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Reactive Extraction of *o*-Aminophenol with Tri-*n*-butyl Phosphate in Different Solvents

Jie Hu Cui,*[†] Chun Guang Li,[†] and Xiu Hong Du[‡]

[†]Zhengzhou Institute of Aeronautical Industry Management, Zhengzhou, 450015, People's Republic of China

[‡]Medical College for Henan Staff and Workers, Zhengzhou, 451191, People's Republic of China

ABSTRACT: Tri-*n*-butyl phosphate (TBP) is used as the extraction agent for the extraction of *o*-aminophenol (OAP) in active solvents and inactive solvents. The effects of aqueous solution pH, solvents, concentration of TBP, and the initial OAP concentration on distribution coefficient (D) are investigated. Results show that the neutral OAP molecule is hydrogen-bonded to TBP effectively into the organic phase, and D was maximum when the equilibrium pH was between pK_{a1} and pK_{a2}. The extraction efficiency is TBP−1-octanol > TBP−kerosene > TBP−carbon tetrachloride > TBP−chloroform, when the concentration of TBP is between (0.3632 and 0.7264) mol·L^{-1}, while the result is TBP−kerosene > TBP−1-octanol > TBP−carbon-tetrachloride > TBP−chloroform when the concentration increases [(1.0896 to 1.8159) mol·dm^{-3}]. Fourier transform infrared spectroscopic analysis shows that the extractive behavior is controlled by hydrogen bonding. An expression for equilibrium D is proposed, and the parameters of the apparent extraction equilibrium constants (K) and the complex ratio (n) (TBP vs OAP) were calculated by fitting the experimental data. It was found that the K and n are 5.97, 5.37, 5.47, and 2.99 and 1.56, 1.51, 1.47, and 1.76 in TBP/kerosene, 1-octanol, carbon tetrachloride, and chloroform, respectively.

INTRODUCTION

Reactive extraction has a high capacity and high selectivity to separate polar organic solutes from dilute solutions. It has received increasing attention because of its simple methodology and low cost. Many organic acid and hydroxybenzene compounds have been studied, for example, formic acid,[1,2] acrylic acid,[3] L-malic acid,[4] propionic acid,[5] phenol,[6] and so forth. For more research on the range of use of a reactive extraction, most researchers explore the extraction of compounds that have two different functional groups, for example, *p*-aminobenzoic acid,[7] aminobenzoic acid,[8] L-tryptophane,[9] L-isoleucine,[10] and so forth. Li and co-workers[11,12] studied the extraction of *p*-aminophenol and established a mathematical model that describes the equilibrium behavior based on the physical extraction and reactive extraction of the solvent. The author also performed the extraction mechanism of *o*-aminophenol,[13] iso-nicotinic acid[14] with di(2-ethylhexyl)-phosphoric acid, trialkylamine as extractant. The results showed that the extraction reaction occurred via both ion-association and ion-exchange reactions, and the two reactions produced the same extraction complex.

o-Aminophenol (OAP) is an important chemical material, commonly used in the dye, pharmaceutical, and biological industries as an intermediate in the production of dyes and pharmaceuticals. It is a key component in industrial effluent from printing and dyeing mills, which is not biodegradable and has serious toxic and contaminative effects. There is no known feasible processing method for removing OAP from such effluents. Thus, it is necessary to adopt a reactive extraction method to recover the organic species from the effluent to reduce pollution.

Tri-*n*-butyl phosphate (TBP) is an organophosphorous extractant,[15] and very little work can be found on the recovery/removal of OAP. In view of this, attempts were made to study the extraction of OAP using TBP in extraction systems. 1-Octanol, chloroform, carbon tetrachloride, and kerosene were also investigated for their ability to affect the extraction power of the extractants over a wide pH range. IR spectroscopic analysis of the organic phase loaded with OAP was investigated to deduce the extraction mechanism.

EXPERIMENTAL SECTION

Materials. OAP from Fluka was analytical reagent grade with a purity of > 0.99 mass fraction. TBP from a Beijing chemical reagent plant was chemical reagent grade with a purity > 0.99 mass fraction. The solvents (1-octanol, chloroform, carbon tetrachloride) were from Luoyang and Tianjin chemical reagent plants and were analytical reagent grade. All of the extractants and solvents were washed with distilled water to remove soluble impurities.

Kerosene was obtained from a local chemical plant. Fractional distillation was used for purification, and the kerosene was collected between (180 and 220) °C. The distilled kerosene was washed with concentrated sulfuric acid (98 %) ($V_{H_2SO_4}$:V_{kerosene} = 1:5) twice and distilled water several times until the aqueous layer became neutral. The density of the sulfonated kerosene was about 0.78 g·cm^{-3}.

Experiments. *Extraction Section.* For the solution preparation, 0.1250 g of OAP was dissolved into a 0.5 L H_2SO_4 solution with a concentration of 2.29·10^{-3} mol·dm^{-3}. Other OAP concentrations were used by a similar method. TBP was used at concentrations of (0.3632, 0.7264, 1.0896, 1.8159, and

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3.6392) $mol \cdot dm^{-3}$ as the basis of solvents in the reactive extraction. Kerosene and carbon tetrachloride can be classified as inactive, while chloroform and 1-octanol be classified as active solvents.

OAP was extracted as follows: all extraction experiments were conducted with 100 mL flasks at 25 °C. Unless otherwise noted, 20 mL of the mixture extraction solvents and 20 mL of OAP solution were added to each flask. pH values of mixture were adjusted from 3 to 10 by the diluted solution of NaOH; then the flask containing the mixture was shaken for about 1 h in a shaker bath with a vibrating rate of 200 rpm.

For clear separation of the two phases after each extraction, the mixed phases were centrifuged at 4000 rpm for 10 min or were left to equilibrate for 5 h or so. The organic phase was removed, and an aqueous phase sample was taken for pH and solute concentration analysis. After the pH value of the aqueous phase was measured with a pH meter (Hanna pH HI9321 model with a deviation of 0.01, calibrated with pH 4.01/7.01/9.18 standard buffer solution, Italy), the pH of the aqueous phase was adjusted to 1 to 1.5 using concentrated H_2SO_4, and the aqueous samples were analyzed for the OAP concentration with a UV-250 spectrophotometer (Shimadzu, Japan) at 271 nm. The OAP content in the organic phase was determined with a mass balance, and consistency was found within 2 %.

IR Spectra. The organic phase solutions were injected to a sample cell with a thickness of 0.05 mm between two CaF_2 plates. IR spectra were taken on a AVATAR360 FTIR spectrometer (Nicolet, America).

Equilibrium Modeling. The reactive extraction equilibrium for polar dilute solution of organic solutes could be described by the mass action law in which the equilibrium behavior can be modeled by postulating the formation of various stoichiometric complexes of acid and amine.[16] A reactive equilibrium description of the system can be written as by a set of reactions of one OAP molecule (HA represents the nondissociated part of the acid present in the aqueous phase) and n TBP molecules to form (1, n) complexes and organic phase species are marked with an overline:

$$n(\overline{\mathrm{TBP}}) + (\mathrm{HA}) \overset{K}{\leftrightarrow} [\overline{(\mathrm{HA})\cdot(\mathrm{TBP})_n}] \qquad (1)$$

where n is the solvation number of TBP. As the OAP-TBP complex is formed, it is rapidly extracted into the organic phase, the equilibrium complexation constant by applying the law of mass action is defined as:

$$K = [\overline{(\mathrm{HA})\cdot(\mathrm{TBP})_n}]/[\mathrm{HA}]\cdot[\overline{(\mathrm{TBP})}]^n \qquad (2)$$

Equilibrium of physical extraction of the solvent:

$$\mathrm{HA} \overset{m}{\leftrightarrow} \overline{\mathrm{HA}}$$

$$m = \frac{[\overline{\mathrm{HA}}]}{[\mathrm{HA}]} \qquad (3)$$

where the overbar denotes species in the organic phase (ignoring dissolution of TBP in the water). If the initial concentration of free extractant can be represented as B_0, which is far higher than that of OAP, and we may assume that the concentration of TBP does not change, the distribution coefficient, D, can be written as:

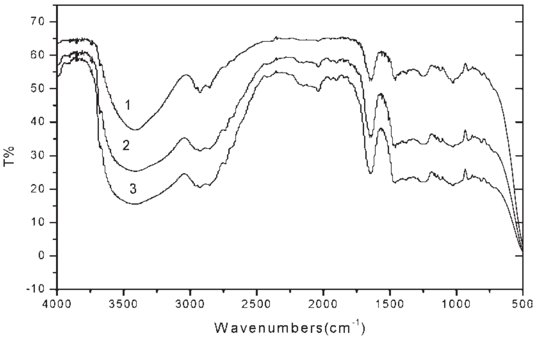

Figure 1. IR spectra for solutions containing TBP in 1-octanol (initial/equilibrium pH 1 to 3.66/3.30, 2 to 7.14/7.00, 3 to 9.06/9.34).

$$\begin{aligned} D &= \frac{[\overline{\mathrm{HA}\cdot\mathrm{TBP}}] + [\overline{\mathrm{HA}}]}{[\mathrm{HA}] + [\mathrm{A}^-] + [\mathrm{H_2A}^+]} \\ &= \frac{K\cdot[\mathrm{HA}]\cdot[\overline{(\mathrm{TBP})}]^n + m\cdot[\mathrm{HA}]}{[\mathrm{HA}]\cdot(1 + 10^{\mathrm{p}K_{a1} - \mathrm{pH}} + 10^{\mathrm{pH} - \mathrm{p}K_{a2}})} \\ &= \frac{K\cdot {B_0}^n}{1 + 10^{\mathrm{p}K_{a1} - \mathrm{pH}} + 10^{\mathrm{pH} - \mathrm{p}K_{a2}}} \\ &\quad + \frac{m}{1 + 10^{\mathrm{p}K_{a1} - \mathrm{pH}} + 10^{\mathrm{pH} - \mathrm{p}K_{a2}}} \end{aligned} \qquad (4)$$

where K_{a1} and K_{a2} are the primary and the second dissociation constant of OAP in water, respectively.

For n-octanol, kerosene, chloroform, and carbon tetrachloride, the m_{max} are all > 0.30, so they cannot be neglected.

$$\log[D\cdot(1 + 10^{\mathrm{p}K_{a1} - \mathrm{pH}} + 10^{\mathrm{pH} - \mathrm{p}K_{a2}}) - m] = \log K + n\cdot\log B_0 \qquad (5)$$

The plot of $\log[D\cdot(1 + 10^{\mathrm{p}K_{a1}-\mathrm{pH}} + 10^{\mathrm{pH}-\mathrm{p}K_{a2}}) - m]$ against $\log B_0$ would provide a straight line with the intercept of $\log K$. From above equation it can be seen that the distribution coefficient of OAP depends on the free extractant concentration in the organic phase.

■ RESULTS AND DISCUSSION

OAP has one Lewis acid group (−OH) and one Lewis base group ($-NH_2$). Two dissociation equilibria exist in aqueous solution as follows, where $\mathrm{p}K_{a1}$ and $\mathrm{p}K_{a2}$ are 4.74 and 9.66, respectively.[17]

$$\mathrm{NH_3}^+\mathrm{ArOH} \overset{k_{a1}}{\leftrightarrow} \mathrm{NH_3}^+\mathrm{ArO}^- + \mathrm{H}^+ \qquad (6)$$

$$\mathrm{NH_2ArOH} \overset{k_{a2}}{\leftrightarrow} \mathrm{NH_2ArO}^- + \mathrm{H}^+ \qquad (7)$$

The cation form of OAP exists at pH < $\mathrm{p}K_{a1}$, while the anionic form appears at pH > $\mathrm{p}K_{a2}$, and neutral OAP dominates at intermediate pH. Therefore, the extraction equilibrium behavior of species with amphoteric functional groups are more complicated than those of nonamphoteric compounds. Therefore, it is essential to understand the effect of pH on the extraction.

Infrared Spectrogram of Reaction Extraction. As shown in Figures 1 and 2, the pH values have little effect on the structure of the complex formed at different pH values. Compared with Figures 1 and 3, it is obvious that the peak at 1247.92 cm^{-1} assigned to the (P=O) stretching vibration of TBP has been

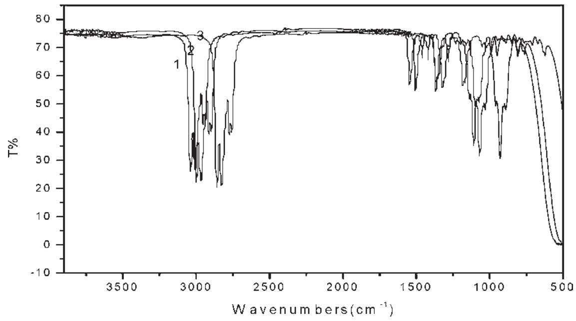

Figure 2. IR spectra for solutions containing TBP in normal heptane (initial/equilibrium pH 1 to 3.52/3.27, 2 to 7.77/7.53, 3 to 8.94/9.32).

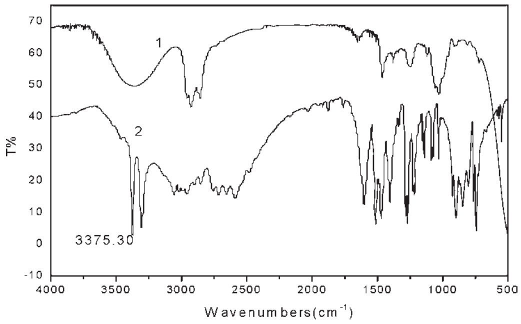

Figure 3. IR spectra of 1, blank organic phase and 2, OAP.

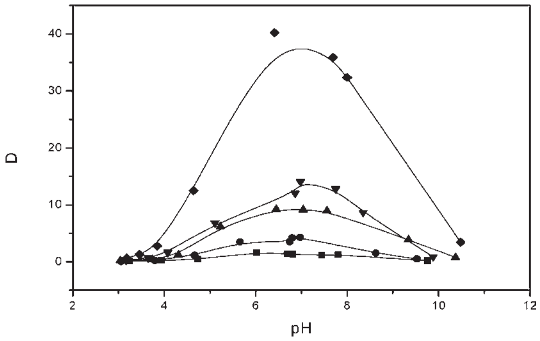

Figure 4. Extraction behavior of OAP with TBP + kerosene, TBP concentration (mol·dm^{-3}): ■, 0.3632; ●, 0.7264; ▲, 1.0896; ▼, 1.8159; ◆, 3.6392.

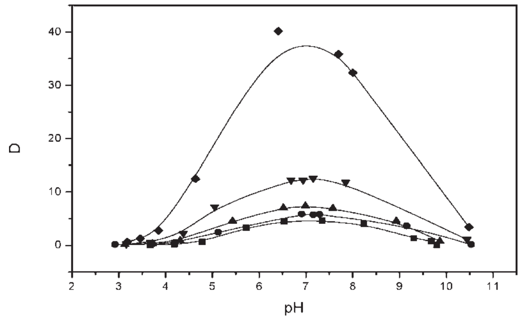

Figure 5. Extraction behavior of OAP with TBP + 1-octanol, TBP concentration (mol·dm^{-3}): ■, 0.3632; ●, 0.7264; ▲, 1.0896; ▼, 1.8159; ◆, 3.6392.

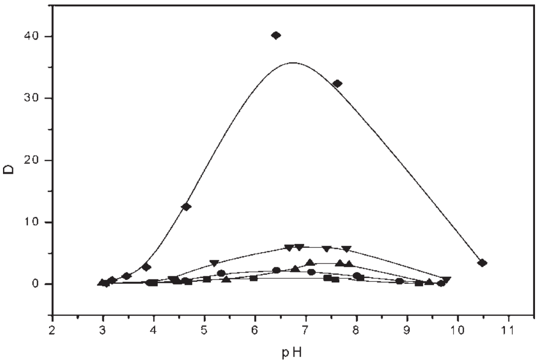

Figure 6. Extraction behavior of OAP with TBP + chloroform, TBP concentration (mol·dm^{-3}): ■, 0.3632; ●, 0.7264; ▲, 1.0896; ▼, 1.8159; ◆, 3.6392.

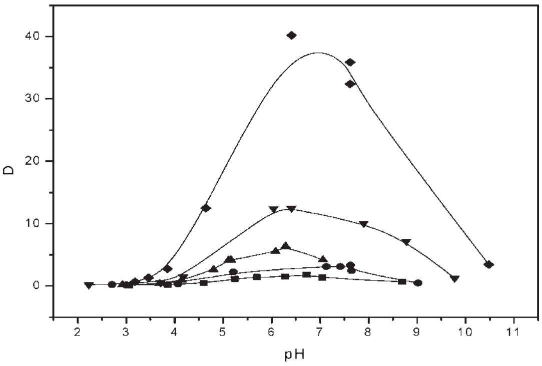

Figure 7. Extraction behavior of OAP with TBP + carbon tetrachloride, TBP concentration (mol·dm^{-3}): ■, 0.3632; ●, 0.7264; ▲, 1.0896; ▼, 1.8159; ◆, 3.6392.

replaced by the peak at 1239.59 cm^{-1}. It is also obvious that the peak at 3375.30 cm^{-1} assigned to the −OH stretching vibration was replaced by the peak at 3421.11 cm^{-1}.

The IR spectrogram showing normal heptane loaded with OAP is in sharp contrast (Figures 2 and 3). As can be seen, the peak at 3375.30 cm^{-1} assigned to −OH stretching vibration disappeared. The peak at 1247.92 cm^{-1} assigned to the (P=O) stretching vibration of TBP has been replaced by the peak at 1236.21 cm^{-1}.

These analyses show that the extraction reaction behavior is controlled by hydrogen bonding without reference to active or inactive solvent and the extraction complex is the same structure ($\overline{(HA)\cdot(TBP)_n}$), so the extraction process react mainly between the neutral molecule of OAP and TBP. The reactive extraction of OAP with TBP can be described by the reaction 1.

Effect of pH. TBP is a Lewis alkali and can receive a proton. As such, it can react with neutral forms of OAP to produce the complex that is extracted into the organic phase. Because the molar fractions of neutral of OAP are a function of pH, *D* greatly depends on the equilibrium pH. As is indicated by the data given in Figures 4 to 7 and Tables 1 to 4, the value of *D* increases with a sharp increase and then decreases in equilibrium pH at the same concentration of TBP, and there is a peak value when the equilibrium pH value is around 6 to 8, which is in accordance with the pH where the neutral OAP dominated

Table 1. Equilibrium Data of OAP between Water and TBP in Kerosene

init. conc. of extractant/mol·dm^{-3}		total equil. conc. of OAP/mg·dm^{-3}		
TBP	init./equil. pH in aq phase	in aq phase	in org phase	distribution coefficient
0.3632	3.21/3.25	216.3	33.7	0.1559
0.3632	4.03/3.94	205.1	44.9	0.2189
0.3632	5.05/4.73	173.5	76.6	0.4406
0.3632	6.16/6.02	95.8	154.2	1.6095
0.3632	7.15/6.69	104.3	145.7	1.3963
0.3632	7.53/6.82	106.2	143.8	1.3541
0.3632	8.01/7.44	115.9	134.1	1.1561
0.3632	8.92/7.81	112.3	137.7	1.2255
0.3632	10.27/9.76	209.7	40.3	0.1922
0.7264	3.07/3.06	229.9	20.1	0.0874
0.7264	4.04/3.80	204.2	45.8	0.2243
0.7264	5.17/4.67	117.1	132.9	1.1347
0.7264	6.04/5.66	55.7	194.3	3.4872
0.7264	7.48/6.75	48.1	201.9	4.1979
0.7264	7.93/6.97	47.4	202.6	4.2758
0.7264	9.23/8.63	98.8	151.2	1.5293
0.7264	10.07/9.53	168.1	81.9	0.4871
1.0896	3.01/3.04	209.7	40.3	0.1922
1.0896	4.02/3.74	182.7	67.3	0.3683
1.0896	5.14/4.31	111.9	138.1	1.2332
1.0896	6.01/5.23	34.8	215.2	6.1846
1.0896	7.09/6.45	24.4	225.6	9.2447
1.0896	7.32/7.04	24.7	225.3	9.1374
1.0896	8.23/7.56	25.1	224.9	8.9550
1.0896	9.05/9.34	51.6	198.4	3.8466
1.0896	10.17/10.37	141.6	108.4	0.7650
1.8159	3.18/3.17	204.2	45.8	0.2243
1.8159	4.14/3.65	149.6	100.4	0.6713
1.8159	5.09/4.08	94.5	155.5	1.6451
1.8159	6.08/5.11	32.1	217.9	6.7917
1.8159	7.08/6.86	19.2	230.8	11.994
1.8159	7.32/6.98	16.6	233.4	14.068
1.8159	8.12/7.75	18.1	231.2	12.7811
1.8159	9.02/8.35	25.9	224.1	8.6571
1.8159	10.08/9.88	132.7	117.3	0.8844
3.6392	3.31/3.18	151.9	98.1	0.6457
3.6392	4.24/3.46	108.9	141.1	1.2954
3.6392	5.05/3.85	66.4	183.6	2.7633
3.6392	6.25/4.64	18.5	231.5	12.4930
3.6392	7.08/6.41	6.1	243.9	40.1968
3.6392	8.05/7.62	6.8	243.2	35.8809
3.6392	9.09/8.0	7.5	242.5	32.3836
3.6392	10.17/10.48	56.4	193.6	3.43585

Table 2. Equilibrium Data of OAP between Water and TBP in 1-Octanol

init. conc. of extractant/mol·dm^{-3}		total equil. conc. of OAP/mg·dm^{-3}		
TBP	init./equil. pH in aq phase	in aq phase	in org phase	distribution coefficient
0.3632	3.12/3.67	224.1	25.9	0.1156
0.3632	4.08/4.19	207.5	42.5	0.20488
0.3632	5.14/4.78	148.6	101.4	0.6822
0.3632	6.22/5.72	58.4	191.6	3.2790
0.3632	6.9/6.53	45.2	204.8	4.5321
0.3632	7.88/7.35	44.5	205.5	4.6204
0.3632	8.87/8.23	49.8	200.2	4.0162
0.3632	9.50/9.3	106.9	143.1	1.3370
0.3632	9.80/9.68	138.2	111.8	0.8096
0.3632	10.65/9.79	226.9	3.1	0.1017
0.7264	3.0/2.92	214.5	35.5	0.1657
0.7264	3.94/3.72	204.2	45.8	0.2243
0.7264	4.95/4.19	171.0	79.0	0.4618
0.7264	5.95/5.12	72.4	177.6	2.4514
0.7264	6.87/6.91	36.3	213.7	5.8906
0.7264	7.26/7.15	37.0	213.0	5.7583
0.7264	7.97/7.29	36.5	213.55	5.8539
0.7264	9.27/9.15	53.5	196.5	3.6769
0.7264	10.6/10.53	218.5	31.5	0.1444
1.0896	3.17/3.13	209.7	40.3	0.1923
1.0896	4.01/3.72	184.9	65.1	0.3521
1.0896	5.05/4.31	127.8	122.2	0.9568
1.0896	6.12/5.43	44.9	205.1	4.5639
1.0896	6.89/6.52	31.1	218.9	7.0509
1.0896	7.34/6.99	29.8	220.2	7.3820
1.0896	8.02/7.57	31.6	218.4	6.9192
1.0896	9.15/8.93	44.8	205.2	4.5799
1.0896	10.15/9.86	141.1	108.9	0.7723
1.8159	3.1/3.16	205.3	44.7	0.2178
1.8159	4.47/3.68	157.3	92.7	0.5890
1.8159	5.48/4.38	77.2	172.8	2.2379
1.8159	6.33/5.05	30.3	219.7	7.2394
1.8159	7.22/6.94	18.9	231.1	12.2167
1.8159	7.89/7.15	18.5	231.5	12.5402
1.8159	8.12/7.85	19.5	230.5	11.8228
1.8159	10.08/9.88	118.5	131.5	1.1103
1.8159	10.19/10.44	132.7	117.3	0.8844
3.6392	3.31/3.18	151.9	98.1	0.6457
3.6392	4.24/3.46	108.9	141.1	1.2954
3.6392	5.05/3.85	66.4	183.6	2.7633
3.6392	6.25/4.64	18.5	231.5	12.4930
3.6392	7.08/6.41	6.1	243.9	40.1968
3.6392	8.05/7.62	6.8	243.2	35.8809
3.6392	9.09/8.0	7.5	242.5	32.3836
3.6392	10.17/10.48	56.4	193.6	3.43585

(pK_{a1} and pK_{a2}). Such a result shows that the reactive process takes place between TBP and OAP, which is further proven through IR spectroscopy.

Generally speaking, TBP reacts with OAP through hydrogen bonding. *D* is lower when pH is lower (1 to 4); the key is that OAP will be all protonated, which will hamper OAP from combining with TBP. *D* increases when pH is higher (4 to 8), because there is hydrogen-bonding between TBP and OAP.

Table 3. Equilibrium Data of OAP between Water and TBP in Carbon Tetrachloride

init. conc. of extractant/mol·dm^{-3}		total equil. conc. of OAP/mg·dm^{-3}		
TBP	init./equil. pH in aq phase	in aq phase	in org phase	distribution coefficient
0.3632	3.02/3.07	225.5	24.5	0.1086
0.3632	3.98/3.86	209.6	40.4	0.1926
0.3632	5.03/4.6	172.2	77.8	0.4520
0.3632	5.98/5.24	119.5	130.5	1.0921
0.3632	7.01/5.7	101.9	148.1	1.4540
0.3632	7.39/6.28	99.9	150.1	1.5032
0.3632	8.05/6.72	89.6	160.4	1.7899
0.3632	9.0/7.05	108.7	141.2	1.2996
0.3632	9.99/8.69	151.2	98.8	0.6535
0.7264	3.01/3.0	222.5	27.5	0.1234
0.7264	4.07/2.71	204.8	45.2	0.2204
0.7264	5.06/4.07	188.4	61.6	0.3266
0.7264	6.04/5.21	77.2	172.8	2.2406
0.7264	6.99/7.13	60.8	189.2	3.1109
0.7264	7.36/7.42	60.7	189.3	3.1153
0.7264	7.95/7.63	57.7	192.3	3.3365
0.7264	8.9/7.65	72.3	177.7	2.4576
0.7264	9.91/9.02	170.4	79.6	0.4668
1.0896	2.94/2.92	212.9	37.1	0.1742
1.0896	4.05/3.69	183.2	66.8	0.3645
1.0896	5.02/4.15	131.4	118.6	0.9029
1.0896	6.03/4.8	68.9	181.1	2.6259
1.0896	7/5.11	48.9	201.1	4.1156
1.0896	7.37/5.16	48.5	201.5	4.1496
1.0896	7.97/6.08	38.4	211.6	5.5084
1.0896	9.01/6.29	33.9	216.1	6.37619
1.0896	10.01/7.06	48.2	201.8	4.1841
1.8159	2.98/2.23	208.2	41.8	0.2008
1.8159	4.04/3.71	158.1	91.9	0.5813
1.8159	4.98/4.18	100.0	150.0	1.5000
1.8159	7.01/6.04	18.6	231.4	12.4462
1.8159	7.41/6.41	18.5	231.5	12.4930
1.8159	8.01/7.9	22.6	227.4	10.0643
1.8159	8.98/8.78	30.5	219.5	7.2044
1.8159	9.97/9.78	111.6	138.4	1.2410
1.8159	10.08/9.88	132.7	117.3	0.8844
3.6392	3.31/3.18	151.9	98.1	0.6457
3.6392	4.24/3.46	108.9	141.1	1.2954
3.6392	5.05/3.85	66.4	183.6	2.7633
3.6392	6.25/4.64	18.5	231.5	12.4930
3.6392	7.08/6.41	6.1	243.9	40.1968
3.6392	8.05/7.62	6.8	243.2	35.8809
3.6392	9.09/8.0	7.5	242.5	32.3836
3.6392	10.17/10.48	56.4	193.6	3.43585

However, with the further increase of pH, the anionic form OAP appears which reacts little with TBP, so *D* decreases with the increase of the solution pH. As a result, the maximum *D* occurs with the pH change.

Table 4. Equilibrium Data of OAP between Water and TBP in Chloroform

init. conc. of extractant/mol·dm^{-3}		total equil. conc. of OAP/mg·dm^{-3}		
TBP	in org phase	init./equil. pH in aq phase	in aq phase	distribution coefficient
0.3632	3.04/3.06	220.7	29.3	0.1329
0.3632	4.04/4.0	216.8	33.2	0.1532
0.3632	4.99/4.69	186.7	63.3	0.3390
0.3632	5.97/5.05	141.3	108.7	0.7690
0.3632	6.96/5.97	128.0	122.0	0.9528
0.3632	7.38/7.43	125.1	124.9	0.9992
0.3632	7.96/8.08	125.2	124.8	0.9961
0.3632	8.95/7.58	144.9	105.1	0.7249
0.3632	9.95/9.23	230.0	20.0	0.0868
0.7264	3.0/3.04	214.4	35.6	0.1660
0.7264	3.98/3.92	205.0	45.0	0.2196
0.7264	5.02/4.62	160.5	89.5	0.5577
0.7264	5.99/5.33	91.5	158.5	1.7328
0.7264	7.0/6.42	77.4	172.6	2.2297
0.7264	7.4/7.11	84.1	165.9	1.9742
0.7264	7.96/8.01	105.2	144.8	1.3757
0.7264	8.98/8.85	167.9	82.1	0.4894
0.7264	10.0/9.67	228.4	21.6	0.0945
1.0896	2.98/2.98	217.4	32.6	0.1497
1.0896	5.01/4.47	174.0	76.0	0.4364
1.0896	6.03/5.43	152.2	97.8	0.6422
1.0896	6.96/6.79	73.9	176.1	2.3821
1.0896	7.37/7.08	56.8	193.2	3.4006
1.0896	8.03/7.67	58.3	191.7	3.2885
1.0896	8.95/7.85	61.0	189.0	3.0979
1.0896	9.94/9.43	202.9	47.1	0.2317
1.8159	3.05/3.07	210.5	39.5	0.1878
1.8159	4.05/3.99	177.3	72.4	0.4097
1.8159	5.05/4.37	130.9	119.1	0.9085
1.8159	5.98/5.19	54.9	195.1	3.5505
1.8159	6.99/6.67	35.9	214.1	5.9649
1.8159	7.45/6.87	35.4	214.6	6.0537
1.8159	8.01/7.41	36.4	213.6	5.8661
1.8159	8.92/7.8	36.7	213.3	5.8058
1.8159	9.87/9.77	134.8	115.2	0.8546
3.6392	3.31/3.18	151.9	98.1	0.6457
3.6392	4.24/3.46	108.9	141.1	1.2954
3.6392	5.05/3.85	66.4	183.6	2.7633
3.6392	6.25/4.64	18.5	231.5	12.4930
3.6392	7.08/6.41	6.1	243.9	40.1968
3.6392	8.05/7.62	6.8	243.2	35.8809
3.6392	9.09/8.0	7.5	242.5	32.3836
3.6392	10.17/10.48	56.4	193.6	3.43585

Effect of Extractant Concentration. TBP concentration has a strong effect on the equilibrium distribution of OAP as shown in Figures 4 to 7. *D* increases as the TBP concentration increases; OAP is extracted into the organic phase more effectively at higher TBP concentrations, which likely results from the extraction equilibrium moving toward the direction of forming an extraction complex (see Formula 1). As a result, the TBP concentration

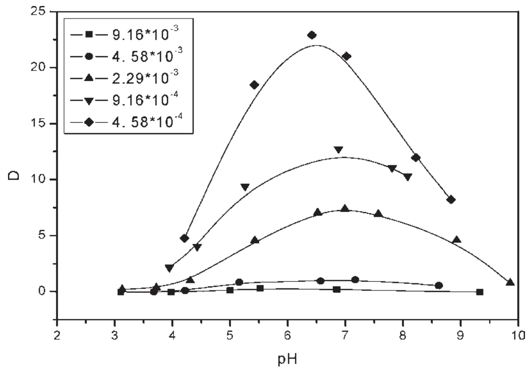

Figure 8. Effect of different OAP concentrations ($mol \cdot dm^{-3}$) on D with 1.0896 $mol \cdot dm^{-3}$ (the concentration of TBP in the 1-octanol phase).

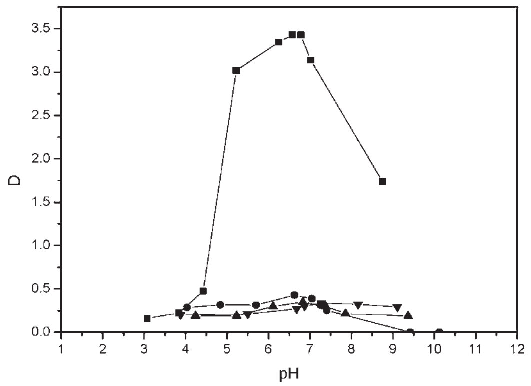

Figure 9. Effect of four solvents on D (OAP concentration is $2.29 \cdot 10^{-3}$ $mol \cdot dm^{-3}$). ■, *n*-octanol; ●, chloroform; ▲, carbon tetrachloride; ▼, kerosene.

must be considered in the extraction process when using extraction technology.

The D value increased more obviously when the TBP concentration increased from (1.8159 to 3.6392) $mol \cdot L^{-1}$ than from (0.3632 to 1.8159) $mol \cdot L^{-1}$ in the four extraction systems. Because the combined strength of TBP helps the extraction complex dissolving easily in extraction system, the dissolving capacity of the extraction complex increases with an increase of TBP concentration.

Effect of the Initial OAP Concentration. When the initial OAP concentrations are $4.58 \cdot 10^{-4}$, $9.16 \cdot 10^{-4}$, $2.29 \cdot 10^{-3}$, $4.58 \cdot 10^{-3}$, and $9.16 \cdot 10^{-3}$ $mol \cdot dm^{-3}$, TBP dissolves in 1-octanol (the concentration of TBP is 1.0896 $mol \cdot dm^{-3}$), and the experiment equilibria are performed. The initial OAP concentration is the key factor in the extraction process as shown in Figure 8: D increases with a decrease of the given initial OAP concentration range ($4.58 \cdot 10^{-4} > 9.16 \cdot 10^{-4} > 2.29 \cdot 10^{-3} > 4.58 \cdot 10^{-3} > 9.16 \cdot 10^{-3}$ $mol \cdot dm^{-3}$), the key is that the extractive capability of reaction reaches saturation with the increase of initial OAP concentration, so D occurs at the minimum value when the initial OAP concentration is maximum. As a result, the initial OAP concentration must be considered in the extraction process before using extraction technology.

Physical Extraction by Solvents. In this work, *n*-octanol, chloroform, carbon tetrachloride, and kerosene were selected as solvents. Because the solvents can be classified into active (*n*-octanol, chloroform) and inactive (carbon tetrachloride and kerosene) solvents, the effect of pure solvent on D needs to be studied. As can be seen from Figure 9 and Table 5, the D value increased in the order of *n*-octanol > chloroform > carbon tetrachloride ≈ kerosene. Compared with other solvents, the polarity of *n*-octanol (OAP is compound of strong polarity) is maximum, and *n*-octanol can react with OAP through hydrogen bonding to enable greater solvation of OAP, so the extraction capacity of *n*-octanol on OAP is higher. The polarity of chloroform is between carbon tetrachloride, kerosene, and *n*-octanol, so the extraction effect of chloroform on OAP is middle among these solvent.

Table 5. Equilibrium Data (D_{max}) of OAP in 1-Octanol, Chloroform, Carbon Tetrachloride, and Kerosene

diluent	D_{max}	pH
1-octanol	3.43	6.78
chloroform	0.428	6.63
kerosene	0.338	7.27
carbon tetrachloride	0.349	6.83

Inert solvents, carbon tetrachloride and kerosene, give very low loadings of OAP, because, being nonpolar, they provide for very little solvation of the polar compound.

Effect of Solvent in the Extraction System. It is known that D depends on the solvents used and the extractant concentration in organic phase. The effect of solvents on extraction equilibrium was studied in the organic phase with *n*-octanol, chloroform, carbon tetrachloride, and kerosene as solvents. As can be seen from Figures 4 to 7, the D value increased in the order of *n*-octanol > kerosene > carbon tetrachloride > chloroform when the TBP concentration is (0.3632 to 0.7264) $mol \cdot dm^{-3}$; however, with the continued increase of TBP concentration [(0.7264 to 1.8159) $mol \cdot dm^{-3}$], the order of the extraction efficiency changed as follows: kerosene > *n*-octanol > carbon tetrachloride > chloroform. Such results are not similar to the efficiency of pure solvent. From the above Figures 4 to 7, it is obvious that the extraction capacity with chloroform as solvent is the minimum without reference to the change of TBP concentration.

Usually, the effect of solvent on D is realized chiefly through physics extraction and dissolution of the reaction complex. There are probably two reasons for above results:

First, the physical extraction only by 1-octanol offers a high D (compared to kerosene, see Figure 9), so its effect cannot be neglected. In addition, the presence of an active solvent will help dissolve the extraction complex. However, with the TBP concentration getting higher, the hydrogen bonding between 1-octanol and TBP get stronger, which hampers the extraction of TBP on OAP. As a result, the D value with 1-octanol as solvent is relatively large at the lower concentration of TBP.

Second, the polarity of the extraction complex is also a key factor on the D value. Because of hydrogen bonding (its polarity is weak) formed between TBP and OAP, the presence of inactive solvent will help dissolve the extraction complex. So, the D value with kerosene as solvent is relatively large at the higher concentration of TBP.

As for the minimum extraction capacity with chloroform as diluent, there is a possibile reason: compared with other solvents, chloroform is an acidic proton-donated solvent, so it not only can react with OAP, but also can react with TBP through hydrogen bonding (which can hamper the extractive capacity of TBP), besides its low physical extractive capacity (see Figure 9). As a

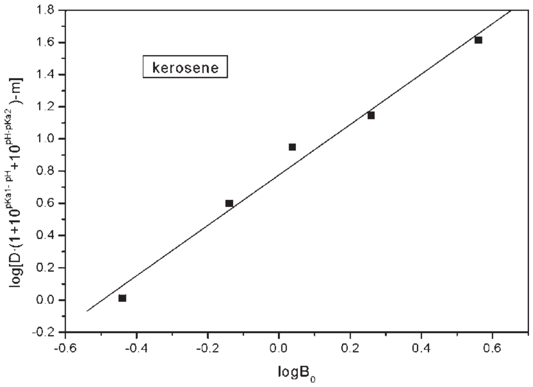

Figure 10. Relation between $\log[D\cdot(1+10^{\mathrm{p}K_{a1}-\mathrm{pH}}+10^{\mathrm{pH}-\mathrm{p}K_{a2}})-m]$ and $\log B_0$ in TBP/kerosene. $\mathrm{pH}_{\mathrm{eq}}$: about 7.0; and —, linear fitting curve: $\log[D\cdot(1+10^{\mathrm{p}K_{a1}-\mathrm{pH}}+10^{\mathrm{pH}-\mathrm{p}K_{a2}})-m] = 0.77 + 1.56 \log B_0$.

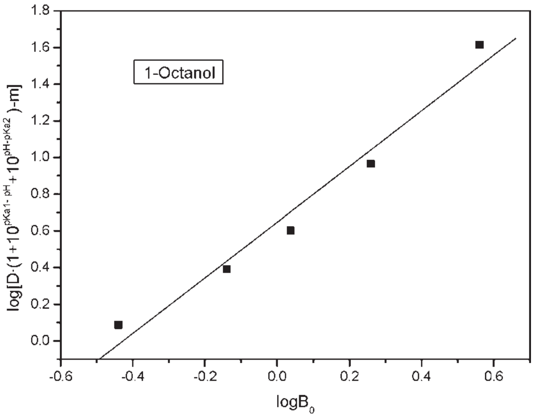

Figure 11. Relation between $\log[D\cdot(1+10^{\mathrm{p}K_{a1}-\mathrm{pH}}+10^{\mathrm{pH}-\mathrm{p}K_{a2}})-m]$ and $\log B_0$ in TBP/1-octanol. $\mathrm{pH}_{\mathrm{eq}}$: about 7.0; —, linear fitting curve: $\log[D\cdot(1+10^{\mathrm{p}K_{a1}-\mathrm{pH}}+10^{\mathrm{pH}-\mathrm{p}K_{a2}})-m] = 0.65 + 1.51 \log B_0$.

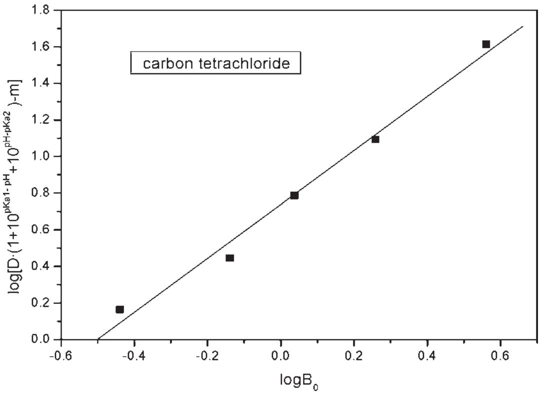

Figure 12. Relation between $\log[D\cdot(1+10^{\mathrm{p}K_{a1}-\mathrm{pH}}+10^{\mathrm{pH}-\mathrm{p}K_{a2}})-m]$ and $\log B_0$ in TBP/carbon tetrachloride. $\mathrm{pH}_{\mathrm{eq}}$: about 7.0; —, linear fitting curve: $\log[D\cdot(1+10^{\mathrm{p}K_{a1}-\mathrm{pH}}+10^{\mathrm{pH}-\mathrm{p}K_{a2}})-m] = 0.74 + 1.471 \log B_0$.

result, the extraction capacity with chloroform as a diluent is at a minimum.

Equilibrium Constants. On the basis of D, m, and pH values of different concentrations of TBP, K and n are then calculated.

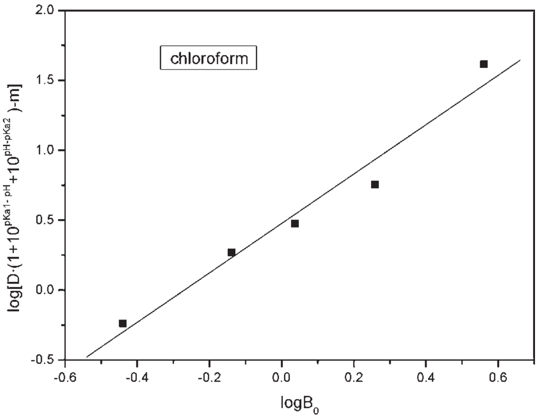

Figure 13. Relation between $\log[D\cdot(1+10^{\mathrm{p}K_{a1}-\mathrm{pH}}+10^{\mathrm{pH}-\mathrm{p}K_{a2}})-m]$ and $\log B_0$ in TBP/chloroform. $\mathrm{pH}_{\mathrm{eq}}$: about 7.0; —, linear fitting curve: $\log[D\cdot(1+10^{\mathrm{p}K_{a1}-\mathrm{pH}}+10^{\mathrm{pH}-\mathrm{p}K_{a2}})-m] = 0.48 + 1.76 \log B_0$.

The relationships between $\log[D(1+10^{\mathrm{p}K_{a1}-\mathrm{pH}}+10^{\mathrm{pH}-\mathrm{p}K_{a2}})-m]$ and $\log B_0$ at $\mathrm{pH}_{\mathrm{eq}}$ is about 7 in TBP/1-octanol, chloroform, carbon tetrachloride, and kerosene are demonstrated in Figures 10 to 13. Figures 10 to 13 show that the linear slope n is 1.56, 1.51, 1.47, and 1.76 ($n = 1.5$, approximately) and that the intercept $\log K$ is 0.78, 0.64, 0.73, and 0.48 with the correlation coefficient r = 0.99, 0.98, 0.99, and 0.99 in TBP/kerosene, 1-octanol, carbon tetrachloride, and chloroform, respectively. These results suggested that (1, 1) and (2, 1) complexes were formed in TBP/chloroform, carbon tetrachloride, kerosene, and TBP/1-octanol. In addition, taking into account 20 % deviation, K was calculated to be 5.97, 5.37, 5.47, and 2.99 in TBP/1-octanol, carbon tetrachloride, kerosene, and chloroform.

According to the K and n obtained above, eq 4 could be denoted by the following.

$$D = \frac{K\cdot\overline{[(\mathrm{TBP})]}_{\mathrm{org}}^{\,n}}{1+10^{\mathrm{p}K_{a1}-\mathrm{pH}}+10^{\mathrm{pH}-\mathrm{p}K_{a2}}} + \frac{m}{1+10^{\mathrm{p}K_{a1}-\mathrm{pH}}+10^{\mathrm{pH}-\mathrm{p}K_{a2}}} \qquad (8)$$

where K = 5.97, 5.37, 5.47, and 2.99 and n = 1.56, 1.51, 1.47, and 1.76 in TBP/kerosene, 1-octanol, carbon tetrachloride, and chloroform, respectively. Thus, eq 8 can be used to predict D of extraction equilibrium when TBP was used for extracting OAP in different TBP systems, respectively.

■ CONCLUSIONS

In this work, the amount of OAP extracted in organic phase increases with the increase of total TBP concentration, and hydrogen-bonding exists in the extraction process through IR spectrum. The pH of aqueous phase is a key factor in the extraction process, and the maximum D appears when the pH is between 6 and 8. Solvents have also a great deal of influence: the extraction efficiency is TBP−1-octanol > TBP−kerosene > TBP-$\mathrm{CCl_4}$ > TBP-$\mathrm{CHCl_3}$ when the concentration of TBP is between (0.3632 and 0.7264) $\mathrm{mol\cdot dm^{-3}}$, while the result is dissimilar (TBP−kerosene > TBP−1-octanol > TBP-$\mathrm{CCl_4}$ > TBP-$\mathrm{CHCl_3}$) when the concentration increases [(1.0896 to 1.8159) $\mathrm{mol\cdot dm^{-3}}$]. These results have great difference from that of extraction on OAP with di(2-ethylhexyl)phosphoric acid as an extractant,[12] so the selection of extractants is also a very important step in the extraction process. An expression of equilibrium D was proposed, and the parameters of the apparent extraction equilibrium constants (K) and the complex ratio (n) (TBP vs OAP) were calculated by fitting the experimental data.

AUTHOR INFORMATION

Corresponding Author

*Tel.: 86-371-66002109. E-mail: cuijiehu@163.com. Fax: 86-371-66002109.

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