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Supplementary material

SUPPLEMENTARY MATERIAL TO

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

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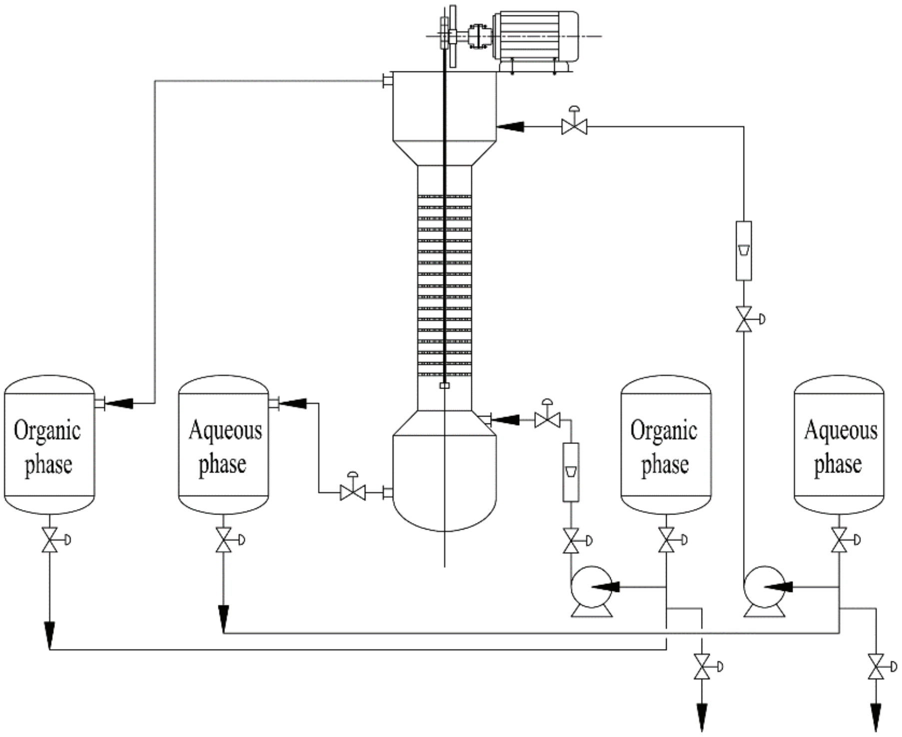

Fig. S-1. Schematic flow diagram of the reciprocating plate extraction column.

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TABLE S-I. Equilibrium data of the extraction system H_3PO_4 (1)$-$$H_2O$ (2)$-$TC (34 % TBP + 66 % cyclohexanol) (3) at 298.2K and atmospheric pressure; *w* is the mass fraction (mass %); blanks: do not exist or not detected

Initial mixture			Aqueous phase			Organic phase		
w_1	w_2	w_3	w_1	w_2	w_3	w_1	w_2	w_3
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

Process stoichiometry

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 $x H_3PO_4 \cdot y TC$[1,2] The extraction reaction can be described as:

$$x\,H_3PO_{4(a)} + y\,TC_{(o)} = x\,H_3PO_4 \cdot y\,TC_{(o)} \tag{S-1}$$

where *x* and *y* are the stoichiometric coefficients of H_3PO_4 and TC in the reaction above, respectively. The subscripts a and o stand for the aqueous and organic phases, respectively.

The equilibrium constant (K_{eq}) of the extraction reaction in Eq. (S-1) is:

$$K_{eq} = \frac{[x\ \mathrm{H_3PO_4} \cdot y\ \mathrm{TC}]_{(o)}}{[\mathrm{H_3PO_4}]_{(a)}{}^{x} \cdot [\mathrm{TC}]_{(o)}{}^{y}} \tag{S-2}$$

The distribution coefficient of H_3PO_4 can be calculated as

$$D = \frac{[H_3PO_4]_{(o)}}{[H_3PO_4]_{(a)}} = \frac{x\ [x\ H_3PO_4 \cdot y\ \mathrm{TC}]_{(o)}}{[H_3PO_4]_{(a)}} \tag{S-3}$$

An indirect approximation method based on slope analysis was used to verify the stoichiometry of the extracted species. Inserting Eq. (S-3) into Eq. (S-2) and then taking the logarithm of both sides of the resulting equation leads to the expression:

$$\log D = \log xK_{eq} + (x-1)\log[\mathrm{H_3PO_4}]_{(a)} + y\log[\mathrm{TC}]_{(o)} \tag{S-4}$$

Inserting Eq. (S-3) into Eq. (S-4) gives:

$$\log[H_3PO_4]_{(o)} = \log xK_{eq} + x\log[H_3PO_4]_{(a)} + y\log[TC]_{(o)} \qquad \text{(S-5)}$$

After determining the values of x and y in the extraction reaction in Eq. (S-1), the stoichiometry of the extracted complexes and the process can be obtained then.

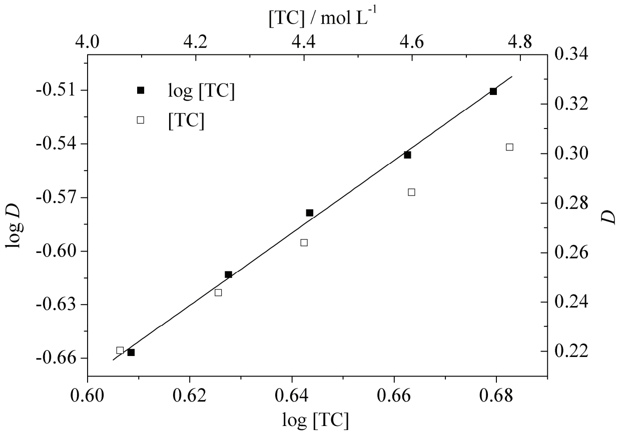

Fig. S-2. Effect of extractant concentration on the distribution coefficient of H_3PO_4: $[H_3PO_4] = 9.16$ mol L^{-1}, O/A = 4, $T = 298.2$ K; ■) log [TC]; □) [TC].

A comparison of the IR spectrum of TC before (A) and after (B) extraction of H_3PO_4 is shown in Figure S-3. The IR spectrum of TC shows a band at 1024 cm^{-1} which corresponds to the P−O−C bond stretching vibration of TBP. The peak at 1024 cm^{-1} broadens after extraction due to the superposition of the vibrations of P−O−C and P−O−H. The peak at 1067 cm^{-1} may be assigned to the stretching vibration of the C−O bond in cyclohexanol. Because of hydrogen bond formation after extraction, the electron cloud is distributed more averagely and the C−O bond stretching vibration frequency is lowered to 1058 cm^{-1}. A band at 1272 cm^{-1} is ascribed to the P=O bond stretching vibration of TBP. The peak at 1272 cm^{-1} shifted to lower frequency at 1253 cm^{-1}, which indicates that hydrogen bonds (P=O···H) formed between the oxygen atom of the phosphoryl group of the TBP molecule and the hydrogen atom of the H_3PO_4 molecule. 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 H_2O 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 H_3PO_4−H_2O−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 H_3PO_4 was extracted into the organic phase as well as H_2O molecules after extraction.[2,3] However, the structures of the extracted complexes and the formation process have not been determined. Further efforts are needed to clarify these issues.

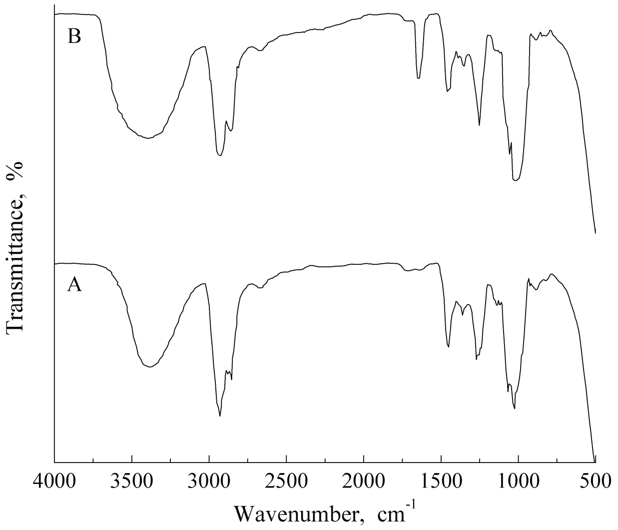

Fig. S-3. IR spectrum of TC before (A) and after (B) extraction.

Effect of temperature on the extraction of H_3PO_4 and impurities

According to the Van't Hoff equation:[4]

$$\frac{\Delta \log D}{\Delta(1/T)} = -\frac{\Delta H}{2.303R} \qquad \text{(S-6)}$$

plots of log D versus T^{-1} are shown in Figs. S-4 and S-5. 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:

$$\log D = -1.35 + 0.22 \times (T^{-1}/10^{-3}),\ r = 0.999 \qquad \text{(S-7)}$$

For Fe^{3+} extraction:

$$\log D = -0.89 - 0.29 \times (T^{-1}/10^{-3}),\ r = 0.998 \qquad \text{(S-8)}$$

For Mg^{2+} extraction:

$$\log D = 2.14 - 1.28 \times (T^{-1}/10^{-3}),\ r = 0.999 \qquad \text{(S-9)}$$

For Al^{3+} extraction:

$$\log D = 1.88 - 1.17 \times (T^{-1} / 10^{-3}), \ r = 0.999 \qquad \text{(S-10)}$$

For F^- extraction:

$$\log D = 1.43 - 0.98 \times (T^{-1} / 10^{-3}), \ r = 0.997 \qquad \text{(S-11)}$$

For SO_4^{2-} extraction:

$$\log D = -0.05 - 0.39 \times (T^{-1} / 10^{-3}), \ r = 0.999 \qquad \text{(S-12)}$$

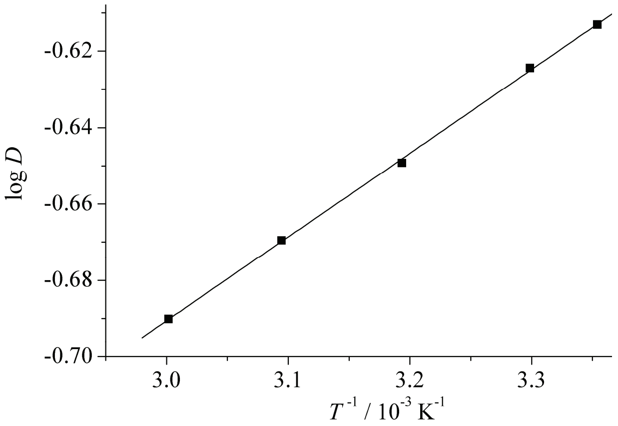

Fig. S-4. Effect of temperature on distribution coefficients of H_3PO_4: [TC] = 4.24 mol L^{-1}, [H_3PO_4] = 9.16 mol L^{-1}, O/A = 4.

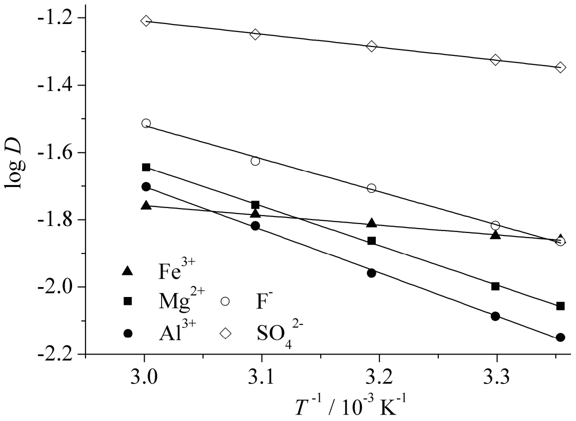

Fig. S-5. Effect of temperature on distribution coefficients of Fe^{3+} , Mg^{2+}, Al^{3+}, F^- and SO_4^{2-}: [TC] = 4.24 mol L^{-1}, [H_3PO_4] = 9.16 mol L^{-1}, O/A = 4; ▲) Fe^{3+}; ●) Mg^{2+}; ■) Al^{3+}; ○) F^-; ◇) SO_4^{2-}.

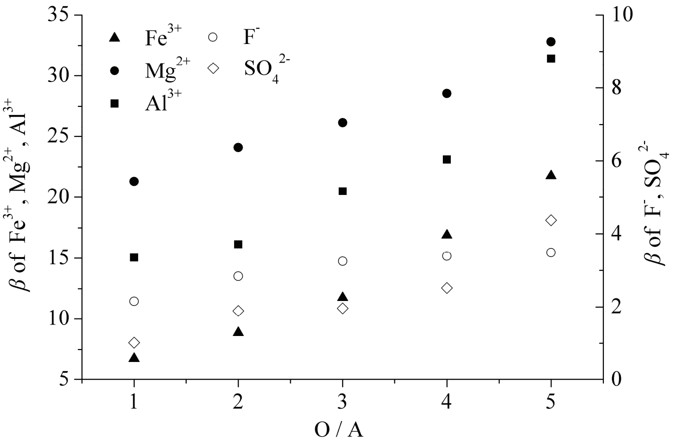

Fig. S-6. Effect of phase ratio on the separation factor for Fe^{3+} , Mg^{2+}, Al^{3+}, F^- and SO_4^{2}: [TC] = 4.24 mol L^{-1}, [H_3PO_4] = 9.16 mol L^{-1}, T = 298.2 K; ▲) Fe^{3+}; ●) Mg^{2+}; ■) Al^{3+}; ○) F^-; ◇) SO_4^{2-}.

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