

Liquid–Liquid Equilibria of Acetic, Formic, and Oxalic Acids between Water and Tributyl Phosphate + Dodecane

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The purpose of this work is to study the extractive capacity of an organophosphorus compound to recover carboxylic acids from the waste water resulting from the ozonation process for the bleaching of pulp in order to reduce the environment pollution. In this work, the selected solvent was composed of a mixture of tributyl phosphate (60 vol %) with dodecane (40 vol %) and the solutes under consideration were acetic, formic, and oxalic acids. With no exception, it is the undissociated acid that is extracted by the solvent. Ternary system solubility diagrams water + carboxylic acid + tributyl phosphate and tie-line data were established at the temperature of 25 °C. In comparison with the conventional extraction solvents such as alcohols, ketones, or ethers, which involve the solvation of the acid by donor bonds, the more basic donor properties of phosphorus-bonded oxygen compounds show the stronger extractive capacity of this group of extractants. Furthermore, the carbon-bonded oxygen solvents are much more soluble in water and hence involve a costly solvent recovery. With regard to the tertiary amine extractants, which have low residual solubilities in water and high extractive power for several acids, the selectivity of organophosphorus compounds with respect to an individual carboxylic acid can be considered as an attractive property of this category of solvent. In this study, partition coefficients between 0.27 and 1.25 were determined for the separate acids.

Introduction

The classical process to recover a carboxylic acid from a wide variety of dilute aqueous effluents including waste waters is based on precipitation of the calcium salt upon addition of calcium hydroxide to the acid aqueous solution. After a complete filtration, the treatment of the solid phase with sulfuric acid leads to preferential precipitation of calcium sulfate. The free organic acid in the resulting aqueous filtrate is first purified by ion exchange resins and then evaporated to give crystals of the acid. In a few cases, since the yield of final crystallization was relatively low, a solvent extraction technique can be considered as an attractive alternative to recover the valuable organic acid. Various solvents have been used for extraction of carboxylic acids (Kertes and King, 1986; King, 1993; Yang *et al.*, 1991). With a phosphorus-bonded oxygen donor extractant such as tributyl phosphate, the extraction process results from the solvating character of the phosphoryl group, which acts as a strong Lewis base. The specific behavior of phosphorus extractants in the process of acid extraction has been investigated in previous works (Lo *et al.*, 1982; Shevchenko and Renard, 1963; Shah and Tiwari, 1981). However, since the tributyl phosphate has a relatively high viscosity (3.56×10^{-3} Pa·s) and a density close to $1 \text{ g}\cdot\text{cm}^{-3}$ ($0.98 \text{ g}\cdot\text{cm}^{-3}$), it is necessary to mix it with a diluent in order to facilitate phase settling after the stirring period with nonmiscible liquids. The influence of the diluent on the extraction properties of the tributyl phosphate is less significant than one would assume on the basis of the solvent effect. For instance, when citric acid is extracted by an organic mixture containing 50 vol % of tributyl phosphate, its partition coefficient is 0.56 with diisopropyl ether as diluent, 0.50 with methyl isobutyl ketone, and 0.33 with aliphatic hydrocarbon (Kertes and King, 1986). In this study, dodecane was chosen as diluent because of its low viscosity (1.1×10^{-3} Pa·s), its low density ($0.75 \text{ g}\cdot\text{cm}^{-3}$),

Table 1. pK_a of Carboxylic Acids in Aqueous Solution at 25 °C

acid	pK_a
acetic	4.75
formic	3.75
oxalic	1st: 1.23 2nd: 4.19

and its low solubility in water. Since dodecane can be considered as chemically inert relative to the extraction process, the percentage of tributyl phosphate in the mixture "extractant + diluent" should be as high as possible to obtain high partition coefficients. Consequently, taking both phase settling and partition coefficient into consideration, previous experiments led us to use a solvent containing 60 vol % of tributyl phosphate and 40 vol % of dodecane. This mixture gives a density of $0.88 \text{ g}\cdot\text{cm}^{-3}$ and a viscosity of 2.44×10^{-3} Pa·s at 25 °C, which are compatible with the decantation process. In comparison with carbon-bonded oxygen donor extractants, which are relatively soluble in water (Duarte *et al.*, 1989; Smaghe *et al.*, 1991; Faizal *et al.*, 1990), the mixture tributyl phosphate + dodecane is practically nonmiscible in the aqueous phase (0.039 mass %).

Experimental Section

Chemicals. Acetic, formic, and oxalic acids, tributyl phosphate, and dodecane were provided by Aldrich Chemical Company and were analyzed by high-performance liquid chromatography (HPLC) in order to confirm the purity of compounds, which was close to 99%. The pK_a values of acetic, formic, and oxalic acids are presented in Table 1 (Weast *et al.*, 1984).

Experimental Procedures. For the determination of solubility isotherms and tie-line data, aqueous solutions of individual carboxylic acid of various concentrations were mixed with varying volumes of solvent in glass-stoppered separatory funnels maintained at the constant temperature

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Table 2. Ternary Diagram for (Tributyl Phosphate (60 vol %) + Dodecane (40 vol %) [w_S]) + Acetic Acid [w_B] + Water [w_A])^a

(a) Binodal Curve Results

aqueous rich side			organic rich side		
100 w_S	100 w_B	100 w_A	100 w_S	100 w_B	100 w_A
0.4	0.0	99.6	68.0	26.5	5.5
0.4	6.0	93.6	72.9	22.1	5.0
0.5	9.4	90.1	78.0	18.1	3.9
0.5	13.6	85.9	80.0	16.4	3.6
0.6	16.9	82.5	83.3	13.3	3.4
0.6	25.0	74.4	86.5	10.5	3.0
1.2	34.6	64.2	88.0	9.1	2.9
3.9	40.2	55.9	89.8	7.4	2.8
10.9	45.1	44.0	91.7	5.5	2.8
13.6	45.4	41.0	97.3	0.0	2.7

(b) Tie-line Data

aqueous phase			organic phase			partition coefficients
100 w_S	100 w_B	100 w_A	100 w_S	100 w_B	100 w_A	
0.5	8.3	91.2	90.4	6.8	2.8	0.82
0.5	11.7	87.8	88.8	8.4	2.8	0.72
0.6	14.6	84.8	87.5	9.6	2.9	0.66
0.6	23.9	75.5	83.7	13.0	3.3	0.54
1.1	28.3	70.6	82.1	14.5	3.4	0.51
1.2	34.3	64.5	80.2	16.3	3.5	0.48
4.9	41.7	53.4	76.6	19.3	4.1	0.46
13.6	45.4	41.0	75.3	20.4	4.3	0.45

^a w is mass fraction with error $\pm 1\%$. Partition coefficients were defined as the ratio of acid concentration in mass percent in the organic phase to that in the aqueous phase.

Table 3. Ternary Diagram for (Tributyl Phosphate (60 vol %) + Dodecane (40 vol %) [w_S]) + Formic Acid [w_B] + Water [w_A])^a

(a) Binodal Curve Results

aqueous rich side			organic rich side		
100 w_S	100 w_B	100 w_A	100 w_S	100 w_B	100 w_A
0.4	0.0	99.6	76.6	17.2	6.2
0.4	0.1	99.5	85.2	11.5	3.3
0.4	13.1	86.5	86.5	10.3	3.2
0.5	17.9	81.6	87.1	9.9	3.0
0.5	24.7	74.8	87.3	9.7	3.0
0.5	28.9	70.6	88.0	9.0	3.0
0.7	32.2	67.1	89.0	8.0	3.0
1.3	39.6	59.1	89.3	7.8	2.9
1.4	40.7	57.9	89.7	7.4	2.9
1.4	40.9	57.7	90.3	6.8	2.9
5.0	47.1	47.9	91.6	5.5	2.9
9.0	48.5	42.5	93.3	3.9	2.8
11.9	49.0	39.1	97.3	0.0	2.7

(b) Tie-line Data

aqueous phase			organic phase			partition coefficients
100 w_S	100 w_B	100 w_A	100 w_S	100 w_B	100 w_A	
0.4	4.2	95.4	93.3	3.9	2.8	0.93
0.4	6.5	93.1	92.1	5.0	2.9	0.77
0.4	12.6	87.0	90.2	6.8	3.0	0.54
0.4	17.9	81.7	89.2	7.8	3.0	0.44
0.5	23.4	76.1	87.9	9.0	3.1	0.38
0.5	28.6	70.9	87.2	9.7	3.1	0.34
0.7	32.4	66.9	86.3	10.4	3.3	0.32
1.1	37.0	61.9	85.6	11.1	3.3	0.30
1.4	40.9	57.7	84.9	11.8	3.3	0.29
5.0	47.1	47.9	83.0	13.1	3.9	0.28
11.9	49.0	39.1	82.7	13.3	4.0	0.27

^a w is mass fraction with error $\pm 1\%$. Partition coefficients were defined as the ratio of acid concentration in mass percent in the organic phase to that in the aqueous phase.

of $(25 \pm 0.1)^\circ\text{C}$ in a thermostated device. A shaking period of $4\text{ h} \pm 10\text{ min}$ is necessary to reach liquid-liquid equilibrium since some previous experiments showed that

Table 4. Ternary Diagram for (Tributyl Phosphate (60 vol %) + Dodecane (40 vol %) [w_S]) + Oxalic Acid [w_B] + Water [w_A])^a

(a) Binodal Curve Results

aqueous rich side			organic rich side		
100 w_S	100 w_B	100 w_A	100 w_S	100 w_B	100 w_A
0.4	0.0	99.6	89.8	7.7	2.5
0.4	2.0	97.6	90.4	7.1	2.5
0.4	3.5	96.1	90.7	6.8	2.5
0.4	4.8	94.8	91.0	6.5	2.5
0.5	6.1	93.4	91.4	6.0	2.6
0.7	7.5	91.8	92.1	5.3	2.6
0.8	9.5	89.7	92.6	4.8	2.6
1.0	10.4	88.6	93.3	4.1	2.6
1.1	12.1	86.8	94.6	2.7	2.7
1.1	14.0	84.9	97.3	0.0	2.7

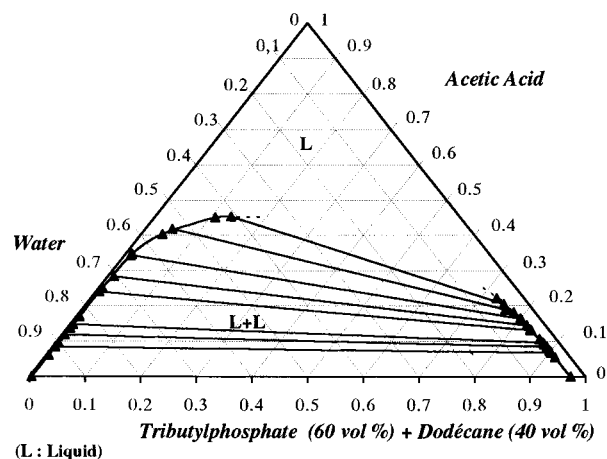
(b) Tie-line Data

aqueous phase			organic phase			partition coefficients
100 w_S	100 w_B	100 w_A	100 w_S	100 w_B	100 w_A	
0.4	2.4	97.2	94.3	3.0	2.7	1.25
0.4	4.4	95.2	92.9	4.5	2.6	1.02
0.5	6.0	93.5	92.2	5.2	2.6	0.87
0.6	7.3	92.1	91.7	5.8	2.5	0.79
0.7	8.8	90.5	91.3	6.2	2.5	0.70
1.0	10.1	88.9	90.8	6.7	2.5	0.66
1.0	10.8	88.2	90.7	6.9	2.4	0.64
1.1	13.5	85.4	90.0	7.6	2.4	0.56
1.1	14.0	84.9	89.9	7.7	2.4	0.55

(c) Mutual Solubility Data

100 w_S	100 w_B	100 w_A
0.0	14.2	85.8
1.1	14.0	84.9
89.8	7.7	2.5
91.5	8.5	0.0

^a w is mass fraction with error $\pm 1\%$. Partition coefficients were defined as the ratio of acid concentration in mass percent in the organic phase to that in the aqueous phase.

**Figure 1.** Ternary diagram for (tributyl phosphate (60 vol %) + dodecane (40 vol %)) + acetic acid + water at 25°C .

the content of acid in both phases did not change beyond a time of $3\text{ h} \pm 10\text{ min}$ in the contacting vessel. After decantation over a period of $2\text{ h} \pm 10\text{ min}$, carboxylic acid, being present in each phase in equilibrium, was titrated with standard sodium hydroxide (0.1 M or 1.0 M) with phenolphthalein as the indicator. In the same phases, the water content was measured with an automatic Karl-Fischer titrator. From each experiment of batch extraction, a material balance, with regard to carboxylic acid, was established in order to confirm the analytical results. The error induced from titrating and weighing was $\pm 1\%$. The average values based upon three readings are reported in

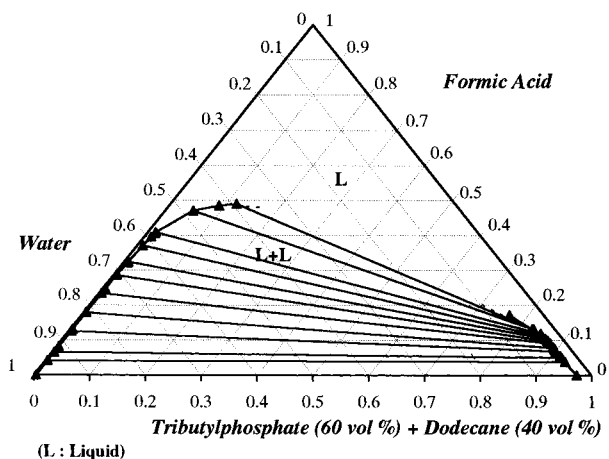


Figure 2. Ternary diagram for (tributyl phosphate (60 vol %) + dodecane (40 vol %) + formic acid + water) at 25 °C.

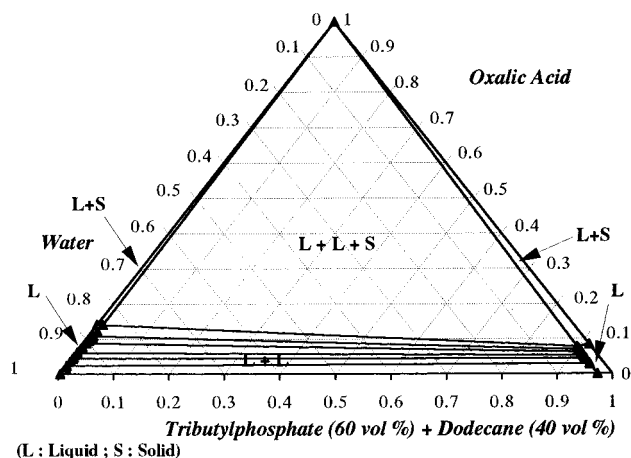


Figure 3. Ternary diagram for (tributyl phosphate (60 vol %) + dodecane (40 vol %) + oxalic acid + water) at 25 °C.

Tables 2–4. Solid–liquid saturation curves that appear in ternary diagram water + oxalic acid + tributyl phosphate (Figure 3) were determined from saturated solutions, and oxalic acid was titrated with standard sodium hydroxide (0.1 M or 1.0 M). For the ternary diagrams, the solvent contents in the extract and the raffinate phases were deduced by difference from the total concentration of the various compounds.

Results and Discussion

Solubility isotherms and tie-lines that are shown in Figures 1–3 have been plotted from the data of Tables 2 to 4 obtained at the temperature of 25 °C. Whereas the liquid–liquid equilibrium shown in Figures 1 and 2 corresponds to a classical model of representation, a zone of

solid phase appears in the ternary system water + oxalic acid + tributyl phosphate (Figure 3), which might belong to the type 4 classification proposed by Treybal (Treybal, 1963). Since the undissociated form of the carboxylic acids is the only one extracted by the solvent, the acidic pH of the initial aqueous solutions is favorable to the extraction process reflected in the partition coefficient values (Tables 2b, 3b, and 4b). The molecular form of a carboxylic acid is predominant in aqueous solution if its pH is below the pK_a of this acid. In the case of oxalic acid, the first dissociation constant determines the acid strength (Table 1). With a strong solvating extractant such as tributyl phosphate, there is no unsolvated species in the organic phase and a quasi-stoichiometric association between the individual phosphoryl group and the individual carboxylic group of the acid occurs in the extract (Kertes and King, 1986). Furthermore, since this solvent can be easily regenerated through back-extraction with an alkaline solution, the tributyl phosphate represents an attractive extractant for the recovery of carboxylic acids from industrial waste waters.

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