

Research Article

Distribution of Picric Acid into Various Diluents

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Extraction constants, defined as $K_{\text{ex}} = [\text{HPic}]_{\text{o}}/[\text{H}^+][\text{Pic}^-]$, for picric acid (HPic) into ten diluents were spectrophotometrically determined at 298 K, where the subscript “o” refers to an organic (o) phase which is composed of the diluent. Their values for the HPic extraction into benzene and chloroform were fairly consistent with those reported before. From the K_{ex} values, distribution constants ($K_{\text{D,HPic}}$) of HPic into the o phases were estimated using the thermodynamic relation $K_{\text{ex}} = K_{\text{D,HPic}}K_{\text{HPic}}$, where K_{HPic} corresponds to a protonation constant of Pic^- in water. Thereby, contributions of functional groups, such as $-\text{Cl}$ and $-\text{CH}_3$, involved in the diluents molecules to $K_{\text{D,HPic}}$ were discussed. The same discussion was also applied for the distribution of the ion pair, composed of CdPic_2 and 18-crown-6 ether, into the diluents.

1. Introduction

Picric acid (HPic) has been widely used for the source of pairing anions in solvent extraction [1–5], application to selective sensors [6], sequential injection analysis with it [7], its separation science [8, 9], theoretical study for its partition [10], its distribution into ionic liquids [11], and so on. Also, many authors have studied extraction and separation of many metal ions by crown compounds from water (w) into various diluents [1–3, 12–17]. In particular, the extraction data of HPic are important for studying the extraction of easily hydrolyzed metal ions, such as Ag^+ and Pb^{2+} , by the compounds into the diluents [1, 2, 18]. However, few systematic studies of the HPic extraction have been reported [5].

In the present paper, we systematically determined at 298 K extraction constants ($K_{\text{ex}}/\text{mol}^{-1} \text{dm}^3$) of HPic into ten diluents having lower polarities, such as *m*-Xylene (mX), toluene (TE), bromobenzene (BBz), chlorobenzene (CBz), and 1-chlorobutane (CBu). These diluents were selected on the basis of the careful consideration by Takeda et al. [3]. From the K_{ex} values, distribution constants ($K_{\text{D,HA}}$) of HPic between the w and organic (o) phases or the diluents were also calculated. Moreover, contributions of functional groups constituting the diluents molecules to $K_{\text{D,HA}}$ were discussed. The same discussion was applied for the distribution of the ion pair of CdPic_2 with 18-crown-6 ether (18C6) into the diluents.

2. Materials and Methods

2.1. Materials. Picric acid (99.5%, $\text{HPic}\cdot x\text{H}_2\text{O}$) was purchased from Wako Pure Chemical Industries, Japan. Sodium hydroxide (97%, Kanto Chemical Co., Ltd., Japan) was used without further purification. Its purity was determined by acid-base titration with potassium hydrogen phthalate (guaranteed pure reagent: GR, 99.9 to 100.2%, Kanto). The chemicals $\text{HPic}\cdot x\text{H}_2\text{O}$ were dissolved in water and then its concentration was determined by acid-base titration with an aqueous NaOH solution of 0.1 mol dm^{-3} . Commercially available diluents (all GR grades, Wako and Kanto) were washed three times with water and kept under the conditions saturated with water. Other chemicals were of GR grade. A tap water was distilled once with the still of the stainless steel and then was purified by passing through the Autopure system (Yamato/Millipore, type WT101 UV). This water was employed for preparation of all aqueous solutions.

2.2. Extraction Procedures and Data Handling. Aqueous HPic solutions of $(0.15\text{--}3.4) \times 10^{-3} \text{ mol dm}^{-3}$ and diluents were mixed at equivalent volume (12 cm^3) in glass tubes of about 30 cm^3 , and then these stoppered glass tubes were vigorously shaken by hand for 1 minute. The tubes were agitated for 2 h by a shaker with water-bath thermostated at 298 K and then, in order to separate the two phases, centrifuged for

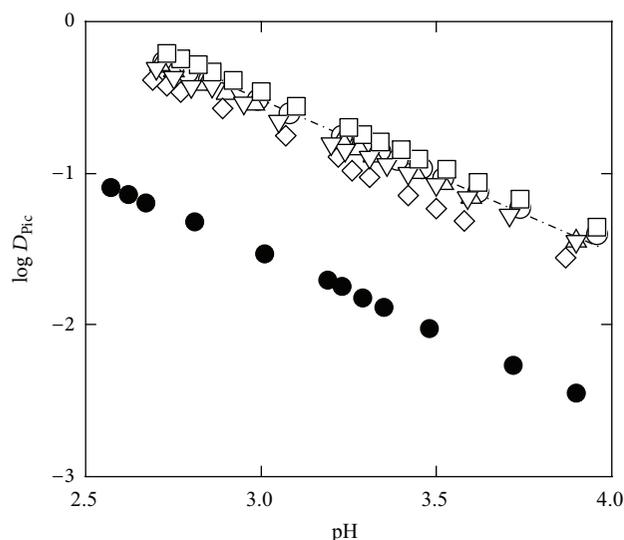


FIGURE 1: Plots of $\log D_{\text{Pic}}$ versus pH for six diluents. Circle: DCE; triangle: DCM; full circle: CBU; diamond: BBz; inverted triangle: Bz; square: mX. A broken line is the regression one for the DCE system based on (2): $\log D_{\text{Pic}} = 2.489 - \text{pH} - \log(1 + 3.86 \times 10^{-\text{pH}})$ at $R = 0.998$.

7 minutes. The pH values of the w phases separated were measured at 298 K: pH readings were in the range of 2.57 to 4.10. A Horiba pH/ion meter (type F-23) equipped with a glass electrode (Horiba, type 9615-10D) was employed for the pH measurements. While the o phases or the diluents separated were transferred into other glass tubes and the aqueous NaOH solutions of 0.1 mol dm^{-3} were added to them, volume ratios (V_o/V) of the separated o phases against the added aqueous solutions with NaOH were 1/1, 1/2, 1/4, 1/5, 1/8, 1/10, 1/12, or 1/25. As similar to the above procedure, the amounts of HPic in the o phases were back-extracted into the aqueous NaOH solutions. Using a 1 cm quartz cell, concentrations of Pic^- in these aqueous solutions were determined spectrophotometrically at 355.0 nm and 298 K, where a spectrophotometer used was of a Hitachi U-2001 type. The operation of the back-extraction was repeated in some cases.

These Pic^- concentrations which were determined at 355.0 nm due to the absorption of Pic^- were assumed to equal the concentrations, $[\text{HPic}]_o$, of HPic in the o phases. Here, the subscript "o" denotes the o phase. From these values and total concentrations, $[\text{HPic}]_t$, of HPic, distribution ratios, D_{Pic} , for Pic^- were calculated, assuming that $[\text{HPic}]_o \gg [\text{Pic}^-]_o + [(\text{HPic})_2]_o$ [19] and then using the equation $D_{\text{Pic}} = [\text{HPic}]_o / ([\text{HPic}]_t - [\text{HPic}]_o)$ (see Section 3.1).

As a software for the analysis of the plots of $\log D_{\text{Pic}}$ versus pH (see Figure 1), a KaleidaGraph (ver. 3.501, Hulinks Inc., Tokyo) was used.

3. Results and Discussion

3.1. A Concise Theoretical Treatment of Extraction Equilibria. We assumed here the following equilibria: $\text{H}^+ + \text{A}^- \rightleftharpoons \text{HA}$ and $\text{HA} \rightleftharpoons \text{HA}_o$ for the overall extraction equilibrium of which

the constant was expressed as $K_{\text{ex}} = [\text{HA}]_o / [\text{H}^+][\text{A}^-]$. For this extraction system [9, 10, 19], the distribution ratio was defined as

$$D_A = \frac{[\text{HA}]_o}{[\text{A}^-] + [\text{HA}]} = \frac{K_{\text{ex}} [\text{H}^+]}{1 + K_{\text{HA}} [\text{H}^+]}. \quad (1)$$

Then, taking logarithms of both sides, the following equation was given:

$$\begin{aligned} \log D_A &= \log K_{\text{ex}} - \text{pH} - \log(1 + K_{\text{HA}} [\text{H}^+]) \\ &= \log K_{\text{ex}} - \text{pH} - \log(1 + K_{\text{HA}} 10^{-\text{pH}}). \end{aligned} \quad (2)$$

Assuming that the K_{HA} values are a constant in a given experimental pH range (see Section 2.2), then we can immediately obtain the $\log K_{\text{ex}}$ value from the plot of $\log D_A$ versus pH. Actually, the K_{HA} values which were averaged for all the values of ionic strength (I) were employed for the analysis of the plots, where $I = (1/2)([\text{H}^+] + [\text{A}^-]) \approx [\text{H}^+]$. Additionally, the $\log K_{\text{D,HA}}$ value can be estimated from the thermodynamic relation: $\log K_{\text{ex}} = \log K_{\text{D,HA}} + \log K_{\text{HA}}$. Also, (2) can approximate to $\log D_A \approx \log K_{\text{ex}} - \text{pH}$ in the present experimental ranges of pH (see Section 2.2).

3.2. Determination of K_{ex} and $K_{\text{D,HPic}}$. Figure 1 shows examples for plots of $\log D_A$ versus pH at $\text{A}^- = \text{Pic}^-$. Thus, the plots yielded linear relationships between $\log D_A$ and pH. The same is also true of the HPic extraction systems with the other four diluents. The extraction data thus obtained are summarized in Table 1. The $\log K_{\text{ex}}$ values of the extraction into benzene, Bz, and chloroform, CF, were in accord with those [1, 2] reported before by Takeda et al. Although the measuring temperature was not described, the $\log K_{\text{ex}}$ value ($=2.28$ [10]) estimated previously for the dichloromethane, DCM, system was also close to our value ($=2.462$). From the $\log K_{\text{HPic}}$ values in Table 1, one can see easily that differences among the present \bar{I} values, the average I ones, have no objection to comparisons among the K_{ex} values or component equilibrium constants, except for the cyclohexane, cHex, system [8].

3.3. Extraction Abilities of the Diluents for HPic. According to the relation $\log K_{\text{ex}} = \log K_{\text{D,HA}} + \log K_{\text{HA}}$, the extraction ability of the diluents employed for HPic is obviously controlled by the $\log K_{\text{D,HA}}$ values (see Table 1). This is supported by the following facts. A plot of $\log K_{\text{ex}}$ versus $\log K_{\text{D,HPic}}$ for the ten diluents gave a straight line with the slope of 1.00₁ and the intercept of 0.58₄ at the correlation coefficient (R) of 0.999. This intercept was also in good agreement with the $\log K_{\text{HPic}}$ values, listed in Table 1, within the experimental errors of ± 0.01 .

3.4. For Interaction of the Diluents Molecules with HPic. The $\log K_{\text{D,HA}}$ values were in the order cHex \ll CBU $<$ CF $<$ oDCBz $<$ BBz, CBz $<$ Bz $<$ DCM, TE \leq DCE $<$ mX (see Table 1 for these abbreviations). This order shows that an interaction with HPic becomes strengthened by going from cHex to mX. We divide here the order into (cHex \ll)

TABLE 1: Extraction constants for HPic into various diluents and their component equilibrium constants (K_{HA} , $K_{D,HA}$) at 298 K.

Diluents ^a	I ^b /mol dm ⁻³	$\log K_{ex}$ ^c	$\log K_{D,HA}$	$\log K_{HA}$ ^{d,e}
DCE	7.8×10^{-4}	2.489 ± 0.006	1.90 ± 0.01	0.59
oDCBz	1.0×10^{-3}	2.170 ± 0.002	1.59 ± 0.01	0.58
DCM	8.4×10^{-4}	2.462 ± 0.002	1.88 ± 0.01	0.59
CBu	1.0×10^{-3}	1.474 ± 0.004	0.89 ± 0.01	0.58
CBz	8.5×10^{-4}	2.310 ± 0.002	1.72 ± 0.01	0.59
BBz	8.7×10^{-4}	2.300 ± 0.007	1.72 ± 0.01	0.59
CF	3.7×10^{-4}	$1.941 \pm 0.003, 1.940^f$	$1.347 \pm 0.006, 1.65_0^f$	$0.594 \pm 0.005, 0.29_0^{f,g}$
cHex ^h	1.0^i	0.66	-0.16	0.82
Bz	8.1×10^{-4}	$2.396 \pm 0.005, 2.393^j$	$1.81 \pm 0.01, 2.10_3^j$	$0.59, 0.29_0^{j,g}$
TE	6.3×10^{-4}	2.473 ± 0.006	1.88 ± 0.01	0.59
mX	7.9×10^{-4}	2.552 ± 0.005	1.97 ± 0.01	0.59

^aDCE: 1,2-dichloroethane; oDCBz: *o*-dichlorobenzene; DCM: dichloromethane; CBu: 1-chlorobutane; CBz: chlorobenzene; BBz: bromobenzene; CF: chloroform; cHex: cyclohexane; Bz: benzene; TE: toluene; mX: *m*-xylene. These diluents are lined up downwards from the high-polar DCE to the low-polar mX. ^bAverage values of I in aqueous solutions. ^c $K_{ex}/\text{mol}^{-1} \text{dm}^3$. ^dAverage values evaluated at I and expressed by $K_{HA}/\text{mol dm}^{-3}$. ^eErrors of all the $\log K_{HA}$ values evaluated here were ± 0.01 except for the CF system. ^fReference [2]. ^g $\log K_{HPic}$ value at ($I/\text{mol dm}^{-3}$) = 0.1. See [21]. ^hReference [8]. ⁱConcentration of HCl. ^jReference [1].

oDCBz < BBz, CBz < Bz < TE < mX for aromatic diluents and CBu < CF < DCM \leq DCE for aliphatic diluents and then will examine these orders in more detail.

The $\log K_{D,HA}$ values were in the order Bz < TE < mX (Table 1). This fact indicates that substitution of -H by -CH₃ increases the interaction of the diluents molecules with HPic. Similar results were obtained for the substitution of -Cl or -Br by -CH₃: namely, CBz or BBz < TE and oDCBz < mX, although the position of the functional group in the latter case differs from each other. On the other hand, those of -Cl by -CH₂CH₂CH₃ and -CH₂CH₃ decreased the interaction with HPic. The corresponding examples were DCM (ClCH₂-Cl) \gg CBu (ClCH₂-CH₂CH₂CH₃) and DCE (ClCH₂CH₂-Cl) \gg CBu (ClCH₂CH₂-CH₂CH₃), respectively. Also, the substitution of -H by -Cl decreased their interaction. These examples were DCM > CF and Bz > CBz > oDCBz. Like the relation between Bz and CBz, the same was also true of that between Bz and BBz. The above results indicate that the functional groups constituting the diluents molecules strengthen the interaction with HPic in the order of -CH₂CH₂CH₃, -CH₂CH₃ \ll -Cl, -Br < -H \leq -CH₃.

The case of cHex \ll Bz suggests that the substitution of -CH₂CH₂- by -CH=CH- strengthens the interaction with HPic, while, there was no difference in the interaction with HPic between -Cl and -Br and accordingly that in $\log K_{D,HA}$ between CBz and BBz (Table 1).

3.5. Application for the Distribution of Ion Pairs with 18C6. The $\log K_{D,MLA2}$ values reported previously [20] at $MLA_2 = Cd(18C6)Pic_2$ were in the order Bz (-6.18) \ll TE (-4.85) < CBu (-4.48) < mX (-4.13) \ll CBz (-2.70) < CF (-2.62) < DCE (-2.53) \leq DCM (-2.52). Comparing these values with the $\log K_{D,HPic}$ ones for given diluents, we can easily see that $Cd(18C6)Pic_2$ more weakly (or more strongly) interacts with the diluents (or water) molecules than HPic does. The high polarity [20] of the $Cd(18C6)Pic_2$ structure is also supported

by this comparison. Similarly, the order was divided into Bz \ll TE < mX \ll CBz for aromatic diluents and CBu \ll CF < DCE \leq DCM for aliphatic diluents.

The same analysis as that described in Section 3.4 gave the order of -H \leq -CH₃ \ll -Cl for the former, while it did that of -CH₂CH₂CH₃, -CH₂CH₃ \ll -Cl \leq -H for the latter. A comparison of these orders with that for the HPic distribution system indicates that the interaction of the aromatic diluents molecules with $Cd(18C6)Pic_2$ differs from that with HPic, while the interaction of the aliphatic diluents ones is essentially similar to it. Especially, it is suggested that the substitution of -H by -Cl in the aromatic diluents molecules or altering Bz into CBz strengthens the interaction with $Cd(18C6)Pic_2$, being contrary to the HPic system. The same is true of the substitution of -CH₃ by -Cl, altering TE into CBz.

4. Conclusions

The K_{ex} and $K_{D,HPic}$ values for the HPic extraction into the ten low-polar diluents were systematically determined at 298 K. The magnitudes of the former constants were exclusively controlled by those of the latter ones from analyzing their thermodynamic relation with K_{HPic} . The contributions of the functional groups constituting the diluents molecules to $K_{D,HPic}$ were clarified subsystematically. That is, it was demonstrated that the interaction of HPic with the diluents molecules is strengthened by introducing a methyl group in their molecules. Also, the contributions to $K_{D,Cd(18C6)Pic_2}$ were partly different from those to $K_{D,HPic}$. The authors cannot now explain essential meanings of such contributions.

Conflict of Interests

The authors do not have any possible conflict of interests with any trademarks mentioned in the paper. Of course, they do not receive any financial gains from the two companies at all.

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