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Yang -Sheng Liu[a]; You -Yuan Dai[a]; Jia -Ding Wang[a]
[a] DEPARTMENT OF CHEMICAL ENGINEERING, TSINGHUA UNIVERSITY, BEIJING, PEOPLE'S REPUBLIC OF CHINA

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Distribution Behavior of L-Tryptophane by Extraction with Di(2-ethylhexyl) Phosphoric Acid

YANG-SHENG LIU, YOU-YUAN DAI,* and JIA-DING WANG
DEPARTMENT OF CHEMICAL ENGINEERING
TSINGHUA UNIVERSITY
BEIJING 100084, PEOPLE'S REPUBLIC OF CHINA

ABSTRACT

To demonstrate that the proton-transfer reaction occurs in the extraction of α-amino acid and to explain the complicated phenomenon present in the extraction of L-tryptophane, a series of extraction equilibrium experiment for L-tryptophane with di(2-ethylhexyl) phosphoric acid (D2EHPA) dissolved in *n*-octane (System A) and a mixture of *n*-octane and *n*-octanol (System B) using L-tryptophane (L-Trp) as a model amino acid were carried out. The effects of L-tryptophane (L-Trp) concentration, D2EHPA concentration, *n*-octanol concentration, and pH on the extraction distribution ratio are discussed in detail. In System A, in the $1.0 < \text{pH} < 3.5$ range, distribution ratio D increases with an increase of pH, but changes slightly in the $3.5 < \text{pH} < 5.0$ range. The data indicate the formation of both (1:1) and (1:2) L-tryptophane-D2EHPA (dimeric) complexes, and the complexes tend to cluster together, away from the low-polarity bulk solvent. The infrared spectrogram of the organic-phase-loaded solute illustrates that the pH condition has little effect on the structure of complex. In System B, both the (1:1) and (1:2) L-tryptophane-D2EHPA (dimeric) complex form, but they do not cluster together because of the diluent that improves the polarity of the bulk solvent. The proton-transfer reaction is again demonstrated in the extraction of α-amino acid with D2EHPA. Expressions of the equilibrium distribution are proposed.

INTRODUCTION

Since 1980s the application of di(2-ethylhexyl) phosphoric acid (D2EHPA) in an emulsion liquid membrane (ELM) as a carrier has attracted much attention from researchers and engineers. It has been reported that

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* To whom correspondence should be addressed.

such amino acids as lysine (1), tryptophane (2), and phenylalanine (2–5) can be separated and concentrated by ELM containing D2EHPA as a carrier. D2EHPA can also separate amino acids as extractant dissolved in different diluent. Liao et al. (6) studied the extraction of isolesine with D2EHPA as the extractant and proposed an extraction equilibrium constant. Teramoto et al. (7) studied the extraction of several amino acids and their related compounds with D2EHPA dissolved in benzene. Shi et al. (8) studied the distribution equilibrium of L-tryptophane by extraction with D2EHPA dissolved in *n*-hexane. A general extraction formula and supposed structure of L-Trp-D2EHPA were proposed. However, the extraction mechanism of amino acids by D2EHPA was limited to a cation-exchange reaction in all of the above works; the extraction equilibria were in the range of $\mathrm{pH} < 3.0$. As to the complicated phenomenon present in the extraction of L-tryptophane with D2EHPA as the extractant, there is no theoretical explanation. There is no suitable model to calculate the distribution ratio. Therefore, it is very important to solve all of these problems.

The authors (9, 10) put forward the ideas that there is a proton-transfer reaction and an ion-exchange reaction in the extraction of L-phenylalanine with D2EHPA as the extractant. To demonstrate that the proton-transfer reaction exists in the extraction of α-amino acid and explain the complicated phenomenon present in the extraction of L-tryptophane, extraction experiments at various pH conditions were carried out using L-tryptophane (L-Trp) as a model amino acid.

MATERIALS AND METHODS

Materials

The D2EHPA used was a product of Chemical Reagent Factory of Beijing, People's Republic of China. It was further purified by recrystallization with copper hydroxide, as described by Patridge and Jensen (11). L-Trp was of chromatographic grade. Other reagents, such as *n*-octane, sulfuric acid (H_2SO_4), sodium sulfate (Na_2SO_4), and sodium hydroxide (NaOH), were all of analytical grade.

Extraction Experiments

All of the extraction experiments were carried out in a bath shaker at 298 ± 0.5 K and 200 ± 2 rpm. Organic solutions, prepared by dissolving D2EHPA in *n*-octane, contained 0.373–0.894 $\mathrm{mol \cdot L^{-1}}$ D2EHPA (dimeric). Aqueous solutions contained 0.296–17.63 $\mathrm{mmol \cdot L^{-1}}$ L-Trp; the ionic strength was fixed at 0.2 $\mathrm{mol \cdot L^{-1}}$. The organic phase (10 mL) and the aqueous phase (10 mL) were stirred in the bath shaker for 1 hour. After equilibrium, the phases were separated by centrifugation.

Analysis

The pH of the aqueous phase was measured with a digital pH meter (model SA 520, USA). The concentration of L-Trp was determined using UV spectrophotometer (model Hp8452, USA) at a wavelength of 280 nm. The concentration of L-Trp in the organic phase was calculated according to the mass balance of L-Trp. Experiments proved that the error was less than 3%. To examine the effect of pH on the structure of the complex in the organic phase, the infrared spectra (model FTIR8200, Japan) of the loaded organic samples at different equilibrium pH values of the aqueous phase were analyzed.

RESULTS AND DISCUSSION

Behavior of Aqueous Solution of L-Trp

L-Trp has one carboxylic group, one amino group, and a side chain (β-indolyl). Two dissociation equilibria *exist* in aqueous solutions:

$$\mathrm{RCH_2(NH_3^+)CHCOOH} \underset{}{\overset{K_{a1}}{\rightleftharpoons}} \mathrm{RCH_2(NH_3^+)CHCOO^-} + \mathrm{H^+} \tag{1}$$

$$\mathrm{RCH_2(NH_3^+)CHCOO^-} \overset{K_{a2}}{\rightleftharpoons} \mathrm{RCH_2(NH_2)CHCOO^-} + \mathrm{H^+} \tag{2}$$

The two dissociation constants for Eqs. (1) and (2) can be described by

$$K_{a1} = \frac{[\mathrm{A}^{\pm}][\mathrm{H}^+]}{[\mathrm{A}^+]} \tag{3}$$

$$K_{a2} = \frac{[\mathrm{A}^-][\mathrm{H}^+]}{[\mathrm{A}^{\pm}]} \tag{4}$$

where A^+, $\mathrm{A}^{\pm}$, and A^- are the cation, zwitterion, and anion of L-Trp, respectively. In aqueous solutions, $\mathrm{p}K_{a1}$ and $\mathrm{p}K_{a2}$ of L-Trp are 2.38 and 9.63, respectively.

System A: Effects of Extractant Concentration and Equilibrium pH on Distribution Ratio

If the extraction of L-Trp with *n*-octane is negligible, the distribution ratio of L-Trp between the organic and the aqueous is defined by

$$D = [A]_{(o)}/[A]_{(w)}$$

where $[A]_{(o)}$ is the concentration of L-Trp in the organic phase and $[A]_{(w)}$ is the concentration of L-Trp in the aqueous phase. As shown in Fig. 1, at a constant extractant concentration (B_0) the distribution ratio D increases with an increase of pH, but the effect of pH on D is not as obvious in the $3.5 < \mathrm{pH} < 5.0$ range. An increase of the initial extractant concentration increases the dis-

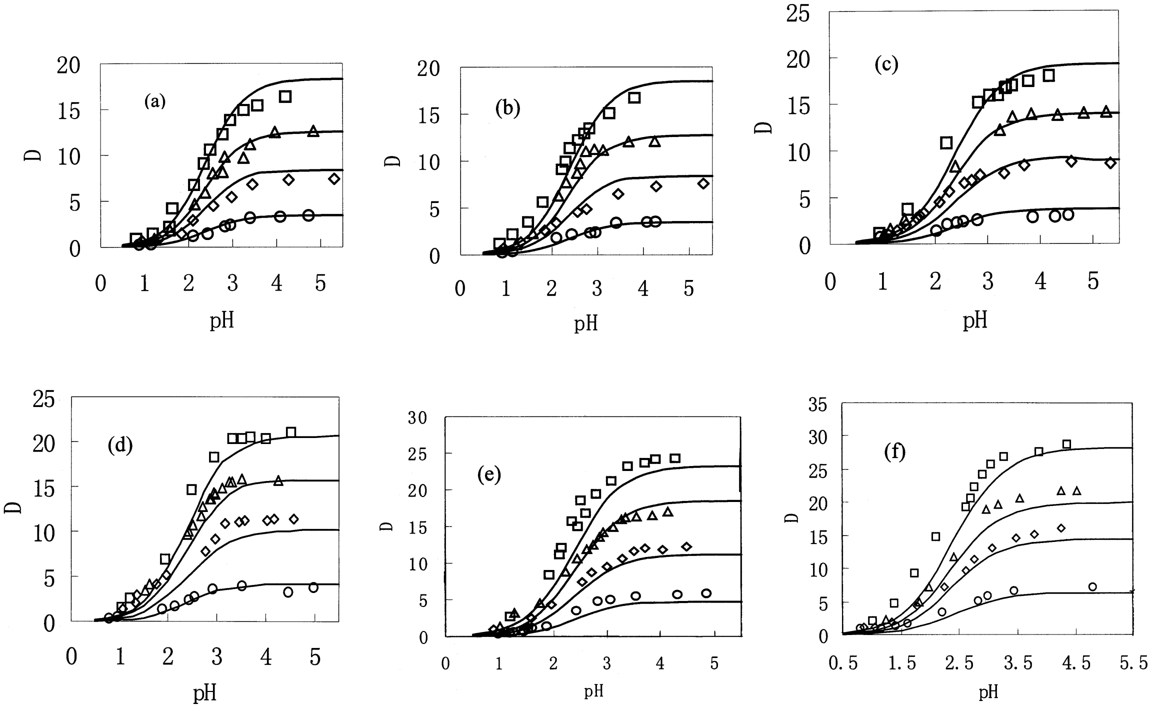

FIG. 1 Effect of pH and concentration of extractant (D2EHPA). Concentration of D2EHPA (mol·L^{-1}): (□) 0.894, (△) 0.740, (◊) 0.600, and (○) 0.373. Initial concentration of L-Trp (mmol·L^{-1}): (a) 0.296, (b) 0.491, (c) 2.453, (d) 4.906, (e) 7.873, and (f) 17.649. Solid lines: Model fits.

tribution ratio; this is ascribed to enhancement of the extraction capacity of the organic phase.

At the same extractant concentration, the difference of the total concentration of L-Trp, C_0, has an obvious effect on the distribution ratio, as seen in Fig. 1. With an increase of C_0, D tends to increase. However, when C_0 is less than 1 mmol·L^{-1}, D remains almost unchanged (see Fig. 1a and 1b).

System B: Effects of Extractant Concentration, Diluent Concentration, and Equilibrium pH on Distribution Ratio

As illustrated in Fig. 2, at a constant extractant concentration (B_0), the distribution ratio D increases with an increase of pH, but the effect of pH condition on D is not as obvious in the higher pH *range*. With an increase of B_0, D tends to increase. These phenomenon are almost the same as those in System A. However, the initial concentration of L-Trp has little effect on the distribution ratio D in System B.

Figure 3 illustrated the relationship between D and the aqueous equilibrium pH. At a constant concentration of D2EHPA, the concentration of *n*-octanol has almost no effect on D.

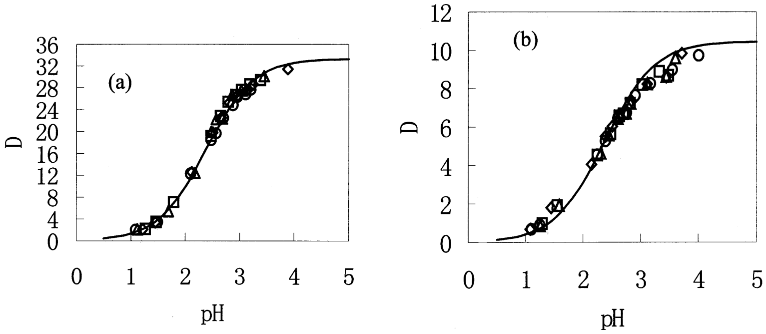

FIG. 2 Effect of pH and initial concentration of L-Trp. Concentration of D2EHPA (mol·L^{-1}): (a) 0.894 and (b) 0.373. Initial concentration of L-Trp (mmol·L^{-1}): (□) 2.894, (◊) 7.155, (△) 9.061, and (○) 15.418. Solid lines: Model fits.

Determination of the Extraction Mechanism

Many workers (2, 6, 8, and 12) considered that the mechanism of the extraction of amino acid with D2EHPA was a cation exchange reaction in the low pH range. Their investigations focused on the cation-exchange reaction in the pH < 3.0 range. In the pH < 5.0 region, the predominant species are A^+ and $A^\pm$. The presence of A^- can be ignored. In the $3.5 <$ pH < 5.0 range, the molar fraction of $A^\pm$ is over 92%, but that of A^+ is less than 8%. It can be concluded from Fig. 1 that the distribution ratio for the extraction of $A^\pm$ is higher. The extraction of $A^\pm$ should attract more attention. The mechanism of the extraction of $A^\pm$ by D2EHPA should be different from that of A^+. Lewis acid D2EHPA in the organic phase is likely to transfer its proton to $A^\pm$ to form an ion-pair complex. This is demonstrated in the infrared spectrogram of the loaded organic phase (ISLOP) (Fig. 4).

The results show that pH has little effect on the structure of the complex (shown in Fig. 4). As illustrated in Fig. 5, in ISLOP the stretching peaks of

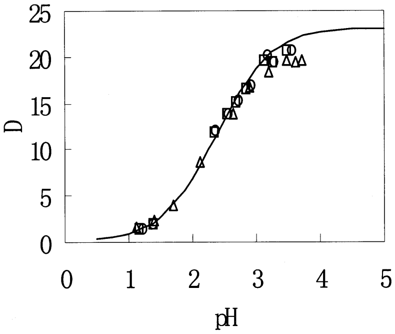

FIG. 3 Effect of pH and concentration of octanol. Concentration of D2EHPA (mol·L^{-1}): 0.740. Initial concentration of L-Trp (mmol·L^{-1}): 7.155. Concentration of octanol: (□) 0.635, (△) 1.269, and (○) 1.904. Solid line: Model fit.

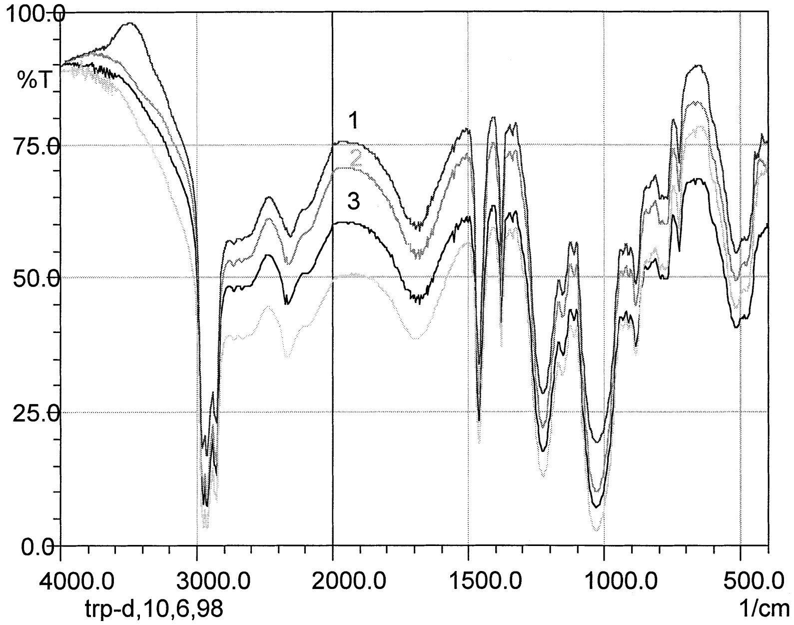

FIG. 4 Infrared spectrograms of loaded organic phase: (1) pH 1.33, (2) pH 2.50, (3) pH 3.12, and (4) pH 4.01.

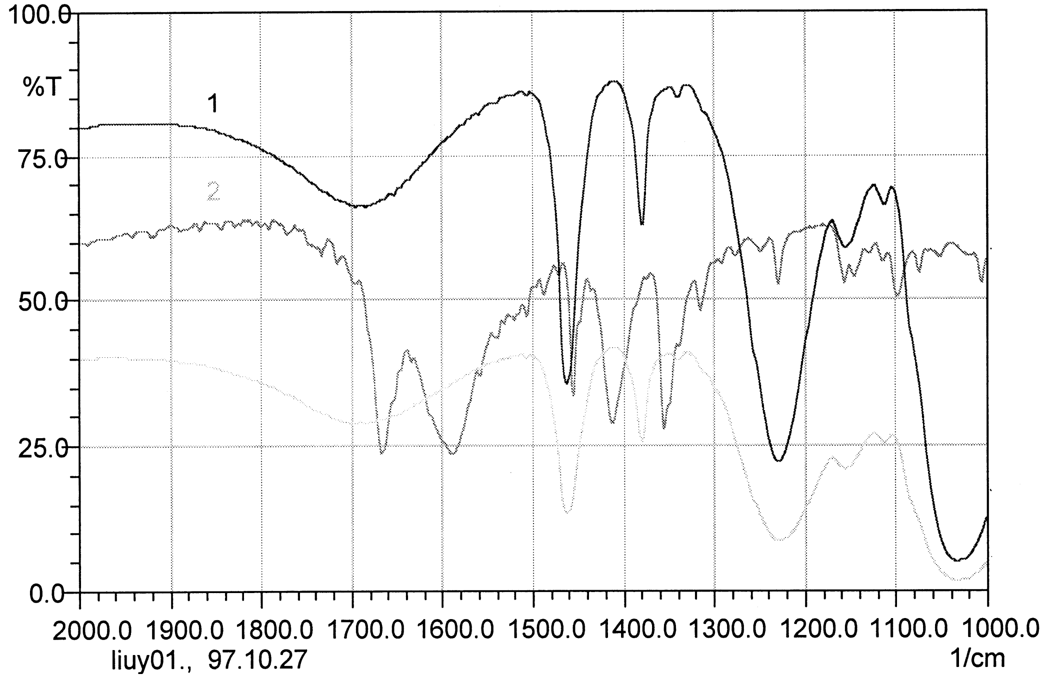

FIG. 5 Infrared spectrograms of loaded organic phase (pH 3.12) and L-tryptophane: (1) L-tryptophane, (2) blank organic phase, and (3) organic phase loaded solute.

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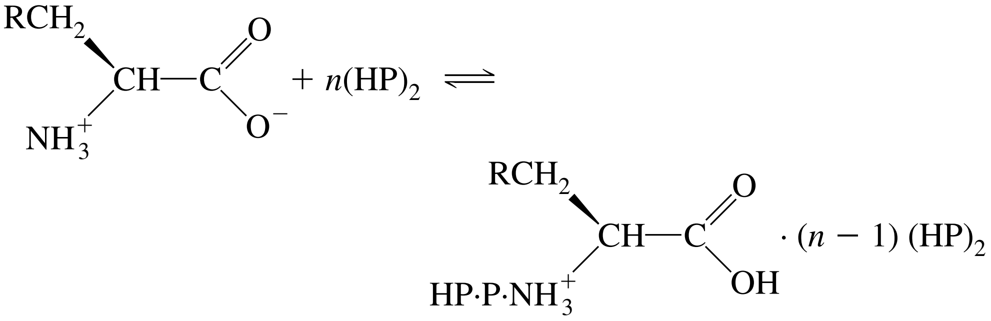
—COO^- at 1413.7, 1591.2, and 1668.3 cm^{-1} are not present, but the absorption peak of —COOH appears at wavenumber 1730.8 cm^{-1}. The characteristic peak of —NH_3^+ near 1500 cm^{-1} is not present, because the stretching is affected by —$(C_8H_{17}O)_2$ $P(O)O^-$ when —NH_3^+ combines with —$(C_8H_{17}O)_2P(O)O^-$.

According to the above analysis, there are two extraction equilibria:



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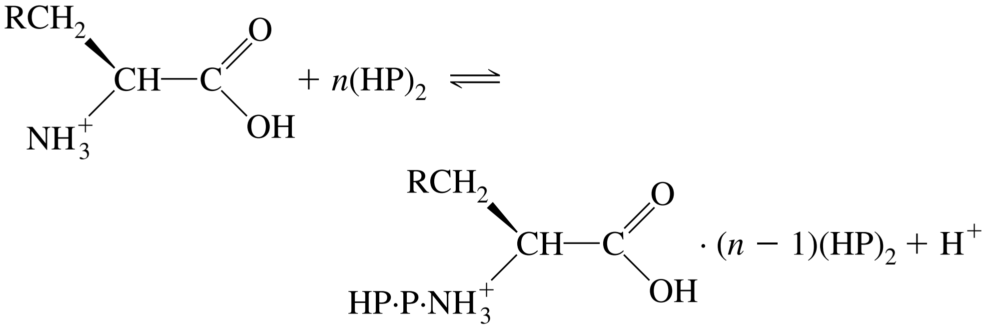

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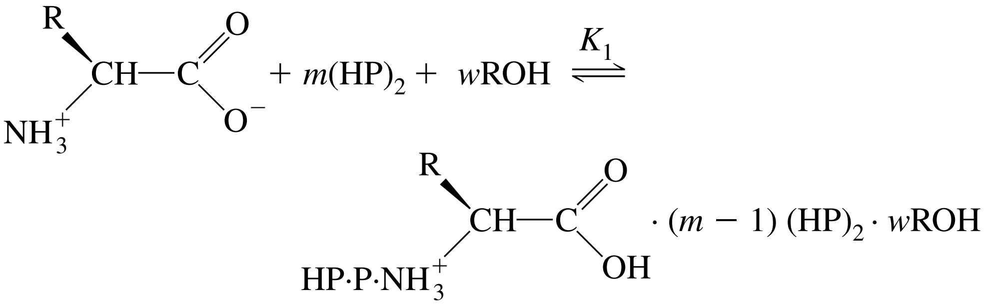
Discussion about the Extraction Mechanism in System B

Based on the above analysis, the following reactions are considered to exist in the extraction:



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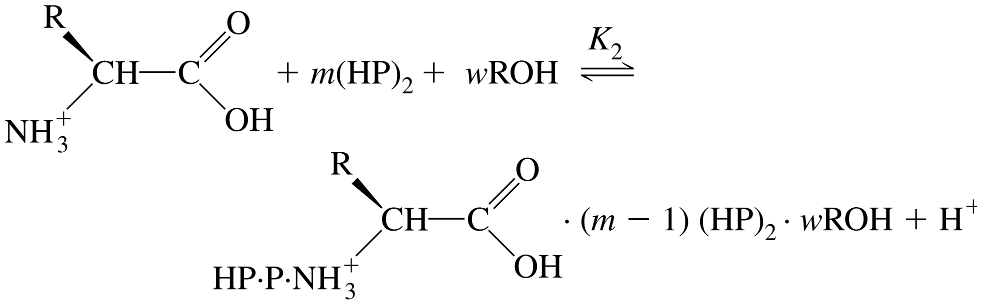


(8)

The extraction equilibrium constants (K_1, K_2) can be expressed as

$$K_1 = \frac{[\overline{\mathrm{PAR}}]}{[\mathrm{A}^{\pm}][\overline{(\mathrm{HP})_2}]^m[\overline{\mathrm{ROH}}]^w} \tag{9}$$

$$K_2 = \frac{[\overline{\mathrm{PAR}}][\mathrm{H}^+]}{[\mathrm{A}^{+}][\overline{(\mathrm{HP})_2}]^m[\overline{\mathrm{ROH}}]^w} = K_1K_{a1} \tag{10}$$

where $\overline{\mathrm{ROH}}$ is *n*-octanol, $\overline{\mathrm{PAR}}$ is the complex, and $\overline{(\mathrm{HP})_2}$ is the dimeric D2EHPA. The organic-phase species are marked with an overbar. If the extraction of L-Trp with *n*-octane is negligible, the distribution ratio of L-Trp between the organic and the aqueous is defined as

$$D' = \frac{[\overline{\mathrm{PAR}}]}{[\mathrm{A}^+] + [\mathrm{A}^{\pm}]} + \phi D_m = \frac{K_1[\overline{(\mathrm{HP})_2}]^m[\overline{\mathrm{ROH}}]^w}{1 + 10^{\mathrm{p}K_{a1}-\mathrm{pH}}} + \phi D_m \tag{11}$$

where D_m is the distribution ratio of the extraction of L-Trp with *n*-octanol, and ϕ is the volume fraction of *n*-octanol in the organic phase. *D_m is around 0.07* (14). By rewriting Eq. (11) and taking the logarithm of both sides, the following equation is obtained:

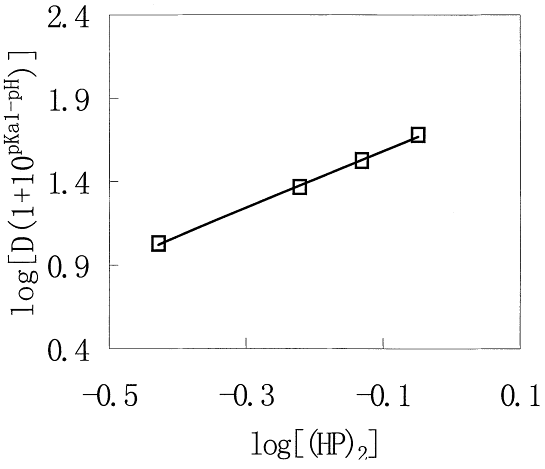


FIG. 6 Log[$D(1 + 10^{\mathrm{p}K_{a1}-\mathrm{pH}})$] vs log[$\overline{(\mathrm{HP})_2}$].

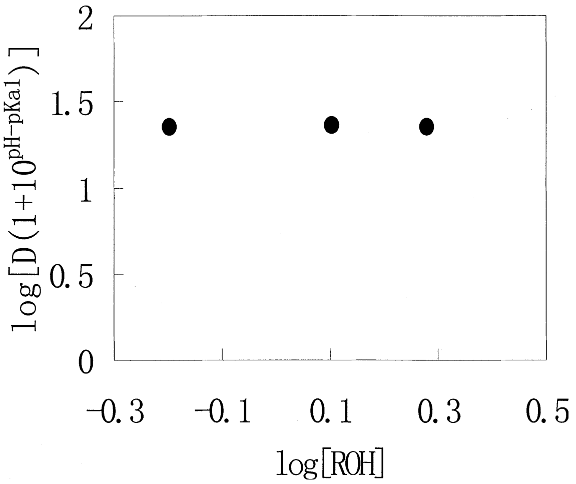


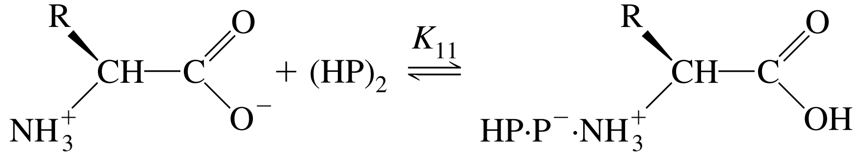
FIG. 7 Log[$D(1 + 10^{\mathrm{pH}-\mathrm{p}K_{a1}})$] vs log[ROH].

$$\log D = \log K_1 + m \log[\overline{(\mathrm{HP})_2}] + w \log[\overline{\mathrm{ROH}}] - \log(1 + 10^{\mathrm{p}K_{a1}-\mathrm{pH}}) \quad (12)$$

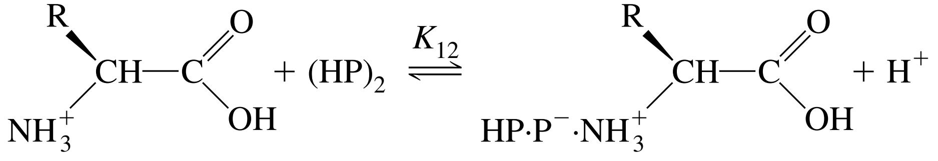
where $D = (D' - \phi D_m)$.

The plot of log[$D(1 + 10^{\mathrm{p}K_{a1}-\mathrm{pH}})$] vs log[$\overline{(\mathrm{HP})_2}$] is shown in Fig. 6. Linearly least-square fitting gives the slope, i.e., $m = 1.7$. The plot of log[$D(1 + 10^{\mathrm{p}K_{a1}-\mathrm{pH}})$] vs log $\overline{\mathrm{ROH}}$ is shown in Fig. 7. Linearly least-square fitting gives the slope, i.e., $w = 0.001 \approx 0$.

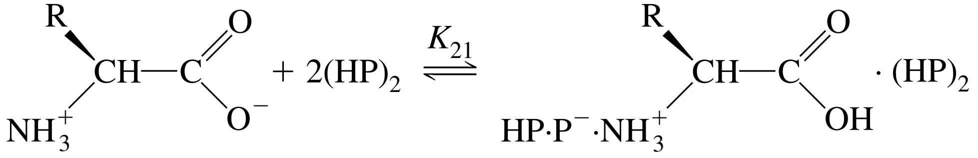
The conclusion can be made that *n*-octanol does not react with the complex of L-Trp–D2EHPA. However, it improves the polarity of the solvent bulk and thus improves the stability of the complex of L-Trp–D2EHPA in the organic phase. Since m is equal to 1.7, both (1:1) and (1:2) L-tryptophane–D2EHPA (dimeric) complexes should form in the extraction.



(13)



(14)



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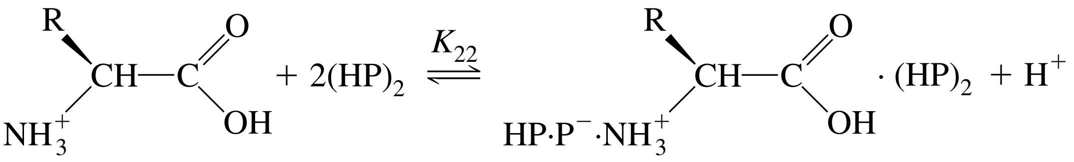

(16)

The extraction equilibrium constants can be described as

$$K_{11} = \frac{[\overline{\mathrm{PA}_{11}}]}{[\mathrm{A}^{\pm}][\overline{(\mathrm{HP})_2}]} \tag{17}$$

$$K_{21} = \frac{[\overline{\mathrm{PA}_{21}}]}{[\mathrm{A}^{\pm}][\overline{(\mathrm{HP})_2}]^2} \tag{18}$$

$$K_{12} = K_{11}K_{\mathrm{a}1} \tag{19}$$

$$K_{22} = K_{21}K_{\mathrm{a}1} \tag{20}$$

The distribution ratio D' and D can be obtained

$$\begin{aligned} D' &= \frac{[\overline{\mathrm{PA}_{11}}] + [\overline{\mathrm{PA}_{21}}]}{[\mathrm{A}^{+}] + [\mathrm{A}^{\pm}]} + \phi D_m \\ &= \frac{K_{11}[(\mathrm{HP})_2] + K_{21}[\overline{(\mathrm{HP})_2}]^2}{1 + 10^{\mathrm{p}K_{\mathrm{a}1}-\mathrm{pH}}} + \phi D_m \end{aligned} \tag{21}$$

$$\begin{aligned} D &= \frac{[\mathrm{PA}_{11}] + [\mathrm{PA}_{21}]}{[\mathrm{A}^{+}] + [\mathrm{A}^{\pm}]} \\ &= \frac{K_{11}[\overline{(\mathrm{HP})_2}]^2 + K_{21}[\overline{(\mathrm{HP})_2}]^2}{1 + 10^{\mathrm{p}K_{\mathrm{a}1}-\mathrm{pH}}} \end{aligned} \tag{22}$$

By using the computer programming to optimize the following object function so that $E(K_{11}, K_{21})$ is minimum:

$$E(K_{11}, K_{21}) = \sum_{i=1}^{i=n} (D_{\mathrm{exp},i} - D_{\mathrm{cal},i})^2 \tag{23}$$

where $D_{\mathrm{exp},i}$ is the experimental value and $D_{\mathrm{cal},i}$ is the calculated value from Eq. (22). K_{11} and K_{21} can be found to be 10.77 $\mathrm{L\cdot mol^{-1}}$ and 46.32 $\mathrm{L^2\cdot mol^{-2}}$, respectively. When the ratio of the volume of the organic phase to that of the aqueous phase is unity, the distribution ratio (D) of L-Trp between the organic phase and the aqueous phase can be calculated by using the following equations:

$$C_0 = (1 + D)[\mathrm{A}^{\pm}]\,(1 + 10^{\mathrm{p}K_{\mathrm{a}1}-\mathrm{pH}}) \tag{24}$$

$$B_0 = [\overline{(\mathrm{HP})_2}] + K_{11}[\overline{(\mathrm{HP})_2}][\mathrm{A}_{\pm}] + K_{21}[\overline{(\mathrm{HP})_2}]^2[\mathrm{A}_{\pm}] \tag{25}$$

$$D = \frac{K_{11}[\overline{(\mathrm{HP})_2}] + K_{21}[\overline{(\mathrm{HP})_2}]^2}{1 + 10^{\mathrm{p}K_{\mathrm{a1}} - \mathrm{pH}}} \tag{26}$$

where C_0 is the initial aqueous concentration of L-Trp and B_0 is the original concentration of D2EHPA in the organic phase. The solid lines in Figs. 2 and 3 are as predicted by this model.

Discussion about the Extraction Mechanism in System A

The research result of Shi et al. (8) showed that the complex ratio of L-Trp–D2EHPA and the extraction equilibrium constant varied with the initial concentration of L-Trp in the aqueous solution. They proposed a supposed structure of L-Trp–D2EHPA, but it was not demonstrated by any experiment. Their investigations focused on the cation-exchange reaction in the $\mathrm{pH} < 3.0$ range. According to the author's researches (9, 10) and the discussions about the mechanism in this paper, proton-transfer and cation-exchange reactions coexist in the extraction of amino acid with D2EHPA. As is known, the equilibrium constant does not vary with the initial concentration of the reactants because it is a stable thermodynamic constant.

King et al. (13) studied the extraction of organic carboxylic acids with a Lewis basic solvent and suggested that if the diluent is a poor solvating medium for the species formed, the polar complexes tend to cluster together to form "micelles" away from the low-polarity bulk solvent. In extreme cases the polar complexes may form a separate phase, a coacervate, or a precipitate.

n-Octanol is a polar diluent in System B. It effectively improves the organic polarity and prevents the polar complexes from interacting. The L-Trp–D2EHPA complex formed in the extraction can be distributed regularly in the organic phase. However, in System A, *n*-octane is an apolar diluent. The low-polarity bulk organic phase can not solvate the complexes formed in the extraction, so the polar L-Trp–D2EHPA complexes tend to cluster together. When the initial concentration of L-Trp increases, the concentration of the complexes in the organic phase will increase too, and the trend to cluster becomes more prominent. However, when the initial concentration of L-Trp is very low, the clustering trend can be ignored.

According to the above analysis, conclusions can be made that in System A there are reactions that form both (1:1) and (1:2) complexes and a "clustering reaction" between the (1:1) complex and the (1:2) complex. The organic polarity of System A is not the same as that of System B, so the extraction equilibrium constants are also different; they are indicated by K'_{11}, K'_{12}, K'_{21}, and K'_{22}, respectively. The reactions which form both (1:1) and (1:2) complexes can still be expressed by Eqs. (13) to (16).

Aside from these reactions in System A, there should be a reaction to represent the clustering trend:

$$p\mathrm{PA}_{11} + q\mathrm{PA}_{21} + m(\mathrm{HP})_2 \xrightleftharpoons{K_{pq}} (\mathrm{PA}_{11})_p(\mathrm{PA}_{21})_q((\mathrm{HP})_2)_m \tag{27}$$

When the initial concentration is low enough, the above reaction can be ignored, as shown in Figs. 1(a) and 1(b). The constants K'_{11}, K'_{12}, K'_{21}, and K'_{22} can be expressed as

$$K'_{11} = \frac{[\overline{\mathrm{PA}_{11}}]}{[\mathrm{A}^{\pm}][(\mathrm{HP})_2]} \tag{28}$$

$$K'_{21} = \frac{[\overline{\mathrm{PA}_{21}}]}{[\mathrm{A}^{\pm}][\overline{(\mathrm{HP})_2}]^2} \tag{29}$$

$$K'_{21} = K'_{11}K_{\mathrm{a1}} \tag{30}$$

$$K'_{22} = K'_{21}K_{\mathrm{a1}} \tag{31}$$

The distribution ratio D of L-Trp between the organic phase and the aqueous phase can be obtained from

$$\begin{aligned} D &= \frac{[\overline{\mathrm{PA}_{11}}] + [\overline{\mathrm{PA}_{21}}]}{[\mathrm{A}^{+}] + [\mathrm{A}^{\pm}]} \\ &= \frac{K'_{11}\,[\overline{(\mathrm{HP})_2}] + K'_{21}\,[\overline{(\mathrm{HP})_2}]^2}{1 + 10^{\mathrm{p}K\mathrm{a1}-\mathrm{pH}}} \end{aligned} \tag{32}$$

By using computer programming to optimize the object function $E(K'_{11}, K'_{21})$, defined as Eq. (23), K'_{11} and K'_{21} are found to be 0.91 $\mathrm{L\cdot mol^{-1}}$ and 21.54 $\mathrm{L^2\cdot mol^{-2}}$, respectively.

When the initial concentration of L-Trp is higher, the clustering reaction, i.e., Eq. (27), should be taken into account. The equilibrium constant K_{pq} can be expressed as

$$K_{pq} = \frac{[\overline{\mathrm{PA_{pq}}m}]}{[\overline{\mathrm{PA}_{11}}]^p[\overline{\mathrm{PA}_{21}}]^q[\overline{(\mathrm{HP})_2}]^m} \tag{33}$$

The distribution ratio can be expressed as

$$\begin{aligned} D &= \frac{[\overline{\mathrm{PA}_{11}}] + [\overline{\mathrm{PA}_{21}}] + (p+q)\,[\overline{\mathrm{PA_{pq}}m}]}{[\mathrm{A}^{+}] + [\mathrm{A}^{\pm}]} \\ &= \frac{K'_{11}[\overline{(\mathrm{HP})_2}] + K'_{21}[\overline{(\mathrm{HP})_2}]^2}{1 + 10^{\mathrm{p}K_{\mathrm{a1}}-\mathrm{pH}}} \\ &\quad + \frac{(p+q)K_{\mathrm{pq}}[\overline{\mathrm{PA}_{11}}]^p[\overline{\mathrm{PA}_{21}}]^q[\overline{(\mathrm{HP})_2}]^m}{[\mathrm{A}^{+} + [\mathrm{A}^{\pm}]} \end{aligned} \tag{34}$$

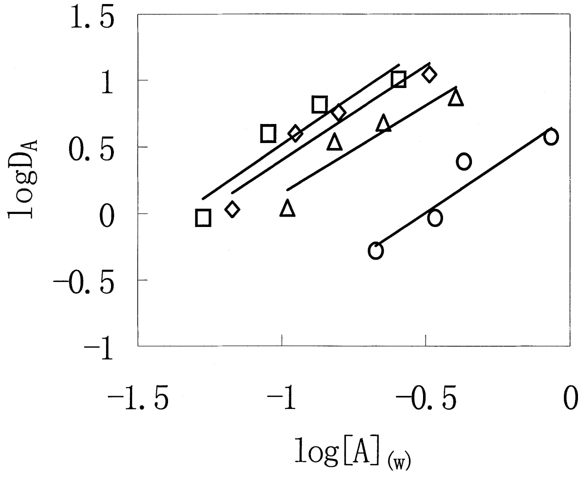

FIG. 8 Plots of log D_A vs $\log[A]_{(w)}$. Aqueous equilibrium pH: 3.36. Concentration of D2EHPA: (□) 0.894, (◊) 0.740, (△) 0.600, and (○) 0.373.

Equation (34) can be rewritten as

$$\log\left[D - \frac{K'_{11}[\overline{(\mathrm{HP})_2}] + K'_{21}[\overline{(\mathrm{HP})_2}]^2}{1 + 10^{\mathrm{p}K_{\mathrm{a1}}-\mathrm{pH}}}\right] = \log\{(p+q) \times K_{pq}\,(K'_{11})^p (K'_{21})^q\} - (p+q)\,\lg(1 + 10^{\mathrm{p}K_{\mathrm{a1}}-\mathrm{pH}}) + (p + 2q + m)\,\lg[\overline{(\mathrm{HP})_2}] + (p + q - 1)\,\lg[A]_{(\mathrm{w})} \tag{35}$$

At constant aqueous equilibrium pH and extractant concentration, plots of log D_{A} vs $\log[A]_{(\mathrm{w})}$ are as shown in Fig. 8; log D_{A} represents the left-hand side of Eq. (35). Linearly least-square fittings give the slopes, i.e., the values of $(p + q - 1)$ in Eq. (34). They are nearly equal to 1.43. At constant aqueous equilibrium pH and aqueous concentration of l-Trp, plots of log D_{A} vs $\log[\overline{(\mathrm{HP})_2}]$ (Fig. 9) give the slopes, i.e., the values of $(p + 2q - m)$ in Eq. (34). They are nearly equal to 3.60.

Computer programming was used to optimize the following object function so that $E(p, q, m, K_{pq})$ is minimum:

$$E(p, q, m, K_{pq}) = \sum_{i=1}^{i=n} (D_{\mathrm{exp},i} - D_{\mathrm{cal},}i)^2 \tag{36}$$

where $D_{\mathrm{exp},i}$ is the experimental value and $D_{\mathrm{cal},i}$ is the calculated value from Eq. (34). The values of p, q, and m are found to be 1.26, 1.17, and 0, respectively. The value of K_{pq} is 7200 $\mathrm{L}^{1.43}\cdot\mathrm{mol}^{-1.43}$, and it reflects the trend of the complexes to cluster together in the low-polarity organic phase (System A). When the ratio of the volume of the organic phase to that of the aqueous phase is unity, the distribution ratio (D) of L-Trp between the or-

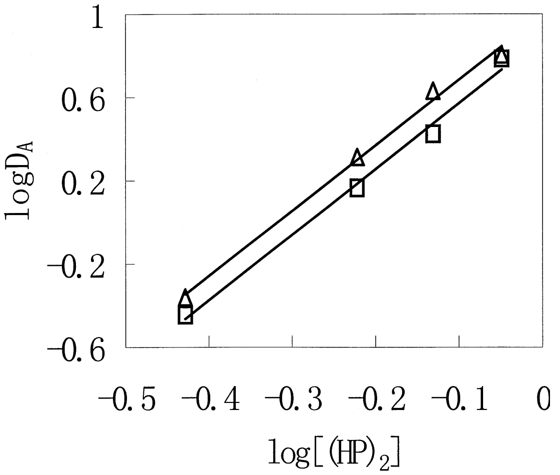

FIG. 9 Plots of log D_A vs log$[\overline{(HP)_2}]$. Aqueous equilibrium pH: (△) 3.53 and (□) 2.55: $[A]_{(w)}$ (mmol·L^{-1}): (△) 0.625 and (□) 0.45.

ganic phase and the aqueous phase in System A can be calculated by using the following equations:

$$C_0 = (1 + D)[A^{\pm}](1 + 10^{pK_{a1}-pH}) \tag{37}$$

$$\begin{aligned} B_0 = {} & [\overline{(HP)_2}] + K'_{11}[\overline{(HP)_2}][A_{\pm}] + 2K'_{21}[\overline{(HP)_2}]^2[A_{\pm}] \\ & + 3.60K_{pq}(K'_{11})^{1.26}(K'_{21})^{1.17}[\overline{(HP)_2}]^{3.60}[A_{\pm}]^{2.43} \end{aligned} \tag{38}$$

$$\begin{aligned} D = {} & \frac{K'_{11}[\overline{(HP)_2}] + K'_{21}[\overline{(HP)_2}]^2}{1 + 10^{pK_{a1}-pH}} \\ & + \frac{3.60K_{pq}(K'_{11})^{1.26}(K'_{21})^{1.17}[\overline{(HP)_2}]^{3.60}[A]_{(w)}^{1.43}}{(1 + 10^{pK_{a1}-pH})^{2.43}} \end{aligned} \tag{39}$$

$$[A_{(w)}] = [A^{\pm}](1 + 10^{pK_{a1}-pH}) \tag{40}$$

The solid lines in Fig. 1 are predictions by the model. Comparation of the equilibrium constants in System A with those in System B shows that $K_{11} > K'_{11}$, and $K_{21} > K'_{21}$, so the polarity of the diluent has a great effect on the equilibrium constants.

CONCLUSIONS

In this paper the extraction of L-tryptophane with D2EHPA dissolved in *n*-octane and *n*-octanol was studied in detail. In System A, in the $1.0 < pH < 3.5$ range, distribution ratio D increases with an increase of pH, but changes only slightly in the $3.5 < pH < 5.0$ range. The data indicate the formation of both (1:1) and (1:2) L-tryptophane–D2EHPA (dimeric) complexes, and the complexes tend to cluster together, away from the low-polarity bulk solvent.

An infrared spectrogram of the organic-phase-loaded solute illustrated that the pH condition had little effect on the structure of the complex. In System B, both (1:1) and (1:2) L-tryptophane–D2EHPA (dimeric) complexes form, but they do not cluster together because of the diluent that improves the polarity of the bulk solvent. The proton-transfer reaction is again demonstrated in the extraction of α-amino acid with D2EHPA. Expressions for the equilibrium distribution are proposed. The experimental data present good agreement to the proposed models.

NOMENCLATURE

A^+	L-tryptophane cation
A^-	L-tryptophane anion
$A^\pm$	L-tryptophane zwitterion
$[A]_{(o)}$	concentration of L-Trp in the organic phase ($L\cdot mol^{-1}$)
$[A]_{(w)}$	concentration of L-Trp in the aqueous phase ($L\cdot mol^{-1}$)
C_0	initial aqueous concentration of L-Trp ($mol\cdot L^{-1}$)
D	distribution ratio (dimensionless)
K_{11}, K'_{11}	equilibrium constant of proton transfer reaction ($L\cdot mol^{-1}$)
K_{12}, K'_{12}	equilibrium constant of cation-exchange reaction (dimensionless)
K_{21}, K'_{21}	equilibrium constant of proton transfer reaction ($L^2\cdot mol^{-2}$)
K_{22}, K'_{22}	equilibrium constant of cation-exchange reaction ($L\cdot mol^{-1}$)
K_{a1}, K_{a2}	dissociation constant of L-Trp ($L\cdot mol^{-1}$)
K_{pq}	"clustering reaction" equilibrium constant ($L^{1.43}\cdot mol^{-1.43}$)
$(HP)_2$	dimeric of D2EHPA
PA	complex of D2EHPA combined with L-tryptophane
PA_{11}	(1:1) complex of D2EHPA combined with L-tryptophane
PA_{21}	(2:1) complex of D2EHPA combined with L-tryptophane

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