

Dear Prof. Menka Petkovska:

Thank you for your letter and for the reviewers' comments concerning our manuscript entitled "Wet process phosphoric acid purification by solvent extraction using tri-n-butyl phosphate and cyclohexanol mixtures" **(Manuscript ID: 3994)**. We are submitting here our revised manuscript together with the itemized response to the reviewers' comments.

The comments are all valuable and very helpful for improving our paper, as well as the important guiding significance to our researches. We think the revised manuscript has been improved based on the comments of the editor and reviewers, and hope it will be accepted for publication in the **JOURNAL OF THE SERBIAN CHEMICAL SOCIETY**.

Journal Manuscript Code: 3994.

Article Title: Wet process phosphoric acid purification by solvent extraction using tri-n-butyl phosphate and cyclohexanol mixtures.

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Article Authors: Xing Li, Jun Li, Yang Jin, Ming Chen, Dongya Feng, Yunhai Guo.

Itemized Response to the Comments:

Comments to the authors from Reviewer #A:

1. Abstract: What is the TC?
2. Page 3: Define the meaning of "a new extraction system" Does it comprise a new extraction equipment? Does it comprise a new extractant, consisting from a mixture of TBP and cyclohexanol with equipment or something else? In the context of this sentence you have not any system, just a mixture of two known extractants.
3. Page 4: You may consider that the composition of WPA in Table 1 is only partly defined. Particularly in a view of other heavy and radioactive metal ions towards which TBP has high affinity! Have you controlled Fe $2+$ ions. Usually ferric and ferrous ions are in equilibrium wherever they are.
4. Page 5: what is the meaning of sickness here. Check this. I think it's a typing error.
5. Page 6: Definition quotations 1 to 3 are too obvious and could be omitted, here in the introductory part of the study. Moreover, this subtitle could be wholly omitted.
6. Page 7: Understandable and obvious. Inorganic acids can be successfully extracted by means of higher alcohols - see A Textbook of Hydrometallurgy by Fathi Habashi. See also the text relating to metal ions extraction by TBP.
7. Page 7: Typing error again! Did you mean previous?
8. Page 7: It is too early to talk about optimum conditions, isn't it?
9. Page 7: I couldn't realize where these percents come from. How did you point out these figures. Explain, please.
10. Page 8: Does the figures 2 and 3 deserve a wider discussion? I think yes. So, do it, please. Please give the volume of the organic and the aqueous phase!
11. Page 8: In the industrial WPA you have, according to the Table 1, approximately 400 mg/L of zinc. If you intend to purify row WPA by the solvent extraction, it would be very useful to consider the distribution of heavy metals, much more toxic than Mg, or Al ions are.
12. Page 9: Denote that it is Hildebrand solubility parameter!
13. Page 9: What is MPa $^{1/2}$? Is this mega pascal or what?
14. Page 10: Give more data in the caption about the triangle diagram and tie lines allowing to a reader to understand better the composition of phases after the extraction and phase separation. Particularly the mass of TC and phosphoric acid.
15. Page 11: Expectable and obvious. 66.66 % of cyclohexanol and balance TBP will

place the curve closer to the pure cyclohexanol

16. Page 11: Put the other information in the caption, as O/A, temperature, phase volume, etc. Or define closely the experimental conditions relating to the subtitle.

17. Page 12: Kinetics of inorganic compounds or ions is considerably high and takes approximately 10 to 15 minutes!

18. Page 12: There is no explanation why D decreases slightly with increasing O/A ration. The decrease is in the range of 20 %. No data about experiments reproducibility, so that it is not possible to split what is an experimental error and what is the phenomenon itself. Volume of phases is missing!

19. Page 12: Replace this subtitle with process stoichiometry.

20. Page 13: What it means "neutral form"? Molecular?

21. Page 14: For a better insight into the process stoichiometry it would be good to establish a diagram: equilibrium concentration of H_3PO_4 in the aqueous phase vs. relative concentration of the extractant expressed in mol/ mol of H_3PO_4 .

22. Page 14: Why 1.8? Can we assume, taking into account eventual experimental and analytical errors, that the stoichiometric number could be: $x = 2$? It seems to me more realistic than 1.8. Please give a comment.

23. Page 14: What is the O/A ratio here. Also give the absolute values of the phase volumes used in the experiments. It would be good to insert the extraction isotherm in its non-linear form in the Fig. 7, in the upper right corner.

24. Page 15: O/A ratio? The same remark as in the previous case. Put non-linear isotherm inside Fig. 8.

25. Page 15: Do not repeat yourself, please. Very similar sentence you already have above at the beginning of the previous subtitle.

26. Page 17: Effect of temperature on what? Extend the subtitle.

27. Page 17: Note somewhere in the text what phosphoric acid you used for this series of experiments - pure, or the industrial acid.

28. Page 17: Explain where this plot comes from? An introductory text is here missing, allowing to readership better understanding of the temperature effect. Otherwise, everything will stay at the phenomenological approach.

29. Page 19: Discussion on the diagrams from Fig. 10 and 11 is missing.

30. Page 20: "... leads to more solvent consumption ...". This sentence must be rewritten! Neither solvent (kerosene) in this case, nor extractant is consumed in solvent extraction. The losses of the organic phase are physical due to a bad phase

separation. Higher O: A ratio means higher investment costs and higher operating costs of handling bigger volumes of organic phase.

31. Page 22: Have you considered the parameters like the oscillation rate, residence time of phases in the extractor and other engineering parameters affecting the extraction, scrubbing and stripping stage?

32. Page 22: Frequency has no unit revolution per minute (rpm)! Or maybe I did not understand this sentence properly. Did you used an oscillation column or a stirring one of a mixer-settler type?

33. Page 22: Meaning of the AR is missing!

34. Page 22: Why did you choose the O/A ratios for scrubbing and stripping operations like these. Have you had some earlier research in this view or some literature evidences about? Give a comment about, please.

35. Page 23: Keep using term phosphoric acid instead of PA, as you did it before, or replace it with PA through the whole text.

36. Page 23: What this table is doing here. Explain its role in the frame of the previous text and its meaning. The title should be adjusted to be more understandable for a reader.

37. Page 23: "...the recycling solvent.." When you say solvent do you mean kerosene or TC? If you mean TC, please use the term extractant! Otherwise you'll make a great confusion to the readership.

38. Page 25: Based on what you have derived the conclusion expressed through the last sentence? You have not mentioned neither power consumption nor ecology aspect of the proposed purification process.

Response to the comments from Reviewer #A:

1. Abstract: What is the TC?

>>>**Re:** Thanks for your question. TC here is an abbreviation for "TBP + Cyclohexanol" which represents the solvent mixtures of tri-n-butyl phosphate and cyclohexanol. We use the abbreviation in the following text to simplify the expression and the explanation is given in the abstract after it first appears.

".....This present work focused on the development of a solvent extraction system, TC, representing tri-n-butyl phosphate (TBP) and cyclohexanol mixtures."

2. Page 3: Define the meaning of "a new extraction system" Does it comprise a new extraction equipment? Does it comprise a new extractant, consisting from a mixture of TBP and cyclohexanol with equipment or something else? In the

context of this sentence you have not any system, just a mixture of two known extractants.

>>>**Re:** Apologies for our inaccurate expression here. We use solvent mixtures of tri-n-butyl phosphate and cyclohexanol in this study which is 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 equipment we use in the continuous extraction study is a reciprocating plate extraction column. The “system” here represents the ternary phase system $\text{H}_3\text{PO}_4\text{--H}_2\text{O--TC}$ (TBP + Cyclohexanol) in the extraction which has not been revealed in other studies. Following the reviewer’s comment, the word “new” is removed in the revised manuscript to avoid misleading.

“In this present work, the research focused on developing a solvent extraction system using TBP and cyclohexanol mixtures, TC, with an optimum composition.”

3. Page 4: You may consider that the composition of WPA in Table 1 is only partly defined. Particularly in a view of other heavy and radioactive metal ions towards which TBP has high affinity! Have you controlled Fe 2+ ions. Usually ferric and ferrous ions are in equilibrium wherever they are.

>>>**Re:** Thanks for your question. In our analysis and data treatment process, the Fe^{2+} ions have already been converted to Fe^{3+} ions. As the reviewer points out, ferric and ferrous ions are usually in equilibrium. We have made an explanatory note under Table 1 as a comment to avoid misleading which is shown as below.

“.....The composition of the industrial WPA is shown in Table 1.

Table 1. Composition of the industrial WPA

Composition	H_3PO_4	SO_4^{2-}	F^-	Fe^{3+}_a	Al^{3+}	Mg^{2+}	Zn^{2+}	Cr^{3+}
wt. %	65.74	3.28	0.334	0.377	0.659	0.732	0.041	0.004

a. ferrous ions have been converted to ferric ions as a sum.”

4. Page 5: what is the meaning of sickness here. Check this. I think it's a typing error.

>>>**Re:** Just as the reviewer says, it is a typing error. We should have meant by “thickness” here. The continuous extraction of the industrial WPA was carried out in a reciprocating plate extraction column. The column plates are several disks and the thickness of each plate is 2 mm. This typing error has been rectified and we are very grateful to the reviewer for the detailed insight. The correction is shown as follows.

“.....The thickness and diameter of the plates are 2 mm and 20 mm, respectively.....”

5. Page 6: Definition quotations 1 to 3 are too obvious and could be omitted, here in the introductory part of the study. Moreover, this subtitle could be wholly omitted.

>>>**Re:** Following the reviewer's suggestion, we have omitted the three equations as well as this subtitle in the introduction here.

6. Page 7: Understandable and obvious. Inorganic acids can be successfully extracted by means of higher alcohols - see A Textbook of Hydrometallurgy by Fathi Habashi. See also the text relating to metal ions extraction by TBP.

>>>**Re:** We have read the documents the reviewer refers here so as to get a better understanding on the results. We appreciate the reviewer very much for the suggestion and guidance.

7. Page 7: Typing error again! Did you mean previous?

>>>**Re:** Apologize for the typing error. We should have meant by "previous" here. We have worked carefully to fix our vocabulary and grammar in the revised manuscript. The correction in this section is shown as below.

".....Cation impurities Fe^{3+} , Mg^{2+} , Al^{3+} have obviously higher separation factors than anion impurities F^- and SO_4^{2-} do, which is in agreement with previous researches."

8. Page 7: It is too early to talk about optimum conditions, isn't it?

>>>**Re:** Following the reviewer's suggestion, we have revised the expression in this section.

".....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."

9. Page 7: I couldn't realize where these percents come from. How did you point out these figures. Explain, please.

>>>**Re:** These percents are derived from our experimental raw data. We did seven experimental points with the weight percent w of cyclohexanol in the solvent mixtures (TBP+ cyclohexanol) ranging from 0 to 100%. The percents are 0%, 26%, 40%, 53%, 66%, 80% and 100%. We use Figure 1 and Figure 2 to present and manage the results instead of revealing every specific data numerically.

10. Page 8: Does the figures 2 and 3 deserve a wider discussion? I think yes. So, do it, please. Please give the volume of the organic and the aqueous phase!

>>>**Re:** Thanks for this comment. Relevant discussion contents have been added in this section which is shown as below.

"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 ml and 56 ml, respectively. The equilibrium distribution results for two different concentration of H_3PO_4 in the initial aqueous phase are compared in Figure 2. The results show that higher cyclohexanol concentration in the solvent mixtures had

better H₃PO₄ extraction efficiency. The increase of H₃PO₄ in the initial aqueous solution from 6.46 mol L⁻¹ 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 Fe³⁺, Mg²⁺, Al³⁺, F⁻ and SO₄²⁻ are shown in Figure 3 with the concentration of H₃PO₄ 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 Fe³⁺, Mg²⁺, Al³⁺ had obviously higher separation factors than anion impurities F⁻ and SO₄²⁻ did, which is in agreement with previous researches.¹⁴ Considering the H₃PO₄ extraction efficiency and selectivity of H₃PO₄, 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.”

11. Page 8: In the industrial WPA you have, according to the Table 1, approximately 400 mg/L of zinc. If you intend to purify row WPA by the solvent extraction, it would be very useful to consider the distribution of heavy metals, much more toxic than Mg, or Al ions are.

>>>**Re:** Thanks for this suggestion. In this study, we choose the three metal elements, Fe, Mg, Al for research due to their high volume in the raw WPA. These metal elements also have considerable effect on the neutralization and crystallization process in the production of phosphate. On the other hand, just as the reviewer mentions, TBP has high affinity towards some heavy metals and radioactive metals. Consequently, solvent extraction using TBP and cyclohexanol will have poor selectivity for H₃PO₄ among those heavy and radioactive metals which though are of comparatively low volume in WPA. Considering the two factors, we did not investigate the distribution of heavy metals. Furthermore, we are studying some other extractants for the removal of those heavy metals if we want to produce phosphoric acid of higher grade. We appreciate it very much for the reviewer’s suggestion and guidance.

12. Page 9: Denote that it is Hildebrand solubility parameter!

>>>**Re:** Appreciation for the suggestion and guidance. We add this in the section which is shown as follows.

“.....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).”

13. Page 9: What is MPa1/2? Is this mega pascal or what?

>>>**Re:** Yes, the “MPa” here is mega pascal. The Hildebrand solubility parameter δ is calculated as

$$\delta = \sqrt{\frac{\Delta H - RT}{V_l}},$$

which is generally measured in MPa^{1/2} or MPa^{0.5} (SI units).

14. Page 10: Give more data in the caption about the triangle diagram and tie lines allowing to a reader to understand better the composition of phases after the extraction and phase separation. Particularly the mass of TC and phosphoric acid.

>>>**Re:** Following the reviewer's suggestion, we have added the equilibrium data 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 in the paper which is shown as below.

“.....The composition data of initial mixtures and equilibrium phases are given in Table 2.

Table 2. Equilibrium data of the extraction system H_3PO_4 (1)– H_2O (2)–TC (34% TBP + 66% Cyclohexanol) (3) at 298.2K ^a

Initial mixtures			Aqueous phase			Organic phase		
w1	w2	w3	w1	w2	w3	w1	w2	w3
51.00	16.00	33.00	69.53	25.49	4.98	48.70	11.97	39.33
48.00	18.00	34.00	64.72	30.78	4.50	41.98	11.92	46.10
40.00	23.00	37.00	55.75	40.41	3.85	31.25	11.62	57.13
33.00	27.00	40.00	48.52	48.46	3.02	22.40	10.55	67.05
26.00	31.00	43.00	41.22	55.84	2.94	17.07	9.78	73.15
18.00	36.00	46.00	35.89	61.40	2.71	14.37	9.20	76.44
11.00	39.00	50.00	26.47	70.52	3.01	7.00	8.89	84.11
8.28	41.72	50.00	15.49	81.26	3.25	2.22	8.42	89.36
	50.00	50.00		97.70	2.30		8.14	91.86

^a w is the mass fraction (%) ; blanks: do not exist or not detected.”

15. Page 11: Expectable and obvious. 66.66 % of cyclohexanol and balance TBP will place the curve closer to the pure cyclohexanol

>>>**Re:** Thanks for your comment. Just as the reviewer suggests, the distribution curve for TC does lie between those two for pure TBP and cyclohexanol and is comparatively closer to that of pure cyclohexanol.

16. Page 11: Put the other information in the caption, as O/A, temperature, phase volume, etc. Or define closely the experimental conditions relating to the subtitle.

>>>**Re:** In this section, the H_3PO_4 equilibrium distribution between the aqueous and organic phases for the extraction system $\text{H}_3\text{PO}_4\text{--H}_2\text{O--TC}$ is obtained in comparison with other two extraction systems using TBP and cyclohexanol separately that are $\text{H}_3\text{PO}_4\text{--H}_2\text{O--TBP}$ and

H₃PO₄-H₂O-Cyclohexanol. The experiment was conducted according to the procedure of equilibrium studies in which certain mass of H₃PO₄, H₂O and extractant were mixed. Thus, the O/A as well as the volumes is not remained constantly for each experimental point. We have given the temperature of equilibrium in the caption.

17. Page 12: Kinetics of inorganic compounds or ions is considerably high and takes approximately 10 to 15 minutes!

>>>**Re:** We are not sure if we have fully understood the meaning of this comment here. The experiments of equilibrium and batch extraction studies are all conducted under equilibrium condition. In this section, the results show that the distribution coefficients increase rapidly in the range of 0-5 min and then remain almost constant which indicates that it takes approximately 5-10 min to attain the equilibrium for extraction. We choose 10 min as extraction time in the further experiments on batch extraction studies in order to ensure the extraction equilibrium is fully achieved.

18. Page 12: There is no explanation why D decreases slightly with increasing O/A ration. The decrease is in the range of 20 %. No data about experiments reproducibility, so that it is not possible to split what is an experimental error and what is the phenomenon itself. Volume of phases is missing!

>>>**Re:** Thanks for this comment. The results show that the increase of phase ratio leads to considerable decrease in the distribution coefficient of H₃PO₄. We are sure that it is the objective experiment phenomenon rather than an experimental error. This is because when the H₃PO₄ 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 H₂O into the organic phase by co-extraction, which is equivalent to the raffinate phase being concentrated.^[a] Thus, distribution coefficient of H₃PO₄ decreases correspondingly with higher phase ratio. We have added the explanation to the text as well as the initial volume which is shown as follows.

“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 H₃PO₄ versus the extraction time with three different phase ratio O / A from 2.0 to 4.0 are shown in Figure 6. The 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 H₃PO₄. This is because when the H₃PO₄ 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 H₂O into the organic phase by co-extraction, which is equivalent to the raffinate phase being concentrated.¹² Thus, distribution coefficient of H₃PO₄ decreases correspondingly with higher phase ratio.”

19. Page 12: Replace this subtitle with process stoichiometry.

>>>**Re:** Following the reviewer's suggestion, we have changed this subtitle to "process stoichiometry" in the text.

20. Page 13: What it means "neutral form"? Molecular?

>>>**Re:** Thanks for your question. In the study of process stoichiometry, we assume the phosphoric acid transfers into the organic phase in the form of H_3PO_4 molecule. We have revised the expression in this section to make it more understandable.

".....Before the application of the solvent mixtures, it is important to know the process stoichiometry, which can be determined by equilibrium studies. For the simplification of analysis method, the assumption is employed in which the binary solvent mixtures (34% TBP + 66% cyclohexanol) are treated as an entirety, TC. Then assuming that the H_3PO_4 transfers from the aqueous phase into the organic phase in the form of H_3PO_4 molecule and exists in the organic phase as a complex of the form $x\text{H}_3\text{PO}_4 \cdot y\text{TC}$"

21. Page 14: For a better insight into the process stoichiometry it would be good to establish a diagram: equilibrium concentration of H_3PO_4 in the aqueous phase vs. relative concentration of the extractant expressed in mol/ mol of H_3PO_4 .

>>>**Re:** Following the reviewer's suggestion, we have inserted the non-linear isotherm in the upper right corner in the Figure 7 which shows the equilibrium concentration of H_3PO_4 in the aqueous and organic phases. We appreciate the reviewer's suggestion and guidance here.

22. Page 14: Why 1.8? Can we assume, taking into account eventual experimental and analytical errors, that the stoichiometric number could be: $x = 2$? It seems to me more realistic than 1.8. Please give a comment.

>>>**Re:** Thanks for this comment. In this section, we use regression analysis to estimate the process stoichiometry 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, $\text{H}_3\text{PO}_4 \cdot \text{TBP}$, $\text{H}_3\text{PO}_4 \cdot 2\text{TBP}$, $\text{H}_3\text{PO}_4 \cdot 3\text{TBP}$, $\text{H}_3\text{PO}_4 \cdot \text{Cyclohexanol}$. If we made the approximation to be $2\text{H}_3\text{PO}_4 \cdot 2\text{TC}$, it means that the extracted complexes are confined to be $\text{H}_3\text{PO}_4 \cdot \text{TBP}$ and $\text{H}_3\text{PO}_4 \cdot \text{Cyclohexanol}$. However, we have not excluded the possibility of other two complexes that are $\text{H}_3\text{PO}_4 \cdot 2\text{TBP}$ and $\text{H}_3\text{PO}_4 \cdot 3\text{TBP}$. Therefore, to be cautious and objective, we estimated it to be $1.8\text{H}_3\text{PO}_4 \cdot 2\text{TC}$. Furthermore, the structures of the extracted complexes and the formation process have not been determined. We are doing further research to clarify these issues. We appreciate the reviewer's suggestion and guidance here.

23. Page 14: What is the O/A ratio here. Also give the absolute values of the phase volumes used in the experiments. It would be good to insert the extraction isotherm in its non-linear form in the Fig. 7, in the upper right corner.

>>>**Re:** Following the reviewer's suggestion, we have inserted the non-linear isotherm in the upper right corner in the Figure 7.

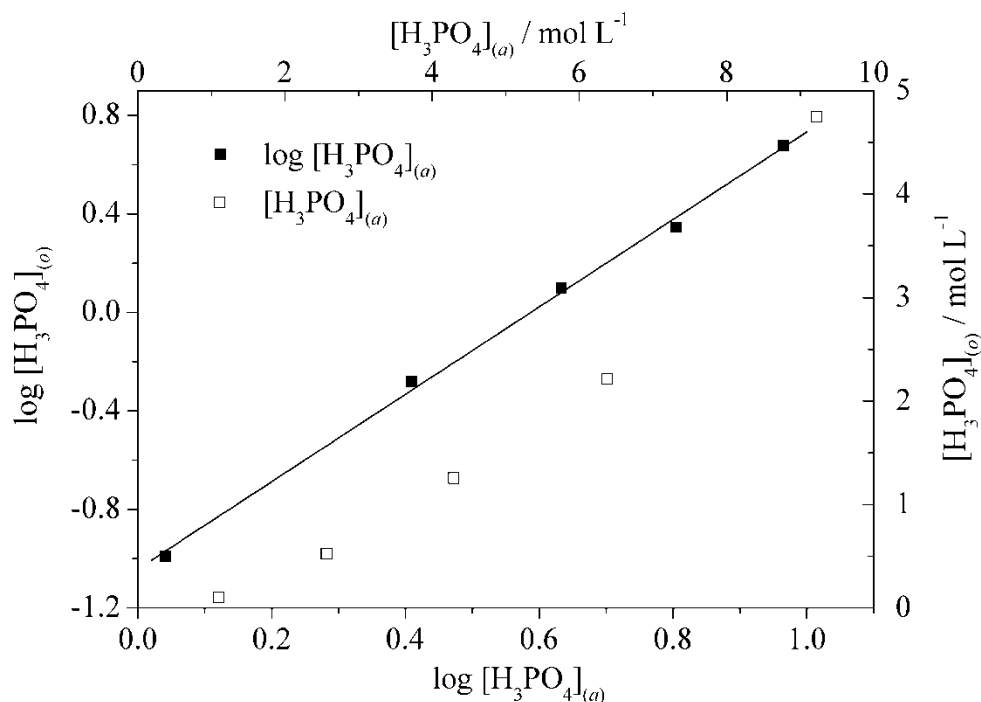


Figure 7. Equilibrium isotherms for the analytical concentrations of the organic phase for the extraction: $[TC] = 4.24 \text{ mol L}^{-1}$, $O / A = 4$, $T = 298.2 \text{ K}$; (■) $\log [H_3PO_4]_{(a)}$; (□) $[H_3PO_4]_{(a)}$.

24. Page 15: O/A ratio? The same remark as in the previous case. Put non-linear isotherm inside Fig. 8.

>>>Re: Following the reviewer's suggestion, we have also inserted the non-linear isotherm in the upper right corner in the Figure 8. We appreciate this valuable guidance in this section.

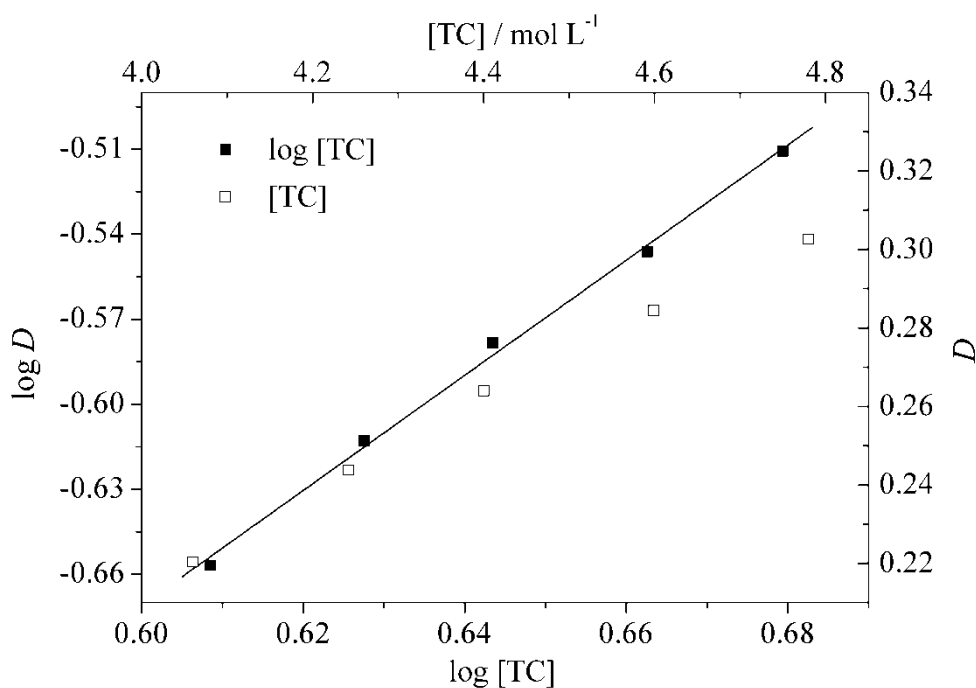


Figure 8. Effect of extractant concentration on the distribution coefficient of H_3PO_4 : $[\text{H}_3\text{PO}_4] = 9.16 \text{ mol L}^{-1}$, $\text{O} / \text{A} = 4$, $T = 298.2 \text{ K}$; (■) $\log [\text{TC}]$; (□) $[\text{TC}]$.

25. Page 15: Do not repeat yourself, please. Very similar sentence you already have above at the beginning of the previous subtitle.

>>>**Re:** We have cut out of the repetition and reorganized the expression in this section which is shown as below

“Based on the simplified regression analysis method above, the extraction process stoichiometry of H_3PO_4 extraction using TC was obtained. The apparent extracted complex of the extraction reaction in Equation (2) 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.....”

26. Page 17: Effect of temperature on what? Extend the subtitle.

>>>**Re:** Following the reviewer’s comment, we have extended the subtitle as below.

“Effect of temperature on the extraction of H_3PO_4 and impurities”

27. Page 17: Note somewhere in the text what phosphoric acid you used for this series of experiments - pure, or the industrial acid.

>>>**Re:** We have added this content in the section which is shown as below.

“The effect of temperature in the range of 298.2-333.2 K on the extraction for the WPA was studied.....”

28. Page 17: Explain where this plot comes from? An introductory text is here missing, allowing to readership better understanding of the temperature effect. Otherwise, everything will stay at the phenomenological approach.

>>>**Re:** Thanks for your valuable suggestion. We have reorganized the text in this section in order to avoid confusion and misleading for readers.

“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 mol L^{-1} and 9.16 mol L^{-1} , respectively.

According to the Van’t Hoff equation²³

$$\frac{\Delta \log D}{\Delta(1/T)} = -\frac{\Delta H}{2.303R} \quad (9),$$

plots of $\log D$ versus $[T^{-1} / 10^{-3}]$ are shown in Figure 10 and Figure 11. Then the values of the enthalpy change of extraction for H_3PO_4 and impurities can be calculated. Using regression analysis, the following relations can be established from the obtained data:

For H_3PO_4 extraction:

$$\log D = -1.35 + 0.22 \times [T^{-1} / 10^{-3}], \quad r = 0.999 \quad (10)$$

For Fe^{3+} extraction:

$$\log D = -0.89 - 0.29 \times [T^{-1} / 10^{-3}], \quad r = 0.998 \quad (11)$$

For Mg^{2+} extraction:

$$\log D = 2.14 - 1.28 \times [T^{-1} / 10^{-3}], \quad r = 0.999 \quad (12)$$

For Al^{3+} extraction:

$$\log D = 1.88 - 1.17 \times [T^{-1} / 10^{-3}], \quad r = 0.999 \quad (13)$$

For F^{-} extraction:

$$\log D = 1.43 - 0.98 \times [T^{-1} / 10^{-3}], \quad r = 0.997 \quad (14)$$

For SO_4^{2-} extraction:

$$\log D = -0.05 - 0.39 \times [T^{-1} / 10^{-3}], \quad r = 0.999 \quad (15)$$

The results show that the distribution coefficients of H_3PO_4 increase with lower temperature.....”

29. Page 19: Discussion on the diagrams from Fig. 10 and 11 is missing.

>>>**Re:** We have restructured the discussion in this section to clarify the effect of temperature on the extraction of H_3PO_4 and impurities which is shown as follows.

“The results show that the distribution coefficients of H_3PO_4 increase with a decrease in temperature. In the range of 298.2-333.2 K, the value of the enthalpy change of H_3PO_4 extraction $\Delta H = -4.21 \text{ kJ mol}^{-1}$ was calculated from the slope of the linear relation in Figure 10, which indicates the extraction of H_3PO_4 is exothermic. Increasing temperature thus has adverse effects on the extraction process. According to Equation (11)-(15), the values of the enthalpy change ΔH of extraction for Fe^{3+} , Mg^{2+} , Al^{3+} , F^{-} , SO_4^{2-} were 5.54, 24.54, 22.48, 18.84, 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 $\text{Mg}^{2+} > \text{Al}^{3+} > \text{F}^{-} > \text{SO}_4^{2-} > \text{Fe}^{3+}$. 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.”

30. Page 20: "... leads to more solvent consumption ...". This sentence must be rewritten! Neither solvent (kerosene) in this case, nor extractant is consumed in solvent extraction. The losses of the organic phase are physical due to a bad phase separation. Higher O: A ratio means higher investment costs and higher operating costs of handling bigger volumes of organic phase.

>>>**Re:** Apologize for our improper expression here. Just as the reviewer comments, by extractant recycling, there is only a little loss of extractant due to the equilibrium solubility of extractant in the raffinate phase and bad separation. We have revised the expression in this section which is shown as below. We appreciate very much for the review’s guidance here.

“.....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.”

31. Page 22: Have you considered the parameters like the oscillation rate,

residence time of phases in the extractor and other engineering parameters affecting the extraction, scrubbing and stripping stage?

>>>**Re:** Thanks for this question. The column structure, oscillation rate and other engineering parameters as well as the resident time of phases in the reciprocating plate column for the continuous purification operation were studied in another article of us which has not been published by far. We appreciate the reviewer's insight and guidance here.

32. Page 22: Frequency has no unit revolution per minute (rpm)! Or maybe I did not understand this sentence properly. Did you used an oscillation column or a stirring one of a mixer-settler type?

>>>**Re:** Apologize for our improper expression here. We did our continuous purifying operations in the reciprocating plate column. The reciprocating motion of the plates was driven by a motor which was running at 175 rpm during the experiment. So the vibration frequency of the column can be converted as: $175/60 \text{ Hz} \approx 3 \text{ Hz}$. We have rectified the expression in the text which is shown as follows.

“.....The vibration frequency of the column was 3 Hz and the amplitude was 25 mm.....”

33. Page 22: Meaning of the AR is missing!

>>>**Re:** Thanks for pointing this out. We have added the meaning of AR after it in the section.

“.....The scrubbing operation was conducted using diluted AR (analytical reagent) phosphoric acid ($[\text{H}_3\text{PO}_4] = 4.23 \text{ mol L}^{-1}$) to strengthen the removing efficiency and reduce the consumption of phosphoric acid.....”

34. Page 22: Why did you choose the O/A ratios for scrubbing and stripping operations like these. Have you had some earlier research in this view or some literature evidences about? Give a comment about, please.

>>>**Re:** In this manuscript, we perform the extraction, scrubbing and stripping operation to make up a complete process of purification. As mentioned in the previous “**Comment 31**”, the structure parameters as well as the resident time, temperature, phase ratio and other operating parameters for the continuous purification operation were studied in another article of us which has not been published by far. Thus those parameters are not discussed in this section.

35. Page 23: Keep using term phosphoric acid instead of PA, as you did it before, or replace it with PA through the whole text.

>>>**Re:** Following the reviewer's suggestion, we have replaced “PA” with “phosphoric acid” in this section for the consistency of expression.

“.....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.....”

36. Page 23: What this table is doing here. Explain its role in the frame of the previous text and its meaning. The title should be adjusted to be more understandable for a reader.

>>>**Re:** Thanks for this comment. This table here shows the phosphoric acid composition of samples taken from the extraction, scrubbing and stripping process in the continuous operation. We use this table to indicate the results of each continuous operation as well as the purified phosphoric acid. Following the reviewer's suggestion, we have revised the title of the table to make it more understandable and it is shown as below.

“.....The phosphoric acid composition of samples taken from the extraction, scrubbing and stripping process in the continuous operation is shown in Table 3.”

Table 3. 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

37. Page 23: "..the recycling solvent.." When you say solvent do you mean kerosene or TC? If you mean TC, please use the term extractant! Otherwise you'll make a great confusion to the readership.

>>>**Re:** Appreciation for the suggestion. We have replaced “solvent” with “extractant” in this section to avoid the confusion and misleading for readers.

“The stability of the extractant in the solvent extraction system is important to the recycling of extractant in the industrial application.....”

38. Page 25: Based on what you have derived the conclusion expressed through the last sentence? You have not mentioned neither power consumption nor ecology aspect of the proposed purification process.

>>>**Re:** Thanks for this comment. In this manuscript, we did not study the power consumption or pollution of this purification process. But we will consider the factors in the further research. We have advised the expression here which is shown as below.

“.....Based on the purification process of extraction, scrubbing and stripping, the extraction system with extractant recycling has good potential prospect for industrial application.”

Reference:

^[a] X. Li, J. Li, J. Luo, Y. Jin, D. Zou, *Solvent Extr. Res. Dev.* **24** (2017) 23

Comments to the authors from Reviewer #B:

The manuscript deals with the purification of wet process phosphoric acid by mix solvent extraction. There are a lot of data and results of different nature, not supported by adequate explanations and discussion. It should be clearly distinguished which results are completely new and which are already reported in the literature.

1. Instead of repeating what was already said in the Abstract section, the last paragraph in the Introduction should clearly emphasize the aim of the investigation. In addition English has to be improved.
2. It is not clear where the equation (7) comes from. This equation states that $[H_3PO_4]_o = x[xH_3PO_4 \cdot yTC]_o$?
3. A comparison of IR spectrum of TC, before and after extraction of phosphoric acid, shows only one big difference by appearance of band at 1647 cm^{-1} . This difference is not clearly explained.
4. Why in the regression analysis applied for examination of the effect of temperature on extraction, $\log D$ is plotted against T^{-1} ?
5. In my opinion it would be better to split the existing manuscript into two parts, the second considering Continuous purification process and Stability of solvent mixtures. The manuscript could be published in the JSCS after a major revision

Response to the comments from Reviewer #B:

1. Instead of repeating what was already said in the Abstract section, the last paragraph in the Introduction should clearly emphasize the aim of the investigation. In addition English has to be improved.

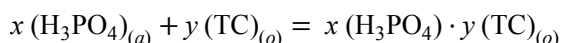
>>>**Re:** Sorry for not emphasizing the aim of the investigation clearly in this section. Related content has been added in the paper which is shown as below.

“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 $H_3PO_4-H_2O-TC$ 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.”

2. It is not clear where the equation (7) comes from. This equation states that $[H_3PO_4]_o = x[xH_3PO_4 \cdot yTC]_o$?

>>>**Re:** Thanks for pointing this out. In this section, we assume that H₃PO₄ transfers from the aqueous phase into the organic phase in a neutral form. The extraction reaction can be described as:



where x and y are the stoichiometric coefficients of H₃PO₄ and TC in the reaction above, respectively. The subscripts a and o stand for the aqueous and organic phases, respectively. It is assumed that the H₃PO₄ exists in the organic phase as a complex of the form xH₃PO₄ · yTC. ^[a] Thus, the molar concentration of [xH₃PO₄·yTC]_o multiplied by the stoichiometric coefficient of H₃PO₄ in the extracted complex, x, is equal to the molar concentration of H₃PO₄ extracted in the organic phase. Mathematically, that can be expressed as $[H_3PO_4]_o = x[xH_3PO_4 \cdot yTC]_o$ for the following method based on slope analysis.

3. A comparison of IR spectrum of TC, before and after extraction of phosphoric acid, shows only one big difference by appearance of band at 1647 cm⁻¹. This difference is not clearly explained.

>>>**Re:** Apologies for our unclear comment on this section. Modified and supplemented content has been added in the paper which is shown as follows:

“Another obvious difference between the spectra of TC before and after extraction is the appearance of bands at 1647 cm⁻¹, which represents O–H bond deformation vibrations. This is because certain amounts of –OH bonds for H₂O were extracted into the organic phase after extraction. The variation is mainly attributed to the partial solubility of water in the extractant, which is in agreement with the result of phase equilibrium study of the system H₃PO₄–H₂O–TC. Moreover, the –OH bond stretching vibration at 3380 cm⁻¹ in cyclohexanol is shifted to a higher frequency at 3395 cm⁻¹ and the peak widened. Based on these changes, it is concluded that H₃PO₄ was extracted into the organic phase as well as H₂O molecules after extraction. ^{20,,}

However, to be honest, the structures of the extracted complexes and the formation process have not been determined definitely. We are doing further experiments to clarify these issues.

4. Why in the regression analysis applied for examination of the effect of temperature on extraction, logD is plotted against T⁻¹?

>>>**Re:** Thanks for your question. According to the Van't Hoff equation ^[b],

$$\frac{\Delta \log D}{\Delta(1/T)} = -\frac{\Delta H}{2.303R}$$

the value of the enthalpy change of H₃PO₄ and impurities can be calculated from the plots of log D versus [T⁻¹ / 10⁻³]. From the plots, we can also learn the effect of temperature on the extraction of H₃PO₄ and impurities from the variation of D at different temperature. The regression analysis was used here to process the phenomenological results. This section has been restructured in the paper to clarify this further which is shown as below:

“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 H₃PO₄ in the initial aqueous phase remained as 4.24 mol L⁻¹ and 9.16 mol L⁻¹, respectively.

According to the Van't Hoff equation²³

$$\frac{\Delta \log D}{\Delta(1/T)} = -\frac{\Delta H}{2.303R} \quad (9),$$

plots of log D versus [T⁻¹ / 10⁻³] are shown in Figure 10 and Figure 11. Then the values of the enthalpy change of extraction for H₃PO₄ and impurities can be calculated. Using regression analysis, the following relations can be established from the obtained data:”

5. In my opinion it would be better to split the existing manuscript into two parts, the second considering Continuous purification process and Stability of solvent mixtures.

>>>**Re:** Thanks for your suggestion. In our consideration, the experimental procedure of this manuscript mainly consists of three sections that are equilibrium studies, batch extraction studies and continuous extraction studies. Each section has its own scheme to integrate and serve the study. The solvent extraction-stripping circulation is designed to evaluate the stability of extractant and the extraction efficiency for H₃PO₄, which is not only important for the continuous purification process, but also appraises the application prospect of the extractant.

Following the reviewer's suggestion, we have also worked to fix our grammar in the revised manuscript, reformatted it and have edited the English expression for clarity by careful revision. We are very grateful to the reviewers for the detailed advice.

Reference:

^[a] Y. Jin, D. Zou, S. Wu, Y. Cao, J. Li, Ind. Eng. Chem. Res. **54** (2015) 108.

^[b] U. K. Deiters, Fluid Phase Equilibr. **336** (2012) 22.

Thanks again for your attention and comments on this paper.

Best regards

Sincerely yours

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