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RESEARCH ARTICLE

Extraction of phosphoric acid from various aqueous solutions using tributyl phosphate (TBP)

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Abstract

Solvent extraction of phosphoric acid from various aqueous solutions has been investigated using tributyl phosphate in kerosene as the extractant. The effect of the nature of the diluent on the extraction of phosphoric acid with TBP has been studied and correlated with the dielectric constant. The extraction equilibrium curve showed that an overall extraction yield of more than 80 % could be reached from aqueous solutions containing 0.8M of sulfuric acid. Pure phosphoric acid was stripped from the loaded organic phase by counter current stripping with distilled water. The produced acid was post treated to eliminate the co-extracted acids and characterized.

Keywords

phosphoric acid · TBP · extraction

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1 Introduction

Wet process phosphoric acid is produced at the General Fertilizer Company G. F. C/Homs-Syria. This acid contains, beside solids and organic matters, many impurities (Shlewit et al. [1] and Khorfan et al. [2]). A pilot plant located at the site of the acid plant is treating 1 m^3/h by removing solid and organic matters before extracting uranium. TBP/kerosene has been examined in laboratory tests, for further purification of the raffinate acid produced at the pilot plant (Shlewit et al. [1] and Shlewit et al. [3]). Results showed that a mixture of diisopropyl ether (DIPE) and TBP in kerosene is an effective solvent for the extraction of phosphoric acid form the commercial wet acid salted out with sulfuric acid and sodium chloride. It was claimed that more than 80% of the acid could be extracted in three counter current stages. TBP+DIPE in kerosene is also used to extract phosphoric acid from the wet H_3PO_4 (Davister et al. [8]). It was concluded that two thirds of the acid can be extracted in four counter current stages at room temperature. Purification of wet phosphoric acid to produce food or pharmaceutical grade acid has received a lot of attention in the recent years. Solvent extraction of phosphoric acid from aqueous solutions has been studied by ether, alcohols, ketones, carboxylate esters, tri-alkylphosphates and various amines by several researchers (Blumberg [4], Berry et al. [5] and Bierman et al. [6]). Furthermore, it was found that co-existing mineral acids enhanced the extraction of phosphoric acid with several solvents (McCorkell et al. [7]). Toyo Sod manufacturing Co. Ltd., Japan (US Pat. 4208389 [9]) presented a procedure for the simultaneous removal of cationic and anionic impurities in the wet H_3PO_4 by extracting the phosphoric acid with n-and isobutyl alcohol after the addition of sulfuric acid to the aqueous feed.

The present work was carried out to improve the overall yield of phosphoric acid extraction using TBP in kerosene after the addition of an optimized amount of some mineral acids.

2 Experimental

2.1 Materials and Methods

Pure phosphoric acid (analytical grade) obtained from MERCK and commercial phosphoric acid produced at the commercial acid plant were used. All chemicals used in this work were of analytical grade. The phosphoric acid extracted into organic phase (TBP/Kerosene) was back-extracted by distilled water. The two phases were agitated using magnetic stirrers at room temperature. The mixing and the settling time were fixed at 10 minutes. Concentration of phosphoric acid in the starting acid solution and the final one resulting from back-extraction was then determined by colorimetric method. It was reacted with molybdic acid after acidification of the solution with hydrochloric acid, the product was then reduced with stannous chloride, extracted into methyl isobutyl ketone and the absorption was measured at 735 nm (Maekawa et al. [10]). Phosphoric acid content of the organic phase was determined by mass balance. The extraction yield Y_E of pure H_3PO_4 is defined as follows:

$$Y_E = \frac{wt\% \text{ of } H_3PO_4 \text{in organic phase}}{wt\% \text{of } H_3PO_4 \text{in the starting aqueous phase}} \times 100.$$

2.2 Pre-purification of the Commercial Phosphoric Acid

Settled acid from the phosphoric acid plant is treated to remove the bulk of sulfate by adding barium carbonate. Solids are removed by adding a suitable flocculent and then by precipitation in a clarifier. The solids remaining should be less than 200 ppm. The fine solids are further removed by filtration in a barite column. The fresh acid containing less than 50 ppm of solids is passed through active carbon columns to remove any organic matter present in the acid.

The above treated acid was pumped to the Syrian uranium recovery pilot-plant to extract uranium using DEHPA/TOPO in kerosene. The raffinate phosphoric acid (free of uranium) produced was then used for H_3PO_4 extraction, Table 1 shows its composition.

Tab. 1. Composition of the raffinate acid

Element	Concentration (ppm)
S	7350
Cl^-	592
Ca	613
Ti	26
V	65
Cr	101
Fe	1850
Ni	13.1
Cu	6.2
As	0.1>
U	1.5
F^-	2%
Zn	204

3 Results and Discussion

3.1 Effect of Nature of Diluent on the Extraction Yield

Diluents have an important bearing on the extractant. The physical properties of the extraction system can often be related to the selection of the diluent. Properties such as dielectric constant, polarity, aromaticity, and solubility parameters of diluents affect the extractability. A number of diluents with different physical properties have been investigated in this work. Two aqueous solutions have been prepared containing 35 and 55 wt% H_3PO_4. The extraction of phosphoric acid has been studied using 80% TBP in various diluents. Table 2 shows the effect of the nature of diluent on the phosphoric acid extraction yield.

Tab. 2. Effect of the diluent nature on the extraction yield of H_3PO_4 using 80% TBP.

Diluent	Dielectric constant (David [11])	Y_E (%) Using 35wt% H_3PO_4	Y_E (%) Using 55wt% H_3PO_4
Kerosene	2	12.29	15.58
Benzene	2.28	11.50	13.99
Toluene	2.38	11.32	13.64
Diisopropyl ether	3.81	10.29	12.45
Chloroform	4.81	4.24	6.22

The results clearly demonstrate that diluents such as kerosene, benzene and toluene having low dielectric constants show higher extraction yield for phosphoric acid. On the other hand, lower extraction yield was observed with diluents having higher dielectric constants such as chloroform and diisopropyl ether. In view of the commercial availability and higher extraction yield kerosene has been chosen as the diluent in the present work.

3.2 Extraction of H_3PO_4 Using 80% TBP/Kerosene from Various Acidic Solutions

The extraction yield (Y_E) of phosphoric acid was changed appreciably by strong acids in the aqueous phase. Fig. 1 shows the extraction yield of phosphoric acid as a function of acid concentration in the range 0 to 1M HX, containing 35 wt% phosphoric acid (where X^- is sulfate, chloride, nitrate or perchlorate ion) and when the organic phase was kerosene initially containing 80% TBP.

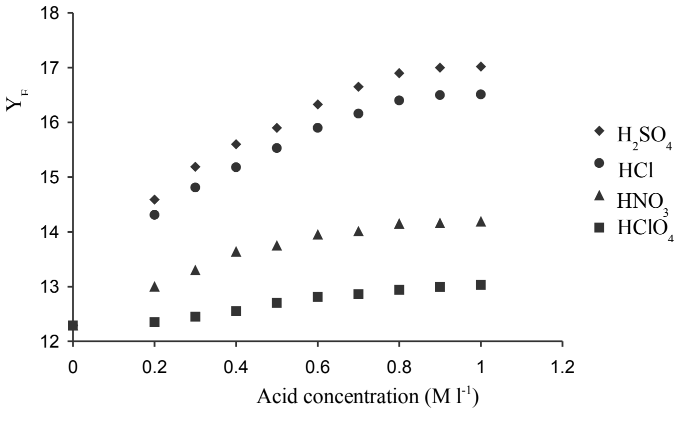

Fig. 1. Phosphoric acid extraction yields (Y_E) as a function of the various acids concentrations in 35 wt% H_3PO_4.

According to Fig. 1, the apparent extraction yield of phosphoric acid was slightly enhanced by perchloric and nitric acid, but it was greatly improved by hydrochloric and sulfuric acid. However, by a further analysis of the data, it was concluded that the latter improvement was due to a decrease in the free TBP concentration caused by an extraction of these strong acids. The net extraction yield of phosphoric acid in these systems with TBP was enhanced by the acids as shown in Fig. 1. The extraction yield from perchlorate and nitrate solutions is nearly independent of the acid concentration. However, the extraction yield from both chlorate and sulfate solutions is greatly enhanced with the increase in the acid concentration. The results showed that adding 0.8M of HX leads to the highest phosphoric acid extraction yield. Thus, it can be concluded as illustrated in Table 3 that the addition of 0.8M HX would lead to an increase in yield of about 0.65%, 1.86%, 4.11% and 4.61% when extracting from aqueous phases containing 0.8M of $HClO_4$, HNO_3, HCl or H_2SO_4 respectively.

Tab. 3. Enhancement values of Y_E in the presence of 0.8M HX compared with initial status (0M HX)

(Y_E) 0M HX	(Y_E) 0.8M HX			
	$HClO_4$	HNO_3	HCl	H_2SO_4
12.29	12.94	14.15	16.40	16.90

This enhancement can be also explained in terms of an extraction of mixed acid species. This statement was confirmed by titration of both phases with standard barium hydroxide solution. Analyses of results showed that a very small amount of the strong acids were extracted. In the extracted species, the protons of an acid can form a hydrogen bond with an oxygen atom and thus its extraction is quite reasonable. However, the solvation number two of the strong acid can only be explained by assuming an extraction of hydrated acid. The oxygen atom of TBP molecules should combine with two hydrogen atoms of the hydrate water molecule which combine with the proton of the strong acid through its oxygen.

The co-extraction of strong acids together with the trisolvated phosphoric acid should occur by a hydrogen bond formation between the phosphoryl oxygen of phosphoric acid and the proton of the strong acid. In the aqueous phase, the phosphoryl oxygen and the three protons of the phosphoric acid should be hydrogen bonded with water molecules, and even after these water molecules are removed by the solvation with TBP, the hydration on the phosphoryl oxygen may continue and this hydration should significantly improve the extraction of the phosphoric acid. In the aqueous phase, a proton dissociated from a strong acid should combine with oxygen atom of water molecules. However, the proton should also be able to combine with the phosphoryl oxygen atom of phosphoric acid solvated with TBP in the organic phase by forming a hydrogen bond, and to replace the abovementioned hydrate water molecule. The enhancement of the extraction shown in Fig. 1 is in the order $H_2SO_4 > HCl > HNO_3 > HClO_4$. The strong acid combined with the phosphoryl oxygen atom of the phosphoric acid should make the total molecular volume of the extracted species larger and more hydrophobic and consequently more extractable, in the same order (Shlewit et al. [3]).

3.3 Phosphoric Acid Extraction Equilibrium

Solvent extraction of H_3PO_4 using 80% TBP in kerosene from 0.8M H_2SO_4 aqueous solutions containing 35 wt% wet phosphoric acid raffinate was carried out at 25^{o}C using different phase ratios of the aqueous/organic phases. The experiment was repeated for 0.8M H_2SO_4 aqueous solutions containing laboratory grade (LG) acid (35 wt% H_3PO_4) at the same temperature. The equilibrium curves are shown in Fig. 2.

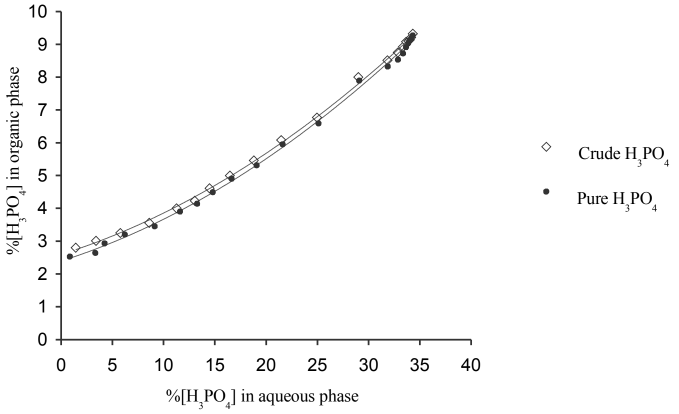

Fig. 2. Extraction equilibrium of H_3PO_4 from LG and crude phosphoric acid

3.4 Number of Stages for H_3PO_4 Extraction

Wet phosphoric acid extraction equilibrium curve from 0.8M H_2SO_4 solution, represented in Fig. 3, was used to calculate the number of counter current stages required to achieve 80% yield of extracted H_3PO_4 at 25 ^{o}C. The operating line was drawn, according to the concentration of the feed acid (35 wt% H_3PO_4). The concentration of the raffinate acid is about 7 wt% and the slope of the operating line is equal to the phase ratio of aqueous/organic phases (1/4). The number of stages to obtain a yield of 80% according to the method of McCabe&Thiele was found to be 2 to 3 stages.

The extraction equilibrium in Fig. 4 for the laboratory grade (LG) acid 35 wt% from 0.8M H_2SO_4 solution was used to calculate the number of counter current stages required to obtain 80% H_3PO_4 extraction at 25^{o}C. The operating line was drawn so that the concentration of the feed acid is 35 wt% H_3PO_4, the concentration of the raffinate acid is about 7 wt% and the slope of the line is equal to the phase ratio of the aqueous/organic phases (1/4). It was found that 2 to 3 stages are needed.

The negligible difference between the equilibrium curves of pure and crude phosphoric acid may be attributed to the presence of certain impurities in the feed raffinate acid shown in Table 1. Impurities here role as salting out agents.

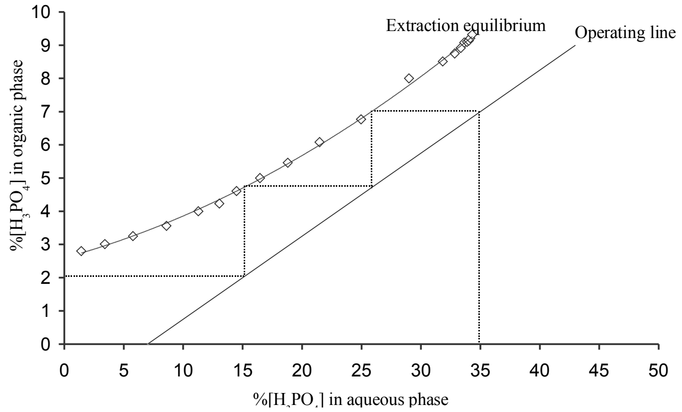

Fig. 3. Number of stages by the McCabe method for wet phosphoric acid raffinate

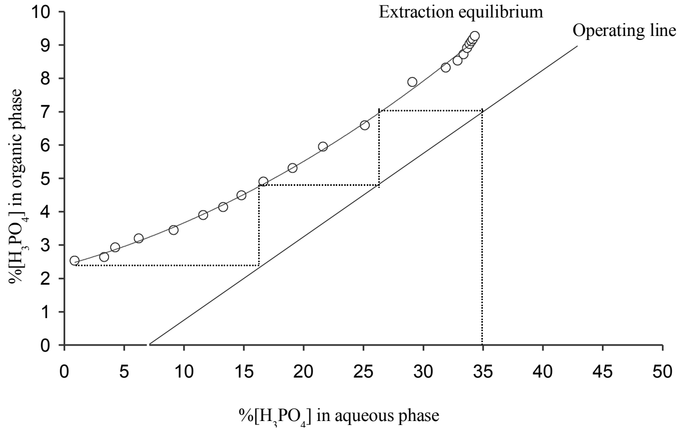

Fig. 4. Number of stages by the McCabe method for LG phosphoric acid.

3.5 Scrubbing and Stripping of Phosphoric Acid

The obtained loaded organic phase from the extraction stages of the feed raffinate acid contains some impurities. Elimination of such impurities were carried out by three scrubbing stages using 35 wt% of LG H_3PO_4 as a scrubbing agent. Phosphoric acid stripping from the scrubbed organic phase was carried out using double distilled water. The outlet stripping liquor was concentrated by evaporation up to 85 wt% H_3PO_4 and characterized using ICP, AAS and XRF analysis techniques. Table 4 shows the characterization of the phosphoric acid produced.

F^- could be eliminated during evaporation by steam stripping technique in the industrial units. Sulfure could be eliminated by precipitation using calcium oxide solution or other conventional methods.

4 Conclusion

The extraction behaviour of phosphoric acid has been investigated using 80% TBP in kerosene as extractant. Kerosene gives the highest extraction yield compared with the other diluents tested. Results demonstrate that H_2SO_4 does enhance the extraction yield of H_3PO_4 to a large extent compared with HCl, HNO_3, or $HClO_4$. McCabe&Thiele method showed that 2 to 3 extraction stages are needed to extract 80% of H_3PO_4 from 0.8M H_2SO_4 solution containing 35 wt% wet phosphoric acid raffinate. Two to three extraction stages were needed also to extract 80% of H_3PO_4 from 0.8M H_2SO_4 solution containing 35 wt% laboratory grade phosphoric acid.

Tab. 4. Characterization of the produced phosphoric acid (85 wt% [H_3PO_4])

Element	Concentration (ppm)
S	260
Cl^-	-
Ca	11
Ti	-
V	-
Cr	-
Fe	7
Ni	-
Cu	1
As	-
U	< 1
F^-	1 %
Zn	-

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