# Study on Solvent Extraction of Phosphoric Acid from Phosphate Ores-HCl Digestion Liquor Using Pure and Mixed Solvent

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Pure and mixed solvents are used to extract phosphoric acid from the dissolution of phosphate ores in HCl medium. Water is used to strip phosphoric acid from the organic layer. The optimum conditions for both extraction and stripping are assigned. The results indicate that the efficiency of both process depend on the nature and composition of the phosphate ore, the nature of solvents, time of contact, the ratio between organic to liquor layers and the number of the applied stages. Also the results indicate that the efficiency of the used solvents have the following order.

tert-amyl alcohol > tributyl phosphate > butanol > pentanol > heptanol > octanol > methyl-isobutyl ketone.

The decrease in the efficiency of extraction with hydrocarbon chain length for alcohols is attributed to the decrease of the active units per unit volume of the alcohol, the association of the alcohol molecules which increases as the hydrocarbon chain increase and electron donor effects of the hydrocarbon chain. By using mixed solvents to extract phosphoric acid, it is found that the mixed solvents improve the separation efficiency and eliminate the emulsion formation during the shaking process of different phases.

#### INTRODUCTION

The aim of this work is the extraction of pure phosphoric acid from the medium of dissolution of phosphate ores in HCl at the optimum conditions. Pure and mixed solvents were used and the optimum conditions of extraction and stripping were assigned in each case.

The choice of the solvent seems to be the most important in the extraction process. Temperature control, shaking speed, contact time and pH of the extracting medium are also important factors in this process, but generally the basic concepts are not largely different among the main routes of extraction.

The foregoing literature<sup>1-4</sup> survey showed that alcohols<sup>5</sup> such as n-butyl, isobutyl-, isoamyl and cyclohexyl alcohols, ethers for example, isopropyl ether<sup>6, 7</sup>, ketones such as methyl ethyl ketone and methyl isobutyl ketone and phosphoric acid esters, for example tributyl phosphate can be used as extracting agents to extract pure phosphoric acid.<sup>8-10</sup> There are several factors should be considered before choosing the required solvent. This may include<sup>11</sup>:

1. Cost, availability and stability of the solvent.

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- 2. High extraction efficiency and high selectivity towards phosphoric acid
- 3. Ease in separating the two phases as well as recovering pure phosphoric acid from the organic phase.
- 4. High solubility in the organic diluent and low aqueous solubility.

Recently, between 1992–1997, Hanna *et al*<sup>12–16</sup> succeeded to purify the wet-process phosphoric acid produced from dissolution of the phosphate ore in sulphuric acid by using the solvent extraction or precipitation methods. This study indicated that the purity of the extracted phosphoric acid and the efficiency of the extraction depend on the nature of the solvent, the time and rate of shaking, the temperature, the number of the extraction steps and the solvent/acid ratio. In the previous papers the authors studied the chemical analysis, X-ray pattern, infrared absorption spectra and the dissolution of Abu-Tartor phosphate ore in some mineral acids. <sup>17, 18</sup>

#### **EXPERIMENTAL**

In this work the main starting materials were the phosphate ores obtained from Sabyia and Abu-Tartor regions (Egypt), in addition to hydrochloric acid (concentration = 3.65%, specific gravity = 1.19). The hydrochloric acid was diluted to 6N before use. Tertiary amyl alcohol, butanol, pentanol, heptanol, octanol, tributyl phosphate and iso-methyl ketone were used as extracting agents of phosphoric acid. The reagent, the solvents and the indicators used in the extraction or the chemical analysis were analytical grade free from water and inorganic impurities.

Method of analysis: To choose a suitable sample for the preparation of phosphoric acid from the ground phosphate ores (Sabyia and Abu-Tartor) representative concentrated samples were taken and exposed to the sieving process through five different sieve meshes. P<sub>2</sub>O<sub>5</sub> and Fe contents were determined spectrophotometrically as that reported before<sup>12</sup>. F contents was determined using fluoride ion selective electrode pH meter "Orion" model 94–09.

Preparation of phosphoric acid: Phosphoric acid was prepared by dissolving phosphate ores in hydrochloric acid at the optimum conditions of dissolution.

Solvent extraction: Solvent extraction technique was used to separate phosphoric acid from CaCl<sub>2</sub> and other salts in the digestion liquor. The efficiency of the acid extraction is affected by different factors such as the nature of solvent, time of shaking, temperature and aqueous: organic ratio. The technique used is single or batch-wise extraction. To study the effect of these factors, sets of experiments were carried out.

Stripping of P<sub>2</sub>O<sub>5</sub> from the organic layer: In this experiment the extracted phosphoric acid in the organic layer was stripped using water. The ratio of organic to aqueous phase and the number of stages for separation was also studied.

### RESULTS AND DISCUSSION

The chemical analysis of both phosphate ores shows that Abu-Tartor phosphate ore contains higher percentage of iron relative to Sabyia ore<sup>16</sup>.

n-Butanol is used to extract phosphoric acid from the dissolution medium of the phosphate ores in HCl at the optimum conditions<sup>17</sup>. In this trial the ratio

between the alcohol and the aqueous layer was adjusted at 1:1, 1.5:1, 2:1, 2.5:1 and 3:1 (Table 1). In case of Sabyia ore, the results indicate that the percentage of extracted P<sub>2</sub>O<sub>5</sub> increases from 28.92 to 63.7 when the ratio between the alcohol to the aqueous layer, increases from 1:1 to 3:1. Similarly, in the case of Abu-Tartor phosphate ore the percentage of P<sub>2</sub>O<sub>5</sub> extracted increases from 26.43 to 51.07 using the previously mentioned ratios.

TABLE-1 THE PERCENTAGE OF P2O5 EXTRACTED BY n-BUTYL ALCOHOL AT DIFFERENT RATIOS OF (org./aq.)

| Vol. of org. | Vol. of aq. | org./aq. | P <sub>2</sub> O <sub>5</sub> % |            |  |
|--------------|-------------|----------|---------------------------------|------------|--|
| (mL)         | (mL)        |          |                                 | Abu-Tartor |  |
| 10           | 10          | 1:1      | 28.92                           | 26.43      |  |
| 15           | 10          | 1.5:1    | 39.30                           | 30.83      |  |
| 20           | 10          | 2:1      | 46.20                           | 35.72      |  |
| 25           | 10          | 2.5:1    | 57.10                           | 45.71      |  |
| 30           | 10          | 3:1      | 63.70                           | 51.07      |  |

TABLE-2 (a) THE PERCENTAGE OF P2O5 EXTRACTED STEP-WISE (1:1) BY n-BUTYL ALCOHOL (SABYIA AND ABU-TARTOR ORES)

| No. of aq./org. |       | Vol.      | of aq.         | Vol.    | of aq.     | P <sub>2</sub> O <sub>5</sub> % |            |
|-----------------|-------|-----------|----------------|---------|------------|---------------------------------|------------|
| Steps           | Ratio | Sabyia    | Abu-Tartor     | Sabyia  | Abu-Tartor | Sabyia                          | Abu-Tartor |
| 1               | 1:1   | 20 mL     | 20 mL          | 20 mL   | 20 mL      | 28.5                            | 26.2       |
| 2               | 1:1   | 15 mL     | 16 mL          | 15 mL   | 16 mL      | 30.8                            | 17.7       |
| 3               | 1:1   | 10.5 mL   | 12 mL          | 10.5 mL | 12 mL      | 4.6                             | 15.7       |
|                 |       | Total Per | centage of P2C |         | 63.9       | 59.5                            |            |

#### (b) THE PERCENTAGE OF P<sub>2</sub>O<sub>5</sub> AND Fe STRIPPED STEP-WISE WITH WATER

| No. of | O=== /U_O                      | Vol. of H <sub>2</sub> O |                | Vol. o | Vol. of Org.   |                | Total Stripped |                |      |  |
|--------|--------------------------------|--------------------------|----------------|--------|----------------|----------------|----------------|----------------|------|--|
| Steps  | Org./H <sub>2</sub> O<br>ratio | Sabyia                   | Abu-<br>Tartor | Sabyia | Abu-<br>Tartor | Sabyia ore (%) |                | Abu-Tartor (%) |      |  |
|        |                                |                          |                |        |                | $P_2O_5$       | Fe             | $P_2O_5$       | Fe   |  |
| 1      | 2:1                            | 12.50                    | 12.50          | 25.00  | 25.00          |                |                |                |      |  |
| 2      | 2:1                            | 12.00                    | 12.25          | 24.00  | 24.50          | 85.20          | 0.26           | 79.26          | 3.26 |  |
| 3      | 2:1                            | 11.80                    | 12.00          | 23.00  | 24.00          |                |                |                |      |  |

Also, the batch-wise procedure was conducted using three steps at a ratio 1:1 of organic solvent to aqueous layer (Table-2a). It was found that on using the step-wise technique, the total percentage of extracted P<sub>2</sub>O<sub>5</sub> amounts to 63.9 and

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59.53% in the case of Sabyia and Abu-Tartor ores, respectively. The obtained results were in agreement with the efficiency obtained by one step extraction for Sabyia ore while it increased from 51.07 to 59.53% for Abu-Tartor ore. This work was extended to strip  $P_2O_5$  from *n*-butanol using  $H_2O$  as stripping agent at an organic-water ratio equals to 2:1 through three loading stages, (Table-2b). The results indicated that these conditions were good for stripping the phosphoric acid with efficiency equals to 85.2% and the iron content was reduced from 0.96% its original value, in Sabyia ore to 0.26%, whereas in case of Adu-Tartor phosphate ore the stripping of  $H_3PO_4$  occurred with an efficiency equals to 79.26% and Fe content was reduced to 3.36% from its original value.

The efficiency of extraction of  $P_2O_5$  becomes 77.83% and the stripping percentage reaches 86.2% when the extraction ratio is 1:3 (aq./org.) and the stripping process carried out at the ratio of 1:2 aqueous to organic, (Table-3a, b), for Abu-Tartor phosphate ore. Simultaneously, in case of Sabyia phosphate ore, the extraction efficiency of  $P_2O_5$  becomes 85.8% at the ratio of (1:3) aqueous to organic and the stripping percentage reaches 98.7% at an aqueous/organic ratio equals 1:2 (Table-2).

Comparing these obtained data for extraction of P<sub>2</sub>O<sub>5</sub> from the medium of dissolution, it may be concluded that:

- 1. In the case of Sabyia phosphate ore, the percentage of P<sub>2</sub>O<sub>5</sub> extracted by *n*-butanol in all ratios is higher than that extracted from Abu-Tartor ore in HCl under the same conditions of extraction.
- 2. The percentage of the stripped iron in case of Abu-Tartor ore (3.26%) is higher than the percentage of iron stripping in case of Sabyia ore (0.26%). This may lead to a decrease efficiency of *n*-butanol in extracting and stripping in case of Abu-Tartor ore.
- 3. As the ratio aqueous to organic in the extraction step increases from 1:1 to 1:3 through the batch-wise process, the percentage of extracted P<sub>2</sub>O<sub>5</sub> increases for the two ores. This increase equals to 30% for Abu-Tartor ore while it amounts to 34% in Sabyia phosphate ore. The difference in the percentage of this increase may be due to the less solubility of Abu-Tartor aqueous layer in *n*-butyl alcohol than the solubility of Sabyia ore, as confirmed by the decrease in the efficiency throughout the extraction process.
- 4. In the stripping step, the percentage of the stripped iron content in Sabyia phosphate ore remains nearly constant (0.23 and 0.26%) when the ratio aq./org. increase from 1:1 to 1:3 in the extraction step, while for Abu-Tartor ore, it increases remarkably and proportionally from 3.26 to 8.90% when the aq./org. ratio is altered from 1:1 to 1:3. This may be attributed to the increase in the efficiency of *n*-butanol to extract  $P_2O_5$  as well as.  $Fe^{3+}$  in addition to the nature of the iron in Abu-Tartor ore. (Table-2).

From the analysis of the obtained data in Tables 1, 2 and 3, it may be concluded that the optimum conditions for extracting  $H_3PO_4$  by *n*-butyl alcohol from the medium of the dissolution for Abu-Tartor phosphate ore are:

 $P_2O_5\%$  extracted = 77.83, aqueous/organic ratio = 1:3, time of the shaking

= 15 min. and temperature = 25°C and the optimum conditions of the stripping stage by water from the organic layer are:  $P_2O_5\% = 86.2$ , Fe = 8.69% ratio of  $H_2O/org. = 1:3$ , time of shaking = 15 min. and temperature = 25°C.

TABLE-3 (a) THE PERCENTAGE OF P2O5 EXTRACTED STEP-WISE (1:1) BY n-BUTYL ALCOHOL (ABU-TARTOR AND SABYIA ORES)

| No. of | aq./org. | Vol. o      | f aq.      | Vol. of aq.                 |        | P <sub>2</sub> O | 5%     |
|--------|----------|-------------|------------|-----------------------------|--------|------------------|--------|
| Steps  | Ratio    | Abu-Tartor  | Sabyia     | Abu-Tartor                  | Sabyia | Abu-Tartor       | Sabyia |
| 1      | 1:3      | 20          | 20         | 60                          | 60     | 50.72            | 62.2   |
| 2      | 1:3      | 11 -        | 9          | 33                          | 27     | 20.72            | 14.6   |
| 3      | 1:3      | 6           | 45         | 18                          | 13.5   | 6.40             | 9.0    |
|        |          | Total Perce | ntage of P | <sub>2</sub> O <sub>5</sub> |        | 77.83            | 85.8   |

## (b) THE PERCENTAGE OF P<sub>2</sub>O<sub>5</sub> AND Fe STRIPPED STEP-WISE WITH RATIO 1:2 BY WATER

| No. of H <sub>2</sub> O/Org.<br>Steps ratio |     | Voi. of H <sub>2</sub> O (mL) |                | Vol. of Org. (mL) |                | Total Stripped% |      |                               |                |
|---|-----|-------------------------------|----------------|-------------------|----------------|-----------------|------|-------------------------------|----------------|
|   |     | Sabyia                        | Abu-<br>Tartor | Sabyia            | Abu-<br>Tartor | Sabyi           |      |                               | Abu-Tartor (%) |
|   |     |                               |                |                   |                | $P_2O_5$        | Fe   | P <sub>2</sub> O <sub>5</sub> | Fe             |
| 1   | 1:2 | 20.0                          | 12.5           | 40.0              | 25             |                 |      |                               |                |
| 2   | 1:2 | 20.0                          | 12.5           | 40.0              | 25             | 98.70           | 0.23 | 86.20                         | 8.96           |
| 3   | 1:2 | 18.8                          | 11.5           | 37.6              | 25             |                 |      |                               |                |

These results are matching with those obtained previously in the case of Sabyia ore<sup>19</sup> and are in agreement with the results obtained by different authors.<sup>20, 21</sup>

The results of using tert-amyl acohol in extracting phosphoric acid from the medium of dissolution of phosphate ore in HCl showed that it has an efficiency of 77.4% in case of Sabyia phosphate ore while it decreased to 68.05% in case of Abu-Tartor ore, Table-4. It was also observed that the efficiency of the extraction increases proportionally with the increasing in the ratio between the aqueous and the organic layers.

TABLE-4 THE PERCENTAGE OF P2O5 EXTRACTED BY tert. AMYL ALCOHOL AT DIFFERENT RATIOS OF org./aq.

| Vol. of aq. | Vol. of org. | ana tan Batia         | P <sub>2</sub> O <sub>5</sub> % |            |  |
|-------------|--------------|-----------------------|---------------------------------|------------|--|
| (mL)        | (mL)         | org./aq. Ratio Sabyia | Sabyia                          | Abu-Tartor |  |
| 10          | 10           | 1:1                   | 46.20                           | 31.43      |  |
| 10          | 20           | 1:2                   | 60.13                           | 52.40      |  |
| 10          | 30           | 1:3                   | 70.65                           | 62.86      |  |
| 10          | 40           | 1:4                   | 77.50                           | 68.05      |  |

Table 5a shows a comparison between the efficiency of *tert*-amyl alcohol in extracting  $P_2O_5$  from the medium of the dissolution of Sabyia and Abu-Taror ores using 1:1 aq./org. ratio in three steps and Table 5a and 5b represents the stripping percentage of both  $P_2O_5$  and Fe by water. The results indicated that both of the extraction and stripping efficiencies of *tert*. amyl alcohol to extract and stripping out  $P_2O_5$  are higher in the case of Sabyia ore than those in Abu-Tartor one. It is note worthy that the reduction of iron content in this process is similar to that observed in case of *n*-butyl alcohol.

TABLE-5 (a) THE PERCENTAGE OF  $P_2O_5$  EXTRACTED STEP-WISE (1:1) BY n-BUTYL ALCOHOL (SABYIA AND ABU-TARTOR ORES)

| No. of aq./org. |           | Vol. of aq. (mL)            |            | Vol. of ac | q. (mL) | P <sub>2</sub> O <sub>5</sub> % |        |  |
|-----------------|-----------|-----------------------------|------------|------------|---------|---------------------------------|--------|--|
| Steps           | Ratio     | Abu-Tartor                  | Sabyia     | Abu-Tartor | Sabyia  | Abu-Tartor                      | Sabyia |  |
| . 1             | 1:1       | 20                          | 20         | 20         | 20      | 30.95                           | 32.51  |  |
| 2               | 1:1       | 14                          | 13         | 14         | 13      | 21.90                           | 25.0   |  |
| 3               | 1:1       | 9                           | 8.5        | 11         | 11.46   | 14.75                           | 9.0    |  |
|                 | Total Per | centage of P <sub>2</sub> C | <b>)</b> 5 |            |         | 64.31                           | 72.26  |  |

(b) THE PERCENTAGE OF P<sub>2</sub>O<sub>5</sub> AND Fe STRIPPED STEPWISE WITH RATIO 1:2 BY WATER

|   |     |        | Vol. of H <sub>2</sub> O (mL) |        | Vol. of Org. (mL) |                               | Total Stripped |                               |      |  |
|---|-----|--------|-------------------------------|--------|-------------------|-------------------------------|----------------|-------------------------------|------|--|
| No. of Org./H <sub>2</sub> O<br>Steps ratio |     |        | Abu-                          |        | Abu-              | Sabyia ore (%)                |                | Abu-Tartor (%)                |      |  |
|   |     | Sabyia | Tartor                        | Sabyia | Tartor            | P <sub>2</sub> O <sub>5</sub> | Fe             | P <sub>2</sub> O <sub>5</sub> | Fe   |  |
| 1 ,   | 2:1 | 12.5   | 12.5                          | 25     | 25.0              |                               |                |                               |      |  |
| 2   | 2:1 | 11.0   | 11.75                         | 23     | 23.5              | 1                             | 0.3            | 89.1                          | 5.74 |  |
| 3   | 2:1 | 10.5   | 10.9                          | 21     | 21.8              |                               |                |                               |      |  |

TABLE-6 THE PERCENTAGE OF  $P_2O_5$  EXTRACTED BY TRIBUTYL PHOSPHATE

| Vol. of aq. | Vol. of org. | / Dati-        | P <sub>2</sub> O | 5%     |
|-------------|--------------|----------------|------------------|--------|
| (mL)        | (mL)         | aq./org. Ratio | Abu-Tartor       | Sabyia |
| 10          | 10           | 1:1            | 30.32            | 35.60  |
| 10          | 20           | 1:2            | 50.72            | 57.11  |
| 10          | 30           | 1:3            | 60.72            | 68.91  |

On the other hand, tri-butyl phosphate, TBP, was used to extract  $P_2O_5$  from the medium of dissolution. In case of Abu-Tartor phosphate ore, the efficiency of TBP equals to 30.32 at (1:1) aq./org. ratio. This value increases proportionally with the increase in the aq./org. ratio reaching 60.72% at (1:3) aq./org., (Table-6).

On using three steps each at 1:1 ratio, the net extraction efficiency equals to 63.22 with a stripping efficiency of 91.04% P<sub>2</sub>O<sub>5</sub> and 61.4% of iron (Table-7). Also, for Abu-Tartor phosphate ore, when three steps were carried out with (1:3) aq./org. ratio the efficiency of extraction increases from 63.22 to 89.00 and the stripping increases from 91.04 to 92.45%. Moreover, the iron content stripping increases from 61.4 to 88.8% of its original value (Table-8a, b).

TABLE-7 (a) THE PERCENTAGE OF P2O5 EXTRACTED STEP-WISE 1:1 BY TRIBUTYL PHOSPHATE (SABYIA AND ABU-TARTOR ORES)

| No. of aq./org. |           | Vol. of a                   | q. (mL) | Vol. of a  | q. (mL) | P <sub>2</sub> O <sub>5</sub> % |        |  |
|-----------------|-----------|-----------------------------|---------|------------|---------|---------------------------------|--------|--|
| Steps           | Ratio     | Abu-Tartor                  | Sabyia  | Abu-Tartor | Sabyia  | Abu-Tartor                      | Sabyia |  |
| 1               | 1:1       | 20                          | 20      | 20.0       | 20.0    | 34.66                           | 31.10  |  |
| 2               | 1:1       | 16.2                        | 17      | 16.2       | 17.0    | 23.80                           | 21.60  |  |
| 3               | 1:1       | 12.5                        | 13.9    | 12.5       | 13.9    | 13.20                           | 12.96  |  |
|                 | Total Per | centage of P <sub>2</sub> C | )5      |            |         | 71.66                           | 63.22  |  |

(b) THE PERCENTAGE OF P2O5 AND Fe STRIPPED STEPWISE WITH RATIO 1:2 BY WATER

|              |                                | Vol. of H <sub>2</sub> O (mL) |        | Vol. of Org. (mL) |               | Total Stripped |         |          |          |
|--------------|--------------------------------|-------------------------------|--------|-------------------|---------------|----------------|---------|----------|----------|
| No. of Steps | Org./H <sub>2</sub> O<br>ratio | Calada                        | Abu-   | Cabada            | Abu-          | Sabyia         | ore (%) | Abu-Ta   | rtor (%) |
|              |                                | Sabyia                        | Tartor | Sabyia            | Sabyia Tartor |                | Fe      | $P_2O_5$ | Fe       |
| 1            | 2:1                            | 12.5                          | 12.5   | 25                | 25            |                |         |          |          |
| 2            | 2:1                            | 12                            | 12.5   | 25                | 25            | 94.19          | 50.31   | 91.04    | 61.4     |
| 3            | 2:1                            | 12                            | 12.5   | 24                | 25            |                |         |          |          |

From Tables 1–7, it is observed that both of the percentage of the extraction and the stripping of P<sub>2</sub>O<sub>5</sub> in case of Sabyia phosphate ore are higher than those obtained from Abu-Tartor phosphate ore. Also, it may be concluded that the more suitable aqueous/organic ratio for the extraction process through three steps is 1:3. These results are in agreement with those obtained by Lembrikov et al.<sup>22</sup> using TBP to purify the wet process phosphoric acid with  $P_2O_5 = 21.7\%$ . Their results indicated that the efficiency of extracting pure phosphoric acid equals 93-96% and the  $R_2O_3$  oxides (R = Fe, Al, ...) percentage decreases from 1.2 to 0.07-0.17%.

On the other hand, Grinerich et al.<sup>23</sup> optimized the TBP/aqueous ratio to be 2.2:1 by using 6 extractions steps and 8 stripping ones. Their data also showed that as the organic/aqueous ratio increases, the number of steps decreases.

The mechanisms of the phosphoric acid extraction with TBP have been studied by different researchers<sup>24</sup>. According to Natio and Suznki<sup>25</sup>, the extraction of the phosphoric acid is due to the adduct formation resulting from the reaction between the acid ions and the TBP molecules. This intermediate adduct can be easily

dissociated by water to give the phosphoric acid and the tributyl phosphate molecules. Higgins and Baldwin<sup>26</sup> found that the value of the distribution coefficient of phosphoric acid between TBP and water increases proportionally with the increase in the acid concentration in the inorganic phase (aqueous). The water accompanying the acid into the TBP is salted out and when the content of TBP, H<sub>3</sub>PO<sub>4</sub> and H<sub>2</sub>O attains the 3:1:6 ratio in the presence of slight excess of HCl. Yagodin *et al.*<sup>27</sup> showed that the extraction of H<sub>3</sub>PO<sub>4</sub> by T.B.P. involves the formation of hydrate di-and mono solvate. At low H<sub>3</sub>PO<sub>4</sub> concentration, H<sub>3</sub>PO<sub>4</sub>-TBP is the main extracted species and the H<sub>3</sub>PO<sub>4</sub>-TBP fraction increases as H<sub>3</sub>PO<sub>4</sub> concentration increases. In general, the extraction of H<sub>3</sub>PO<sub>4</sub> by TBP occurs through an aggregate formation between the acid and the solvent, hence:

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^ H_3PO_4 \rightleftharpoons 2H^+ + HPO_4^{2-}$$
 $(BuO)_3P \rightleftharpoons O + H_2PO_4^- \rightarrow (BuO)_3P \rightleftharpoons O - - - H_2PO_4^-$ 

At high concentration:

$$(BuO)_3P = O - - H_2PO_4^- \xrightarrow{H^+} H_3PO_4^- + (BuO)_3P = O$$
(mono-solvate)

At low concentration, where the ionization of acid is relatively high:

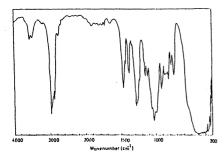
$$(BuO)_3P = O + H_2PO_4 \rightarrow [(BuO)_3P = O]_2 - - HPO_3^2$$
disolvate

| No. of aq./org. |       | Vol. o     | f aq.  | Vol. o     | f aq.  | P <sub>2</sub> O <sub>5</sub> % |        |  |
|-----------------|-------|------------|--------|------------|--------|---------------------------------|--------|--|
| Steps           | Ratio | Abu-Tartor | Sabyia | Abu-Tartor | Sabyia | Abu-Tartor                      | Sabyia |  |
| 1               | 1:3   | 20         | 20     | 60         | 60     | 68.10                           | 61.19  |  |
| 2               | 1:3   | 12         | 13     | 36         | 39     | 23.3                            | 19.76  |  |
| 3               | 1:3   | 7.5        | 8      | 22.5       | 24     | 5.13                            | 9.05   |  |
|                 |       | 93.53      | 89.9   |            |        |                                 |        |  |

# (b) THE PERCENTAGE OF $P_2O_5$ AND Fe STRIPPED STEPWISE WITH RATIO 1:2 BY WATER

|          |                             | Vol. of H | 20 (mL) | Vol. of O | org. (mL) |          | Total St | ripped%  |          |
|----------|-----------------------------|-----------|---------|-----------|-----------|----------|----------|----------|----------|
| No. of O | Org./H <sub>2</sub> O ratio | Cabrila   | Abu-    | Cabria    | Abu-      | Saby     | ia ore   | Abu-Ta   | rtor (%) |
| •        |                             | Sabyia    | Tartor  | Sabyia    | Tartor    | $P_2O_5$ | Fe       | $P_2O_5$ | Fe       |
| 1        | 2:1                         | 12.5      | 12.5    | 25        | 25        |          | -        |          |          |
| 2        | 2:1                         | 12.3      | 12.5    | 24.6      | 25        | 95.2     | 76.9     | 92.45    | 88.8     |
| 3        | 2:1                         | 12.0      | 12.4    | 24        | 24.8      |          |          |          |          |

On the other hand (BuO)<sub>3</sub>P=O is important for metal extraction, such as Zr, Fe, ...) from either chloride or nitrate solution and the mechanism is generally considered to involve coordination of the phosphoryl (P=O) group directly to the metal irons as in MO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>.2TBP. So, it is useful to follow the ability of Fe to be extracted by using TBP in case of the phosphate of Abu-Trator where iron is higher than that of Sabyia ore. Table 11b reveals that the extraction of P<sub>2</sub>O<sub>5</sub> is accompanied by the extraction of iron content. In case of Abu-Tartor phosphate ore, the efficiency of TBP to strip iron content reaches 88.8%. The infrared spectrum of pure TBP (Fig. 1a), has very strong bands at 970, 1053 and 1060



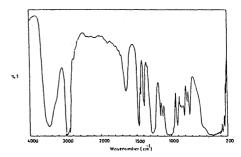


Fig. 1 The IR-spectra of pure tributyl phosphate (a) and after loaded with phosphoric acid (b).

cm<sup>-1</sup> due to (P-O-)-C stretching vibration, whereas the P-O mode band is at 1290 cm<sup>-1</sup>. The broad (P)-OH bands appear at 2845, 2900 cm<sup>-1</sup>. Also, a weak intensity band at about 1650 cm<sup>-1</sup> is attributed to (P)-OH deformation. The infrared spectrum of TBP after loaded with phosphoric acid, (Fig. 1b), through the extraction process exhibits:

- 1. A conversion of the weak intensity band at 1650 cm<sup>-1</sup> to a sharp strong one which may confirm the formation of a complex between phosphoric acid and TBP.
- 2. The sharp band with medium intensity at 1030 cm<sup>-1</sup> containing two shoulders around it, is converted to broad and strong intensity band.
- 3. The medium absorption band at 1290 cm<sup>-1</sup> is converted to a strong broad one. This may suggest the formation of a complex between Fe and TBP.

From the results of infrared, it may be concluded that TBP extracts P<sub>2</sub>O<sub>5</sub> as well as Fe from the medium of dissolution of phosphate ore in HCl.

Different solvents much as: tert-amyl alcohol, butanol, pentanol, heptanol, octanol and methyl isobutyl ketone were also used to extract P<sub>2</sub>O<sub>5</sub> from the medium of dissolution. The results in Table-9 indicate that the efficiency of the used solvents have the following order:

Tert-amyl alcohol > tributyl phosphate > butanol > pentanol > heptanol > octanol > methyl isobutyl ketone.

The decrease of efficiency of extraction with hydrocarbon chain length for alcohol may be due to:

- 1. The decrease of the active units per unit volume of the alcohol.
- 2. The association of alcohol molecules which increases with the increase of

length of the hydrocarbon chain. This association decreases the interaction effects between alcohol and  $H_3PO_4$ .

3. The electron donor effect decreases as the hydrocarbon chain increases which decreases the alcohol-phosphoric acid aggregate formation.

In this study, in light of the literature survey<sup>28</sup>, a number of solvent mixtures with different ratios were used, namely,

- 1. Tert-amyl alcohol + methyl isobutyl ketone (15:1 v/v%).
- 2. Tributyl phosphate + acetone (5:1 v/v%) and (10:1 v/v%).
- 3. Tert-amyl alcohol + pentanol (2:1), (1:1), and (1:2 v/v%)
- 4. Tert-amyl alcohol + tributyl phosphate (2:3 v/v%).
- 5. Tert-amyl alcohol + acetone (5:1), (2:1) and (1:1 v/v%).

The obtained results are tabulated in Table-10. The results indicate that tert-amyl alcohol/methyl isobutyl ketone and TBP/acetone have the highest efficiency for extraction of H<sub>3</sub>PO<sub>4</sub> acid where methyl isobutyl ketone and acetone act as diluent for the alcohol and TBP, respectively.

From these results it may be concluded that the mixed solvents improve the separation efficiency and eliminate the emulsion formation during the shaking process of different phases.

TABLE-9
THE PERCETAGE OF P<sub>2</sub>O<sub>5</sub> EXTRACTED BY DIFFERENT SOLVENTS

| Solvent                | og Josep Datio   | P <sub>2</sub> O <sub>5</sub> (%) |            |  |
|------------------------|------------------|-----------------------------------|------------|--|
| Solvent                | aq./org. Ratio – | Sabyia                            | Abu-Tartor |  |
| Tert-amyl alcohol      | 1:1              | 46.20                             | 31.43      |  |
|                        | 1:2              | 60.13                             | 52.40      |  |
|                        | 1:3              | 70.65                             | 62.86      |  |
|                        | 1:4              | 77.40                             | 68.90      |  |
| Tributyl phosphate     | 1:1              | 35.95                             | 30.32      |  |
|                        | 1:2              | 57.11                             | 50.72      |  |
|                        | 1:3              | 68.91                             | 60.72      |  |
|                        | 1:4              | 75.43                             | 66.50      |  |
| Butanol                | 1:1              | 39.30                             | 26.43      |  |
|                        | 1:2              | 46.20                             | 35.72      |  |
|                        | 1:2.5            | 57.10                             | 45.71      |  |
|                        | 1:3              | 63.70                             | 51.71      |  |
| Pentanol               | 1:3              | 46.19                             | 38.92      |  |
| Heptanol               | 1:3              | 27.54                             | 21.85      |  |
| Octanol                | 1:3              | 25.00                             | 19.13      |  |
| Methyl isobutyl ketone | 1:3              | 15.67                             | 9.17       |  |
|                        |                  |                                   |            |  |

| TABLE-10   |
|--|
| THE EFFICIENCY OF THE PHOSPHORIC ACID EXTRACTION |
| USING MIXED SOLVENTS                             |

| Mix                      | Ratio of aq./org. | Efficiency (%) |  |
|--------------------------|-------------------|----------------|--|
| T.A.A. + Isobutyl ketone | 1:3               | 69.1           |  |
| (15:1)                   | 1:2               | 57.44          |  |
| TBP + Acetone            |                   |                |  |
| (5:1)                    | 1:3               | 68.4           |  |
| (10:1)                   | 1:3               | 68.26          |  |
| T.A.A. + Pentanol        |                   |                |  |
| (2:1)                    | 1:3               | 51.27          |  |
| (1:1)                    | 1:3               | 47.88          |  |
| (1:2)                    | 1:3               | 44.49          |  |
| T.A.A. + TBP(2:3)        | 1:3               | 53.49          |  |
| T.A.A. + acetone         |                   |                |  |
| 5:1                      | 1:3               | 76.69          |  |
| 2:1                      | 1:3               | 86.44          |  |
| 1:1                      | 1:3               | 89.62          |  |

T.A.A.—tert. amyl alcohol.

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