EXTRACTION OF H_3PO_4 FROM WET PHOSPHORIC ACID BY nC4 – nC7 ALCOHOLS

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Abstract

Most phosphate rocks are used to manufacture phosphoric acid by digestion with concentrated sulfuric acid by the wet method. Many impurities dissolve also in the acid and then go to the fertilizer which makes this acid unsuitable for food or pharmaceutical uses. Pure phosphoric acid for food purposes is obtained by reduction of the phosphate rocks in an electric furnace to obtain P_2O_5 by the dry method. This method consumes a lot of energy and so it is rather expensive. There has been an increased interest in the past few years in purifying commercial wet phosphoric acid to obtain a pure acid. Several methods were developed on the pilot plant or commercial scales but most of the works are still in the developmental stage.

This paper studies extraction of H_3PO_4 by nC4 – nC7 alcohols by liquid-liquid extraction. The alcohol mainly used is n-heptanol. The effect of temperature and mixing time on distribution ratio is studied. The results show that nC7 alcohol is a suitable solvent for H_3PO_4 extraction. The temperature has a slight negative influence on extraction. The extraction is enhanced by increasing P_2O_5 and alcohol concentrations. The extraction decreases by increasing the number of carbon atoms or the molecular weight of the n-alcohol, but phase separation is slower. Extraction of uranium and heavy metals is negligible while extraction of fluorine and iron is relatively small.

Keywords: alcohols, extraction, phosphoric acid, purification.

1. Introduction

There has been a wide interest over the last few years to develop a process to purify commercial wet phosphoric acid to obtain a pure acid. Most of the works are still in the developmental stage. Many solvents were tried but aliphatic alcohols have the advantages of being cheap, easy to use, separate quickly and do not pollute the food grade acid.

Purification of wet phosphoric acid was studied by DAVISTER [1] by liquid-liquid extraction with a mixture of diisopropylether (DIPE) and tributylphosphate (TBP) in kerosene diluent. Two thirds of P_2O_5 were extracted in 4 counter current stages at $5 - 25\,°C$. Sulfate (SO_4^{2-}) was removed from the acid by adding fine phosphate powder while fluoride (F^-) was removed by adding silica during concentration of the acid by evaporation in vacuum. The pure phosphoric acid was recovered from the solvent by stripping with distilled water under higher temperatures. The color was adjusted by active carbon.

CUER and FLOREANCIG [2] published that P_2O_5 could be extracted by tri-octylamine (TOA) but with more difficulty. Alcohols could also be used with higher selectivity for higher molecular weights. Ethers such as DIPE and dinormalpropyl-ether (DNPE) could also be used at low temperatures of $5-25\,°C$. Phosphoorganic solvents especially TBP could be used to extract P_2O_5 from wet phosphoric acid since it has a low solubility in water and it is a common solvent. A mixture of TBP and DIPE in kerosene was used in a Ugine-Kuhlman pilot plant.

NAIR [3] published that FACT Co of India had developed a liquid-liquid extraction process to purify wet phosphoric acid. The process used an alcohol with low solubility in water such as butanol in the presence of ammonia or organoamines. The acid was then stripped from the solvent by contact with distilled water. It was also possible to recover the pure P_2O_5 in the form of an alkaline phosphate by extraction with alkaline solvents.

MCCULLOUGH [4] published that Occidental Oil developed a process to extract H_3PO_4 from wet phosphoric acid by liquid-liquid extraction using n-heptanol. It was possible to remove 97% of the metals and 82% of the fluoride. Oxidation was used to remove the color of the acid. TVA Co used methanol with a small amount of ammonia to precipitate most metallic impurities in the form of M NH_4PO_4 (M for metallic cations). Acetone could also be used with a small amount of ammonia to do the same.

BIERMAN [5] 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. The mixture was separated into two phases. One phase consists of hexanol with pure H_3PO_4 and the other is a methanol phase rich in metallic and anionic impurities.

LANOE [6] claims a procedure in a patent where strong wet phosphoric acid is pretreated and extracted with 80% of tributyl phosphate (TBP) and 20% of saturated hydrocarbon by volume in counter-current extraction at ambient temperature.

A MEAB report [7] describes processes to purify wet phosphoric acid using partially immiscible solvents such as alcohols, ketones, ethers and esters. The rejection of cationic impurities is marked and when operating with a concentrated acid feed the selectivity is poor. When ethers are selected as solvent, the effect of temperature is very important, while with alcohols and ketones it is not important.

2. Experimental

2.1. Materials

Normal aliphatic alcohols n-C4 to n-C7 from British drug house (BDH)/England with 99% wt purity were used. A commercial wet phosphoric acid from the General Fertilizer Company GFC Homs/Syria with 36.5% wt P_2O_5 and a density of 1.392 g/cm^3 was used after being separated from solids and organics in the pilot plant for extraction of uranium. Another commercial phosphoric acid separated

from solids with 27.1% wt P$_2$O$_5$ and a density of 1.26 g/cm^3 and containing 59 ppm uranium was also used.

2.2. *Apparatus and Procedures*

Extraction was carried out in a beaker with a magnetic stirrer placed in a thermostat to control the temperature. The aqueous and organic phases were stirred for 5 minutes and were allowed to separate for 20 minutes in a funnel. The concentration of the acid in the aqueous phase was measured by a potentiometric titration with 0.1 NaOH. The potentiometer E536 from Metrohm Co was used. The concentration of P$_2$O$_5$ in the solvent was calculated from the material balance. The yield was calculated from the equation:

$$\text{Yield Y\%} = \{[\text{P}_2\text{O}_5] \text{ feed acid} - [\text{P}_2\text{O}_5] \text{ raffinate}\}/[\text{P}_2\text{O}_5] \text{ feed acid.} \quad (1)$$

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

$$D = [\text{P}_2\text{O}_5] \text{ solvent}/[\text{P}_2\text{O}_5] \text{ raffinate}, \quad (2)$$

where [P$_2$O$_5$] $=$ wt % of P$_2$O$_5$.

The fluoride concentration was determined by titration with thorium nitrate. The uranium concentration was determined by complexing it with ammonium thiocyanate and measuring the absoption by a UV spectrophotometer of type Spectronic 601 from Bausch & Lomb Co. The iron concentration in the acid was determined by complexing it with 1–10 phenonitroline in the range of pH 4 to 6 and measuring the absorption by the UV spectrophotometer at 510 nm. The concentrations of cations such as Cd^{2+}, CU^{2+}, Zn^{2+} were measured by a polarograph, Model 693 (VA) Processor from Metrohm Co. The degree of phase separation was determined by measuring the change of height of the interface from the bottom of the column with time.

3. Results and Discussion

3.1. *Extraction by n-C4 to n-C7 Alcohols*

The effect of the molecular weight of the n-alcohol was investigated by extraction with different alcohols from n-C4 to n-C7 and the time of separation of the phases was measured under the same experimental conditions ($T = 25\,°\text{C}$, O/A $= 5/1$, P$_2$O$_5 = 36.5\%$ wt). The results are plotted in *Fig. 1* in the form of D versus number of carbon atoms of the solvent and in *Fig. 2* in the form of time of separation versus number of carbon atoms of the solvent.

It is clear that extraction decreases rapidly, as expected, with the increase of the molecular weight or the number of carbon atoms of the solvent and ease of
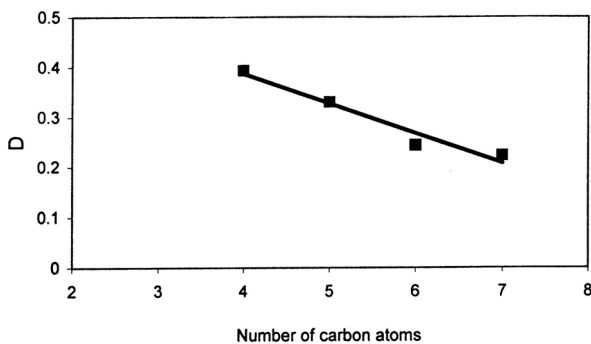
Fig. 1. Effect of molecular weight of n-alcohol on extraction of H_3PO_4
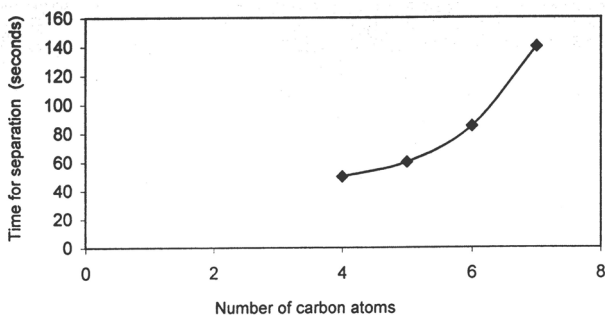(P$_2$O$_5$ = 36.5% wt, O/A = 5/1, T = 25 °C)

Fig. 2. Effect of molecular weight of n-alcohol on time for separation
(P$_2$O$_5$ = 36.5% wt, O/A = 5/1, T = 25 °C)

separation of the two phases decreases with the increase of the molecular weight of
the solvent. A compromise should be made between ease of separation, solubility
of solvent in the acid, stability of solvent, selectivity and extraction efficiency.
Further experiments were carried out on n-heptanol (n-C7) only, because it has
lower solubility and higher stability [8].

3.2. Effect of Time of Mixing on Extraction

The effect of time of mixing on extraction was investigated. The extraction was
carried out under the same conditions as previously (P$_2$O$_5$ = 36.5% wt, O/A = 5/1,
T = 25 °C). The time of mixing was varied form 25 to 180 seconds. The results
are represented in Fig. 3 in the form of D versus time of mixing. The results show

that D increases very slightly from a value of 0.55 to 0.57 at 25 to 50 seconds, respectively, and remains constant after that. This shows that the reaction is rapid and diffusion which is influenced by stirring has very little influence on extraction. The mixing time was fixed at 5 minutes for other experiments.
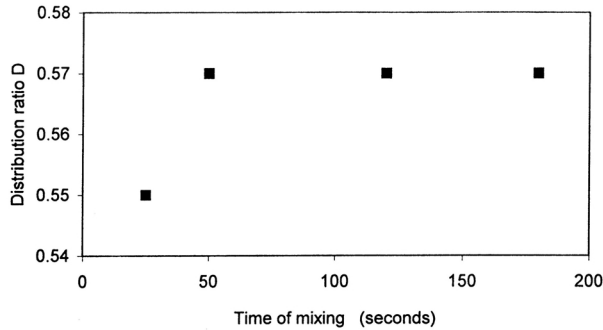

Fig. 3. Effect of time of mixing on extraction by n-C7
(P$_2$O$_5$ = 36.5% wt, O/A = 5/1, T = 25 °C)

3.3. Determination of the Extraction Isotherm

The extraction isotherm of H$_3$PO$_4$ with n-heptanol from raffinate phosphoric acid taken from a pilot plant performing the extraction of uranium was determined. The extraction was carried out at (T = 25°C, P$_2$O$_5$ = 36.5% wt.). The results are shown in *Fig. 4*, where P$_2$O$_5$ in the solvent is plotted versus P$_2$O$_5$ in the raffinate. The experiment was repeated under the same conditions but for commercial phosphoric acid treated against solids only. The conditions were (27.1% P$_2$O$_5$, T = 25 °C). The results are represented in the same figure.

3.4. Effect of Temperature

The effect of temperature was investigated by extracting H$_3$PO$_4$ from 36.5% wt P$_2$O$_5$ raffinate phosphoric acid with n-heptanol using a phase ratio O/A = 5/1 but varying the temperature from 25 to 50 °C. The results are plotted in *Fig. 5* in the form of ln D versus $1/T$ °K$^-$. The results fit a straight line equation with a slope value 0.0591. The relation between the equilibrium constant K and the temperature is given by Van Hoff's equation:

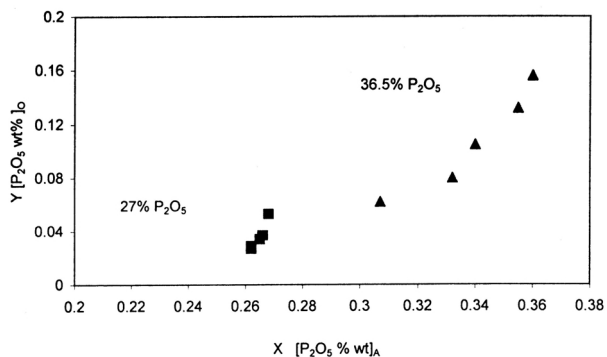$$d \ln K / dT = \Delta H / R \cdot T^2. \tag{3}$$

Fig. 4. Isotherm of extraction of H_3PO_4 by n-C7
($P_2O_5 = 36.5\%$ wt, $P_2O_5 = 27.0\%$ wt, $T = 25\ °C$)

By integration

$$\ln K = (-\Delta H/R)(1/T) + a. \tag{4}$$

And since the distribution ratio D is related by definition to the equilibrium constant K the previous equation could be written:

$$\ln D = (-\Delta H/R)(1/T) + a' \tag{5}$$

Comparing the two slopes $(-\Delta H/R)$ and (0.0591) it is possible to calculate $\Delta H = -490$ J/mol. The results show that temperature has a slight negative effect on the extraction of H_3PO_4 by n-heptanol. Therefore it is a usual practice to carry out the extraction at room temperature.
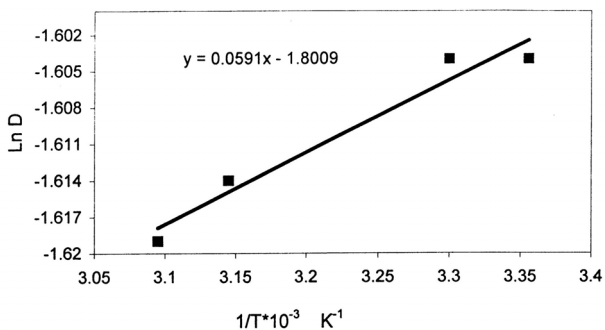

Fig. 5. Effect of temperature on extraction by n-C7
($P_2O_5 = 36.5\%$ wt, O/A = 5/1)

3.5. Effect of n-heptanol Concentration

The effect of n-heptanol concentration in kerosene was studied using raffinate phosphoric acid at 25 °C and phase ratio O/A = 5/1. The concentration of n-heptanol in kerosene was varied from 50% to 100% by volume. The results are represented by Fig. 6 in the form of ln D versus ln[n − C7] mol/L. The results fit a straight line with a slope = 1.346. This indicates that the results are satisfactory and the extraction dependency is 1. The extraction increases by increasing the solvent concentration in the diluent. It is a usual practice to use n-heptanol without a diluent since phase separation is quick.
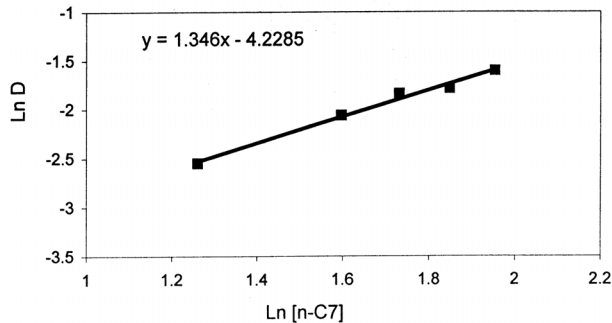

Fig. 6. Effect of n-C7 concentration on extraction
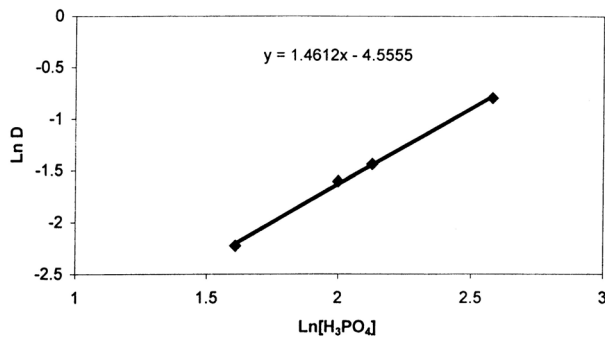(P$_2$O$_5$ = 36.5% wt, O/A = 5/1, T = 25 °C)

Fig. 7. Effect of phosphoric acid concentration on extraction by n-C7
(O/A = 5/1, T = 25 °C)

3.6. Effect of Phosphoric Acid Concentration

The effect of phosphoric acid concentration was studied by varying the concentration of the acid from 27% wt to 49.5 % wt P_2O_5, while keeping other conditions constant ($T = 25\,°C$, O/A $= 5/1$). The results are represented in *Fig. 7* in the form of ln D versus ln[H_3PO_4] mol/L. The results show that D increases significantly by an increase in the concentration of the acid. The results are represented by a straight line with a slope $= 1.4612$. This indicates that the results are satisfactory and the extraction dependency is unity in the extraction system with n-heptanol.

3.7. Effect of Phase Ratio on the Separation Time

The effect of separation time was studied using different phase ratios (O/A $= 1, 2, 5$) of n-heptanol with raffinate phosphoric acid 36.5% wt P_2O_5 at 25 °C. The results are represented by *Fig. 8*. Higher phase ratio (O/A) gives better separation.
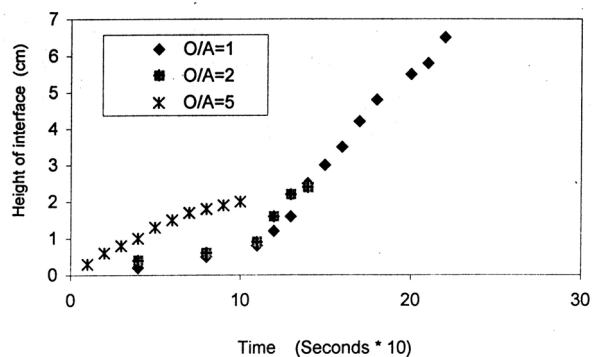

Fig. 8. Separation of n-heptanol and phosphoric acid
            ($P_2O_5 = 36.5\%$ wt, $T = 25\,°C$)

3.8. Extraction of Uranium, Fluoride, Iron and Heavy Metals

An experiment was carried out to extract H_3PO_4 from wet phosphoric acid treated against solids only with 36.5% wt P_2O_5 concentration and containing 55 mg/L U and 16 g/L Fe and 1.21% wt F^-. The acid was treated with n-heptanol with O/A $= 4/1$ at 25 °C. The concentrations of iron and F^- in the acid raffinate were measured. The results shown in *Fig. 9* give the yield of extraction for these elements. The results show that the yield for iron and fluoride is small, and that for uranium is negligible. This means that the solvent is selective for the extraction of H_3PO_4 which is in

agreement with results by other workers [4]. The extraction of heavy metals by n-heptanol was investigated by carrying out experiments on raffinate phosphoric acid with 27% wt P_2O_5 concentration at 25 °C and $O/A = 5/1$. The results are shown in *Fig. 10* where the distribution ratios of Cd, Zn, Cu are represented. The results show that extraction of these elements is negligible.
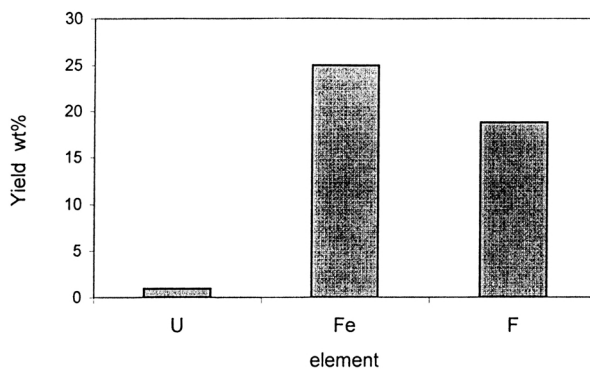

Fig. 9. The yield of extraction of U, Fe and F^- by n-heptanol
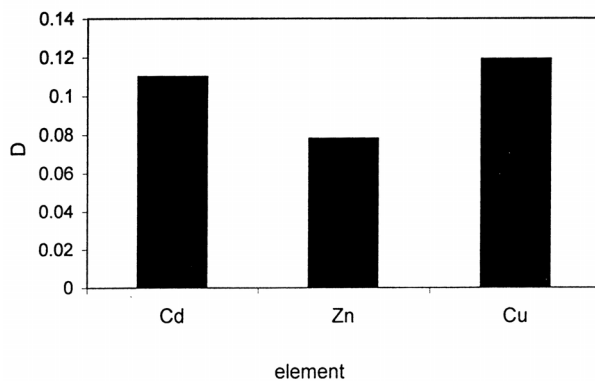($P_2O_5 = 36.5\%$ wt, $O/A = 4/1$, $T = 25$ °C)

Fig. 10. Distribution ratios of extraction of Cd, Zn and Cu by n-heptanol
($P_2O_5 = 27\%$ wt, $O/A = 5/1$, $T = 25$ °C)

4. Conclusions

The previous results show that:

1. The solvent is selective to H_3PO_4. Extraction of uranium and heavy metals is negligible, while that for iron and fluoride is small.
2. The temperature has a small negative effect on the extraction in the range studied so extraction could be carried out at ordinary temperatures.
3. The time of mixing has a small effect on extraction which indicates that extraction is not diffusion controlled.
4. The concentration of n-heptanol has a positive effect on the extraction so the solvent is used without diluent.
5. The concentration of phosphoric acid has a positive effect on extraction so it is recommended to use high strength phosphoric acid.
6. The higher ratio O/A gives higher extraction and the ease of separation is also better. A phase ratio O/A = 5/1 is used to get a high yield and quick phase separation.
7. Extraction decreases with an increase of the molecular weight of the solvent. The solubility and stability of the alcohols is higher with lower molecular weight so n-heptanol is used as a compromise.

Acknowledgement

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