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Wet process of phosphoric acid purification by solvent extraction using tri-*n*-butyl phosphate and cyclohexanol mixtures

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Abstract: Solvent extraction is an efficient, economical and widely-used technology for the purification of wet process phosphoric acid (WPA). This present work focused on the development of a solvent extraction system, TC, representing tri-*n*-butyl phosphate (TBP) and cyclohexanol mixtures. The equilibrium phase diagram of the system $\text{H}_3\text{PO}_4\text{--H}_2\text{O--TC}$ at 298.2 K and atmospheric pressure was obtained. The effects of extraction time, phosphoric acid concentration, extractant concentration, temperature and phase volume ratio on extraction efficiency were studied. The extracted complexes were estimated to be $1.8\text{H}_3\text{PO}_4 \cdot 2\text{TC}$. The extraction process of H_3PO_4 was exothermic and the enthalpy change, ΔH , was obtained. The solvent mixtures had a high efficiency for phosphoric acid purification *via* multi-stage counter-current extraction from the industrial WPA in a reciprocating plate extraction column with an H_3PO_4 extraction yield of 85.08 % at 313.2 K. The stability, extraction efficiency and recycling capability of TC for H_3PO_4 extraction were also estimated.

Keywords: mixing extractant; equilibrium phase diagram; extracting mechanism; reciprocating plate column.

INTRODUCTION

Phosphoric acid is a type of basic raw material widely used in many areas such as agricultural feed, fertilizers, detergents and food additives. Commercial phosphoric acid is commonly manufactured by thermal and wet process. Wet process phosphoric acid (WPA) is produced by decomposition of phosphate rock with mineral acid which is thus far acknowledged as a more economical, environmental-friendly method of production.^{1,2} However, WPA is accompanied by a number of undesirable impurities beside solids and organic matters so that purification must be conducted during the downstream production. Several physicochemical treatment techniques have been investigated for purifying WPA

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including adsorption, crystallization, ion exchange, ion precipitation and solvent extraction.^{3,4}

Experimental and technical researches indicate that solvent extraction is a practical, efficient and economical method for WPA purification which is accepted as the most widely-used technique applied in the industrial production process at present.^{5,6} Many types of organic solvents have been investigated to serve as the extractant, *e.g.*, esters,⁷ alcohols⁸ and ketones.⁹ Tri-*n*-butyl phosphate (TBP) is extensively used in WPA purification due to its good selectivity to phosphoric acid, immiscibility with the aqueous solution and easy recovery. However, TBP is easy to emulsify because of its partial hydrolysis in the acid solution, which has negative effect on phase separation.¹⁰ Aliphatic alcohols, such as butanol, pentanol and octanol, have been studied for purifying WPA which have the advantages of good extraction efficiency, low toxicity and quick phase separation without emulsification. Cyclohexanol has been used for leaching and extraction. It has lower density and viscosity than octanol, which can provide better flowability. The solubility of cyclohexanol in aqueous solution is also lower than that of butanol and pentanol. The experimental results indicate its favorable extraction efficiency of H₃PO₄ and good stability in liquid–liquid systems.^{11,12} The main aim of this study was to investigate the purification process of WPA using TBP and cyclohexanol mixtures. Kerosene was used as diluent to decrease the viscosity of the two-phase mixtures and accelerate the phase separation process.¹³

In this present work, the research focused on developing a solvent extraction system using TBP and cyclohexanol mixtures with an optimum composition. The solvent mixtures were expected to eventually combine the advantages of good selectivity from TBP and good extraction efficiency from cyclohexanol while avoiding their disadvantages at the same time. The equilibrium phase diagram of the system H₃PO₄–H₂O–TC at 298.2 K and atmospheric pressure was obtained as well as the phase equilibrium data of the extraction system. The extracted complexes and the process stoichiometry were studied in order to estimate the transferring mechanism. A multi-stage counter-current extraction in a reciprocating plate extraction column with scrubbing and stripping of the loaded organic phase were applied to obtain the purified phosphoric acid from industrial WPA. The stability and recycling capability of TC for H₃PO₄ extraction were also appraised. The study is capable of enriching theoretical foundation and technical guidance for the phosphoric acid purification process.

EXPERIMENTAL

Materials

TBP and cyclohexanol, provided by Jingcui Chemical Reagent Co. (Sichuan, China), were both of analytical reagent grades and used without any further purification. Analytically pure H₃PO₄ (purity ≥ 85 %) was obtained from Kelong Chemical Reagent Co. (Sichuan,

China). Kerosene was provided by Zhongcui Chemical Co. (Sichuan, China). Before use, kerosene was washed with concentrated sulfuric acid and neutralized with 5 % Na₂CO₃ solution then washed with water until the pH was neutral and finally distilled at 458.2–528.2 K. Deionized water was used throughout the experiments. The industrial raw WPA was supplied by Furui Chemical Plant (Yunnan, China), which was obtained by decomposing phosphate ore using sulfuric acid. The composition of the industrial WPA is shown in Table I.

TABLE I. Composition of the industrial WPA; ferrous ions have been converted to ferric ions as a sum

| Component | H ₃ PO ₄ | SO ₄ ²⁻ | F ⁻ | Fe ³⁺ _a | Al ³⁺ | Mg ²⁺ | Zn ²⁺ | Cr ³⁺ |
|----------------|--------------------------------|-------------------------------|----------------|-------------------------------|------------------|------------------|------------------|------------------|
| Content, wt. % | 65.74 | 3.28 | 0.334 | 0.377 | 0.659 | 0.732 | 0.041 | 0.004 |

Procedure

Equilibrium studies. Experiments were carried out at 298.2 K and atmospheric pressure in a water thermostat (± 0.1 K). Known amounts of aqueous phase (diluted analytically pure phosphoric acid) and organic phase (TBP and cyclohexanol mixtures) were mixed and shaken for 1 h until equilibrium was reached and then left to settle for 1 h to completely separate the two liquid phases. The concentration of phosphoric acid in the two phases was determined by the quinoline phosphomolybdate gravimetric method with an accuracy of ± 0.1 %.⁷ The water content in the organic phase was determined by the Karl-Fisher potentiometric titration method using a compact potentiometric titrator (Methohm 916 Ti-Touch, Switzerland) with an accuracy of ± 0.1 %.⁷ FT-IR spectroscopy (Nicolet 7100, USA) was used for the analysis of the organic phase.

Batch extraction studies. The extraction temperature was controlled and maintained in a water thermostat (± 0.1 K). Certain amounts of phosphoric acid were diluted with deionized water to prepare the aqueous phase while TBP and cyclohexanol mixtures were diluted in kerosene to prepare the organic phase. Then the two prepared phases were mixed and stirred for a certain time. After standing for a sufficient time, the mixtures completely separated into two equilibrated phases. The organic phase and the raffinate aqueous phase were then weighed and taken for analysis. Measurement of Fe³⁺ concentration in the aqueous solution was performed using a UV-Vis spectrophotometer (Mapada UV-1100, China) at a wavelength of 510 nm with an accuracy of ± 0.5 %.¹² Measurement of the concentration of other metallic ions (Al³⁺, Mg²⁺, Zn²⁺ and Cr³⁺) in the aqueous solution was performed with an ICP-AES (Thermo Fisher Iris Adv, USA) with an accuracy of ± 0.5 %.¹⁰ The fluoride composition in the aqueous phase was determined by an ion meter (Jingke DDS-307, China) using a fluoride selective electrode with a saturated calomel electrode as the reference electrode with an accuracy of ± 1 %.¹⁴ The concentration of SO₄²⁻ in the aqueous solution was identified using a UV-Vis spectrophotometer at a wavelength of 440 nm with an accuracy of ± 0.5 %.⁵ The volume of the liquid phases was also determined (± 0.1 mL).

Continuous extraction studies

The continuous extraction of the industrial WPA was carried out with multi-stage counter-current operations in a reciprocating plate extraction column.¹⁵ The temperature of the column was maintained by a heating belt (± 0.1 K). The diameter and effective height of the column are 22 and 1300 mm, respectively. The material of the column plates is PTFE. The number of the column plates is 35 with the plate spacing to be 25 mm. The thickness and diameter of the plates are 2 and 20 mm, respectively. Schematic flow diagram of the reciprocating plate extraction column is shown in Fig. S-1 of the Supplementary material to this

paper. The organic phase and the raffinate aqueous phase after extraction were weighed and taken for analysis.

RESULTS AND DISCUSSION

Composition of solvent mixtures

The effect of the weight percent, w , of cyclohexanol in the solvent mixtures (TBP+cyclohexanol) ranging from 0 to 100 % on the extraction was studied at 298.2 K. The initial volumes of organic and aqueous phases were remained as 224 and 56 ml, respectively. The equilibrium distribution results for two different concentration of H_3PO_4 in the initial aqueous phase are compared in Fig. 1. The results show that higher cyclohexanol concentration in the solvent mixtures had better H_3PO_4 extraction efficiency. The increase of H_3PO_4 in the initial aqueous solution of 6.46 to 9.16 mol L^{-1} led to an obvious increase for the distribution coefficient. This indicates that the raw WPA can be pre-concentrated to get better extraction efficiency. The effect of the composition of solvent mixtures on the separation factors for five impurities: Fe^{3+} , Mg^{2+} , Al^{3+} , F^- and SO_4^{2-} , are shown in Fig. 2 with the concentration of H_3PO_4 in the initial aqueous phase remained at 9.16 mol L^{-1} . As the results show, TBP had better selectivity than cyclohexanol in the solvent mixtures. For all impurities, the separation factors passed through a minimum as the cyclohexanol percentage of the mixtures increase. Cation impurities: Fe^{3+} , Mg^{2+} and Al^{3+} had obviously higher separation factors than anion impurities F^- and SO_4^{2-} did, which is in agreement with previous researches.¹⁴ Considering the H_3PO_4 extraction efficiency and selectivity of H_3PO_4 , the composition of TC were obtained for a cyclohexanol weight percent of 66 % in the solvent mixtures. Thus, the solvent mixtures were maintained as 34 % TBP + 66 % cyclohexanol for the following experiments.

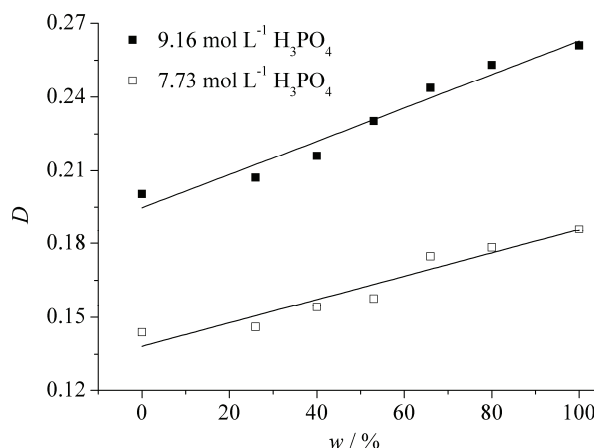


Fig. 1. Effect of cyclohexanol content in solvent mixtures on the distribution coefficient of H_3PO_4 ; O/A = 4, $T = 298.2$ K; $[\text{H}_3\text{PO}_4] = 9.16$ mol L^{-1} (■); $[\text{H}_3\text{PO}_4] = 6.46$ mol L^{-1} (□).

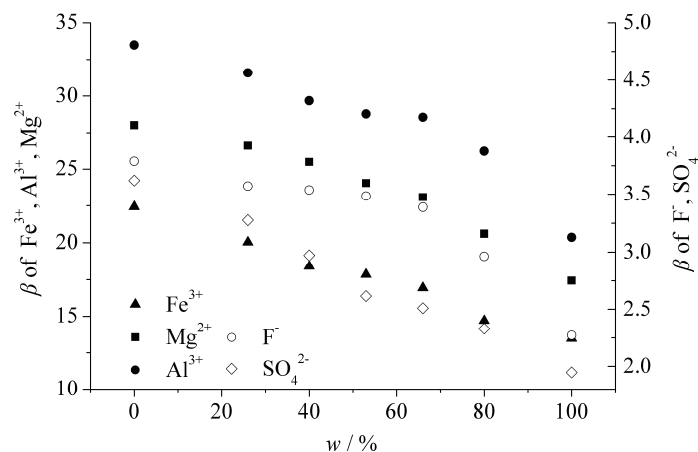


Fig. 2. Effect of cyclohexanol content in solvent mixtures on the separation factor for Fe^{3+} , Mg^{2+} , Al^{3+} , F^- and SO_4^{2-} : $[\text{H}_3\text{PO}_4] = 9.16 \text{ mol L}^{-1}$, $\text{O/A} = 4$, $T = 298.2 \text{ K}$; Fe^{3+} (▲); Mg^{2+} (●); Al^{3+} (■); F^- (○); SO_4^{2-} (◇).

Equilibrium studies of extraction system $\text{H}_3\text{PO}_4\text{-H}_2\text{O}$ solvent mixtures

Mutual solubility of TBP and cyclohexanol. The solvent mixtures in this study consisted of TBP and cyclohexanol. They are both non-polar molecules with low solubility in H_2O . Based on the theory that similar compounds can be easily dissolved in one another, mutual solubility of TBP and cyclohexanol was considered using the Hildebrand solubility parameter (δ).¹⁶ δ is calculated as:

$$\delta = \sqrt{\frac{\Delta H - RT}{V_1}} \quad (1)$$

where δ is solubility parameter, $\text{MPa}^{1/2}$, ΔH is heat of gasification, J mol^{-1} , T is absolute temperature, K , R is the gas constant, $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$, V_1 is molar volume of liquid, $\text{m}^3 \text{ mol}^{-1}$.

At 293.2 K , the solubility parameters δ of TBP and cyclohexanol are 20.24 and $22.51 \text{ MPa}^{1/2}$, respectively. The results calculated show that TBP and cyclohexanol have similar solubility parameter δ and good mutual solubility.¹⁷ The mutual solubility was also proved by mixing different concentrations of TBP and cyclohexanol at different temperature. Therefore, the extraction system $\text{H}_3\text{PO}_4\text{-H}_2\text{O-TBP-cyclohexanol}$ can be regarded as a ternary system $\text{H}_3\text{PO}_4\text{-H}_2\text{O-TC}$ (TBP+cyclohexanol) during the equilibrium studies.

Phase diagram of the system $\text{H}_3\text{PO}_4\text{-H}_2\text{O-TC}$ at 298.2 K . It is necessary to establish the equilibrium phase diagram of the extraction system to reveal the distribution of H_3PO_4 between the aqueous and organic phases. Based on the optimum composition of solvent mixtures obtained, the phase diagram of the system $\text{H}_3\text{PO}_4\text{-H}_2\text{O-TC}$ (34 % TBP+66 % cyclohexanol) at 298.2 K and atmo-

spheric pressure is shown in Fig. 3. The conjugated phases were connected with tie-lines for each mixtures. The plait-point marked in the phase diagram was established according to the Hand method.¹⁸ The composition data of initial mixtures and equilibrium phases are given in Table S-I of the Supplementary material to this paper.

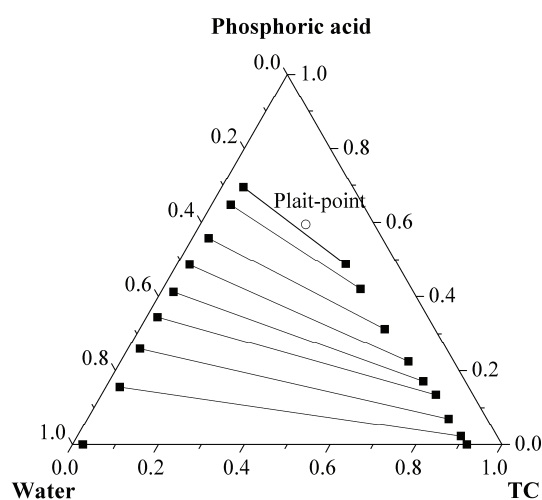


Fig. 3. Equilibrium phase diagram of the extraction system $\text{H}_3\text{PO}_4\text{-H}_2\text{O-TC}$ (34% TBP + 66% Cyclohexanol) at 298.2 K and atmospheric pressure.

As the phase diagram shows, the pseudo-ternary system has two completely miscible liquid pairs, $\text{H}_3\text{PO}_4+\text{H}_2\text{O}$ and $\text{H}_3\text{PO}_4+\text{TC}$. It also has one partially miscible liquid pair, $\text{H}_2\text{O}+\text{TC}$. The plait-point of the system indicates good capability of the solvent mixtures for H_3PO_4 extraction due to the ability of the organic phase to load high H_3PO_4 concentration, 59.46 %. The solvent mixtures have low solubility in the aqueous solution, which is less than 5 %, leading to little consumption of solvent for the scrubbing and stripping operation after extraction. In addition, the solubility of water in the solvent mixtures increases slowly from 8.14 to 11.97 % as the mass fraction of H_3PO_4 increases from 2.22 to 48.70 % in the organic phase. The phase equilibrium study of the system indicates that the solvent mixtures can be considered as favorable candidates for the extraction of H_3PO_4 .

Equilibrium distribution of H_3PO_4 for three different solvent extraction systems. Based on the equilibrium studies, the H_3PO_4 distribution between the aqueous and organic phases for the extraction system $\text{H}_3\text{PO}_4\text{-H}_2\text{O-TC}$ was obtained in comparison with other two extraction systems using TBP and cyclohexanol separately at 298.2 K. The weight percent of H_3PO_4 in organic phase and aqueous phase at equilibrium are represented as $w_{(o)}$ and $w_{(a)}$, respectively. Figure 4 shows that the distribution curve for TC lies between those for other two solvents. For high H_3PO_4 concentration, cyclohexanol performs better than TC

on the capability of loading H_3PO_4 , which is in turn superior to TBP. This trend is obviously inversed for low H_3PO_4 concentration. The results indicate that the solvent mixtures can performance well with favorable extraction efficiency combing the advantages of each pure solvent while avoiding their disadvantages in a wide range of H_3PO_4 concentration.

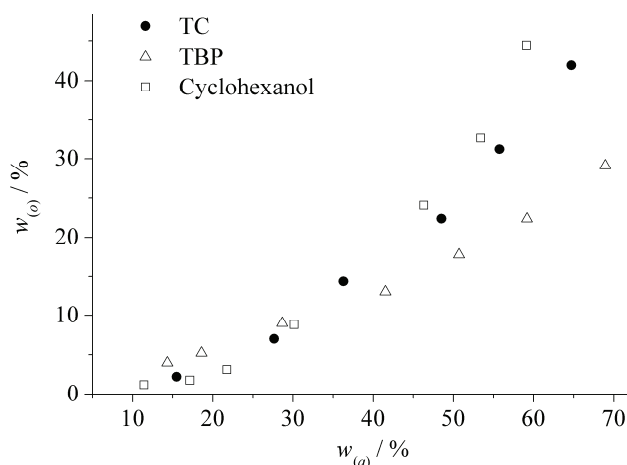


Fig. 4. Equilibrium distribution of H_3PO_4 for different solvent extraction systems at 298.2 K: TC (●); TBP (△); cyclohexanol (□).

Effect of extraction time on the extraction efficiency

The effect of extraction time on the extraction efficiency in the range of 0–60 min was investigated. The initial volumes of aqueous phases were remained as 56 ml. Plots of the distribution coefficient D of H_3PO_4 versus the extraction time with three different phase ratio O/A from 2.0 to 4.0 are shown in Fig. 5. The

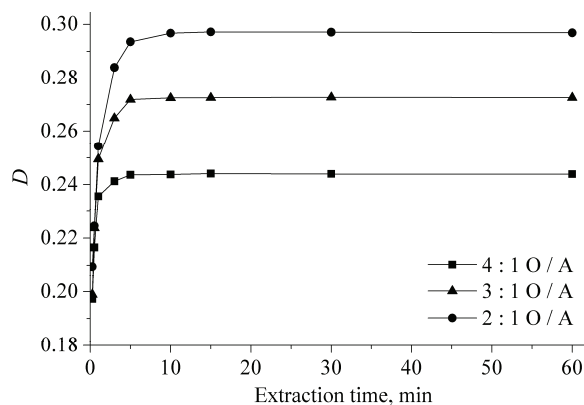


Fig. 5. Effect of extraction time on the distribution coefficient of H_3PO_4 ; [TC] = 4.24 mol L^{-1} , $[\text{H}_3\text{PO}_4] = 9.16 \text{ mol L}^{-1}$, $T = 298.2 \text{ K}$; O/A: 4 (■); 3 (▲); 2 (●).

results show that the distribution coefficients increase rapidly in the range of 0–5 min and then remain almost constant which indicates that it took approximately 5–10 min to attain the equilibrium for extraction. The extraction time of 10 min was used for further experiments to ensure that the extraction equilibrium was achieved. The results also indicate that the increase of phase ratio leads to considerable decrease in the distribution coefficient of H_3PO_4 . This is because when the H_3PO_4 content in the aqueous phase is constant, increasing the phase ratio means more cyclohexanol in the extraction equilibrium. More cyclohexanol leads to higher volume of H_2O into the organic phase by co-extraction, which is equivalent to the raffinate phase being concentrated.¹² Thus, distribution coefficient of H_3PO_4 decreases correspondingly with higher phase ratio.

Effect of H_3PO_4 concentration

The effect of H_3PO_4 concentration on the extraction was investigated. The H_3PO_4 concentration was varied in the range of 1.10–9.22 mol L^{-1} . The concentration of TC in the initial organic phase remained 4.24 mol L^{-1} and the temperature was maintained at 298.2 K constantly. The plot of $\log [\text{H}_3\text{PO}_4]_{(o)}$ versus $\log [\text{H}_3\text{PO}_4]_{(a)}$ is shown in Fig. 6. Using regression analysis, the following relation was established from the obtained data:

$$\log [\text{H}_3\text{PO}_4]_{(o)} = -1.04 + 1.77 \log [\text{H}_3\text{PO}_4]_{(a)}, r = 0.998 \quad (2)$$

where r is the correlation coefficient.

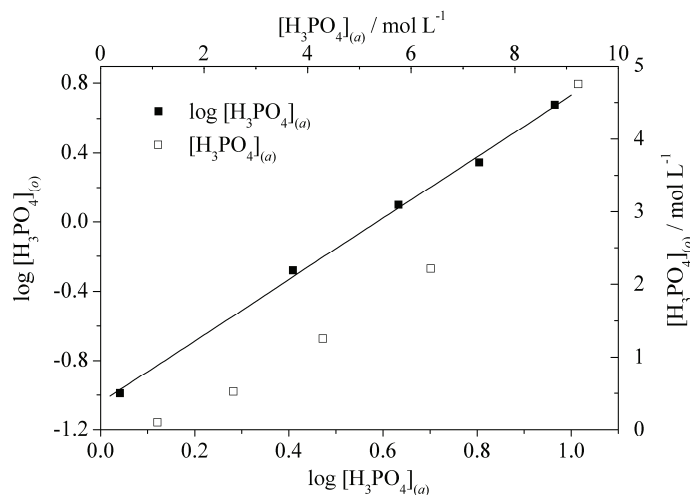


Fig. 6. Equilibrium isotherms for the analytical concentrations of the organic phase for the extraction: $[\text{TC}] = 4.24 \text{ mol L}^{-1}$, $\text{O/A} = 4$, $T = 298.2 \text{ K}$; $\log [\text{H}_3\text{PO}_4]_{(a)}$ (■); $[\text{H}_3\text{PO}_4]_{(a)}$ (□).

The H_3PO_4 concentration in the organic phase increases obviously with an increase of H_3PO_4 concentration in the aqueous phase. The slope of the line is 1.77. According to the slope of the line, x in Eq. (2) equals approximately 1.8.

Effect of TC concentration

The effect of the solvent mixtures concentration in the range of 4.06–4.78 mol L^{-1} on the extraction was studied at 298.2 K. The concentration of H_3PO_4 in the initial aqueous phase remained at 9.16 mol L^{-1} . As Fig. S-2 shows (Supplementary material), the distribution coefficients increase as the TC concentration is raised. Higher extractant concentration leads to better extraction efficiency. Using regression analysis, the following relation was established from the obtained data:

$$\log D = -1.89 + 2.03 \log [\text{TC}], r = 0.997 \quad (3)$$

According to Eq. (3), the slope of the plot of $\log D$ versus $\log [\text{TC}]$ is 2.03, which would give the number of molecules of $[\text{TC}]$ engaged in the reaction (Eq. (S-1)). Therefore, y in Eq. (S-1) approximately equals 2.

IR absorption spectra of the extracted complexes

Based on the simplified regression analysis method above, the extraction process stoichiometry of H_3PO_4 using TC was obtained. The apparent extracted complex of the extraction reaction in Eq. (S-1) was suggested to be $1.8\text{H}_3\text{PO}_4 \cdot 2\text{TC}$. Considering that the solvent mixtures consist of 34 % TBP and 66 % cyclohexanol, there may be four types of extracted complexes, $\text{H}_3\text{PO}_4 \cdot \text{TBP}$, $\text{H}_3\text{PO}_4 \cdot 2\text{TBP}$, $\text{H}_3\text{PO}_4 \cdot 3\text{TBP}$, $\text{H}_3\text{PO}_4 \cdot \text{cyclohexanol}$, which are formed during the reaction.^{19,20} These issues are examined through IR spectra, which is presented in Supplementary material.

Effect of temperature on the extraction of H_3PO_4 and impurities

The effect of temperature in the range of 298.2–333.2 K on the extraction for the WPA was studied. The concentration of TC in the initial organic phase and the concentration of H_3PO_4 in the initial aqueous phase remained as 4.24 and 9.16 mol L^{-1} , respectively. This analysis is given in Supplementary material.

The results show that the distribution coefficients of H_3PO_4 increase with lower temperature. In the range of 298.2–333.2 K, the value of the enthalpy change of H_3PO_4 extraction of $-4.21 \text{ kJ mol}^{-1}$ was calculated from the slope of the linear relation, which indicates the extraction of H_3PO_4 is exothermic. Increasing temperature thus has adverse effects on the extraction process. According to Eqs. (S-1)–(S-5), the values of the enthalpy change of extraction for Fe^{3+} , Mg^{2+} , Al^{3+} , F^- and SO_4^{2-} were 5.54, 24.54, 22.48, 18.84 and 7.40 kJ mol^{-1} , respectively. The values calculated indicate that the co-extraction of these five impurities is endothermic and the changes of enthalpy are sorted as $\text{Mg}^{2+} > \text{Al}^{3+}$

$> F^- > SO_4^{2-} > Fe^{3+}$. Therefore, the results show that increase of temperature has negative effect on the selectivity to H_3PO_4 for the purification. Volatilization of the extractant also increases at higher temperature. Based on the studies above, this extraction system can perform well at room temperature with good selectivity and low energy consumption so that it has good prospects for industrial application.

Effect of phase ratio on the extraction of H_3PO_4 and impurities

The effect of phase volume ratio (O/A) ranging from 1.0 to 5.0 on the extraction for WPA was studied. The concentration of TC in the initial organic phase and the concentration of H_3PO_4 in the initial aqueous phase remained as 4.24 and 9.16 mol L⁻¹, respectively. The temperature was maintained at 298.2 K constantly. As Fig. 7 shows, when $[H_3PO_4]$ is 9.16 mol L⁻¹, the extraction yields of H_3PO_4 increase from 24.39 to 65.28 % with the increasing rate slowing down as the phase ratio rises from 1.0 to 5.0. This is because the H_3PO_4 content in the aqueous phase was constant; increasing the phase ratio can lead to higher extraction equilibrium values, thereby increasing the extraction yield. On the other hand, the extraction yields decrease comparatively with lower concentration of H_3PO_4 in the initial aqueous phase, which indicates that the raw WPA can be pre-concentrated for better extraction yield. Figure S-6 of the Supplementary material indicates that the separation factors are also raised with higher phase ratio. Selectivity for metal ionic impurities, Fe^{3+} , Mg^{2+} and Al^{3+} , is considerably better than that for F^- and SO_4^{2-} . However, higher phase ratio means higher viscosity of the two-phase mixtures and leads to higher investment costs as well as operating costs of handling bigger volumes of organic phase.²¹

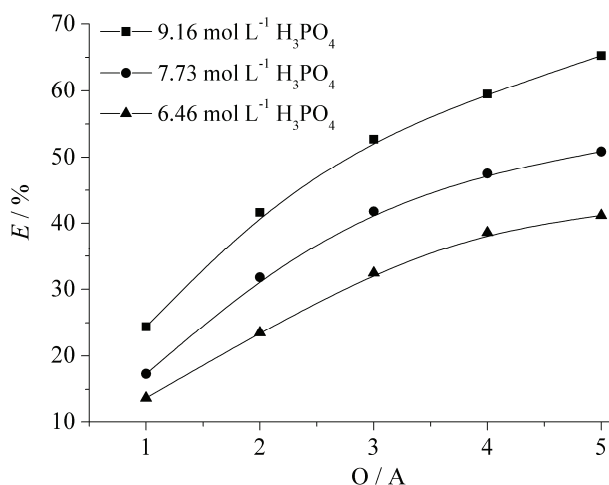


Fig. 7. Effect of phase ratio on extraction yield of H_3PO_4 : $[TC] = 4.24 \text{ mol L}^{-1}$, $T = 298.2 \text{ K}$; $[H_3PO_4]$: (■) 9.16; (●) 7.73; (▲) 6.46 mol L⁻¹.

Continuous purification process

Multi-stage counter-current extraction of H₃PO₄. In the industrial purification process of WPA, the multi-stage counter-current extraction process is often conducted to increase the yield of H₃PO₄. In this work, the extraction of the industrial WPA (Table S-I) was carried out with continuous operations in a reciprocating plate extraction column. The temperature of the column was controlled and maintained at 313.2 K. The vibration frequency of the column was 3 Hz and the amplitude was 25 mm. The feed flow rates of the aqueous and organic phase were 6 and 30 mL min⁻¹, respectively. The composition of the extracted organic phase is shown in Table II. The total extraction yield of H₃PO₄ is 85.08 %, which indicates high extraction efficiency from the industrial WPA via a multi-stage counter-current extraction using the reciprocating plate extraction column.

TABLE II. Composition of phosphoric acid in extraction, scrubbing and stripping process

| Type | [H ₃ PO ₄] wt. % | [SO ₄ ²⁻] wt. % | [F] ppm | [Fe ³⁺] ppm | [Al ³⁺] ppm | [Mg ²⁺] ppm |
|--------------------------|--|---|------------|----------------------------|----------------------------|----------------------------|
| Extracted organic phase | 14.63 | 0.36 | 341.0 | 145.6 | 186.4 | 166.4 |
| Scrubbed organic phase | 13.81 | 0.22 | 304.7 | 53.6 | 98.7 | 81.6 |
| Stripped phosphoric acid | 36.15 | 0.18 | 225.9 | 9.5 | 4.9 | 2.1 |

Scrubbing and stripping. After extraction process, the organic phase loading H₃PO₄ contained some impurities with equilibrium concentration due to co-extraction. Thus scrubbing of the organic phase at a phase ratio O/A of 15 was conducted to remove these undesirable impurities. The scrubbing operation was conducted using diluted AR (analytical reagent) phosphoric acid ([H₃PO₄] = 4.23 mol L⁻¹) to strengthen the removing efficiency and reduce the consumption of phosphoric acid. After scrubbing, the stripping (re-extraction) of H₃PO₄ from the scrubbed loaded organic phase was carried out with O/A phase ratio of 5 using deionized water. The scrubbing and stripping operations were also conducted in the reciprocating sieve plate column at 323.2 K. The phosphoric acid composition of samples taken from the extraction, scrubbing and stripping process in the continuous operation is shown in Table II. As Table II shows, the scrubbing operation is able to remove impurities efficiently, especially for metallic ions, with less than 1 % consumption of H₃PO₄. By the above purifying process of extraction, scrubbing and stripping, the metallic impurities are successfully removed to less than 10 ppm in the purified phosphoric acid without any other purifying technology. In order to remove the sulfate ions further, chemical precipitation using barium carbonate or calcium carbonate is generally conducted before or after extraction. The fluoride ions residual in the purified diluted phosphoric acid after stripping can be removed in the concentration process to

produce phosphoric acid of food and analytical grade.²² The study of the purification process is capable of providing technical guidance and improvement while adopting batch or continuous column extraction approaches.

The stability of the extractant in the solvent extraction system is important to the recycling of extractant in the industrial application. A solvent extraction–stripping circulation was designed to evaluate the stability of TC and the extraction efficiency for H_3PO_4 .²³ The extraction process was conducted at a phase ratio O/A of 1 and 298.2 K with $[\text{TC}] = 4.24 \text{ mol L}^{-1}$, $[\text{H}_3\text{PO}_4] = 7.06 \text{ mol L}^{-1}$. The loaded organic phase was stripped completely at O/A phase ratio of 1 and 323.2 K using deionized water. The organic phase recycled was then contacted with fresh phosphoric acid solution under identical operation condition repeatedly for 10 cycles. The variation of the distribution coefficient for H_3PO_4 and the density of the recycled solvent mixtures as a function of extraction cycles is shown in Fig. 8. The results show that the distribution coefficients change slightly and the average value of the distribution coefficients is 0.201. The density of the recycled solvent mixtures ρ also fluctuates slightly around 870 kg m^{-3} as the increase of the extraction cycles. Therefore, it can be concluded that the solvent mixtures TC have a high stability for the H_3PO_4 extraction.

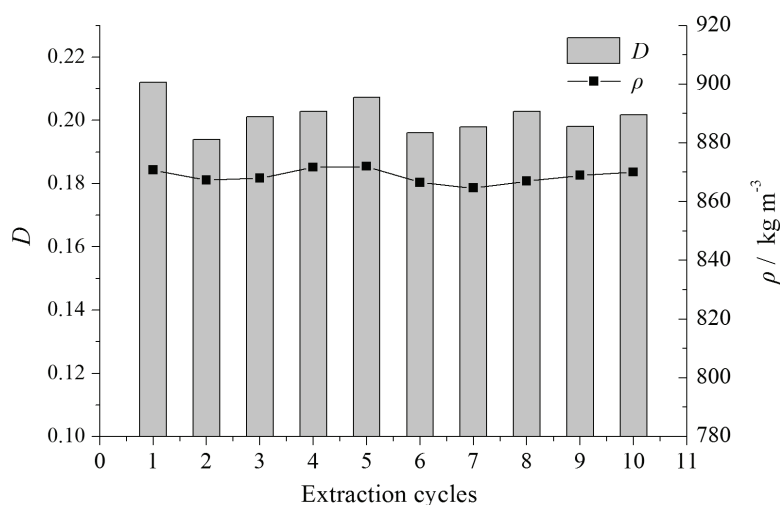


Fig. 8. Variation of the distribution coefficients and density of the solvent mixtures as a function of extraction cycles: $[\text{TC}] = 4.24 \text{ mol L}^{-1}$, $[\text{H}_3\text{PO}_4] = 7.06 \text{ mol L}^{-1}$, O / A = 1.

CONCLUSIONS

In this study, a new extraction system for purifying the wet process phosphoric acid using TBP and cyclohexanol mixtures was investigated. The optimum composition of the solvent mixtures, TC, was obtained to be 34 % TBP+66 % cyclohexanol giving consideration to the extraction yield and selectivity of

H₃PO₄. Based on the good mutual solubility of TBP and cyclohexanol, the equilibrium phase diagram of the system H₃PO₄–H₂O–TC at 298.2 K was obtained. The increase of initial H₃PO₄ and extractant concentration both had positive effects on the extraction. Thus the crude WPA should possibly undergo a pre-treatment process in order to increase the extraction efficiency as well as reducing the concentrations of the co-extracted impurities. The apparent stoichiometry of the extracted complexes was estimated to be 1.8H₃PO₄·2TC. The extraction of H₃PO₄ was exothermic with the value of the enthalpy change of –4.21 kJ mol^{–1} in the range of 298.2–333.2 K. The values of the enthalpy change of extraction for Fe³⁺, Mg²⁺, Al³⁺, F[–], SO₄^{2–} were 5.54, 24.54, 22.48, 18.84 and 7.40 kJ mol^{–1}, respectively, indicating that the extraction of these impurities was endothermic. *Via* a multi-stage counter-current extraction in a reciprocating plate extraction column, the solvent mixtures showed a high efficiency for purification of industrial WPA with an H₃PO₄ extraction yield of 85.08 % at 313.2 K. Based on the purification process of extraction, scrubbing and stripping, the extraction system with extractant recycling has good potential prospect for industrial application.

NOMENCLATURE

Roman symbols

| | | |
|-----------------------|----------------------------|----------------------------------|
| E | Extraction yield | % |
| $V_{(o)}, V_{(i)}$ | Volume | m ³ |
| D | Distribution coefficient | |
| $[C]$ | Molar concentration | mol dm ^{–3} |
| H | Enthalpy | J mol ^{–1} |
| $w, w_{(o)}, w_{(a)}$ | Weight percent | % |
| T | Temperature | K |
| V_1 | Molar volume of liquid | m ³ mol ^{–1} |
| K_{eq} | Equilibrium constant | |
| x, y | Stoichiometric coefficient | |
| r | Correlation coefficient | |

Greek symbols

| | | |
|----------|----------------------|--------------------|
| β | Separation factor | |
| δ | Solubility parameter | MPa ^{1/2} |
| ρ | Density | kg m ^{–3} |

SUPPLEMENTARY MATERIAL

Additional data and considerations are available electronically at the pages of journal website: <http://www.shd.org.rs/JSCS/>, or from the corresponding author on request.

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ИЗВОД
ПРОЦЕС ТЕЧНЕ ЕКСТРАКЦИЈЕ ЗА ПРЕЧИШЋАВАЊЕ ФОСФОРНЕ КИСЕЛИНЕ
ПОМОЋУ СМЕШЕ ТРИ-*n*-БУТИЛ-ФОСФАТА И ЦИКЛОХЕКСАНОЛА

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Течна екстракција је ефикасан и економичан поступак који се широко користи у технологији за пречишћавање фосфорне киселине (WPA). Рад се бави развојем растварача за екстракциони систем, ТС, са смешом три-*n*-бутил-фосфата (ТВР) и циклохексанола. Добијен је равнотежни фазни дијаграм система $\text{H}_3\text{PO}_4\text{-H}_2\text{O-ТС}$ на 298,2 К и атмосферском притиску. Испитивани су ефекти времена екстракције, концентрације фосфорне киселине, концентрације екстрагенса, температуре и запреминског односа фаза на ефикасност екстракције. Процењено је да су издвојени комплекси састава $1,8\text{H}_3\text{PO}_4\text{-2ТС}$. Процес екстракције H_3PO_4 је егзотерман, и израчуната је промена енталпије, ΔH . Смеша растварача је имала високу ефикасност од 85,08 % на 313,2 К за пречишћавање WPA вишестепеном противструјном екстракцијом у екстракционој колони са наизменичним струјањем преко плоча. Такође су процењени стабилност и ефикасност екстракције и рециклирања ТС за екстракцију H_3PO_4 .

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