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Liquid−Liquid Equilibria of the Ternary System Water + Phosphoric Acid + Tributyl Phosphate at 298.15 K and 323.15 K

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Solubilities and liquid−liquid-phase equilibria for the ternary system water + phosphoric acid + tributyl phosphate are presented at (298.15 and 323.15) K. The binodal curves, tie lines, and distribution curves have been determined. The plait point compositions have been calculated by Hand's method. The extraction power of tributyl phosphate for phosphoric acid has been compared to those of methyl isobutyl ketone, dibutyl ether, isoamyl alcohol, and diethyl ketone. The extraction chemistry of H_3PO_4 by tributyl phosphate is also discussed.

Introduction

Many areas for phosphoric acid applications such as liquid fertilizers, metal treatment products, feed grade calcium phosphate, food products, and so forth call for an acid quality ranging between those of furnace grade and conventional wet process phosphoric acid. Recently, an increasing proportion of such needs have been met by wet process acid purified by solvent extraction.[1] For this purpose a considerable number of polar solvents have been studied as extractants for H_3PO_4, including alcohols,[2−4] ketones,[5−8] ethers,[9,10] and esters.[11]

Interactions between tributyl phosphate (TBP), phosphoric acid (H_3PO_4), and water have been studied at 298.15 K by Higgins.[11] However, many data, related to the purification behavior of TBP for wet process phosphoric acid, were still unavailable. Three patented processes, also using TBP as an extractant, are described in the literature.[12−14] Nevertheless, these papers provide only technical data for the process scheme. To our knowledge, the phase equilibrium diagram of the ternary system $H_2O + H_3PO_4$ + TBP has not yet been published.

To study a solvent extraction process adapted in an optimal way to the quality of the Tunisian raw material and to the specification of the final products, methylisobutyl ketone (MIBK) has been previously tested as an extractant.[15,16]

The present work is concerned with a full characterization of the ternary phase diagram of $H_2O + H_3PO_4$ + TBP at (298.15 and 323.15) K. $T = 298.15$ K has been selected to compare our results to those existing in the literature for other solvents, while $T = 323.15$ K has been selected to approximate the industrial conditions, which are imposed by the viscosities of acids and TBP.

Experimental Section

Materials. The following reagents were used in this investigation: TBP with a purity higher than 99%, a density of 0.976 g/cm^3 at 293.15 K, and a water content of 0.1 mass %, determined using the Karl−Fisher method;[17] 85% analytical grade phosphoric acid of density 1.70 g/cm^3 at 293.15 K; crystallized analytical grade phosphoric acid (higher than 99% H_3PO_4); analytical grade toluene of density 0.867 g/cm^3 at 293.15 K. All were supplied by Fluka (Buchs Switzerland) and were used without further purification. Pure water with a resistivity of (16 to 18) MΩ·cm was used.

Procedure. The equilibrium between the liquid phases was studied in a transparent water thermostat at (298.15 and 323.15) K. The temperature was controlled within ±0.2 K.

To cover, at a given temperature, the whole heterogeneous domain of the ternary diagram, extractions were performed using different two-phase mixtures each containing known masses of 85% phosphoric acid, water, and TBP. The mixture was stirred vigorously for 20 min in a separatory funnel and was then allowed to settle for between (2 and 24) h depending on the stability of the formed emulsion. After separation, the aqueous and organic phases were weighed and analyzed. The compositions of conjugated phases allowed us to construct the tie lines. Joining the extremities of the tie lines enabled us to draw the binodal curve. The upper part of the saturation curve was constructed using the cloud point method as described elsewhere.[15] Crystallized phosphoric acid was used for this purpose.

Phosphoric acid was titrated in both phases with NaOH in the presence of bromocresol green and phenolphthalein as indicators.[18] The amount of TBP in the aqueous phases was determined indirectly by the total organic carbon method[19] in a Shimadzu TOC 500 apparatus fitted with an IR detector ($\lambda = 4300$ nm). Single-phase samples with known contents of TBP were used to establish a calibration curve. The amount of water in the organic phases was determined by the Karl−Fisher method[17] using a Metrohm E551 Karl−Fisher titrator. The average deviation obtained for analysis was 0.5% for H_3PO_4, 2% for TBP, and 2% for water. The amounts of water in the aqueous phases and those of TBP in the organic ones were determined by the material balance for each phase. The accuracy of the global mass balances ranged between (3 and 4)%.

To obtain a clearer picture about the acid−solvent interaction, further extraction experiments were accomplished at 298.15 K by equilibrating aqueous solutions containing 12 M initial H_3PO_4 with equal masses of TBP at various concentrations in toluene as diluent. The procedures of extraction, phase separation, and analysis were the same as those described above.

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Table 1. Compositions (mass %) of Initial Heterogeneous Mixtures and Coexisting Phases in the System H_2O (1) + H_3PO_4 (2) + TBP (3) at 298.15 K

initial mixtures			equilibrium aqueous phases			equilibrium organic phases		
w_1	w_2	w_3	$(w_1)_{aq}$	$(w_2)_{aq}$	$(w_3)_{aq}$	$(w_1)_{org}$	$(w_2)_{org}$	$(w_3)_{org}$
41.05	10.70	48.26	81.37	18.60	0.0330	5.40	4.20	90.40
38.20	11.70	50.10	79.57	20.40	0.0320	5.20	5.00	89.80
34.20	15.60	50.20	72.97	27.00	0.0290	4.80	7.80	87.40
27.40	18.50	54.10	66.27	33.70	0.0270	4.50	10.30	85.20
26.50	24.50	49.00	58.77	41.20	0.0245	4.10	14.00	81.90
17.80	32.70	49.50	43.77	56.20	0.0210	3.60	20.80	75.60
12.82	63.97	23.21	18.98	81.00	0.0240	4.00	41.94	54.06
12.60	68.52	18.88	17.81	82.17	0.0245	3.80	44.00	52.20

Table 2. Compositions (mass %) of Initial Heterogeneous Mixtures and Coexisting Initial Mixture Phases in the System H_2O (1) + H_3PO_4 (2) + TBP (3) at 323.15 K

initial mixtures			equilibrium aqueous phases			equilibrium organic phases		
w_1	w_2	w_3	$(w_1)_{aq}$	$(w_2)_{aq}$	$(w_3)_{aq}$	$(w_1)_{org}$	$(w_2)_{org}$	$(w_3)_{org}$
45.50	8.50	46.00	84.76	15.20	0.0410	5.40	1.50	93.10
44.60	10.90	44.50	81.76	18.20	0.0395	5.30	2.40	92.30
41.50	17.50	41.00	73.37	26.60	0.0360	5.00	5.70	89.30
37.70	24.60	37.70	62.77	37.20	0.0320	4.70	9.60	85.70
33.60	32.90	33.50	52.97	47.00	0.0300	4.30	13.00	81.90
29.20	42.30	28.50	46.27	53.70	0.0300	3.20	19.10	77.70
26.50	47.70	25.80	39.67	60.30	0.0310	3.70	22.20	74.10
23.50	52.10	24.50	34.97	65.00	0.0335	3.50	24.70	71.80
13.96	74.88	11.35	16.05	83.90	0.0520	3.80	41.30	54.90
7.39	72.72	19.90	10.80	89.13	0.0655	3.80	55.00	41.10
7.98	80.34	11.68	9.73	90.20	0.0700	4.00	58.10	37.90

Table 3. Compositions Corresponding to Points Obtained by the Cloud Point Method at (298.15 and 323.15) K for the System H_2O (1) + H_3PO_4 (2) + TBP (3)

	T = 298.15 K		T = 323.15 K	
w_1	4.86	5.90	5.02	5.88
w_2	86.49	93.51	89.33	93.20
w_3	8.65	0.59	5.65	0.93

Results and Discussion

Unless stated otherwise, concentrations are expressed in mass fraction (given in percent) and symbolized by $(w_i)_\phi$, where i stands for the component analyzed (i = 1 for H_2O, i = 2 for H_3PO_4, and i = 3 for TBP) and ϕ for the nature of the phase considered (aq for the aqueous phase and org for the organic one).

Establishment of the Ternary Diagrams. The compositions of initial heterogeneous mixtures and those of equilibrium phases at (298.15 and 323.15) K are given in Tables 1 and 2, respectively. Table 3 shows the compositions corresponding to points of binodal curves determined by the cloud point method.

The equilibrium diagram at 298.15 K of the ternary system H_2O + H_3PO_4 + TBP is shown in Figure 1. The heterogeneous region of the system occupies practically the same area at (298.15 and 323.15) K.

In practice, a greater number of tie lines would be needed for extractor computation design. Direct interpolation of the observed tie lines is difficult on a triangular diagram. Interpolation can be achieved with the Hand method.[20] The correlation curves carried out at (298.15 and 323.15) K by using Hand's method represent the dependence of the ratio $(w_2/w_3)_{org}$ on the ratio $(w_2/w_1)_{aq}$ in logarithmic coordinates. Figure 2 shows the correlation curve obtained at 298.15 K. The tie line correlations are represented by the relationships

$$\log(w_2/w_3)_{org} = 0.674 + 0.929 \log(w_2/w_1)_{aq} \quad (r^2 = 0.994) \text{ at } 298.15\text{ K}$$

$$\log(w_2/w_3)_{org} = 0.799 + 1.076 \log(w_2/w_1)_{aq} \quad (r^2 = 0.976) \text{ at } 323.15\text{ K}$$

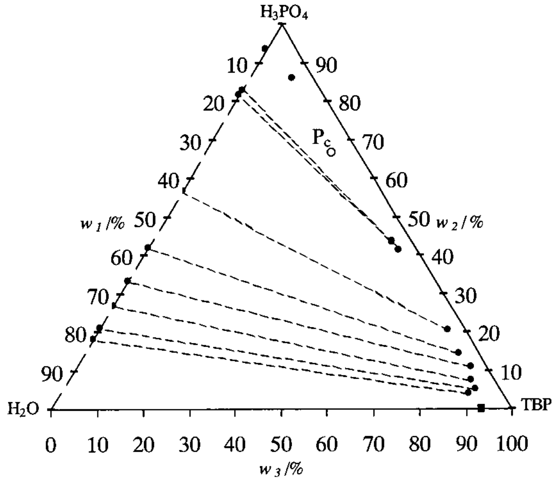

Figure 1. Ternary liquid−liquid equilibria for the system H_2O (1) + H_3PO_4 (2) + TBP (3) at 298.15 K.

The extrapolation of the tie line curve crosses the solubility curve at the plait point P_C, as shown in Figure 2. The plait point compositions are

$$w_1 = 4.96\%; \quad w_2 = 67.05\%; \quad w_3 = 27.99\% \text{ at } 298.15\text{ K}$$

$$w_1 = 4.63\%; \quad w_2 = 70.15\%; \quad w_3 = 25.22\% \text{ at } 323.15\text{ K}$$

Solvent Solubility. The solubility of TBP in the aqueous phase is very low when compared to that of other solvating solvents.[2−10,15] Figure 3 depicts the amount of TBP dissolved in the aqueous phase as a function of its phosphoric acid concentration. The solubility of TBP decreases first with increasing H_3PO_4 concentration, and then increases at higher H_3PO_4 concentration. Anhydrous phosphoric acid dissolves TBP in all proportions at (298.15 and 323.15) K. Moreover, at a given H_3PO_4 concentration in the aqueous phase, the solubility increases slightly with temperature (Figure 3). The shape of the curves obtained in this work is similar to that observed by Higgins at 298.15 K (Figure 3). However, the solubility values of TBP determined in

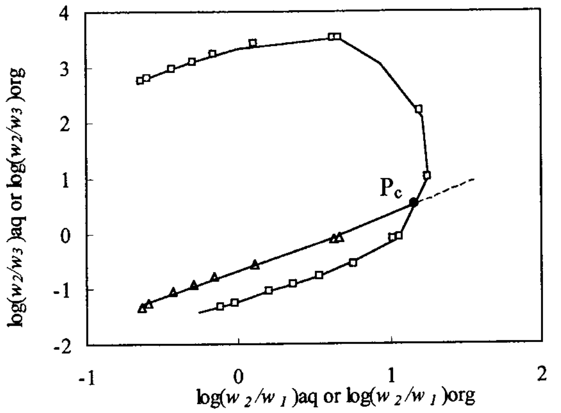

Figure 2. Hand's coordinate for the system H_2O (1) + H_3PO_4 (2) + TBP (3) at 298.15 K: △, tie line correlation curve; □, solubility curve.

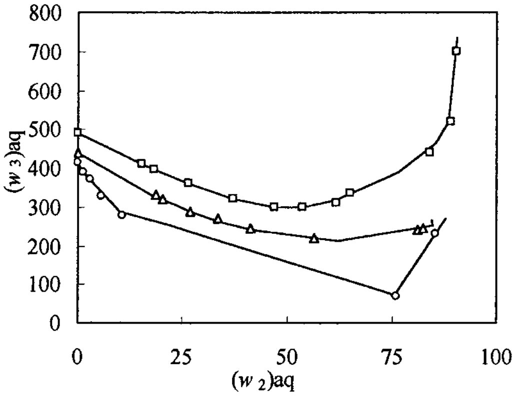

Figure 3. Solubility of TBP (3) in aqueous phosphoric medium: △, $T = 298.15$ K (this work); □, $T = 323.15$ K (this work); ○, results obtained by Higgins at 298.15 K.

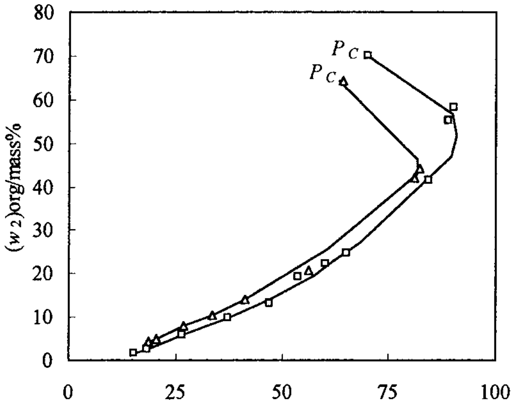

Figure 4. Phosphoric distribution curves: △, $T = 298.15$ K; □, $T = 323.15$ K.

Table 4. Solubility S of TBP in Water

S/mass % at 298.15 K	0.0414[11]	0.0390[21]	0.0440 (this work)
S/mass % at 323.15 K	-	-	0.0490 (this work)

Table 5. Effect of KH_2PO_4 Addition on the Distribution Coefficient of P_2O_5 ($T = 323.15$ K; Initial Ratio Org/Aq = 1)

total P_2O_5/mass %	59.42	59.42	59.42	59.42	59.42	59.42
$P_2O_5{}^a$	0	0.67	2.13	4.42	6.90	9.14
$D_{P_2O_5}{}^b$	0.423	0.416	0.405	0.389	0.365	0.351

[a] P_2O_5 introduced as KH_2PO_4/mass %. [b] $D_{P_2O_5} = (w_{P_2O_5})_{org}/(w_{P_2O_5})_{aq}$.

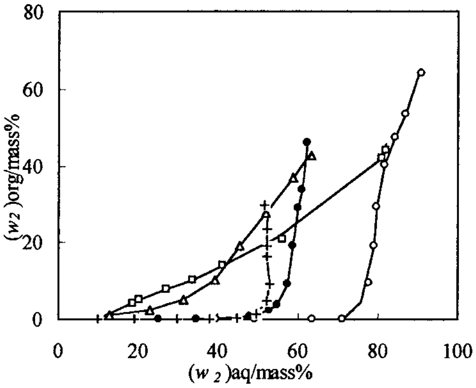

Figure 5. Phosphoric acid distribution curves for different solvents at 298.15 K: □, TBP; △, iA; +, DEK; ●, MIBK; ○, DBE.

aqueous phosphoric media (Figure 3) and in pure water (Table 4) are relatively higher than those reported in the literature.[11,21]

Phosphoric Acid Extraction. Figure 4 represents the H_3PO_4 distribution curves obtained at (298.15 and 323.15) K. As can be seen, the H_3PO_4 distribution coefficient ($D = (w_2)_{org}/(w_2)_{aq}$) is not constant but increases as the H_3PO_4 concentration in the aqueous phase increases. Nevertheless, the extraction of H_3PO_4 is noticed to be slightly sensitive to temperature in the range (298.15−323.15) K. It is worth noting that the results obtained in this work at 298.15 K agree with those reported elsewhere.[11]

The shape of phosphoric acid distribution curves obtained with TBP can be explained by considering the extraction mechanism of weak acids by solvating solvents. Indeed, the extraction of H_3PO_4 should be expected as a result of the competition between water and the solvent for the solvation, by hydrogen bonds, of the neutral species H_3PO_4.[22] Thus, as the H_3PO_4 concentration of the aqueous phase increases, the proportion of undissociated H_3PO_4 increases, whereas water activity decreases.[23] So the solvation of H_3PO_4 by the solvent and its subsequent transfer to the organic phase becomes favored. This assumption is confirmed by extraction data obtained when using, as aqueous feeds, different mixtures of H_3PO_4 and KH_2PO_4 whose total P_2O_5 content equals 59.42 mass % (Table 5). Indeed, the distribution coefficient of P_2O_5 decreases when the amount of KH_2PO_4 in the initial aqueous mixture increases.

In the following paragraph the extraction power of TBP for H_3PO_4 is compared to those of other solvents, namely, isoamyl alcohol (iA),[4] dibutyl ether (DBE),[8] methylisobutyl ketone (MIBK),[15] and diethyl ketone (DEK).[7] Figure 5 shows the H_3PO_4 distribution curves for TBP and these solvents. As seen, each solvent becomes an effective extractant for phosphoric acid only when the H_3PO_4 concentration in the aqueous phase exceeds a limit, which increases in the following order: TBP $\sim$ iA $<$ DEK $<$ MIBK $<$ DBE.

Moreover, according to Figure 5, TBP and iA extract H_3PO_4 even from a dilute phosphoric medium. These solvents present the advantage of yielding, with concentrated feed acids, highly exhausted raffinates with regard to H_3PO_4. In return, the other solvents present interesting stripping conditions of H_3PO_4 from the organic phase, releasing with water a highly concentrated reextracted acid. In addition, we have suggested elsewhere[16] that the order of the extraction power of any carbon-bonded oxygen donor solvent is related to the solubility of water in the pure solvents rather than to their polarity or their dielectric constant. Experimental results obtained here with TBP

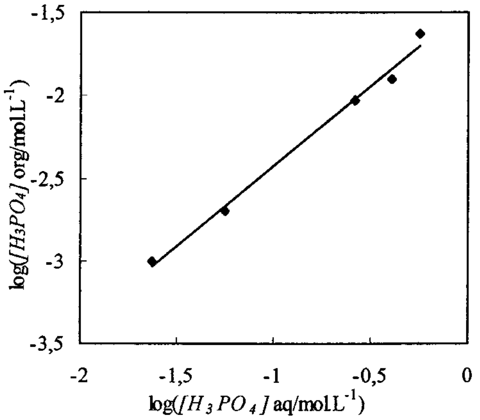

Figure 6. Variation of log $[H_3PO_4]_{org}$ versus log$[H_3PO_4]_{aq}$.

Table 6. Dipole Moment μ, Water Solubility S, and Dielectric Constant ϵ for the Different Solvents Considered

	iA	TBP	DEK	MIBK	DBE
μ/D	1.82[24]	3.07[21]	2.82[7]	2.79[25]	1.18[24]
S/mass % at 298.15 K	9.6[4]	4.67[21]	2.43[7]	1.8[15]	0.1[8]
ϵ[24]	14.70	7.96	17.00	13.11	3.08

confirm this global tendency despite the difference between the solvent functional groups (Table 6).

From partition data of a solute between organic and aqueous phases, we have often been able to deduce which solvent complex is formed.[21,22,26–29] In this matter, the solvation of H_3PO_4 with TBP is now discussed.

Let us postulate that H_3PO_4 exists in the TBP phase as a complex of the formula pH$_3$PO$_4$·qTBP. Slope analyses of the detailed extraction results support the following solvation equilibrium:[21,22,26–30]

$$p(H_3PO_4)_{aq} + q(TBP)_{org} \leftrightarrow p(H_3PO_4)\cdot q(TBP)_{org}$$

with the thermodynamic extraction constant

$$K = \frac{(a_{p(H_3PO_4)\cdot q(TBP)})_{org}}{(a_3)^{q}_{org} \times (a_2)^{p}_{aq}}$$

where p is the degree of association of the extracted H_3PO_4, q is the solvation number, and a_j is the molar activity of species j.

Phosphoric acid extraction from dilute phosphoric media with pure TBP allows p to be determined.[29] In fact, when confounding activity and molar concentration, the variation of log $[H_3PO_4]_{org}$ with log $[H_3PO_4]_{aq}$ is linear, and p is given by the slope of the curve (Figure 6). In our case $p = 0.97$ (Figure 6).

Carrying out extractions with TBP diluted in inert solvent (like benzene, toluene, kerosene, ...) and keeping the aqueous phase constant in composition allow us to obtain the value of q provided that p remains constant. Thus, it can be shown under these conditions that the variation of log D (D is the H_3PO_4 distribution coefficient expressed in the molar scale: $D = [H_3PO_4]_{org}/[H_3PO_4]_{aq}$) with log [TBP] is linear and q is given by the slope of the curve.[26] Figure 7 illustrates the variation of log D versus log [TBP] obtained in this work with fresh portions of 12 M phosphoric acid solution and TBP in various concentrations in toluene. It is important to notice that this aqueous phase molarity allows diluted TBP in toluene to extract the H_3PO_4 appreciably. Considering the linear part of the curve, the solvation number q is equal to 2.1. As seen, the linearity is followed at low TBP concentrations (0.033−0.250) M, but deviations occur at higher TBP concentrations (>0.250 M), owing to the nonideality of the TBP phase and/or simultaneous formation of a number of complexes in the organic phase.[22,27]

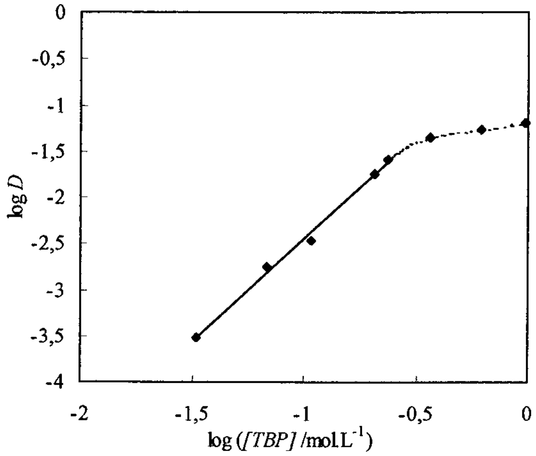

Figure 7. Variation of log D as a function of log[TBP].

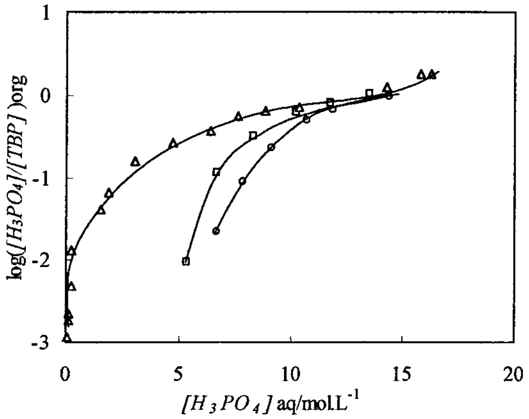

Figure 8. Partition of H_3PO_4 between TBP phases and aqueous phosphoric media: ○, 0.366 M TBP; □, 0.969 M TBP; △, 3.66 M TBP.

Figure 8 shows the molar concentration ratio of phosphoric acid to TBP in the organic phase as a function of the phosphoric acid concentration (mol·L^{-1}) in the conjugated aqueous one when pure TBP and TBP diluted in toluene (0.366 and 0.969 mol·L^{-1}) are used as solvents. First, regardless of the shape of the curves, the fact that the extraction ability of TBP diluted in toluene is lower than that of undiluted TBP should be a result of a decrease in polarity of the organic phase. On the other hand, it is seen that the molar ratio of H_3PO_4 to TBP first increases and then tends toward a limit at concentrated aqueous media. This limit translates the saturation effect of the organic phase when the molar ratio H_3PO_4/TBP is about 1.

According to information from Figures 6−8, it appears that the composition of the extracted complex globally ranges between H_3PO_4·2TBP and H_3PO_4·TBP depending upon the amount of TBP present in the organic phase. Moreover, it can also be seen from Figure 8 that, for pure TBP as solvent, the $[H_3PO_4]_{org}/[TBP]_{org}$ ratio departs greatly from unity (it reaches about 4) at highly concentrated aqueous media (>15 mol·L^{-1}). This fact cannot be explained by a simple extraction mechanism and indicates the formation of aggregates (polymerization reaction in the organic phase at the higher acidities). This has also been

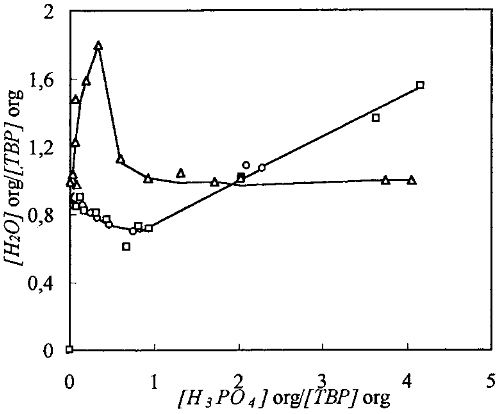

Figure 9. Water extraction by TBP: ○, $T = 298.15$ K (this work); □, $T = 323.15$ K (this work); △, results of Higgins at 298.15 K.

suggested by several authors who studied the extraction of mineral acids by solvating solvents.[11,27]

Finally, the results obtained here with TBP do not lead to an unequivocal assignment of the solvation number. In this matter, the same situation was previously noted by many workers when studying the extraction chemistry of mineral acids with neutral solvating solvents.[21,22] This may be explained by the dependence of solvation degree on the concentrations of both aqueous and organic phases. Moreover, for such an extraction system, it was also suggested that more than one solvate may coexist in equilibrium.

Water Extraction. From the data in Tables 1 and 2, we can analyze quantitatively the water coextraction behavior. Figure 9 shows the variation of the molar ratio $[H_2O]/[TBP]$ in the organic phase versus the ratio $[H_3PO_4]/[TBP]$ in the same phase. The results obtained at (298.15 and 323.15) K appear to be noticeably identical to the experimental pitfalls. So we have represented the experimental results by only one curve. As can be observed from curve a of Figure 9, H_3PO_4 forces water from the organic phase until a 1:1 ratio of H_3PO_4 to TBP is reached. As additional H_3PO_4 goes into the TBP phase, the water content of the latter begins to increase. The minimum in the $[H_2O]_{org}/[TBP]_{org}$ ratio occurs when the organic phase reaches the approximate composition $TBP{\cdot}H_3PO_4{\cdot}{}^3/_4H_2O$. It is worth noticing that the same behavior of water was observed[22] in the $H_2O + HNO_3 + TBP$ system, for which the minimum occurs when the composition of the organic phase is close to $TBP{\cdot}HNO_3{\cdot}{}^1/_3H_2O$.[22] In return, our results present significant differences with respect to those reported by Higgins[11] (Figure 9). The great amounts of extracted water observed by Higgins[11] may be due to the fact that TBP leads to very stable emulsions, notably at low H_3PO_4 concentrations of the aqueous phases. For the first part of curve a of Figure 9, the monotonically decreasing values of the ratio $[H_2O]_{org}/[TBP]_{org}$ tend to indicate that H_3PO_4 is extracted as an anhydrous species which competes with water in the P→O sites of the TBP phase. On the other hand, the increasing values observed beyond the 1:1 ratio of H_3PO_4 to TBP suggest that water is probably extracted as a hydrated complex of phosphoric acid. The extracted water is likely to be associated with aggregate formation in the TBP phase (cross linkages) at the higher organic acidities.[22]

When comparing the water behavior in the systems $H_2O + H_3PO_4 + TBP$ (this work) and $H_2O + H_3PO_4 + MIBK$[15] (Figure 10), it appears that MIBK coextracts water to a higher extent than TBP. Indeed, in the whole range of the $[H_3PO_4]_{org}/[MIBK]_{org}$ ratio experimentally permitted, MIBK extracts two moles of water per mole of H_3PO_4 transferred into the organic phase (slope of curve b of Figure 10). So, TBP, which is more basic than MIBK,[21] competes favorably with water for the solvation of H_3PO_4, extracting a less hydrated H_3PO_4 species.

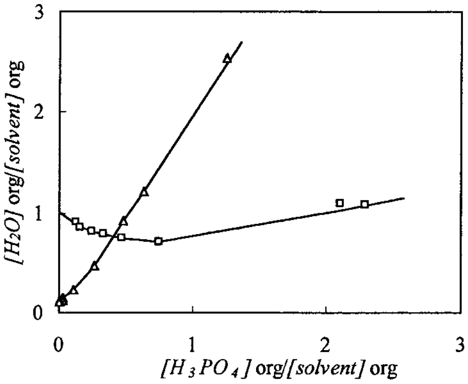

Figure 10. Water extraction by TBP and MIBK at 298.15 K: □, TBP (this work); △, MIBK.

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