyzed total-concentration of Pb(II)]$_o$}. Thus, [the analyzed total-concentrations of Pb(II)]$_o$ can mean mixtures of the species with Pb(II), because their total concentrations of Pb(II) were determined by AAS measurements. If the ratio of Pb^{2+}:L is 1:1, then the slope of the plot should be close to unity. A ratio of A^- to Pb^{2+}:L (=1:1) also can be supported by a counterbalance in charge between Pb^{2+} and A^-, and is accordingly reflected to the exponent of $[A^-]$ in $D/[A^-]^2$. This has been verified experimentally [2,12]. In addition, the conditions of $1 \gg r$ and $1 \gg s$ were assumed in the equation of log $(D/[A^-]^2)$ = log $\{[(1 + r)/(1 + s)] \times D_M/[A^-]^2\}$ = log $[L]_o$ + log K_{ex}^{mix} with $r = ([MLA^+]_o + [ML^{2+}]_o + [ML_2A_2]_o + \cdots)/[MLA_2]_o$, $s = ([ML^{2+}] + [MA^+] + [MLA^+] + \cdots)/[M^{2+}]$, and $D_M = [MLA_2]_o/[M^{2+}]$ [2–4,12]. As a first diagnosis, hence, one can estimate extraction-abilities and -selectivities of L, A^-, or diluents against M^{2+} from the log K_{ex}^{mix} values, which are intercepts for the plots of log $(D/[A^-]^2)$ versus log $[L]_o$.

The experimentally obtained slopes of the above plots were 0.67 for the extraction into NB, 1.05 for 1,2-dichloroethane, DCE, 0.91 for *o*-dichlorobenzene (oDCBz), 1.18 for dichloromethane, DCM, 0.80 for 1-chlorobutane (CBu), 0.96 for chlorobenzene, CBz, 0.95 for bromobenzene (BBz), 1.06 for chloroform (CF), 0.93 for benzene, Bz, 0.98 for toluene (TE), and 0.92 for *m*-xylene, mX. These diluent systems, except for the NB, DCM, and CBu ones, indicated the extraction of $Pb(18C6)Pic_2$ as the major species.

As examples, Fig. 1 shows the plots for the Pb(II) extraction into NB, DCM, CBu, and Bz, together with the calculated straight lines which have the hypothetical slope of unity for the NB, DCM, and CBu systems. The value of the slope for the NB system reflects a dissociation of $Pb(18C6)Pic_2$ into $Pb(18C6)Pic^+$ (and Pic^-) in the lower $[18C6]_{NB}$ range [6,12]. The fractions of $Pb(18C6)Pic^+$ against the total amounts of the Pb(II) species extracted into the NB phases were in the range of 0.37 to 0.73 {see Eq. (A10) in Appendix A}. As shown in Fig. 1, the value for the DCM system suggests a formation of $Pb(18C6)_2Pic_2$ or $[Pb(18C6)Pic_2]_2$ in the higher $[18C6]_{DCM}$ range [5,15], while that for CBu does a dimerization of 18C6 itself in the higher $[18C6]_{CBu}$ range from its shape of the plot [16]. The former was predicted from a gradual increase in the slope (>1), while the latter was done from a gradual decrease in the slope (<1). In the determination of K_{ex} and $K_{ex\pm}$ for the NB, CBu, and DCM systems, the formation of $Pb(18C6)Pic_2$ and $Pb(18C6)Pic^+$ with Pic^- was assumed and then their data were curve-fitted using Eqs. (14a) and (14b).