Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Studies on Reactive Extraction of Meta-Aminophenol Using Trialkylphosphine-Oxide

Zhixian Chang[a]; Ling Zhang[a]; Deliang Li[a]
[a] College of Chemistry and Chemical Engineering, Henan University, Kaifeng, China

To cite this Article Chang, Zhixian , Zhang, Ling and Li, Deliang(2007) 'Studies on Reactive Extraction of Meta-Aminophenol Using Trialkylphosphine-Oxide', Separation Science and Technology, 42: 9, 2099 — 2109
To link to this Article: DOI: 10.1080/15363830701313578
URL: http://dx.doi.org/10.1080/15363830701313578

Separation Science and Technology, 42: 2099–2109, 2007
Copyright © Taylor & Francis Group, LLC
ISSN 0149-6395 print/1520-5754 online
DOI: 10.1080/15363830701313578

Studies on Reactive Extraction of Meta-Aminophenol Using Trialkylphosphine-Oxide

Zhixian Chang, Ling Zhang, and Deliang Li
College of Chemistry and Chemical Engineering, Henan University,
Kaifeng, China

Abstract: Distribution of meta-aminophenol (MAP) between water and trialkylphosphine oxide (TRPO), dissolved in different diluents (1-octanol and kerosene), as well as a comparison with the extraction equilibrium of pure diluent alone has been studied. The influence of the pH value of aqueous solutions, the TRPO concentration and diluents on the distribution ratio *D* has been discussed. The results indicate that the pH value and the TRPO concentration are the key factors that affect *D*. The non-polar diluent (kerosene) is favorable for extracting MAP when TRPO is used as extractant. MAP can be extracted with both acidic and neutral extractants (Di(2-ethylhexyl)phosphoric and TRPO) efficiently in kerosene while the basic one (Alamine 336) in 1-octanol, and their efficient pH region is 2.5–3.5, 4.5–6.5, and 6.5–7.8, respectively. The extraction ability shows the order of TRPO/kerosene $\geq$ Di(2-ethylhexyl)phosphoric/kerosene $>$ Alamine 336/1-octanol. The best selection is TRPO/kerosene with initial pH at 5.5–9.5.

Keywords: Reactive extraction, meta-aminophenol, trialkylphosphine-oxide

INTRODUCTION

Reversible reactive extraction is a new technique for separating and recovering the polar organic species from diluents with high efficiency and selectivity (1). Recently, researchers have applied this technique to treat polar organic diluents, such as carboxyl acids (2–6), alamines (7), phenols (8), and

Received 13 November 2006, Accepted 28 January 2007

Address correspondence to Zhixian Chang, College of Chemistry and Chemical Engineering, Henan University, Kaifeng 475001, China. Tel./Fax: (+86)03783881589; E-mail: chzx19@163.com

gained encouraging results. For example, using trioctylamines (TOA) as extractant, Li et al. (9, 10) carried on the systematic study of the monocarboxylic acid. Their results showed that the extractability depended on the hydrophobicity and the acidity of the acids. Based on the extraction equilibrium behavior, mathematical models were developed to describe the extraction behavior of monocarboxylic acid with TOA under the mass action law. The models indicated that the extraction equilibrium constant depended on the acid hydrophobicity, the acid acidity, and the specific basicity of TOA. These models can serve as guidelines for the selection of the extractant during the separation of monocarboxylic acid. Su et al. (11) studied the effects of pKa of amines, complexing agent concentration, and pH of solutions by using Di(2-ethylhexyl)phosphate (D2EHPA) as the extractant and kerosene as the diluent. In their study, they proposed an equilibrium distribution equation that includes chemical complexation and physical dissolution simultaneously. Tanase et al. (12) conducted a study on phenol and o-cresol using sulfuric acid salts of trioctylamine and obtained a consistent experimental result. Especially, systematic research by Dai's research team of Tsinghua University provided successful treatment of the wastewater containing phenols of the Wuxi Chemical Plant and ten other factories. This was key to enabling waste water processing to achieve a discharging standard. This technique had gained substantial economic and the social efficiencys and broadened the ways for processing highly concentrated organic waste water.

There also have been reports on the complex extraction research of amphoteric organic compounds. Aynur Senol (13) discussed the extraction equilibria of nicotinic acid using Alamine 336 in various diluents in their study. Li et al (14) investigated the equilibrium distribution coefficient of sulfanilic acid using trialkylamine in a long range of pH. Cui et al. (15) worked on wastewater from the production of Tobias acid with PCW-1 and gained good results. Tang et al. (16) studied the CLT acid waste using TOA as the extractant and kerosene as the diluent. D. Cascaval et al. (17) summarized the selective separation condition of amino acids by reactive extraction using D2EHPA. Li et al. (18–20) systematically studied the influence of diluents, pH on distribution coefficients of o-aminophenol and p-aminophenol, using trialkylphosphorous-oxide as extractant. They further studied the mixture extractant of trialkylamine and D2EHPA in heptane on to the p-aminophenol, and discovered that the couple had the obvious synergistic effect (21). However, research on the complexing extraction rule of this kind of compounds is insufficient. It requires further research to sequentially supply the foundation for its extraction theory and its industrial application.

Meta-aminophenol (MAP) is an important intermediate of dye, para-aminosalicylic acid, anti-tuberculosis medicines, photographic developer, and color film etc. MAP contains a Lewis acid group -OH and a Lewis base group -NH_2, and it has strong toxicity. Therefore, it is a hazardous environmental pollutant. In this paper, we studied the reactive extraction characteristics of MAP using trialkylphosphine-oxide (TRPO) dissolved in 1-octanol and kerosene. The key factors that affect *D* and the extraction mechanism are discussed and an analytic expression of the relationship between the initial pH and the equilibrium pH are proposed, which will provide useful information for further investigation of MAP and its industrial application.

EXPERIMENTAL DETAILS

TRPO, an industrial product by CYTEC Canada Incorporation, is a C_8-C_{10} saturated straight-chain trialkylphosphine-oxide mixture (purity $\geq$ 93%) with an average molecular weight of 350 g/mol and a density of 0.88 g/cm^3 (25°C). It was first pre-treated with 5% NaOH solution ($V_{NaOH}:V_{TRPO} = 1:5$), then washed with distilled water until the aqueous layer became neutral.

Kerosene, an alkyl mixture, is obtained from a local chemical plant. Before being used in the experiment, it was washed with H_2SO_4 (98%) ($V_{H2SO4}:V_{kerosene} = 1:5$) until the bottom became achromatism transparent. It was then washed with distilled water several times until the aqueous layer became neutral. The final product's density is about 0.78 g/cm^3 and its content of arene is less than 10%.

MAP, analytical grade (99.0%, GC), was furnished by China Medicine (Group) Shanghai Chemical Reagent Corporation. All the other chemicals are from the Tianjin Kermel Chemical Reagent Development Center, with chemical reagents purity $\geq$ 99%.

All extraction experiments were performed with 100 mL flasks at 25 ± 0.5°C. The equal volumes (20 mL) of initial aqueous and organic phases were shaken for 1.5 hour and then left to settle for 1 hour at fixed temperature (25 ± 1°C) and pressure (101.3 kPa). Before the organic phase was added, the aqueous-phase pH, which was measured with a pH meter (pH211, HANNA, Italy), was adjusted with a saturated NaOH solution and a diluent H_2SO_4 solution. After separation, the volumes of both phases (there were no significant changes before and after extraction) were measured, and the same method was used to measure aqueous-phase pH. It was then adjusted to pH of 1.5–2.0 with H_2SO_4 (98%). It was finally analyzed at 272 nm (the maximum adsorption wavelength of MAP) with a UV-250 spectrometer (Shimadzu, Japan). The interest concentrations in organic phases were calculated by material balance. The deviation of this method was less than 2% (21).

RESULTS AND DISCUSSION

Existing Forms of MAP

MAP has a Lewis acid group -OH and a Lewis base group -NH_2, exhibiting Lewis acid-base character. It exists in three forms in aqueous solution:

$^+H_3NArOH$ (H_2A^+), H_2NArOH (HA), and H_2NArO^- (A^-). Two dissociation balances exist in aqueous solution as follows:

$$H_2A^+ \xrightleftharpoons{K_{a1}} HA + H^+$$

$$HA \xrightleftharpoons{K_{a2}} A^- + H^+$$

with pK_{a1} and pK_{a2} are 4.13 and 9.83 (22), respectively.

The effect of the aqueous pH on molar fractions of various MAP is shown in Fig. 1. Apparently, the cation MAP exists at lower pH ($pH < pK_{a1}$), while the anion appears at higher pH ($pH > pK_{a2}$), and neutral MAP dominates at an intermediate pH ($pK_{a1} < pH < pK_{a2}$). The extraction behavior is distinct at different pH.

Effect of pH Value on *D*

In general, TRPO mainly reacts with the neutral MAP by forming hydrogen-bonds, which is supported by various *D* upon pH in different systems in Figs. 2 and 3. We can see that the *D* values increase with pH first and then decrease. There is a maximum *D* of each system with equilibrium pH at 4.5–6.5, which is a bit different from the pH at the maximum molar fraction of the neutral MAP. This is because TRPO is a neutral phosphorous-oxide extractant of general reagent grade, which contains phosphorous acids (R_2POH) (23) and aliphatic acids (24). According to other researchers (23), these kinds of acids cannot be eliminated by alkali completely. These impurities may, on the one hand, have some extraction action on MAP at lower pH (25), and

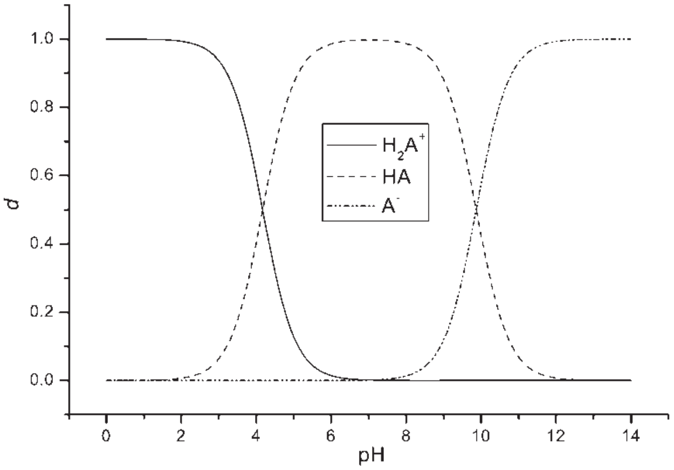

Figure 1. Effect of the aqueous pH on molar fractions of various MAP.

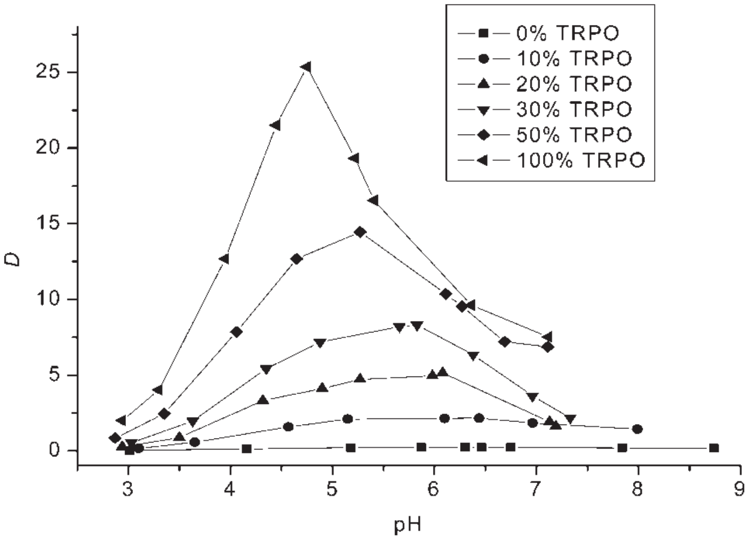

Figure 2. Extraction equilibrium of MAP with kerosene as diluent.

cause *D* to rise; on the otherhand, they may enter the aqueous phases during the extraction process, and cause the pH value to decrease. These may be the reasons that the higher the concentration of TRPO is, the more remarkable the deviation of maximum *D* is.

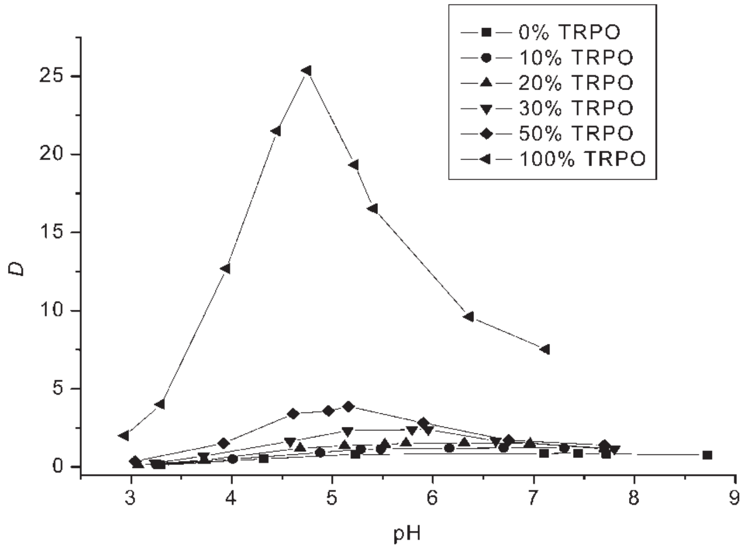

Figure 3. Extraction equilibrium of MAP with 1-octanol as diluent.

Effect of the Concentration of TRPO on *D*

As can be seen from Figs. 2 and 3, the *D* value increases with the increase of TRPO concentration (B_0). This phenomenon confirms to the reaction equilibrium. The increase of B_0 made the equilibrium concentration of TRPO (B) increase, and led to the chemical reaction move towards the direction of forming complexation and caused *D* to increase.

Effect of Diluents on *D*

Comparing Fig. 2 with Fig. 3, we can see that the extraction ability of pure 1-octanol is higher than that of pure kerosene; but as far as the mixtures are concerned, the extraction ability of TRPO/kerosene is much higher than that of TRPO/1-octonal. *D* of the same concentration of TRPO(10%) in kerosene or 1-octonal is given in Fig. 4. This may be owing to the hydrogen-bonds between TRPO and polar diluent 1-octonal, which can weaken the extract ability of the mixture, and make the total extract ability decrease ulterior. But in the TRPO/kerosene, the molecular interaction is so weak that kerosene could not affect the extraction ability of TRPO much.

Change of pH

It is known that *D* mainly depends on the pH value of equilibrium (pH_{eq}), while pH_{eq} is related to the initial pH (pH_{in}). Especially during the industrial

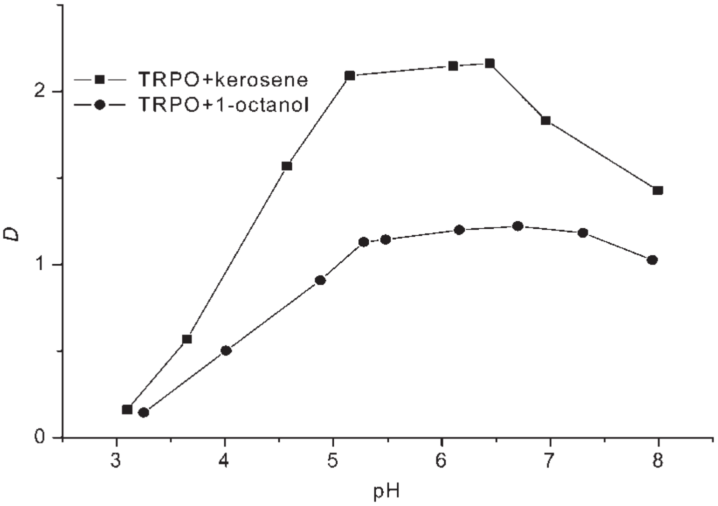

Figure 4. Effect of diluents on *D*.

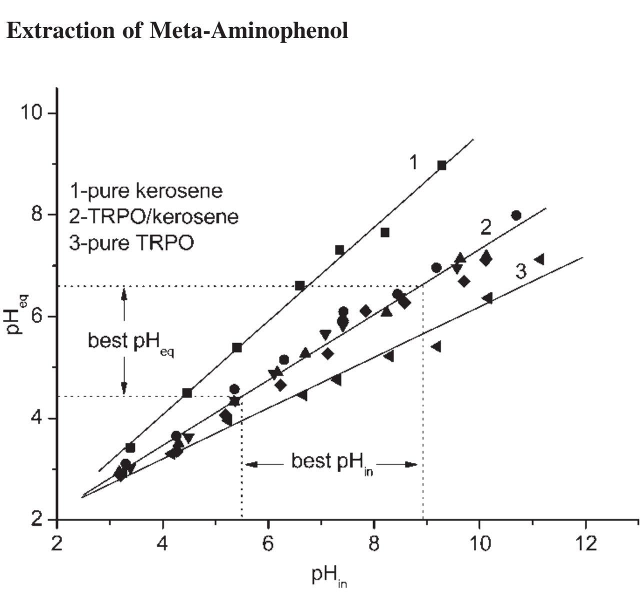

Figure 5. Linear relationship between pH_{ep} and pH_{in} in TRPO/kerosene.

separation process, pH_{in} is much more significant. So we present the relationship between pH_{eq} and pH_{in} of all systems in Figs. 5 and 6 and Table 1. A linear relationship is obtained with related coefficient $R > 0.98$ and standard deviation $SD < 0.36$. Obviously, the best pH_{in} is 5.5–9.5, while the best pH_{eq} is 4.5–6.5 in both TRPO/kerosene and TRPO/1-octanol systems.

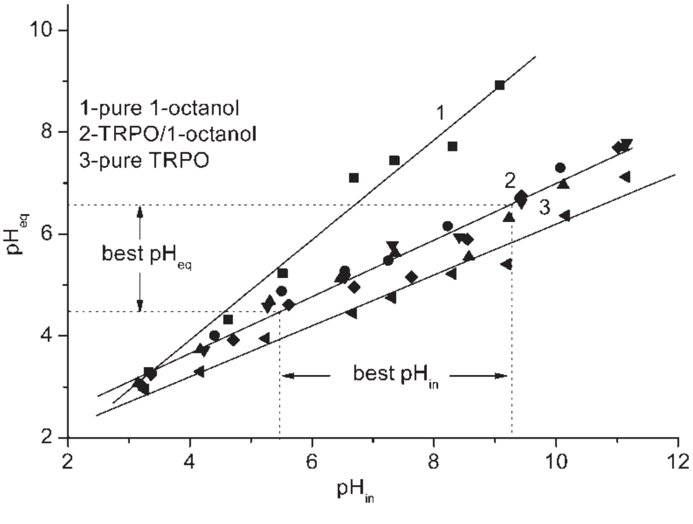

Figure 6. Linear relationship between pH_{ep} and pH_{in} in TRPO/1-octanol.

Table 1. Linear equation of pH_{eq} and pH_{in} in different systems

system	$pH_{eq} \sim pH_{in}$	R	SD
Pure kerosene	$pH_{eq} = 0.375 + 0.923\ pH_{in}$	0.997	0.17
Pure 1-octanol	$pH_{eq} = -0.0101 + 0.983\ pH_{in}$	0.988	0.35
TRPO/kerosene	$pH_{eq} = 0.880 + 0.645\ pH_{in}$	0.991	0.20
TRPO/1-octanol	$pH_{eq} = 1.429 + 0.557\ pH_{in}$	0.987	0.23
Pure TRPO	$pH_{eq} = 1.199 + 0.500\ pH_{in}$	0.989	0.22

Comparison with other Extractants

In order to study the extraction function of TRPO/kerosene versus MAP further, and look for the suitable condition for the industrial process, we selected the common acidic phosphorus-oxide extractant Di(2-ethylhexyl)-phosphate (D2EHPA) and basic trialkylamine extractant (Alamine 336) for comparison. Figure 7 displays the comparison of their extraction behavior versus MAP among 30% D2EHPA, 30% TRPO in kerosene, and 30% Alamine 336 in 1-octanol. It can be seen that their extraction ability shows the order of TRPO/kerosene $\geq$ D2EHPA/kerosene $>$ Alamine336/1-octanol, indicating that whether the acid, neutral, or basic extractant can be used for extracting MAP. It's noticeable that pH values on the peak *D* of D2EHPA, TRPO and Alamine 336 are 2.5–3.5, 4.5–6.5, and 6.5–7.8, respectively. Based on the resutls, we can select appropriate extractants

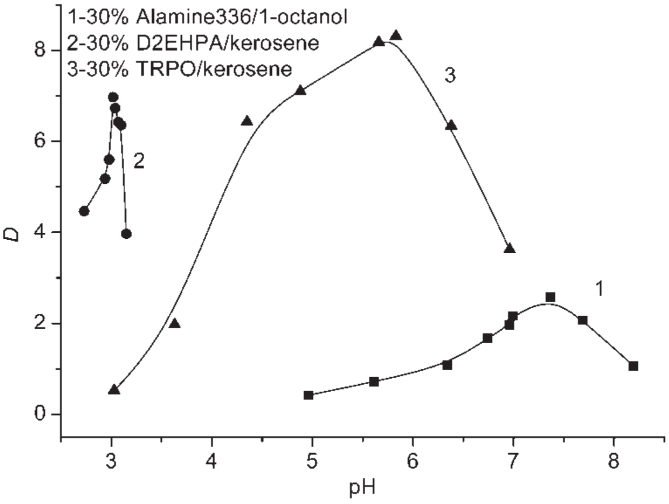

Figure 7. Comparison of other extractants with TRPO on extraction equilibrium of MAP.

for different real systems in industry, and avoid the side-effect to extraction equilibrium of a great deal of salt producing from the regulation of pH during the process.

In summary, when TRPO is adopted to treat the waste water with MAP, it is more suitable to use kerosene as the diluent. Furthermore, the TRPO/kerosene system costs less, and the operation parameters, such as viscidity, density, and interface tensions are also appropriate.

CONCLUSIONS

TRPO mainly reacts with neutral MAP. The phase-transfer of MAP occurs readily by forming hydrogen-bonds between TRPO and neutral MAP. D value depends primarily on the equilibrium pH in aqueous phase and the concentration of TRPO in organic phase. The polar diluent can weaken the extraction ability of TRPO versus MAP. TRPO/kerosene can extract MAP efficiently at pH 4.5–6.5, while D2EHPA/kerosene at 2.5–3.5 and Alamine 336/1-octanol at 6.5–7.8. And the best selection is TRPO/kerosene with initial pH at 5.5–9.5.

NOMENCLATURE

D	distribution coefficient
K_{a1}	the first dissociation constant of MAP, $\mathrm{mol \cdot L^{-1}}$
K_{a2}	the second dissociation constant of MAP, $\mathrm{mol \cdot L^{-1}}$

REFERENCES

1. King, C. J. (1987) Handbook of separation process technology. *Separation Process Based on Reversible Chemical Complexation*; John Wiley & Sons: New York, 760–774, Chapter15.
2. Nikhade, B.P. and Pangarkar, V.G. (2005) Equilibria and kinetics of extraction of citric acid from aqueous solutions in Alamine 336-cyclohexanone system. *Separation Science and Technology*, 40 (12): 2539–2554.
3. Marinova, M., Albet, J.L., Molinier, J., and Kyuchoukov, G. (2005) Specific influence of the modifier (1-decanol) on the extraction of tartaric acid by different extractants. *Industrial & Engineering Chemistry Research*, 44 (17): 6534–6538.
4. Hong, Y.K. and Hong, W.H. (2005) Removal of acetic acid from aqueous solutions containing succinic acid and acetic acid by tri-n-octylamine. *Separation and Purification Technology*, 42 (2): 151–157.
5. Huang, Y.Y., Zhang, J., and Dai, Y.Y. (2000) Study on extraction of aromatic acid based on chemical complexation. *Environmental Chemistry (China)*, 19 (2): 136–141.

6. Wasewar, K.L., Heesink, A.M., Versteeg, G.F., and Pangarkar, V.G. (2002) Reactive extraction of lactic acid using alamine336 in MIBK:equilibra and kinetics. *Journal of Biotechnology*, 97 (1): 59–68.
7. Gao, H.C., Shen, X.H., and Wu, J. (1994) The study of extraction mechanism with Amine. *Chemical Journal of Chinese Universities*, 15 (10): 1425–1428.
8. Jin, X.H. and Wang, Y.X. (2002) Extraction of amino-phenol in wastewater based on complexation. *Environmental Science and Technology*, 25 (6): 29–31.
9. Li, Z.Y., Qin, W., and Dai, Y.Y. (2004) Extraction equilibria behavior of monocarboxylic acids by Trioctylamine (I): extraction equilibria. *Journal of Chemical Industry and Engineering (China)*, 55 (1): 54–58.
10. Li, Z.Y., Qin, W., and Dai, Y.Y. (2004) Extraction equilibria behavior of monocarboxylic acids by Trioctylamine (II): apparent extraction equilibrium constantand correlation. *Journal of Chemical Industry and Engineering (China)*, 55 (1): 59–64.
11. Su, H.J., Xu, L.L., and Dai, Y.Y. (1997) Extraction of organic amines from diluent solution based on chemical complexation. *Journal of Chemical Industry and Engineering (China)*, 48 (6): 713–720.
12. Tanase, D., Anicuta, G.S., and Octavian, F. (1999) Reactive extraction of phenols using sulfuric acid salts of trioctylamine. *Chemical Engineering Science*, 54 (10): 1559–1563.
13. Senol, A. (2001) Extraction equilibria of nicotinic acid using Alamine 336 and conventional solvents: effect of diluent. *Chemical Engineering Journal*, 83: 155–163.
14. Li, Z.Y., Yang, Y.Y., and Dai, Y.Y. (2000) Extraction of aminobeniene sulfonic acid with trinkylamine (7301) based on chemical complexation. *Journal of Chemical Industry and Engineering (China)*, 51 (1): 85–89.
15. Cui, S.H., Jiang, C.Y., Wang, Y.P., and Peng, P.Y. (2000) Extracting method on chemical complexion applied in treatment of wastewater from the production of tobias acid. *Journal of Nanjing Normal University (Natural Science)*, 23 (3): 52–55.
16. Tang, H.P., Li, Z.H., Yang, S.F., Zhu, W.P., and Yang, Z.H. (2000) Extraction technology for CLT-acid recovery (CLT). *Environmental Science*, 21 (4): 57–60.
17. Cascaval, D., Oniscu, C., and Galaction, A.I. (2001) Selective separation of amino acids by reactive extraction. *Biochemical Engineering Journal*, 7 (3): 171–176.
18. Li, D.L., Qin, W., and Dai, Y.Y. (2003) Extraction equilibrium of p-aminophenol with TRPO. *Journal of Chemical Industry and Engineering (China)*, 54 (3): 339–343.
19. Li, D.L., Liu, X.Q., and Qin, W. (2005) Complexation extraction of o-aminophenol with TRPO. *Journal of Chemical Engineering of Chinese Universities*, 19 (5): 588–592.
20. Li, D.L., Liu, X.Q., and Cui, J.H. (2006) Reactive extraction of o-aminophenol using trialkylphosphine oxide. *Chinese J. Chem. Eng.*, 14 (1): 46–50.
21. Qin, W., Li, D.L., and Dai, Y.Y. (2003) Liquid-liquid equilibria of p-aminophenol between water and trialkylamine, trialkylphosphine oxide and Di (2-ethylhexyl) phosphoric acid in heptane. *Journal of Chemical and Engineering Data*, 48: 1606–1609.
22. Dean, J.A. (1985) Lange's Handbook of Chemistry; McGraw-Hill Book Company: New York.

23. Lu, X.Y. (1964) The synthesis of acidic organophosphorus extractants. *Atomic Energy Science and Technology(China)*, 6: 627–635.
24. Xin, R.X., Wu, W., Jiao, J.X., Zhang, P., Liang, J.F., and Song, C.L. (2001) Determination of trace fatty acids in tri-alkyphosphine oxide by pyrolysis methylation Gas Chromatography. *Chinese Journal of Analysis Laboratory*, 20 (1): 8–11.
25. Cui, J.H., Li, D.L., and Zhang, L. (2005) Complexation extraction of p-aminophenol with Di(2-ethylhexyl)phosphoric acid in different diluent. *Chinese Journal of Spectroscopy Laboratory*, 22 (2): 307–311.