

Study on the Extraction of *L*-Phenylalanine with Organo-phosphoric Acid in Two and Three-phase System

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The extraction behaviors of *L*-phenylalanine by di-(2,4,4-trimethylpentyl) phosphinic acid, di-(2,4,4-trimethylpentyl)-monothiophosphinic acid and di-(2-ethylhexyl) phosphoric acid were studied in both two-phase and three-phase systems respectively. The equilibrium constants for these extraction reactions were calculated.

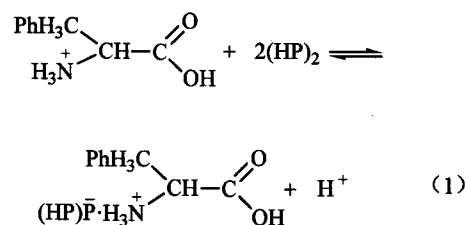
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Introduction

The extraction of amino acids has recently attracted a great deal of attention. They could be extracted into reverse micelles or microemulsions with a surfactant such as AOT [sodium di-(2-ethylhexyl) sulfosuccinate]. Leaididis *et al.* investigated the partition of amino acids between water and reverse micelle interfaces, and discussed the related factors influencing the distribution in their series of papers.¹⁻⁴ Adachi *et al.*⁵ reported that the extraction of amino acid was given by the sum of the contribution of solubilization in the water pool and that of association at the interface. Rabie *et al.*⁶ studied the effect of amino acids at zwitterionic condition on the water uptake of AOT reverse micelle system and showed that the water uptake increased almost linearly with the initial amino acid concentration. Fu *et al.*⁷ measured the equilibrium constants for the association of AOT anions with amino acid in its cationic form (A^+) and the constants for the

association of AOT molecule with its zwitterionic form (A^\pm), respectively, at different temperatures, and found that the associated A^+ at the interface decreased the water uptake in the reverse micelles.

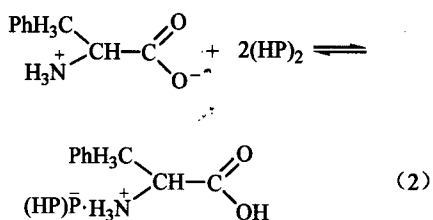
Amino acid could also be extracted into organic solution by complexing method with extractant, such as di-(2-ethylhexyl) phosphoric acid (HDEHP, trade mark P204 in China), but the relative studies were limited to the cationic exchange between A^+ and H^+ in a lower aqueous pH range.⁸⁻¹⁰ Liu *et al.*¹¹ expanded the experimental pH range and investigated the extraction of *L*-phenylalanine with HDEHP. They confirmed the cationic exchange between A^+ and H^+ at pH 1—3 written as the Eq. (1), where the partition coefficient (D) of amino acid between two phases increased with the increase of pH. But they found that in higher pH of 3—5, the extractant reacted with A^\pm by proton-transfer, see Eq. (2), to form the same complex as in the lower pH. In this case D was influenced little by aqueous pH values.



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Cyanex272 [containing about 87% di-(2,4,4-trimethylpentyl) phosphinic acid, HDTMPP], and Cyanex302 [containing about 84% di-(2,4,4-trimethylpentyl) monothiophosphinic acid, HDTMTP] (abbreviated as HP) are important extractants used in the extraction of metal ions. In the process of neutralization of their organic solution with NaOH, the volumes of organic phase increase with the increase of neutralization fraction α , and the organic solutions even separate into two phases,¹²⁻¹⁵ *i. e.*, the third phase forms. This is because the sodium salt of organo-phosphinic acid (NaP) has a hydrophilic head and two hydrophobic tails like AOT, showing the characteristics of an anionic surfactant.

This paper aims to investigate the extractions of *L*-phenylalanine with HDTMPP and HDTMTP over a wider aqueous pH range of 1–10 in both two-phase and three-phase systems, and to compare them with the extraction behavior of HDEHP and AOT.

Experimental

Cyanex272 and Cyanex302 were kindly supplied by Cytec Co. in Canada, P204 was supplied by Shanghai Institute of Organic Chemistry. Cyanex272 and P204 were purified with the middle phase microemulsion method¹⁴ and Cyanex302 was purified with cobalt salt precipitation method.¹⁵ Their purities were all higher than 99%. *L*-Phenylalanine, sodium hydroxide and sodium sulfate were of all A. R. grade. Hydrogenated gasoline was purchased from Qilu Petroleum Chemical Company in China without further purification.

Equal volumes (10.00 mL each) of gasoline solution of extractant and aqueous solution of phenylalanine (initial concentration was 2.0 mmol/L) containing Na₂SO₄ (0.2 mol/L) to maintain the ionic strength, and NaOH for adjusting the aqueous pH or the neutralization fraction (α) of the acidic extractants, were mixed in stoppered tubes, shaken and equilibrated in a water bath at 298 K

for at least 24 h. The volumes of each phase were recorded carefully (the accuracy could be within 0.02 mL). After the phase separation, the contents of phenylalanine in the aqueous phase were analyzed by spectrophotometry¹⁶ with a 721 spectrophotometer (Shanghai, China), and the pH was measured with a pH-2 pH meter. The water contents in the organic phase were determined by Karl-Fischer titration (WS-2 micro-water instrument, Keson Co., China). The concentration of amino acid in the organic phase for the two-phase system was obtained by difference. In the three-phase system, our analysis confirmed that the upper phase had no amino acid, so the content in the middle phase was also obtained by calculation.

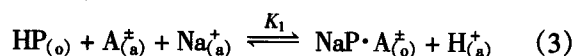
Results and discussion

Extraction of phenylalanine with HDEHP, HDTMPP and HDTMTP in two-phase system

The equilibrium aqueous pH < 7 has been chosen to study the extraction of amino acid. In this case, the equilibrium phase volume changes a little (increases about 0.1–0.2 mL), and no third phase forms.

The plots of the partition coefficient (*D*) of phenylalanine between organic and aqueous phase with increasing equilibrium aqueous pH are shown in Fig. 1. The plot in Fig. 1(a) shows that the *D* increased with the increase of pH at pH 1–3 and changed little at pH 3–5 in P204 system. This was consistent with the result reported in the reference.¹¹ But the extraction behaviors by C272 and C302 were different from P204. Phenylalanine was extracted very weakly at pH < 6, but *D* increased sharply with increasing at pH from then.

In neutral aqueous solution (pH = 6–7), phenylalanine exists in its zwitterionic form of A[±] (the acidic ionization constants of phenylalanine are p*K*_{a1} = 1.83 and p*K*_{a2} = 9.13), the extraction reaction is supposed to be:



where a, o represent aqueous and organic phase respectively. The experimental data are listed in Table 1.1 and Table 1.2, and lg *K*_{1,C272} = -6.07 ± 0.04, lg *K*_{1,C302} = -6.04 ± 0.04 are obtained respectively.

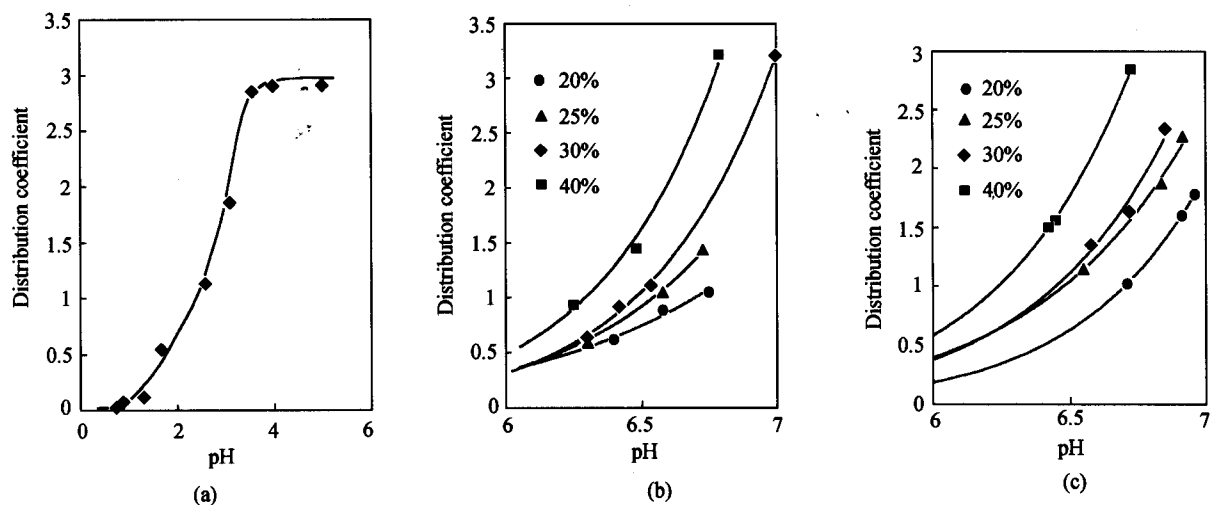


Fig. 1 Plots of the partition coefficient D of phenylalanine vs. the equilibrium aqueous pH. (a) P204 (25%, V/V); (b) C272; (c) C302.

Table 1.1 Extraction of phenylalanine with HDTMPP in two-phase system

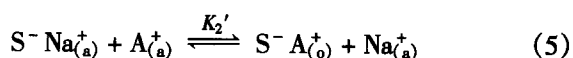
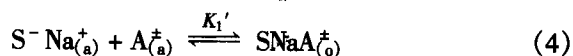
c_{HDTMPP} (V/V%)	20%			25%			30%			40%		
c_{HDTMPP} (mol/L)	0.613			0.766			0.919			1.226		
$c_{\text{NaOH}}^{\text{in}}$ (mol/L)	0.08	0.24	0.32	0.08	0.24	0.40	0.16	0.32	0.48	0.20	0.40	0.60
pH	6.40	6.58	6.75	6.30	6.58	6.73	6.42	6.54	7.00	6.25	6.48	6.79
$c_{\text{Na}^+\text{A}^-}^{\text{f}}$ (mmol/L)	0.77	0.94	1.02	0.77	1.02	1.08	0.95	1.05	1.52	0.97	1.08	1.52
$c_{\text{A}^+}^{\text{f}}$ (mmol/L)	1.23	1.06	0.98	1.23	0.98	0.82	1.05	0.95	0.48	1.03	0.82	0.48
$c_{\text{Na}^+}^{\text{f}}$ (mol/L)	0.48	0.64	0.72	0.48	0.64	0.80	0.56	0.72	0.88	0.60	0.80	1.00
c_{HP}^{f} (mol/L)	0.533	0.374	0.294	0.686	0.526	0.459	0.758	0.595	0.437	1.025	0.825	0.625
D_{A^+}	0.62	0.88	1.04	0.62	1.04	1.44	0.90	1.10	3.21	0.93	1.44	3.21
$\lg K_1$	-6.01	-6.01	-6.06	-6.03	-6.08	-6.04	-6.10	-6.14	-6.07	-6.07	-6.15	-6.08
$\lg \bar{K}_1$	-6.07 ± 0.04											

Table 1.2 Extraction of phenylalanine with HDTMPP in two-phase system^a

c_{HDTMPP} (V/V%)	20%			25%			30%			40%		
c_{HDTMPP} (mol/L)	0.587			0.733			0.879			1.174		
$c_{\text{NaOH}}^{\text{in}}$ (mol/L)	0.08	0.24	0.27	0.08	0.24	0.40	0.16	0.32	0.48	0.20	0.40	0.64
pH	6.71	6.91	6.96	6.55	6.84	6.92	6.58	6.72	6.85	6.42	6.45	6.73
$c_{\text{Na}^+\text{A}^-}^{\text{f}}$ (mmol/L)	1.01	1.23	1.28	1.07	1.30	1.39	1.15	1.24	1.40	1.20	1.22	1.48
$c_{\text{A}^+}^{\text{f}}$ (mol/L)	0.99	0.77	0.72	0.93	0.70	0.61	0.85	0.76	0.60	0.80	0.78	0.52
$c_{\text{Na}^+}^{\text{f}}$ (mmol/L)	0.48	0.64	0.67	0.48	0.64	0.80	0.56	0.72	0.88	0.60	0.80	1.04
c_{HP}^{f} (mol/L)	0.507	0.347	0.317	0.653	0.493	0.333	0.719	0.559	0.399	0.974	0.774	0.534
D_{A^+}	1.02	1.60	1.78	1.15	1.86	2.28	1.35	1.63	2.23	1.50	1.56	2.85
$\lg K_1$	-6.09	-6.05	-6.04	-5.99	-6.07	-5.99	-6.05	-6.11	-6.03	-6.01	-6.05	-6.02
$\lg \bar{K}_1$	-6.04 ± 0.07											

^a $V_0^{\text{in}} = V_a^{\text{in}} = 10.00$ mL, $c_{\text{A}^+}^{\text{in}} = 2.0$ mmol/L, $c_{\text{Na}_2\text{SO}_4}^{\text{in}} = 0.2$ mol/L.

In the system of AOT-*n*-heptane-phenylalanine-NaCl (0.1 mol/L) we studied previously,⁷ both reactions of



were considered at 298 K in the aqueous pH range of 1.5–7, and $K_1' = 2.29 \pm 0.09$, $K_2' = 116.2 \pm 1.4$, respectively. The value of K_2' was about 50 times of K_1' indicating that the high extraction was caused by the electrical combination of S^- with A^+ .

There is also a strong electrical force between P^- and A^+ in P204 extraction system. Considering the acidic ionization constants, $pK_{a,HDEHP} = 2.79$ ¹⁷ is lower than $pK_{a,HDTMTP} = 3.12$ ¹⁵ and $pK_{a,HDTMPP} = 3.73$.¹² The stronger acidity of HDEHP might be a reason for explaining big difference between the extraction behavior by HDEHP and by the other two extractants. H^+ in P204 is easier to be exchanged by A^+ [Eq. (1)], it can even be transferred into A^{\pm} resulting also the combination of P^- with A^+ . We have also noticed that the polar heads of SO_3^- and PO_4^- in AOT and HDEHP, respectively, have more oxygen atom than that in HDTMPP (PO_2^-) and HDTMPTP (PSO^-). More oxygen atom should make the extractant hydrophilic heads have more chance to combine with A^+ in aqueous solutions.

The extraction behaviors of the systems Cyanex272 and Cyanex302 are very similar even their pK_a values are different. In the pH range of 6–7, the neutralized fraction (α) of the organic acids is about 15%–55%. In this range, reverse micelle or w/o microemulsion formed in the organic phase, where the free acid (HP) took part in the structure as a co-surfactant like an alcohol.^{18,19} The volumes of the organic phases in the system of HP (0.4 mol/L)-kerosene- H_2O (NaOH, Na_2SO_4 0.1 mol/L) increased about 5% for Cyanex272 and about 12% for Cyanex302 system (see Fig. 3 in the Ref. 15) owing to the water solubilization. The sodium salts NaDTMPP and NaDTMPTP with surfacial activities should locate at the interface of the reverse micelle or microemulsion, so the combination of the extractant with A^{\pm} should be there too. The molecules of H_2O and/or HP associated with the polar head P^- would be replaced by the extracted amino acid. The experiment here showed that the volume increase of the organic solutions loaded amino acid was less

than 2%, which was omitted in the calculation of the data in Table 1 and 2 respectively. The data indicated that the extraction of amino acid was neither attributed to cationic exchange between A^+ and H^+ , nor the proton-transfer from HP to A^{\pm} as in the HDEHP system, but to the association of the sodium salt with amino acid in the zwitterionic form at the interface.

The Lewis basicity of the bond $P=O$ in NaDTMPP was stronger than that in NaDEHP, which was proved by the 1H NMR spectra measurements for their microemulsions.²⁰ It was also reported that the hydrophilic property of NaDTMPTP was stronger than that of NaDTMPP. This order was supported by the data of formation heats ($-\Delta H_{NaDTMPP} > -\Delta H_{NaDTMPTP}$) and of dipole moments ($D_{HDTMPP} < D_{HDTMPTP}$).¹⁹ The similar values of $\lg K_{1,C272}$ and $\lg K_{1,C302}$ might be resulted by the association competition of amino acid A^{\pm} , unneutralized organic acid HA and water with the polar head of the extractant at the interface of the reverse micelle or microemulsion. We have tried to write a direct reaction in the form of NaP with A^{\pm} as Eq. (4) in the AOT system, but we found that the unneutralized organic acid had an effect on the extraction.

Extraction of phenylalanine in three-phase system

In this part, the extraction is discussed based on the following assumptions:

(1) The sodium salt NaP is accumulated in the interfacial zone of the middle phase microemulsion.^{14,15}

$$c_{NaP}^m = c_{HP}^{o,in} \cdot \alpha \cdot \frac{V^{o,in}}{V^m} \quad (6)$$

where m represents the middle phase and in represents the initial state.

(2) The amino acid exists in both the middle phase and aqueous phase, but is not soluble in the light organic phase composed mainly with gasoline.

$$c_A^{a,in} \cdot V^{a,in} = c_A^{a,f} \cdot V^{a,f} + c_A^m \cdot V^m \quad (7)$$

where f represents the final state.

(3) The amino acid extracted in the middle phase is the sum of the phenylalanine solubilized in the water pool and that associated with surfactant at the interfacial zone.

$$c_A^m = c_A^{m,b} + c_A^{m,s} \quad (8)$$

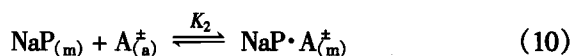
where b and s represent the bonding and solubilizing respectively.

(4) The water pool has the same composition and properties as the bulk aqueous phase because the water content in the middle phase microemulsion is much larger than that in reverse micelles of the organic solution.

$$c_A^{m,s} = c_A^{a,f} \quad (9)$$

The experimental conditions chosen in this study are as follows: All initial volumes of both organic and aqueous solutions, initial concentrations of phenylalanine and Na_2SO_4 in aqueous are as the same as those in the two-phase system, but the organic acid is almost completely neutralized by NaOH ($\alpha = 1.0$ for both of Cyanex272 and P204, $\alpha = 0.9$ for Cyanex302 respectively). Under these conditions, the equilibrium aqueous pH values are ranged between 7–10, where phenylalanine exists in its zwitterionic and anionic forms (A^\pm and A^-), and their fractions f_\pm and f_- can be calculated by the values of K_{a1} , K_{a2} and pH.

Suppose that the anionic surfactant NaP associates with A^\pm become $\text{NaP} \cdot \text{A}^\pm$ at the interfacial zone in the middle phase microemulsion:



$$K_2 = \frac{c_A^{m,b}}{c_A^{a,f} \cdot f_\pm \cdot c_{\text{NaP}}^m} \quad (11)$$

where c_{NaP}^m is given by Eq. (6) and is calculated by Eq. (12) which is derived from Eqs. (7) and (8):

$$c_A^{m,b} = (c_A^{a,in} \cdot V^{a,in} - c_A^{a,f} \cdot V^{a,f} - c_A^{a,f} \cdot V^{m,s}) / V^m \quad (12)$$

where $V^{m,s}$ represents the volume of aqueous solution solubilized in the middle phase microemulsion.

The three-phase extraction data are listed in Table 2.1, 2.2 and 2.3, and the equilibrium constants obtained are $K_{2,C272} = 1.96 \pm 0.18$, $K_{2,C302} = 2.15 \pm 0.09$ and $K_{2,P204} = 2.21 \pm 0.20$ respectively.

These equilibrium constants are very close again and even close to $K'_{1,AOT} = 2.29 \pm 0.01$ for Eq. (4). In AOT-heptane-phenylalanine- NaCl (0.1 mol/L)- H_2O system, where the volume of water solubilized in organic

phase was about 20% in the equilibrium organic solution at 298 K and pH 6. The solubilized water has also a contribution to the extraction as the system studied in this part. At the same time, all the initial organo-phosphoric acids are neutralized by NaOH , (in Cyanex302 system, its neutralized fraction $\alpha = 90\%$, higher than this value made aqueous $\text{pH} > 10$, then f_{A^\pm} will be too low to be

Table 2.1 Extraction of phenylalanine with HDTMPTP in three-phase system

c_{HDTMPTP} (V/V%)	10	15	20	25	30
c_{HDTMPTP} (mol/L)	0.293	0.440	0.587	0.733	0.879
c_{NaOH} (mol/L)	0.264	0.397	0.528	0.660	0.791
V_{upper} (mL)	7.84	6.23	4.57	3.10	1.61
V_{middle} (mL)	5.20	7.35	9.90	12.22	14.39
V_{lower} (mL)	6.96	6.42	5.53	4.68	4.00
pH	8.35	8.43	8.44	8.49	8.57
f_{A^\pm}	0.86	0.83	0.83	0.81	0.78
$c_{\text{A}^\pm}^{a,f}$ (mmol/L)	1.35	1.19	1.03	0.92	0.84
$c_{\text{A}^\pm}^{\text{mid}}$ (mmol/L)	2.04	1.68	1.44	1.28	1.16
$c_{\text{NaP}}^{\text{mid}}$ (mol/L)	0.51	0.54	0.53	0.54	0.55
$V^{m,s}$ (mL)	3.04	3.58	4.47	5.32	6.00
E (%)	53	62	71	78	83
Solubilization (%)	38.7	34.5	31.9	31.2	30.2
Association (%)	61.3	65.5	68.1	68.8	69.8
K_2	2.11	2.09	2.15	2.19	2.25
\bar{K}_2	2.15 ± 0.09				

Table 2.2 Extraction of phenylalanine with HDTMPP in three-phase system

c_{HDTMPP} (V/V%)	10	15	20	25	30
c_{HDTMPP} (mol/L)	0.306	0.459	0.613	0.766	0.919
c_{NaOH} (mol/L)	0.306	0.459	0.613	0.766	0.919
V_{upper} (mL)	7.70	8.10	5.00	3.90	3.10
V_{middle} (mL)	5.30	5.90	9.70	11.60	12.80
V_{lower} (mL)	7.00	6.00	5.30	4.50	4.10
pH	9.10	9.30	9.56	9.60	9.66
f_{A^\pm}	0.50	0.40	0.27	0.26	0.24
$c_{\text{A}^\pm}^{a,f}$ (mmol/L)	1.52	1.52	1.52	1.42	1.36
$c_{\text{A}^\pm}^{\text{mid}}$ (mmol/L)	1.76	1.84	1.23	1.17	1.13
$c_{\text{NaP}}^{\text{mid}}$ (mol/L)	0.58	0.58	0.63	0.66	0.72
$V^{m,s}$ (mL)	3.00	4.00	4.70	5.50	5.90
E (%)	47	55	60	68	72
Solubilization (%)	48.7	55.8	59.8	57.4	55.6
Association (%)	51.3	44.2	40.2	42.6	44.4
K_2	2.06	1.71	1.89	2.01	2.13
\bar{K}_2	1.96 ± 0.18				

Table 2.3 Extraction of phenylalanine with HDEHP in three-phase system

c_{HDEHP} (V/V%)	10	15	20	25	30
c_{HDEHP} (mol/L)	0.278	0.417	0.557	0.696	0.835
c_{NaOH} (mol/L)	0.278	0.417	0.557	0.696	0.835
V_{upper} (mL)	7.16	4.85	3.58	2.29	1.58
V_{middle} (mL)	4.82	7.60	10.13	12.13	13.25
V_{lower} (mL)	8.02	7.55	6.29	5.58	5.17
pH	7.02	7.07	7.12	7.17	7.33
$f_{\text{A}^{\pm}}$	0.99	0.99	0.99	0.99	0.98
c_{A}^{of} (mmol/L)	1.20	1.05	0.94	0.80	0.71
$c_{\text{A}}^{\text{mid}}$ (mmol/L)	2.15	1.59	1.39	1.28	1.23
$V_{\text{NaP}}^{\text{mid}}$ (mol/L)	0.58	0.55	0.55	0.57	0.63
$V^{\text{m},\text{s}}$ (mL)	1.98	2.45	3.71	4.42	4.83
E (%)	51.8	60.4	70.4	77.6	81.5
Solubilization (%)	22.8	21.4	24.5	22.7	21.1
Association (%)	77.2	78.6	75.5	77.3	78.9
K_2	2.41	2.19	2.05	2.19	2.21
\bar{K}_2	2.21 \pm 0.20				

extracted). The effect of the unneutralized free acid on the extraction discussed in above part can be neglected, so there is more similarity between the extractant systems and AOT system. In a word, the obtained extraction constants imply that the association between S^- or P^- with A^{\pm} is little affected by the surfactants when they locate at the interface. The different hydrophilic-hydrophobic properties of these four extractants make a different phase behavior and a different extraction contribution by the solubilization. The biggest contribution by solubilization of higher than 50% has been found in the system of Cyanex272.

The third phase formation at 298 K in AOT extraction system had been observed just at $\text{pH} < 1.5$. In that strong acidic medium, the head group of $-\text{SO}_3\text{Na}$ in AOT molecules was supposed to be changed to $-\text{SO}_3\text{H}$. Both the marked association competition between A^+ and H^+ with $-\text{SO}_3^-$ and the low volume of the middle phase made the extraction efficiency of the amino acid decrease.

Summary

Summarizing the extractions of phenylalanine with AOT, HDEHP, HDTMPP and HDTMPTP, it is found that there are three forces to make the amino acid be extracted into organic phase or middle phase from aqueous solution.

(1) Electrical combination of S^- (or P^-) with A^+ .

(2) Association of the surfactant SNa or NaP with A^{\pm} at the interface.

(3) Solubilization of amino acid in the water pool of reverse micelle or middle phase microemulsion.

The first force in AOT and HDEHP systems is much stronger than that in HDTMPP and HDTMPTP systems. The high extraction from the lower pH medium in the former systems is caused by the electrical combination of anionic S^- or P^- with A^+ .

Concerning about the second force, association between the surfactant molecule SNa or NaP with A^{\pm} at the interface, the association constants are almost the same for the four systems, $K_{2,\text{NaDEHP}} = 2.21 \pm 0.20$, $K_{2,\text{NaDTMPP}} = 1.96 \pm 0.18$, $K_{2,\text{NaDTMPTP}} = 2.15 \pm 0.09$ for Eq. (10) and $K'_{1,\text{AOT}} = 2.29 \pm 0.09$ for Eq. (4), respectively. The results indicate that the association is little affected by molecule structure of the surfactants when they locate at the interface.

Finally, the contribution to the extraction by the solubilized water in the middle phase could be higher than 50%, much higher than that in the two-phase reverse micelle system.

Acknowledgements

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References

- 1 Leadidis, E. B.; Hatton, T. A. *J. Phys. Chem.* **1990**, *94*, 6400.
- 2 Leadidis, E. B.; Hatton, T. A. *J. Phys. Chem.* **1990**, *94*, 6411.
- 3 Leadidis, E. B.; Bommarius, A. S.; Hatton, T. A. *J. Phys. Chem.* **1991**, *95*, 5943.
- 4 Leadidis, E. B.; Hatton, T. A. *J. Phys. Chem.* **1991**, *95*, 5957.
- 5 Adachi, M.; Harada, M.; Shioi, A.; Sato, Y. *J. Phys. Chem.* **1991**, *95*, 7925.
- 6 Rabie, H. R.; Vera, J. H. *Fluid Phase Equilib.* **1997**, *135*, 269.
- 7 Fu, X.; Li, J.-L.; Ma, Y.; Zhang, L.; Wang, D.-B.; Hu, Z.-S. *Colloids Surf. A* **2001**, *179*, 1.
- 8 Liao, S.-S.; Lin, Z.; Jiang, G.-H.; Zhang, D. *Solvent Extr. Ion Exch.* **1993**, *11*, 849.

- 9 Shi, Q.; Sun, Y.; Liu, L.; Bai, S. *Sep. Sci. Technol.* **1997**, *32*, 2051.
- 10 Cao, H.-J.; Wang, D.-B.; Liu, P.-Y.; Wu, Z.-S.; Yan, Z. *Chem. J. Chin. Univ.* **1996**, *17*, 386 (in Chinese).
- 11 Liu, Y.-S.; Dai, Y.-Y.; Wang, J.-D. *J. Chem. Ind. Eng.* **1999**, *50*, 289 (in Chinese).
- 12 Fu, X.; Hu, Z.-S.; Liu, Y.-D.; Golding, J. A. *Solvent Extr. Ion Exch.* **1990**, *8*(4&5), 573.
- 13 Hu, Z.-S.; Xin, H.-Z.; Pan, Y.; Liu, Z.-X.; Fu, X. *Chin. J. Appl. Chem.* **1995**, *12*(5), 10.
- 14 Hu, Z.-S.; Pan, Y.; Ma, W.-W.; Fu, X. *Solvent Extr. Ion Exch.* **1995**, *13*, 965.
- 15 Fu, X.; Xiong, Y.-H.; Xue, S.-Y.; Zhang, S.-N.; Hu, Z.-S. *Solvent Extr. Ion Exch.* **2002**, *20*(3), 331.
- 16 Greonstain, T. P.; Winitz, M. *Chemistry of the Amino Acids*, Wiley, New York, **1961**.
- 17 Geng, P.-W.; Wang, X.-Y. *J. Beijing Univ.* **1982**, (5), 59.
- 18 Fu, X.; Xin, H.-Z.; Hu, Z.-S.; Liu, Z.-X. *Acta Chim. Sinica* **1993**, *51*, 1151 (in Chinese).
- 19 Fu, X.; Xiong, Y.-H.; Wei, Q.-L.; Xue, S.-Y.; Zhang, S.-N.; Hu, Z.-S. *Study on the Thiophosphinic Extractants II, Thermodynamic Functions and Structure Parameters of the w/o Microemulsion of the Saponified Acid Systems*, accepted by *Colloids Surf. A*.
- 20 Fu, X.; Pan, Y.; Xin, H.-Z.; Hu, Z.-S.; Yu, H. *Acta Chim. Sinica* **1995**, *53*, 178 (in Chinese).

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