

# Study of the multicomponent system wet process phosphoric acid–methyl isobutyl ketone at 40 °C phase equilibria and extraction performances

M. Feki<sup>a</sup>, M. Stambouli<sup>b</sup>, D. Pareau<sup>b</sup>, H.F. Ayedi<sup>a,\*</sup>

<sup>a</sup> *Laboratoire de Chimie Industrielle, Ecole Nationale d'Ingénieurs de Sfax, B.P.W, 3038 Sfax, Tunisia*

<sup>b</sup> *Laboratoire de Chimie et Génie des Procédés, Ecole Centrale Paris, 92 295 Chatenay-Malabry Cedex, France*

Received 26 February 2001; received in revised form 19 September 2001; accepted 17 October 2001

## Abstract

This work concerns the purification of wet process phosphoric acid (WPA) by solvent extraction with methyl isobutyl ketone (MIBK) at 40 °C. For this purpose, an exhaustive study of the multicomponent extraction system WPA–MIBK was carried out. In a first step, the distribution of the main components (H<sub>3</sub>PO<sub>4</sub>, H<sub>2</sub>O, MIBK) and the major impurities of WPA (Ca<sup>2+</sup>, Mg<sup>2+</sup>, Al<sup>3+</sup>, Fe<sup>3+</sup>, SO<sub>4</sub><sup>2-</sup>, F<sup>-</sup>) between the conjugated phases was systematically studied. Then, expression of phase compositions in terms of H<sub>3</sub>PO<sub>4</sub>, H<sub>2</sub>O and MIBK on an impurity-free basis enabled us to compute the characteristics of the H<sub>3</sub>PO<sub>4</sub> countercurrent multistage extraction using the Mac Cabe–Thiele method. Both as-received and water-saturated MIBK were considered as solvent. From graphical results, optimum conditions to conduct the extraction of H<sub>3</sub>PO<sub>4</sub> from concentrated WPAs (53.5–58% P<sub>2</sub>O<sub>5</sub>) were determined. To validate experimentally the obtained results, continuous countercurrent extractions were performed on a laboratory-scale mixer-settler unit. A good agreement was observed. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Wet process phosphoric acid; Solvent extraction; Methyl isobutyl ketone

## 1. Introduction

Many phosphoric acid applications (such as making non-sludging liquid fertilisers, surface treatment products and feed-grade calcium phosphate for animal supplements) call for acid of intermediate quality between that of high purity furnace-grade acid (thermal acid) and impure conventional wet process phosphoric acid (WPA) [1,2]. Thermal acid is used only in applications where its price can be justified such as in pharmaceutical products, foodstuffs and detergents [2,3]. Solvent extraction purification of the cheaper and more widely available WPA is a better alternative to produce a range of specifications up to foodstuff quality [2].

In previous papers [4,5], dealing with WPA purification by solvent extraction with methyl isobutyl ketone (MIBK), we reported solubility and liquid–liquid phase equilibrium data for the ternary system H<sub>2</sub>O–H<sub>3</sub>PO<sub>4</sub>–MIBK [4], and compared the selectivity of MIBK [5] to those of other solvents described in the literature. Since WPA and analytical phosphoric acid behave so differently against MIBK, essen-

tially with respect to mutual phase solubility at high H<sub>3</sub>PO<sub>4</sub> concentrations and water coextraction [4], the ternary phase diagram H<sub>2</sub>O–H<sub>3</sub>PO<sub>4</sub>–MIBK established previously could not be used to compute the characteristics of countercurrent multistage extractions.

The aim of the present work is to carry out an exhaustive study of the multicomponent system WPA–MIBK at 40 °C. For this purpose, the distribution of the components H<sub>3</sub>PO<sub>4</sub>, H<sub>2</sub>O, MIBK and the major impurities of WPA (Ca<sup>2+</sup>, Mg<sup>2+</sup>, Al<sup>3+</sup>, Fe<sup>3+</sup>, SO<sub>4</sub><sup>2-</sup>, F<sup>-</sup>) between the conjugated phases obtained when WPA (from Tunisian rock) is brought into equilibrium with MIBK was first studied systematically. The expression of phase compositions in terms of H<sub>3</sub>PO<sub>4</sub>, H<sub>2</sub>O and MIBK on an impurity-free basis (reduced coordinates) enabled us to transform the multicomponent system WPA–MIBK into a pseudo-ternary system H<sub>2</sub>O–H<sub>3</sub>PO<sub>4</sub>–MIBK. Mac Cabe–Thiele method [6] was then used to calculate, under different conditions, the number of theoretical extraction stages required to achieve a given yield of H<sub>3</sub>PO<sub>4</sub> from WPAs. In order to validate the graphical results, continuous countercurrent extractions were conducted using a laboratory-scale mixer-settler unit.

\* Corresponding author. Tel.: +216-4-274-088; fax: +216-4-275-595.

Table 1  
Composition (wt.%) of the basic WPA

H <sub>3</sub> PO <sub>4</sub> (P <sub>2</sub> O <sub>5</sub> )	Mg <sup>2+</sup> (MgO)	Ca <sup>2+</sup> (CaO)	Al <sup>3+</sup> (Al <sub>2</sub> O <sub>3</sub> )	Fe <sup>3+</sup> (Fe <sub>2</sub> O <sub>3</sub> )	SO <sub>4</sub> <sup>2-</sup>	F <sup>-</sup>	H <sub>2</sub> O	Total
75.9 (55.0)	0.712 (1.180)	– <sup>a</sup>	0.376 (0.710)	0.288 (0.412)	2.24	0.0990	19.6	99.2 <sup>b</sup>

<sup>a</sup> Concentration below the detection limit.

<sup>b</sup> Deviation from 100% was essentially ascribable to the precision of analyses.

## 2. Experimental

### 2.1. Raw materials

The basic WPA used in this work was prepared by treating Tunisian phosphate rock with sulphuric acid. Before carrying out the extraction experiments, the dark crude acid was partially defluorinated with bentonite [7] and then treated with activated carbon (supplied by NORIT) so as to reduce its humic matter content. This treatment was used to prevent crude formation during solvent extraction experiments. The composition of the resulting green acid is shown in Table 1.

Other acids obtained by dilution with water or concentration of the basic WPA were also considered. All the WPAs used practically present the same ratio of impurities/H<sub>3</sub>PO<sub>4</sub>.

MIBK with a purity higher than 99% was supplied by Fluka. Its water content, determined in the laboratory by the Karl Fischer method [8], was 0.09 wt.%. The reagent was used without dilution.

### 2.2. Procedures

All the experiments were carried out at about 40 °C. This temperature achieves a satisfactory compromise between an economical cooling of the feed WPA (industrially produced at about 80 °C) and the latter's acceptable viscosity. Moreover, at this temperature, losses of MIBK by evaporation remain negligible.

#### 2.2.1. Batch experiments

The distribution of the components of the system WPA–MIBK at 40 °C was studied by the ratio solvent to feed variation method [9]. Using the feed acid described in Table 1, weight phase ratios from 0.25 to 14 were used. Experiments were performed under thermostatic conditions at 40 ± 0.2 °C.

To avoid mass loss due to liquid pouring, each initial heterogeneous mixture was directly prepared in a weighed separatory funnel. The mixture was vigorously shaken for 20 min to achieve equilibrium and was then allowed to settle

for 1 h. The phases were next separated, weighed and samples of each phase were taken for H<sub>3</sub>PO<sub>4</sub>, H<sub>2</sub>O, MIBK and impurity analysis.

#### 2.2.2. Continuous experiments

Continuous countercurrent extractions were conducted at 40 ± 3 °C in a polyethylene mixer-settler unit of ROBATEL design (mixer volume: 35 ml; settler volume: 200 ml). The total feed flow rate accepted by the battery was in the range 2–5 l h<sup>-1</sup>. For each run the steady state was confirmed by H<sub>3</sub>PO<sub>4</sub> analysis in the organic stream and by verification of the mass flow rates balance. The maximum deviation of the latter was 2%.

### 2.3. Analysis

H<sub>3</sub>PO<sub>4</sub>, H<sub>2</sub>O and impurities in both aqueous and organic phases were analysed using the methods described elsewhere [5].

MIBK dissolved in aqueous raffinate was determined by hypiodite oxidation in alkaline medium [10]. After oxidation, the samples were acidified and the excess iodine was back titrated with sodium thiosulfate. The end point was detected by potentiometry with platinum polarised electrodes. The method was first validated using WPA samples containing known amounts of MIBK. A precision of 5% was obtained. When considering all the constituents of each aqueous raffinate, the deviation of mass balance was generally less than 3%.

MIBK in organic extracts was computed from the overall mass-balance established for this component. For each organic phase, the average deviation of material balance was 0.5% (maximum deviation was 1%).

## 3. Results and discussion

### 3.1. Extraction chemistry

The results considered here were obtained in batch operations. Nomenclature for expressing phase compositions and deriving subsequent equations is given in Fig. 1.

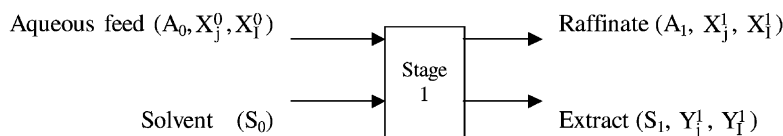


Fig. 1. Single-stage extraction.

Table 2  
H<sub>3</sub>PO<sub>4</sub>, H<sub>2</sub>O and MIBK composition (wt.%) of the phases A<sub>1</sub> and S<sub>1</sub>

No. of experiments	Weight ratio of the phases		Composition of the phases A <sub>1</sub> and S <sub>1</sub>					
	S <sub>0</sub> /A <sub>0</sub>	S <sub>1</sub> /A <sub>1</sub>	X <sub>H<sub>3</sub>PO<sub>4</sub></sub> <sup>1</sup>	Y <sub>H<sub>3</sub>PO<sub>4</sub></sub> <sup>1</sup>	X <sub>H<sub>2</sub>O</sub> <sup>1</sup>	Y <sub>H<sub>2</sub>O</sub> <sup>1</sup>	X <sub>MIBK</sub> <sup>1</sup>	Y <sub>MIBK</sub> <sup>1</sup>
1	0.25	1.16	71.5	52.4	21.64	10.74	0.60	36.7
2	0.5	2.19	69.6	43.6	23.22	8.94	0.58	48.3
3	0.75	3.13	66.2	36.6	24.36	7.50	0.55	56.4
4	1	3.94	64.6	31.6	25.00	6.41	0.40	62.5
5	1.5	5.61	64.3	24.7	25.40	5.07	0.38	70.6
6	2	7.28	63.5	20.5	25.20	4.20	0.34	75.7
7	3	10.44	62.2	15.1	25.86	3.11	0.28	82.1
8	4	13.71	61.7	12.3	25.80	2.49	0.26	85.8
9	5	17.45	61.4	10.0	26.03	2.06	0.25	88.0
10	6	21.58	61.3	8.7	26.06	1.78	0.22	89.6
11	7	26.78	61.3	7.7	26.30	1.59	0.22	90.7
12	9	37.11	60.5	6.2	27.50	1.27	0.21	92.4
13	10.5	45.94	60.4	5.4	28.00	1.12	0.20	93.2
14	12	56.02	60.2	4.8	28.48	1.02	0.20	93.9
15	14	74.00	59.8	4.1	29.97	0.92	0.18	94.5

Phase quantities A<sub>0</sub>, S<sub>0</sub>, A<sub>1</sub> and S<sub>1</sub>, and concentrations X<sub>j</sub>, Y<sub>j</sub>, X<sub>I</sub> and Y<sub>I</sub> of each component *j* (H<sub>3</sub>PO<sub>4</sub>, H<sub>2</sub>O, MIBK) or *I* (any WPA impurity) are expressed in weight and in wt.%, respectively.

It is convenient to precise that in all that follows, phosphoric acid concentration is expressed, indifferently, in terms of wt.% H<sub>3</sub>PO<sub>4</sub> or wt.% P<sub>2</sub>O<sub>5</sub> (wt.% H<sub>3</sub>PO<sub>4</sub> = 1.38 wt.% P<sub>2</sub>O<sub>5</sub>).

### 3.1.1. Species distribution

Tables 2 and 3 indicate the complete composition of the conjugated phases generated in batch by the initial mixtures WPA–MIBK described in Table 2.

To evaluate quantitatively the extraction power of MIBK against H<sub>3</sub>PO<sub>4</sub>, H<sub>2</sub>O and impurities we calculate—from the results in Tables 2 and 3—the percentage extracted (Ex, %) of each component *j* or *I* in the organic phases

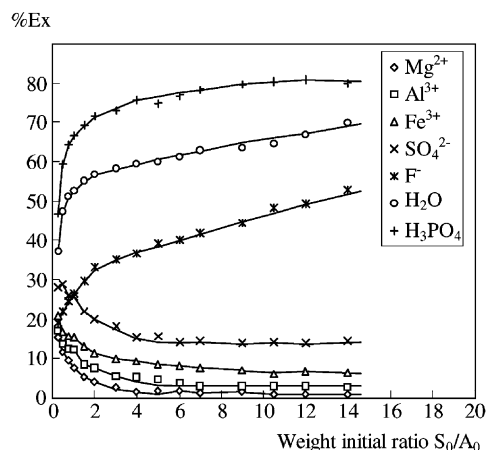


Fig. 2. Percentage of each component extracted of the WPA–MIBK system vs. S<sub>0</sub>/A<sub>0</sub>.

Table 3  
Impurity composition (wt.%) of the phases A<sub>1</sub> and S<sub>1</sub>

No. of experiments	X <sub>Mg<sup>2+</sup></sub> <sup>1</sup>	Y <sub>Mg<sup>2+</sup></sub> <sup>1</sup>	X <sub>Al<sup>3+</sup></sub> <sup>1</sup>	Y <sub>Al<sup>3+</sup></sub> <sup>1</sup>	X <sub>Fe<sup>3+</sup></sub> <sup>1</sup>	Y <sub>Fe<sup>3+</sup></sub> <sup>1</sup>	X <sub>SO<sub>4</sub><sup>2-</sup></sub> <sup>1</sup>	Y <sub>SO<sub>4</sub><sup>2-</sup></sub> <sup>1</sup>	X <sub>F<sup>-</sup></sub> <sup>1</sup>	Y <sub>F<sup>-</sup></sub> <sup>1</sup>	∑ X <sub>I</sub> <sup>1</sup>	∑ Y <sub>I</sub> <sup>1</sup>
1	1.060	0.162	0.540	0.0946	0.404	0.0888	2.79	0.930	0.1392	0.0276	4.93	1.303
2	1.340	0.0787	0.690	0.0498	0.510	0.0466	3.38	0.629	0.1646	0.0209	6.08	0.825
3	1.521	0.0505	0.776	0.0355	0.574	0.0336	3.92	0.437	0.1769	0.0181	6.97	0.575
4	1.625	0.0339	0.817	0.0284	0.602	0.0278	4.12	0.359	0.1803	0.0163	7.34	0.465
5	1.783	0.0177	0.911	0.0149	0.663	0.0176	4.63	0.231	0.1851	0.0137	8.17	0.295
6	1.887	0.0108	0.962	0.0105	0.706	0.0123	4.95	0.170	0.1836	0.0123	8.69	0.216
7	1.981	0.00534	1.017	0.0056	0.743	0.00771	5.26	0.110	0.1845	0.0095	9.19	0.138
8	2.050	0.00324	1.050	0.0041	0.769	0.00568	5.60	0.0719	0.1852	0.0077	9.65	0.0927
9	2.151	0.00220	1.104	0.0030	0.811	0.00429	5.83	0.0605	0.1861	0.0068	10.08	0.0768
10	2.278	0.00170	1.168	0.0021	0.860	0.00354	6.23	0.0462	0.1920	0.0059	10.73	0.0594
11	2.446	0.000997	1.268	0.0014	0.926	0.00276	6.68	0.0409	0.2012	0.0053	11.52	0.0514
12	2.679	0.000927	1.392	0.0011	1.023	0.00205	7.39	0.0310	0.2114	0.0045	12.69	0.0395
13	2.880	0.000560	1.492	0.00092	1.104	0.00154	7.87	0.0276	0.2102	0.0042	13.56	0.0348
14	3.098	0.000449	1.602	0.00085	1.178	0.00151	8.48	0.0240	0.2213	0.0038	14.58	0.0306
15	3.553	0.000361	1.832	0.00065	1.349	0.00123	9.62	0.0213	0.2353	0.0035	16.57	0.0270

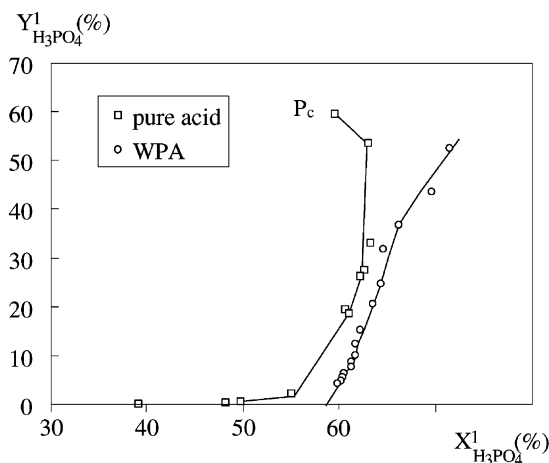


Fig. 3.  $\text{H}_3\text{PO}_4$  distribution curves for WPA and pure acid ( $P_c$  denotes the critical point).

as follows:

$$\text{Ex}(j) = \left( \frac{S_1 Y_j^1}{A_0 X_j^0} \right) \times 100 \quad (1)$$

Fig. 2 shows the percentage of  $\text{H}_3\text{PO}_4$ ,  $\text{H}_2\text{O}$  and impurities extracted by MIBK versus the initial phase ratio  $S_0/A_0$ . According to this figure, we have the following:

- (i) The percentage of  $\text{H}_3\text{PO}_4$  extracted increases, rapidly for a ratio  $S_0/A_0 < 2$  and moderately beyond this range.
- (ii) Metallic impurities and  $\text{SO}_4^{2-}$  practically follow the same trend, whereas  $\text{F}^-$  seems to behave differently. Indeed, while  $\text{F}^-$  coextraction is much more pronounced as  $S_0/A_0$  increases, metallic impurities and  $\text{SO}_4^{2-}$  tend rather to concentrate in the aqueous raffinate. Nevertheless,  $\text{SO}_4^{2-}$  seems to be more extractable in organic phases than metallic species.
- (iii) Like  $\text{H}_3\text{PO}_4$ , water is coextracted to a higher extent by MIBK.
- (iv) For initial phase ratios greater than unity, the extraction power of MIBK for impurities decreases in the order  $\text{F}^- > \text{SO}_4^{2-} > \text{Fe}^{3+} > \text{Al}^{3+} > \text{Mg}^{2+}$ .

Fig. 3 shows  $\text{H}_3\text{PO}_4$  distribution curves at  $40^\circ\text{C}$  for both systems WPA–MIBK (this work) and  $\text{H}_2\text{O}$ – $\text{H}_3\text{PO}_4$ –MIBK [4]. As it can be noticed, the most exhausted extraction raffinate obtained from WPA contains about 59%  $\text{H}_3\text{PO}_4$ . In return, the aqueous concentration level beyond which  $\text{H}_3\text{PO}_4$  is transferred from pure acid to the organic phase is about 50%  $\text{H}_3\text{PO}_4$ . WPA impurities that concentrate in the extraction raffinates are the cause of this  $\text{H}_3\text{PO}_4$  extractability difference (salting in effect). Beyond these aqueous concentration limits,  $\text{H}_3\text{PO}_4$  extraction becomes more favourable and this tendency is more pronounced for pure acid.

### 3.1.2. MIBK selectivity

Selectivity of MIBK for  $\text{H}_3\text{PO}_4$  against each impurity  $I$  is expressed in terms of decontamination factor  $\alpha_{\text{H}_3\text{PO}_4/I}$  is

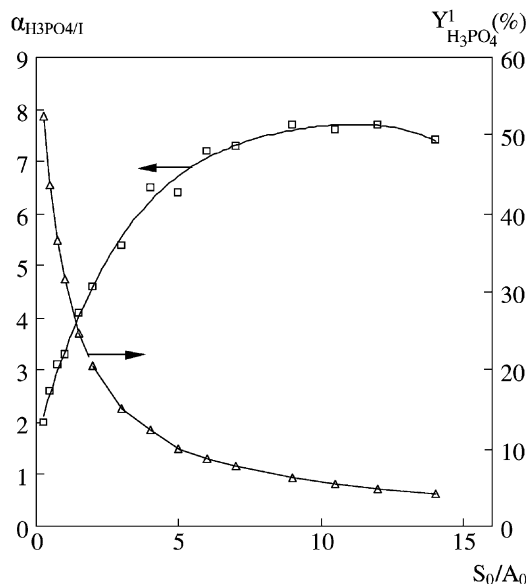


Fig. 4. Decontamination factor against the whole impurities and  $\text{H}_3\text{PO}_4$  concentration in the organic phase vs. the initial phase ratio  $S_0/A_0$ .

defined as follows:

$$\alpha_{\text{H}_3\text{PO}_4/I} = \frac{(\text{H}_3\text{PO}_4/I)_{\text{output}}}{(\text{H}_3\text{PO}_4/I)_{\text{input}}} = \frac{(S_1 Y_{\text{H}_3\text{PO}_4}^1 / S_1 Y_I^1)}{(A_0 X_{\text{H}_3\text{PO}_4}^0 / A_0 X_I^0)} \quad (2)$$

As shown in Fig. 4, where  $Y_{\text{H}_3\text{PO}_4}^1$  and the decontamination factor against the whole impurities  $\alpha_{\text{H}_3\text{PO}_4/I}$  are plotted as a function of  $S_0/A_0$ , an increase in the solvent/feed ratio leads to an organic extract less concentrated in  $\text{H}_3\text{PO}_4$  but more purified. This result illustrates the fact that performances of extraction (in terms of a good use of the MIBK extractive capacity) and selectivity are at first sight antagonistic and cannot be simultaneously reached in a simple extraction step. Consequently, a scrubbing section is necessary for the overall purification process in order to reduce to a lower extent the amount of coextracted impurities.

### 3.1.3. Water coextraction

Fig. 5 relates the amounts of water ( $Y_{\text{H}_2\text{O}}^1$ ) present in the organic extracts to those of  $\text{H}_3\text{PO}_4$  ( $Y_{\text{H}_3\text{PO}_4}^1$ ) in the same phases for both WPA (55%  $\text{P}_2\text{O}_5$ ) (this work) and analytical acid [4]. It can be observed that all points obtained in each case of acid could be well correlated by a straight line. For WPA, the relationship is as follows:

$$Y_{\text{H}_2\text{O}}^1 = (0.21 \pm 0.01) Y_{\text{H}_3\text{PO}_4}^1 \quad (3)$$

This implies a molar ratio  $\text{H}_2\text{O}/\text{H}_3\text{PO}_4$  in the organic phases equal to  $1.14 \pm 0.05$ . For pure phosphoric acid, the corresponding expression is as follows:

$$Y_{\text{H}_2\text{O}}^1 = (0.34 \pm 0.02) Y_{\text{H}_3\text{PO}_4}^1 \quad (4)$$

This leads to a molar ratio  $\text{H}_2\text{O}/\text{H}_3\text{PO}_4$  in the extracts equal to  $1.9 \pm 0.1$ .

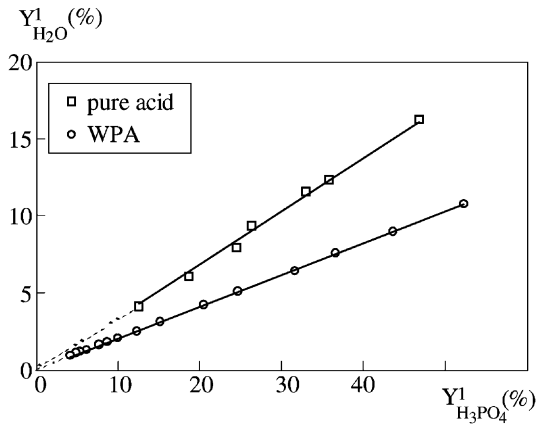


Fig. 5. Water coextraction for systems WPA–MIBK and H<sub>2</sub>O–H<sub>3</sub>PO<sub>4</sub>–MIBK.

Comparing water coextraction from WPA and pure acid proves that WPA impurities decrease the water uptake of the organic phase.

When considering water coextraction by MIBK at 40 °C from other WPAs obtained by dilution or by concentration of the basic acid described in Table 1, it was noted that the slope of the straight line

$$Y_{\text{H}_2\text{O}}^1 = aY_{\text{H}_3\text{PO}_4}^1 \quad (5)$$

depends on the concentration of H<sub>3</sub>PO<sub>4</sub> and consequently of water in the feed acid (Table 4). The correlation obtained is as follows:

$$a = -0.0145X_{\text{H}_3\text{PO}_4}^0 + 1.3165 \quad (6)$$

### 3.1.4. MIBK solubility in the aqueous raffinate

Fig. 6 shows the solubility of MIBK at 40 °C in the extraction raffinates generated by the system WPA–MIBK: the solvent solubility decreases with the H<sub>3</sub>PO<sub>4</sub> concentration in the aqueous raffinates (therefore, the impurity concentration of the raffinates increases). Nevertheless, the extraction raffinates from pure phosphoric acid [4] dissolve more MIBK than those from WPA (salting out effect). In this connection, it is important to note that the higher the extractant solubility, the higher its recovery costs from both the extraction raffinate and the stripped acid.

## 3.2. Extraction engineering

From equilibrium data in Table 2, the weight fractions of H<sub>2</sub>O, H<sub>3</sub>PO<sub>4</sub> and MIBK in aqueous and organic conju-

Table 4  
Values of the parameter *a* for different feed acids *A*<sub>0</sub>

$X_{\text{H}_3\text{PO}_4}^0$ (%)	$X_{\text{P}_2\text{O}_5}^0$ (%)	<i>a</i>
73.8	53.5	0.25
75.9	55	0.21
78	56.5	0.18
80	58	0.16

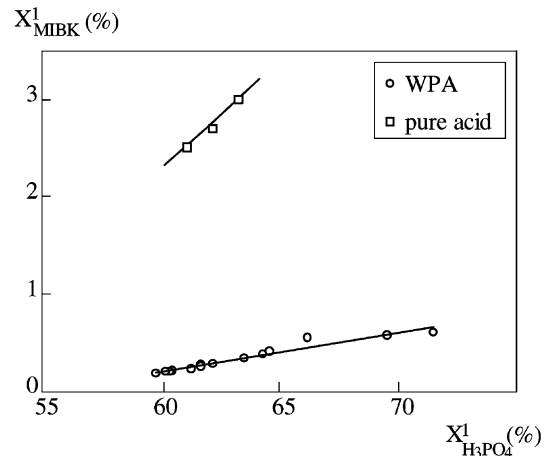


Fig. 6. MIBK solubility in raffinates generated by WPA and pure acid.

gated phases may be expressed in terms of reduced coordinates (coordinates on impurity-free basis)  $\bar{X}_j$  and  $\bar{Y}_j$  in the following way:

$$\bar{X}_j = \frac{X_j^1}{X_{\text{H}_3\text{PO}_4}^1 + X_{\text{H}_2\text{O}}^1 + X_{\text{MIBK}}^1} \quad (7)$$

$$\bar{Y}_j = \frac{Y_j^1}{Y_{\text{H}_3\text{PO}_4}^1 + Y_{\text{H}_2\text{O}}^1 + Y_{\text{MIBK}}^1} \quad (8)$$

where *j* stands for H<sub>2</sub>O, H<sub>3</sub>PO<sub>4</sub> or MIBK. Thus, the multicomponent extraction system WPA–MIBK may be transformed into a reduced ternary system H<sub>2</sub>O–H<sub>3</sub>PO<sub>4</sub>–MIBK. In these conditions, Mac Cabe–Thiele method can be used to determine the characteristics of multistage countercurrent extractions provided that the operating curve can be established. Subsequent paragraphs deal with this approach.

### 3.2.1. Determination of the distribution curve

From data in Table 2 and Eq. (7),  $\bar{X}_{\text{H}_3\text{PO}_4}$  values were calculated for all the aqueous phases considered. For organic phases, concentration of total impurities (Mg<sup>2+</sup>, Al<sup>3+</sup>, Fe<sup>3+</sup>, SO<sub>4</sub><sup>2-</sup>, F<sup>-</sup>) which all do not exceed 1.3% (see Table 3) will be neglected. Thus, reduced coordinates  $\bar{Y}_{\text{H}_3\text{PO}_4}$  become identical with normal  $Y_{\text{H}_3\text{PO}_4}$ . Fig. 7 shows the distribution curve plotted on  $\bar{X}_{\text{H}_3\text{PO}_4}$  and  $Y_{\text{H}_3\text{PO}_4}$  coordinates.

### 3.2.2. Operating curve equation

In order to establish the equation of the operating curve for H<sub>3</sub>PO<sub>4</sub>, it will be assumed that both concentration of total impurities in the organic phases and the solubility of MIBK in aqueous raffinates (this does not exceed 0.8% according to Table 3) can be neglected. Furthermore, concerning water coextraction, we will take into account the relationship (Eq. (5)) established previously and the fact that the slope *a* is dependent on the feed acid concentration.

An extraction cascade in which WPA (aqueous feed) is contacted countercurrently with MIBK is now considered.

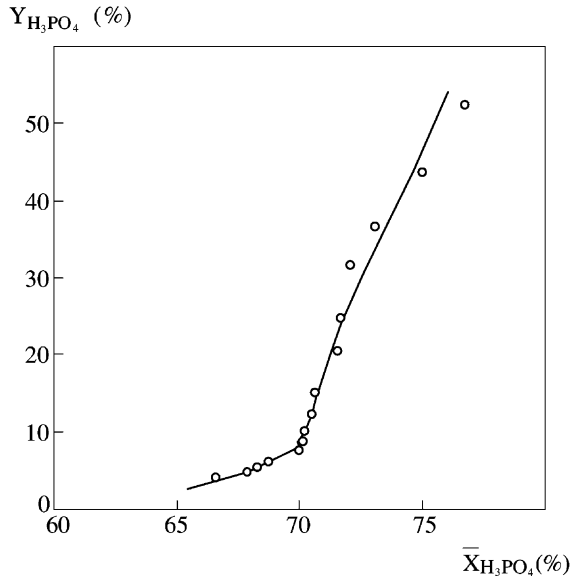


Fig. 7. H<sub>3</sub>PO<sub>4</sub> distribution curve on an impurity-free basis.

The nomenclature of weight flow rates, H<sub>3</sub>PO<sub>4</sub> concentrations and stage numbers is shown in Fig. 8. It will be assumed that equilibrium between both phases leaving each stage and steady state are reached.

In accordance with the nomenclature in Fig. 8, the composition on an impurity-free basis of the counterflowing phases can be written as

$$\bar{A}_0 \begin{cases} \text{H}_3\text{PO}_4 : \bar{X}_{\text{H}_3\text{PO}_4}^0 \\ \text{H}_2\text{O} : 1 - \bar{X}_{\text{H}_3\text{PO}_4}^0 \\ \text{MIBK} : 0 \end{cases}, \quad S_{n+1} \begin{cases} 0 \\ 0 \\ 1 \end{cases}, \quad \bar{A}_i \begin{cases} \bar{X}_{\text{H}_3\text{PO}_4}^i \\ 1 - \bar{X}_{\text{H}_3\text{PO}_4}^i \\ 0 \end{cases}, \quad S_i \begin{cases} Y_{\text{H}_3\text{PO}_4}^i \\ aY_{\text{H}_3\text{PO}_4}^i \\ 1 - (1+a)Y_{\text{H}_3\text{PO}_4}^i \end{cases}$$

For normal coordinates, the material balances for stages *i*–*n* are as follows:

total balance :  $A_{i-1} + S_{n+1} = S_i + A_n$  (9)

MIBK balance :  $S_{n+1} = (1 - (1+a)Y_{\text{H}_3\text{PO}_4}^i)S_i$  (10)

H<sub>3</sub>PO<sub>4</sub> balance :  $A_{i-1}X_{\text{H}_3\text{PO}_4}^{i-1} = S_iY_{\text{H}_3\text{PO}_4}^i + A_nX_{\text{H}_3\text{PO}_4}^n$  (11)

total impurity balance :  $A_{i-1} \sum X_I^{i-1} = S_i \sum Y_I^i + A_n \sum X_I^n$  (12)

Eq. (11) can be directly written in reduced coordinates as follows:

$$\bar{A}_{i-1}\bar{X}_{\text{H}_3\text{PO}_4}^{i-1} = S_iY_{\text{H}_3\text{PO}_4}^i + \bar{A}_n\bar{X}_{\text{H}_3\text{PO}_4}^n$$
 (13)

By subtracting Eq. (12) from Eq. (9), the total balance in terms of reduced flow rates is written as follows:

$$\bar{A}_{i-1} + S_{n+1} = S_i + \bar{A}_n$$
 (14)

Considering Eqs. (10), (13) and (14), the relationship obtained for the operating curve is

$$Y_{\text{H}_3\text{PO}_4}^i = \frac{\bar{X}_{\text{H}_3\text{PO}_4}^{i-1} - \bar{X}_{\text{H}_3\text{PO}_4}^n}{[(1+a)(1 - (S_{n+1}/\bar{A}_n))] \bar{X}_{\text{H}_3\text{PO}_4}^{i-1} - (1+a)\bar{X}_{\text{H}_3\text{PO}_4}^n + (S_{n+1}/\bar{A}_n)}$$
 (15)

### 3.2.3. Stagewise computations using McCabe–Thiele constructions

3.2.3.1. Effect of the flow rate *S<sub>n+1</sub>/A<sub>0</sub>* ratio. For an aqueous feed *A<sub>0</sub>* (WPA) with given H<sub>3</sub>PO<sub>4</sub> composition *X<sub>H3PO4</sub><sup>0</sup>* and a total impurity content  $\sum X_I^0$ , the reduced quantities  $\bar{A}_0$  and  $\bar{X}_{\text{H}_3\text{PO}_4}^0$  were calculated as follows:

$$\bar{A}_0 = A_0(1 - \sum X_I^0)$$
 (16)

and

$$\bar{X}_{\text{H}_3\text{PO}_4}^0 = \frac{X_{\text{H}_3\text{PO}_4}^0}{1 - \sum X_I^0}$$
 (17)

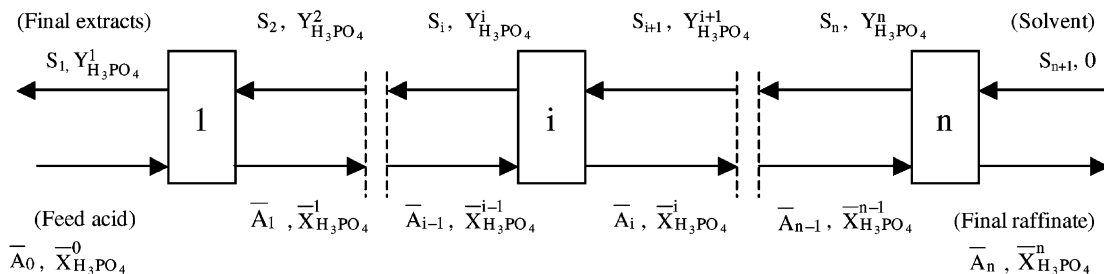


Fig. 8. Flow sheet of continuous countercurrent multistage extraction.

For a specified recovery (yield),  $\rho$  (%) of the main solute  $\text{H}_3\text{PO}_4$  (or  $\text{P}_2\text{O}_5$ ) is given as follows:

$$\rho = \left( \frac{S_1 Y_{\text{H}_3\text{PO}_4}^1}{A_0 X_{\text{H}_3\text{PO}_4}^0} \right) \times 100 \quad (18)$$

A material balance for this component about the entire cascade in Fig. 8 provides

$$Y_{\text{H}_3\text{PO}_4}^1 = \frac{\rho \bar{X}_{\text{H}_3\text{PO}_4}^0}{\rho(1+a)\bar{X}_{\text{H}_3\text{PO}_4}^0 + (S_{n+1}/\bar{A}_0)} \quad (19)$$

$$\frac{\bar{A}_n}{S_{n+1}} = \frac{\bar{A}_0}{S_{n+1}} [1 - \rho(1-a)\bar{X}_{\text{H}_3\text{PO}_4}^0] \quad (20)$$

$$\bar{X}_{\text{H}_3\text{PO}_4}^n = \frac{(\bar{A}_0/S_{n+1})(1-\rho)\bar{X}_{\text{H}_3\text{PO}_4}^0}{\bar{A}_n/S_{n+1}} \quad (21)$$

Considering the distribution curve  $Y = f(\bar{X})$  in Fig. 7 and the operating curve plotted by using Eq. (15), Mac Cabe–Thiele constructions were made to evaluate the effect of  $S_{n+1}/A_0$  ratio on the number of theoretical stages ( $n_{\text{th}}$ ) required to achieve a given yield  $\rho$ . For example, when the specified feed composition, the flow rate ratio and the specified recovery to be obtained are given as follows:

$$X_{\text{H}_3\text{PO}_4}^0 = 75.9\%, \quad \sum X_I^0 = 3.7\%, \\ S_{n+1}/A_0 = 1.5, \quad \rho = 77.5\%$$

The equations previously derived yield

$$Y_{\text{H}_3\text{PO}_4}^1 = 26.6\%, \quad \frac{\bar{A}_n}{S_{n+1}} = 0.168,$$

$$\bar{X}_{\text{H}_3\text{PO}_4}^n = 67.9\%$$

and

$$Y_{\text{H}_3\text{PO}_4}^i = \frac{\bar{X}_{\text{H}_3\text{PO}_4}^{i-1} - 0.679}{5.144 - 6.008\bar{X}_{\text{H}_3\text{PO}_4}^{i-1}} \quad (22)$$

The Mac Cabe–Thiele diagram (Fig. 9) corresponding to such an example leads to a number of theoretical extraction stages equal to 2.

For  $X_{\text{H}_3\text{PO}_4}^0 = 75.9\%$  and  $\rho = 77.5\%$ , results showing the effect of  $S_{n+1}/A_0$  ratio on the extraction characteristics

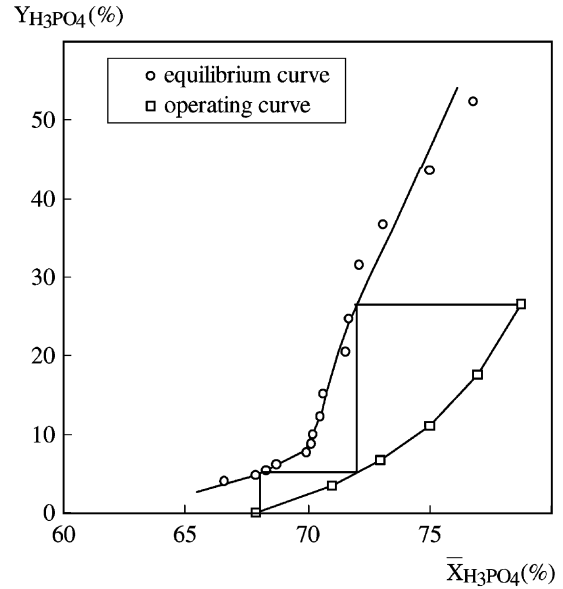


Fig. 9. Mac Cabe–Thiele construction for  $X_{\text{H}_3\text{PO}_4}^0 = 75.9\%$ ,  $S_{n+1}/A_0 = 1.5$  and  $\rho = 77.5\%$ .

are summarised in Table 5. As we can see, an increase in the flow ratio  $S_{n+1}/A_0$  induces quite naturally a decrease in the number of theoretical stages but leads to a more diluted extract ( $Y_{\text{H}_3\text{PO}_4}^1$  decreases) though more purified ( $\alpha_{\text{H}_3\text{PO}_4}/I$  increases). These conclusions are qualitatively similar to those obtained in batch experiments. Thus, a scrubbing section would necessarily required to achieve good performances for both extraction and purification of the acid.

In these same specified extraction conditions, the minimum ratio ( $S_{n+1}/A_0$ ) which occurs for an infinite number of stages (i.e. when the operating curve intersects the equilibrium one) is equal to about 0.4 (Fig. 10).

If we consider the data corresponding to the number of theoretical stages ( $n_{\text{th}}$ ) and  $S_{n+1}/A_0$  ratios (Table 5), it appears that  $n_{\text{th}}$  rapidly increases for  $S_{n+1}/A_0 < 1.5$  and remains almost unchanged for  $S_{n+1}/A_0 > 2$ . Therefore, a flow ratio in the range 1.5–2 seems to be judicious in order to carry out the extraction step.

3.2.3.2. Effect of the feed acid concentration. For a constant flow ratio  $S_{n+1}/A_0 = 1.5$ , we determined for the

Table 5  
Counter-current extraction characteristics for different ratios solvent to feed ( $X_{\text{H}_3\text{PO}_4}^0 = 75.9\%$  and  $\rho = 77.5\%$ )

$S_{n+1}/A_0$	$Y_{\text{H}_3\text{PO}_4}^1$ (%)	$\bar{A}_n/S_{n+1}$	$\bar{X}_{\text{H}_3\text{PO}_4}^n$ (%)	$\bar{A}_0/\bar{A}_n$	$\sum Y_I^1$ (%)	$\alpha_{\text{H}_3\text{PO}_4}/I$	$n_{\text{th}}$
4	12.5	0.0629	0.679	3.83	0.10	6.1	1.4
3	15.8	0.0838	0.679	3.83	0.15	5.1	1.5
2	21.7	0.126	0.679	3.83	0.25	4.2	1.7
1.5	26.6	0.168	0.679	3.83	0.34	3.8	2
1	34.4	0.251	0.679	3.83	0.53	3.2	2.6
0.75	40.2	0.335	0.679	3.83	0.70	2.8	3.3
0.5	48.5	0.503	0.679	3.83	1.07	2.2	5.2
0.33	56.5	0.762	0.679	3.83	1.57	1.8	$\infty$

<sup>a</sup> Deduced from the curve  $\sum Y_I^1 = f(Y_{\text{H}_3\text{PO}_4}^1)$  plotted with data in Tables 2 and 3.

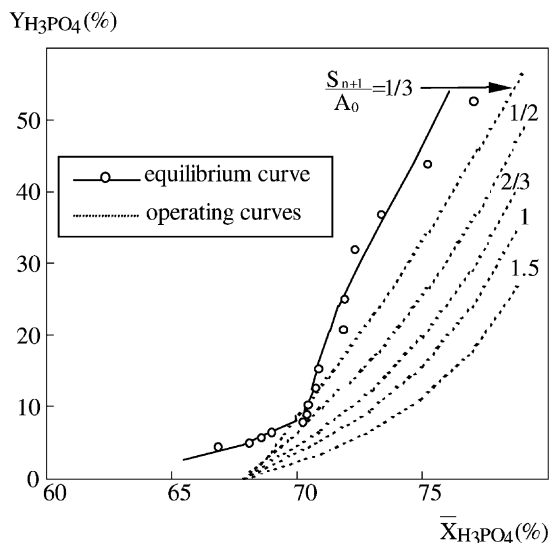


Fig. 10. Minimum ratio  $S_{n+1}/A_0$ .

following concentrations of the aqueous feeds (WPAs): 53.5, 55, 56.5 and 58%  $P_2O_5$ , the number of theoretical extraction stages needed to achieve different yields  $\rho$  of  $H_3PO_4$  (Fig. 11). From this figure, and for entire number of theoretical stages equal to 1–4, the following can be concluded:

- (i) Regardless of the number of extraction stages, the recovery of  $H_3PO_4$  is highly favoured when increasing  $P_2O_5$  (%) in the feed acid.
- (ii) For a given concentration of the aqueous feed, the enhancement of  $H_3PO_4$  yield is relatively pronounced when passing from one to two stages, moderate from two to three stages and poor beyond  $n_{th} = 3$ .

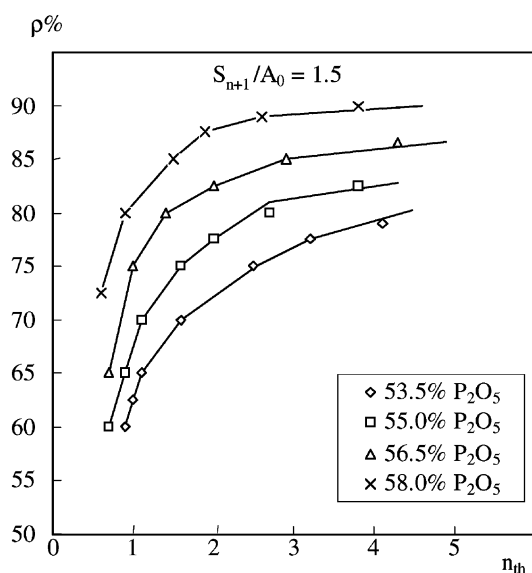


Fig. 11. Variations of  $H_3PO_4$  yield vs. the number of theoretical stages for different feed acid concentrations.

Considering the whole results previously described, the optimum conditions to conduct the extraction step are as follows:

- A  $P_2O_5$  concentration of the feed acid as high as practical.
- A solvent/feed ratio between 1.5 and 2.
- A number of theoretical stages equal to 2 or 3.

### 3.2.4. Incidence of MIBK saturated with water

The above described stagewise computations were made with “anhydrous” MIBK as solvent (i.e. fresh solvent). In fact, for a global purification process including the three sections: extraction, scrubbing and stripping, the recovered MIBK leaving the stripping step and recycled normally as such to the first extraction section is saturated with 2%  $H_2O$  [4].

To examine the effect of a water-saturated MIBK (2%  $H_2O$ ) on the extraction performances, preliminary experiments with different solvent/WPA ratios ( $S_0/A_0$ ) were conducted in batch at 40 °C (refer to Fig. 1). For this purpose, WPA containing 55%  $P_2O_5$  (Table 1) was used. Results obtained, compared to those with “anhydrous” MIBK, are listed in Table 6. Data in this table show how water content of MIBK affects the aqueous phase ratio  $A_1/A_0$  and the  $H_3PO_4$  yield  $\rho$ . As it can be clearly seen, for a single-stage extraction with saturated MIBK an optimum recovery of  $H_3PO_4$  is obtained for a solvent/feed ratio equal to about 2.5. The variation obtained with saturated MIBK can be explained when considering dilution of the feed acid induced by water content of the solvent. Thus,

- (i) for  $S_0/A_0 < 2.5$ , the negative effect of the feed acid dilution attenuates the known positive effect expected by an increase in the solvent/feed ratio;
- (ii) for  $S_0/A_0 > 2.5$ , the negative effect of the dilution prevails over the effect of the solvent/feed ratio.

Since the water content of MIBK induces a dilution of the feed acid, the treatment, for example, of 100 g WPA (55%  $P_2O_5$ ) with 150 g MIBK containing 2%  $H_2O$  should be similar to the treatment with 147 g anhydrous MIBK of a solution obtained by mixing 100 g WPA (55%  $P_2O_5$ ) with 3 g of water (i.e. 103 g WPA (53.4%  $P_2O_5$ )). The experimental confirmation of this assumption is given in Table 7.

Now, for both anhydrous and saturated MIBK, a slight variation ( $\leq 5\%$ ) of the solvent/feed ratio around 1.5 implies only a poor modification of the extraction yield (Table 6). In these conditions, the performances of the previously described multistage extractions can be practically extrapolated to saturated MIBK by modulating only the concentration of the feed acid. For example, the extraction performances previously obtained with a solvent/feed ratio equal to 1.5, a WPA containing 55%  $P_2O_5$  and anhydrous MIBK simulate practically those expected, for the same solvent/feed ratio, with WPA (56.7%  $P_2O_5$ ) and MIBK containing 2%  $H_2O$ .

Adopting this procedure, results obtained for  $S_{n+1}/A_0$  ratio equal to 1.5 are shown in Fig. 12. In the same figure



Table 6  
Batch extractions at 40 °C with anhydrous and water-saturated MIBK (feed acid A<sub>0</sub>: WPA (55% P<sub>2</sub>O<sub>5</sub>))

S <sub>0</sub> /A <sub>0</sub>	S <sub>0</sub> for anhydrous MIBK				S <sub>0</sub> for water-saturated MIBK			
	S <sub>1</sub> /A <sub>1</sub>	A <sub>1</sub> /A <sub>0</sub>	Y <sub>H<sub>3</sub>PO<sub>4</sub></sub> <sup>1</sup> (%)	ρ (%)	S <sub>1</sub> /A <sub>1</sub>	A <sub>1</sub> /A <sub>0</sub>	Y <sub>H<sub>3</sub>PO<sub>4</sub></sub> <sup>1</sup> (%)	ρ (%)
1	3.94	0.405	31.6	66.4	3.51	0.443	30.4	62.3
1.25	4.80	0.387	27.8	68.0	4.10	0.442	26.3	62.9
1.5	5.61	0.378	24.7	69.0	4.68	0.440	23.6	63.9
1.75	6.40	0.369	22.1	70.0	5.29	0.437	21.2	64.7
2	7.28	0.362	20.5	70.6	5.87	0.436	19.4	65.4
2.5	8.80	0.355	17.5	71.6	7.08	0.437	16.2	66.1
3	10.44	0.350	15.1	72.6	7.83	0.452	13.9	64.8
3.5	12.05	0.344	13.5	73.4	8.65	0.466	12.0	63.5

Table 7  
Results showing the dilution of the feed acid by the water content of MIBK

Extraction procedure	Results			
	A <sub>1</sub> /A <sub>0</sub>	S <sub>1</sub> /A <sub>1</sub>	Y <sub>H<sub>3</sub>PO<sub>4</sub></sub> <sup>1</sup> (%)	ρ (%)
100 g WPA (55% P <sub>2</sub> O <sub>5</sub> ) + 100 g MIBK containing 2% H <sub>2</sub> O	0.443	3.51	30.4	62.3
100 g WPA (55% P <sub>2</sub> O <sub>5</sub> ) + 2 g H <sub>2</sub> O + 98 g fresh MIBK	0.442	3.51	30.3	62.1
100 g WPA (55% P <sub>2</sub> O <sub>5</sub> ) + 150 g MIBK containing 2% H <sub>2</sub> O	0.440	4.68	23.6	63.9
100 g WPA (55% P <sub>2</sub> O <sub>5</sub> ) + 3 g H <sub>2</sub> O + 147 g fresh MIBK	0.443	4.74	23.6	64.0
100 g WPA (55% P <sub>2</sub> O <sub>5</sub> ) + 200 g MIBK containing 2% H <sub>2</sub> O	0.436	5.87	19.4	65.4
100 g WPA (55% P <sub>2</sub> O <sub>5</sub> ) + 4 g H <sub>2</sub> O + 196 g fresh MIBK	0.438	5.84	19.2	64.7

are given, for comparison, results for anhydrous MIBK. As it can be noticed, extraction yields are notably decreased when using saturated MIBK. Indeed, for specified values of both  $X_{\text{H}_3\text{PO}_4}^0$  and  $n_{\text{th}}$  an absolute reduction of H<sub>3</sub>PO<sub>4</sub> yield of the order of seven to eight points is observed.

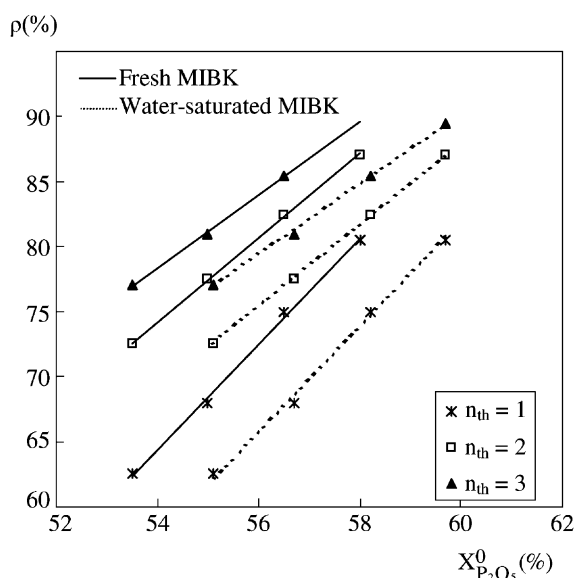


Fig. 12. Effect of the concentration of the feed acid and the number of theoretical stages on the H<sub>3</sub>PO<sub>4</sub> yields (ρ) for fresh and water-saturated MIBK.

### 3.2.5. Feasibility tests for a continuous extraction

To validate the graphical results obtained by Mac Cabe–Thiele method, continuous countercurrent extractions were performed at 40 ± 3 °C on the laboratory-scale mixer-settler unit.

From a complete study of the purification process of Tunisian WPA by MIBK, to be published, we describe here results obtained with two- and three-staged countercurrent extractions using water-saturated MIBK (2% H<sub>2</sub>O) as solvent and feed acids (WPAs) containing 55 and 58% P<sub>2</sub>O<sub>5</sub>. The global feed flow rate of the mixer-settler battery was reduced to about 2 l h<sup>-1</sup> so that the stage efficiency of 100% was practically reached. Results obtained in steady-state conditions are given in Table 8. As it can be concluded, a close agreement between observed H<sub>3</sub>PO<sub>4</sub> yields and those predicted from Fig. 12 is obtained. Furthermore, the increase in the observed H<sub>3</sub>PO<sub>4</sub> yield with increasing the number of extraction stages is as expected by graphical constructions (Fig. 12).

### 3.2.6. Quality of the acid produced by simple extraction

Simple extraction (i.e. without scrubbing step) performances in terms of H<sub>3</sub>PO<sub>4</sub> yield were already elucidated, the quality of the produced acid is discussed here.

Considering the organic extract produced by the three-stage continuous extraction on the mixer-settler unit (Table 8), H<sub>3</sub>PO<sub>4</sub> and coextracted impurities present in this phase were stripped continuously at 40 °C with pure water.

Table 8  
H<sub>3</sub>PO<sub>4</sub> yields of two- and three-staged countercurrent extractions

n <sub>th</sub>	X <sub>H<sub>3</sub>PO<sub>4</sub></sub> <sup>0</sup>	S <sub>n+1</sub> /A <sub>0</sub>	ρ observed in mixer-settler runs (%)				Global ρ expected graphically (%)
			First stage	Second stage	Third stage	Global	
2	75.9	1.45	63.9	9.2	–	73.1	72.5
	80.0	1.45	73.7	8.2	–	81.9	82.5
3	75.9	1.42	63.1	8.3	4.0	75.4	77.0

Table 9  
Composition (wt.%) of both purified and feed acids (this work and Albright process)

Reference	Phosphoric medium	Composition					
		H <sub>3</sub> PO <sub>4</sub>	Mg <sup>2+</sup>	Al <sup>3+</sup>	Fe <sup>3+</sup>	SO <sub>4</sub> <sup>2-</sup>	F <sup>-</sup>
This work	Purified acid	76.2	0.0580	0.0485	0.0567	0.742	0.0420
	Feed acid	75.9	0.712	0.376	0.288	2.24	0.0990
	α <sub>H<sub>3</sub>PO<sub>4</sub>/I</sub>	–	12.3	7.8	5.1	3	2.4
Albright process	Purified acid	56	0.0005	–	0.0025	0.5	–
	Feed acid	77.4	0.25	–	0.23	1.31	–
	α <sub>H<sub>3</sub>PO<sub>4</sub>/I</sub>	–	362	–	66.6	1.9	–

A judicious choice of H<sub>2</sub>O/extract flow ratio allowed to produce, in a single stage of the mixer-settler battery, a recovered solvent containing 2% H<sub>2</sub>O and 0.59% H<sub>3</sub>PO<sub>4</sub> and a purified phosphoric acid containing 50% H<sub>3</sub>PO<sub>4</sub> (36.2% P<sub>2</sub>O<sub>5</sub>), saturated with 1.6% MIBK. The stripping efficiency of H<sub>3</sub>PO<sub>4</sub> and impurities was beyond 98%. Concentration, under reduced pressure, of the stripped acid allowed to recover the dissolved MIBK and to produce a marchand-grade phosphoric acid, i.e. containing at least 54% P<sub>2</sub>O<sub>5</sub>. The composition of the resulting concentrated acid, compared to that of the feed WPA, is shown in Table 9. As it can be noticed, the produced acid has already reached, by simple extraction, a relatively high purity level, especially with respect to metallic impurities. However, it is still far away from technical-grade phosphoric acids like the one produced by the Albright process [11] which uses the same solvent MIBK but includes a multistage-scrubbing step (Table 9). Thus, phosphoric acid from simple extraction can be used favourably as such for the preparation of relatively low quality products like superphosphoric acid (P<sub>2</sub>O<sub>5</sub> > 70%) and liquid fertilisers [1,12]. For detergents, food and surface treatment, the crude organic extract should undergo a scrubbing step and possibly a chemical post-treatment in order to reduce the concentrations of coextracted impurities so as to reach the required specifications.

#### 4. Conclusion

Distribution data for the multicomponent system WPA–MIBK show that extraction of H<sub>3</sub>PO<sub>4</sub> becomes

effective only from concentrated aqueous phosphoric medium. Moreover, MIBK presents globally a good purification behaviour with regard to WPA metallic impurities but is unsuitable for anionic impurity purification, especially F<sup>-</sup>.

Expression of conjugated phase compositions on an impurity-free basis permitted us to transform the multicomponent system WPA–MIBK into a reduced ternary system H<sub>2</sub>O–H<sub>3</sub>PO<sub>4</sub>–MIBK. Mac Cabe–Thiele method was then used to check the effect of different extraction parameters on the number of theoretical stages required to achieve a given yield of H<sub>3</sub>PO<sub>4</sub> from WPAs. Graphical results were validated experimentally by performing continuous countercurrent extraction runs on a laboratory-scale mixer-settler unit.

#### References

- [1] I. Raz, Chem. Eng. 10 (1974) 52.
- [2] J. Bergdorf, R. Fischer, Chem. Eng. Prog. (1978) 41.
- [3] P. Mangin, Inf. Chimie 152 (1976) 135.
- [4] M. Feki, M. Fourati, M.M. Chaabouni, H.F. Ayedi, Can. J. Chem. Eng. 72 (1994) 939.
- [5] M. Feki, H.F. Ayedi, Sep. Sci. Technol. 33 (1998) 2609.
- [6] R.E. Treybal, Liquid Extraction, 2nd Edition, McGraw-Hill, New York, 1963.
- [7] J. Ezzeddine, D. Hechmi, Brev. Fr. 2,375,142 (1978).
- [8] J. Bizot, Bull. Soc. Chim. Fr. 1 (1967) 151.
- [9] S. Stenström, G. Aly, Hydrometallurgy 14 (1985) 257.
- [10] S. Siggia, J. Hanna, Quantitative Organic Analysis Via Functional Groups, 4th Edition, R.E. Krieger Publishing Company, Florida, 1988.
- [11] T. Williams, German Patent 2,320,877 (1973).
- [12] I. Moldovan, Phosphorous and Potassium 12 (1964) 16.