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RESEARCH ARTICLE

Synergistic effect of some alcohols on the extraction of H_3PO_4 from Syrian wet phosphoric acid by TBP

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Abstract

This paper studies the synergistic effect of some alcohols such as isoamyl alcohol, pentanol, hexanol and heptanol on the Extraction of H_3PO_4 from Syrian phosphoric acid by (TBP). The possibility to use these alcoholic compounds as a diluent instead of kerosene was also studied. The results show that the alcohols have higher extraction yeild than (TBP) diluted in kerosene. The alcohols have an important synergistic effect, when they were used asdiluent instead of kerosene, on the Extraction of H_3PO_4 by (TBP) and they have a higher extraction yeild and a quicker phase separation compared with kerosene. Extraction of uranium, fluoride, sulfate and heavy metals by these reagents is relatively small.

Keywords

extraction · alcohol · phosphoric acid · tributylphosphate

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1 Introduction

Liquid-liquid extraction is the most important method for purification of commercial wet phosphoric acid and the tributylphosphate (TBP) is the most common phosphoorganic solvent which used for this purpose. Lanoe [1] claimed in a patent a procedure where strong wet phosphoric acid is pretreated and extracted with 80 % of tributylphosphate (TBP) and 20 % of saturated hydrocarbon by volume in counter-current extraction at ambient temperature. The pure phosphoric acid was recovered from the solvent by stripping with distilled water under higher temperatures. The color was adjusted by active carbon. Bierman [2] extracted H_3PO_4 from wet phosphoric acid by a high molecular weight hydrophobic alcohol such as hexanol. For extracting the metallic impurities a low molecular weight hydrophilic alcohol such as methanol was used. Other investigators [3–5] described processes to purify wet phosphoric acid using partially immiscible solvents such as alcohols, ketones, ethers and esters.

In our earlier paper [6] we have studied the liquid-liquid extraction of H_3PO_4 by nC4 – nC7 alcohols. The alcohol mainly used for extraction is n-heptanol because of its stability, low solubility and selectivity to H_3PO_4. The extraction of the impurities shuch as uranium, heavy metals, iron and fluoride from wet phosphoric acid by n-heptanol is very small. In our previous paper [7] we have studied the synergistic effect of etheric compounds on the extraction of H_3PO_4 from syrian wet phosphoric acid by TBP. In this paper we will continue to study synergistic effect of alcoholic compounds on the extraction of H_3PO_4 from syrian wet phosphoric acid by TBP.

2 Experimental

2.1 Materials

Tributylphosphate (TBP) 99 % wt., isoamyl alcohol, pentanol, hexanol and heptanol from BDH were used. A commercial wet phosphoric acid 27 % wt P_2O_5, 3 ppm uranium and a specific gravity of 1.26 from the General Fertilizer Company GFC Homs /Syria were used after being treated in the pilot plant for extraction of uranium. Kerosene (flash point 76 °C, < 5% aromatics, 3 mg/kg sulfur) supplied from Pemco Chemical Co. was used.

2.2 Apparatus and Procedures

Extraction was carried out in a beacher with a magnetic stirrer placed in a thermostat to control the temperature. The speed of the stirrer was 560 rpm, the length 12 mm. The mixture of both aqueous and organic phases was stirred for 5 minutes then left for 20 minutes to separate in a funnel. The concentration of the acid in the aqueous phase was measured by potentiometric titration with 0.1 NaOH. A potentiometer Type E536 from Metrohm Co was used. The concentration of P_2O_5 in the solvent was calculated from material balance. The yield was calculated from the equation:

$$\text{Yield Y \%} = \{[P_2O_5]\text{feed acid} - [P_2O_5]\text{raffinate}\}/[P_2O_5]\text{feed acid} \quad (1)$$

The distribution ratio (D) was calculated from the equation :

$$D = [P_2O_5]\text{solvent}/[P_2O_5]\text{raffinate} \quad (2)$$

where $[P_2O_5]$ = Concentration of P_2O_5 wt. %.

Fluoride concentration in the aqueous phase was determined by ion selective electrode using ion selective/pH meter from Metrohm Co. Uranium concentration was determined by complexing it with ammonium thiocynate and measuring the absorption at λ_{max} = 365 nm by a UV-Vis spectrophotometer Type Spectronic 601 from Bausch&Lomb Co. The concentration of sulfate in the aqueous phase was determined by ion chromatography Type Metrohm 792 basic IC. The concentrations of cations such as Cd^{2+} and Cu^{2+} were measured by polarograph Model 693 (VA) Processor from Metrohm. The arsenic was measured by netron activation analysis. The ease of phase separation was determined by measuring variation of the height of the interface from bottom of the column with time.

3 Results & Discussions

3.1 Determination of the Extraction Isotherm with TBP

The extraction isotherm of H_3PO_4 with 80% TBP/kerosene from treated wet phosphoric acid was determined. The extraction was carried out at $T = 25\,^{\circ}$C, $P_2O_5 = 27\,\%$wt in the common range of concentrations. The results are shown in Fig. 1 where concentration of P_2O_5 wt.% in the solvent is plotted versus concentration of P_2O_5 wt.% in the refined.

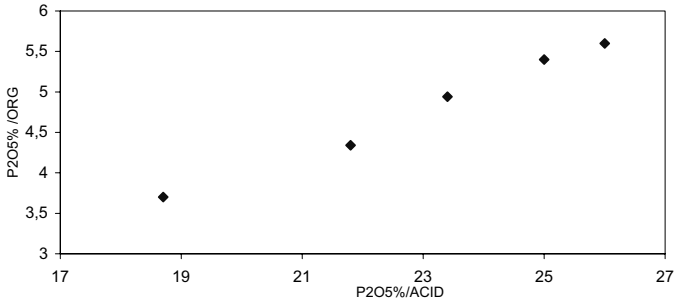

Fig. 1. Extraction isotherm of H_3PO_4 by TBP/kerosene ($P_2O_5 = 27\,\%$ wt., $T = 25^{\circ}$)

3.2 Study of the Synergistic Effect of Alcoholic Compounds

Synergistic effect of alcoholic compounds on the extraction of H_3PO_4 from Syrian phosphoric acid by TBP was investigated. The components isoamyl alcohol, pentanol, hexanol, heptanol and kerosene were added to TBP with different concentrations from 20 % to 80 % v/v of TBP. Extraction was carried out at $T = 25^{\circ}$C, O/A = 5/1, $P_2O_5 = 27\,\%$wt. and the time of separation of the phases was measured under the same experimental conditions. The results are plotted in Figs. 2, 3 in the form of Y and D versus concentrations of TBP respectively. It is clear that both Y and D increase as expected rapidly with increasing concentration of TBP according to the following:

$$\text{TBP/kerosene} < \text{TBP/heptanol} < \text{TBP/hexanol} < \text{TBP/pentanol} < \text{TBP/isoamyl alcohol}$$

The ease of separation of the two phases is low for TBP/kerosene but increases with decreasing concentration of TBP/kerosene while it is very high with other solvents, it takes only five minuets to complete separation. A compromise should be made between ease of separation, the selectivity and extraction efficiency. So, experiments were further carried out on TBP/isoamyl alcohol only.

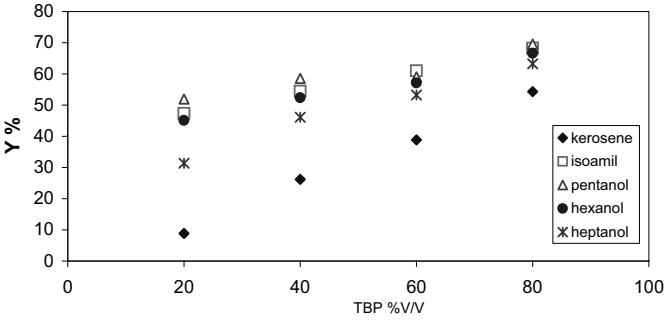

Fig. 2. Effect of concentration of TBP on extraction yield ($P_2O_5 = 27\,\%$wt., O/A = 5/1, $T = 25^{\circ}$C)

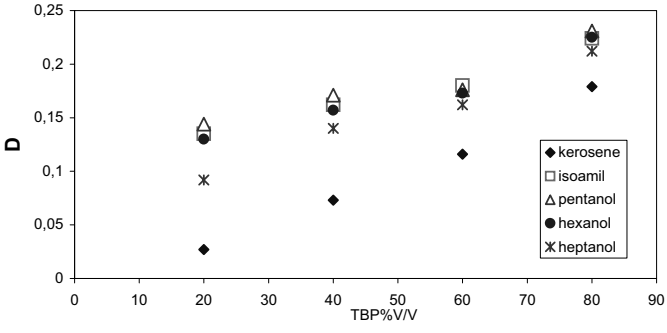

Fig. 3. Effect of concentration of TBP on distribution ratio ($P_2O_5 = 27\,\%$wt., O/A = 5/1, $T = 25^{\circ}$C)

3.3 Determination of the Extraction Isotherm with TBP/isoamyl Alcohol

The extraction isotherm of H_3PO_4 with 60% TBP/isoamyl alcohol from treated wet phosphoric acid was determined. The

extraction was carried out at $T = 25°C$, $P_2O_5 = 27\,\%$wt. The results are shown in Fig. 4 where P_2O_5 in the solvent is plotted versus P_2O_5 in the refined. The number of stages for extraction of H_3PO_4 with 60 % TBP/isoamyl alcohol from wet phosphoric acid was calculated by McCabe & Thiele method which shows that four stages are enough to reduce the P_2O_5 content in wet phosphoric acid to less than 10 %wt.

3.4 Effect of Temperature on Extraction

The effect of temperature was investigated by extracting H_3PO_4 from 27 % wt P_2O_5 raffinate phosphoric acid with TBP/isoamyl alcohol using a phase ratio O/A=5/1 but varying the temperature from 25 to 45 °C. The results are plotted in Fig. 5 in the form of Y% versus temperature °C. The results show that the extraction yield decreases when temperature increases.

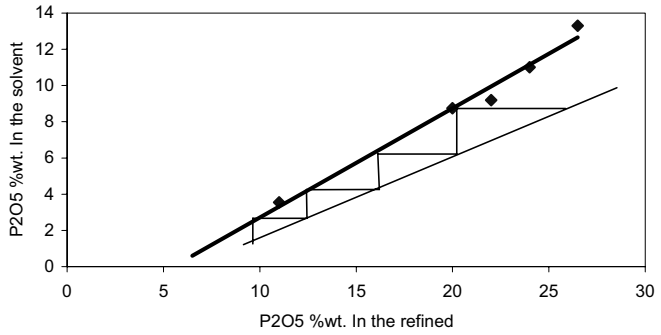

Fig. 4. Extraction isotherm of P_2O_5 by TBP/isoamil ($P_2O_5 = 27\,\%$ wt., $T = 25°$)

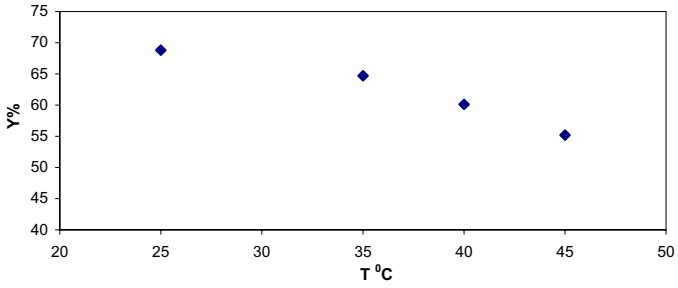

Fig. 5. Effect of temperature on extraction ($P_2O_5 = 27\,\%$wt., O/A = 5/1,)

3.5 Effect of Time of Mixing on Extraction

The effect of time of mixing on the extraction was investigated by using 60 % TBP/ isoamyl alcohol. The extraction was carried out under the same previous conditions $P_2O_5 = 27\,\%$ wt., O/A = 5/1, $T = 25\,°C$. The time of mixing was varied from 30 to 240 seconds. The results are represented in Fig. 6 in the form of Y versus time of mixing. The results show that Y increases very slightly from a value of 0.45 to 0.68 at 30 to 180 seconds respectively and remains constant after then. This indicates that the reaction is rapid and diffusion which is influenced by stirring has very little influence on the extraction. The mixing time was fixed at 5 minutes for other experiments.

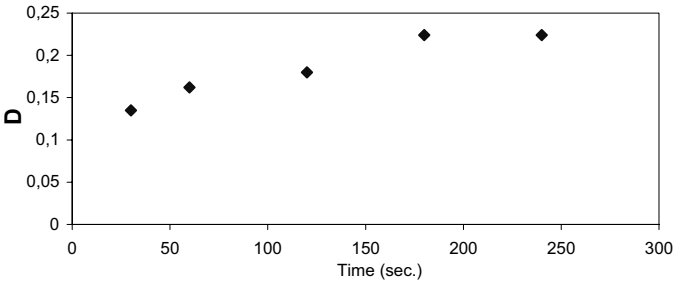

Fig. 6. Effect of time of mixing on the extraction ($P_2O_5 = 27$%wt., O/A = 5/1, $T = 25°C$)

3.6 Determination of the Stripping Isotherm

The stripping isotherm of H_3PO_4 from loaded TBP/isoamyl alcohol by distilled water was determined. The stripping was carried out at $T = 40°C$, $P_2O_5 = 15\,\%$wt. The results are shown in Fig. 7 where P_2O_5 % in the barren solvent is plotted versus P_2O_5 % in the water. The number of stages for stripping of H_3PO_4 from loaded TBP/isoamyl alcohol was calculated by McCabe & Thiele method which shows that three stages are enough to reduce the P_2O_5 content in solvent to about 1%wt. This result is identical to the operation of a stripping unit in a commercial plant.

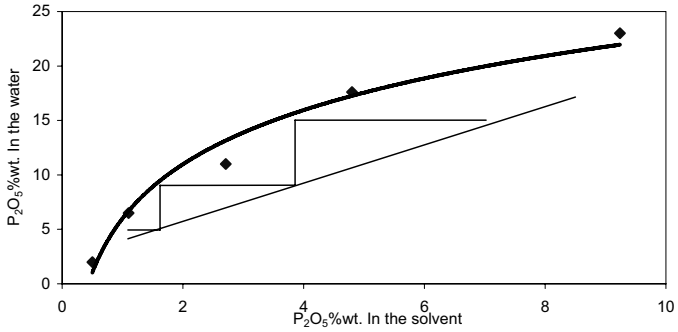

Fig. 7. Stripping isotherm (P_2O_5=15%wt., $T = 40°C$)

3.7 Effect of Temperature on Stripping

The effect of temperature was investigated by stripping H_3PO_4 from loaded TBP/isoamyl alcohol 15 %wt.P_2O_5 by distilled water using a phase ratio O/W=5/1 but varying the temperature from 25 to 50 °C. The results are plotted in Fig. 8 in the form of Y% versus temperature °C. The results show that the stripping yield increases with temperature.

3.8 Extraction of Uranium, Arsenic, Cadmium, Copper, Fluoride and Sulfate

An experiment was carried out to extract H_3PO_4 from wet phosphoric acid treated from solids with 27 %wt. P_2O_5 concentration and contains 65 mg/L uranium, 4 mg/L arsenic, 2.9 mg/L cadmium, 5.6 mg/L copper, 4.3 g/ L sulfate and 16.9 g/L fluoride. The acid was treated with 60 % TBP/ isoamyl alcohol at O/A = 5/1 and $T = 25°C$. The experiment was repeated under the same conditions but with 80% TBP/kerosene. The

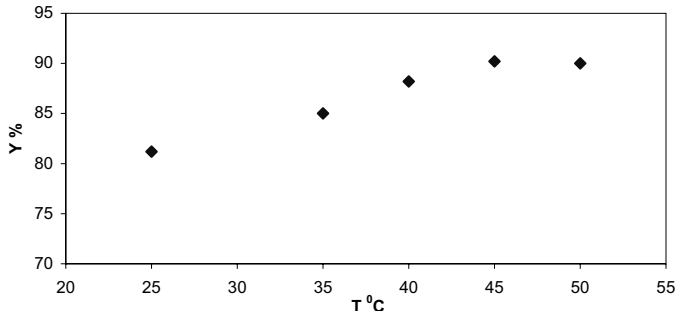

Fig. 8. Effect of temperature on stripping (P_2O_5=15%wt., O/A=5/1)

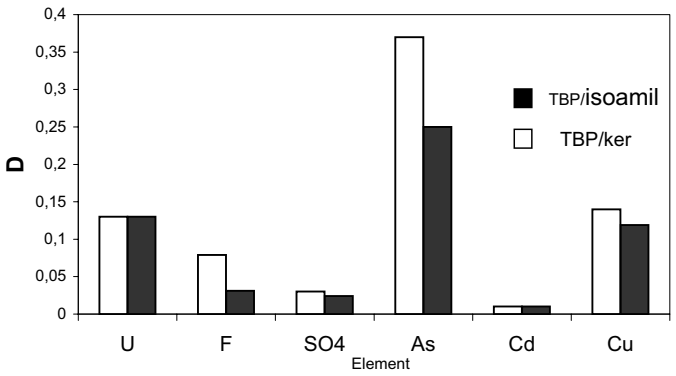

Fig. 9. Comparison of selectivity between TBP/isoamil and TBP/kerosene

concentrations of uranium, arsenic, cadmium, copper, fluoride and sulfate in the acid refined were measured. The results are shown in Fig. 9, which gives the distribution ratios for these elements. The results show that the distribution ratios for these elements are relatively small what indicates that extraction of these elements by the above solvents is negligible and that the selectivity for 60% TBP/ isoamyl alcohol is better than for 80% TBP/kerosene.

4 Conclusions

The previous results show that:

1 The alcohols play an important synergistic role when they are used as diluents for TBP and they inhance the extraction efficiency.

2 The time of mixing has a small effect on extraction which indicates that extraction is not diffusion controlled.

3 The separation time for the extraction by TBP with alcohols as diluent is smaller than that by TBP with kerosene with phase ratio $O/A = 5/1$.

4 The temperature has a negative effect on the extraction of H_3PO_4 but it has a positive effect on the stripping. According to McCabe & Thiele method extraction process needs four stages while stripping process needs three stages.

5 Extraction of uranium, arsenic, cadmium, copper, fluoride and sulfate is little or negligible and the 60 % TBP/isoamyl alcohol solvent is more selective than 80 % TBP/kerosene solvent.

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