

Solubility Measurements for Water + Tartaric Acid + (Tributyl Phosphate + Dodecane) at 25, 35, and 45 °C

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Tartaric acid is recovered from distillery wastewater by solvent extraction. The use of tributyl phosphate + dodecane as a solvent was studied. Solubility relationships were established at 25, 35, and 45 °C in order to study the use of tributyl phosphate as an extractant. The tributyl phosphate + dodecane mixture was a very selective solvent for extracting tartaric acid from wastewater. Distribution coefficients range from 0.18 to 0.33.

Introduction

Tartaric acid, C₄H₆O₆, is mainly used in food and pharmaceutical applications because of its acidulant properties and high solubility in water (1).

In wine distillery the treatment of grape must using ion-exchange resins produces a pollutant aqueous effluent which contains essentially tartaric and malic acids. Tartaric acid can be recovered from the effluent by the technique of solvent extraction.

Previous studies concerning the extraction of tartaric acid from aqueous solutions were made using solvents such as 2-methyl-1-propanol, 1-pentanol, 3-methyl-1-butanol, and 4-methyl-2-pentanone which belong to the category of carbon-bonded oxygen-donor compounds (2-5). The solubilities of these solvents in water are relatively high (at 25 °C, 8.23 mass % for 2-methyl-1-propanol, 2.04 mass % for 1-pentanol, and 2.61 mass % for 3-methyl-1-butanol) which would make a solvent recovery cycle costly and yield a poor process economy.

The solvent selected for our studies was tributyl phosphate. It contains a phosphoryl group which is a stronger Lewis base than the carbon-bonded oxygen compounds. Further this solvent is less soluble in water (<0.6 mass %) than those solvents mentioned above.

Since tributyl phosphate has a relatively high viscosity of 3.56×10^{-3} Pa·s and a specific gravity close to unity (0.98), it is necessary to mix it with a diluent in order to facilitate good phase separation. Dodecane was chosen because of its low viscosity (1.15×10^{-3} Pa·s), its weak specific gravity (0.75), and furthermore its insolubility in water. The percentage of tributyl phosphate in the mixture should be as high as possible in order to obtain the highest partition coefficients. Taking both the partition coefficient and phase separation into consideration, we have chosen the mixture of 75 vol % tributyl phosphate + 25 vol % dodecane as the solvent.

Experimental Section

Chemicals. For the extraction experiments, tributyl phosphate, dodecane, and tartaric acid with a minimum purity of 99% were obtained from Aldrich Chemical Co. The analysis by high-performance liquid chromatography (HPLC) confirmed these purities.

Experimental Procedures. Solubility isotherms and tie-line data for the ternary system water + tartaric acid +

Table I. Ternary System Water (A) + Tartaric Acid (B) + (Tributyl Phosphate (75 vol %) + Dodecane (25 vol %)) (S) at 25 °C

Binodal Curve Results for the Organic-Rich Side (E)						
100w _{AE}	100w _{BE}	100w _{SE}	100w _{AE}	100w _{BE}	100w _{SE}	
4.2	0.0	95.8	3.2	6.9	89.9	
4.1	0.2	95.7	3.1	8.0	88.9	
4.0	0.9	95.1	3.0	9.2	88.8	
3.9	2.0	94.1	2.8	11.1	86.1	
3.8	3.3	92.9	2.7	12.1	85.2	
3.6	5.3	91.1				
Binodal Curve Results for the Aqueous-Rich Side (R)						
100w _{AR}	100w _{BR}	100w _{SR}	100w _{AR}	100w _{BR}	100w _{SR}	
43.3	55.2	1.5	88.7	10.6	0.7	
50.6	48.1	1.3	91.7	7.7	0.6	
57.3	41.5	1.2	93.9	5.5	0.6	
64.2	34.7	1.1	96.4	3.1	0.5	
73.1	25.9	1.0	98.5	1.1	0.4	
80.9	18.4	0.7	99.6	0.0	0.4	
85.5	13.8	0.7				
Mutual Solubility Data						
100w _A	100w _B	100w _S	100w _A	100w _B	100w _S	
41.5	58.55	0.0	0.9	11.3	87.8	
2.7	11.9	85.4	0.5	11.1	88.4	
1.9	11.7	86.4	0.0	11.3	88.7	
Tie-Line Data						
aqueous phase (R)			organic phase (E)			
100w _{AR}	100w _{BR}	100w _{SR}	100w _{AE}	100w _{BE}	100w _{SE}	m
98.4	1.1	0.5	4.1	0.4	95.5	0.33
96.9	2.6	0.5	4.0	0.8	95.2	0.31
93.6	5.8	0.6	3.9	1.6	94.5	0.27
90.8	8.6	0.6	3.9	2.2	93.9	0.26
87.4	11.9	0.6	3.8	3.4	92.8	0.24
79.4	19.8	0.7	3.8	4.5	91.7	0.23
75.9	23.3	0.8	3.7	4.9	91.4	0.21
69.4	29.5	1.1	3.5	5.9	90.6	0.20
61.5	37.4	1.1	3.2	7.4	89.4	0.20
56.2	42.6	1.2	3.0	8.6	88.4	0.20
48.9	49.7	1.4	2.9	9.8	87.3	0.20
43.3	55.2	1.5	2.7	12.1	85.2	0.22

(tributylphosphate + dodecane) were determined at 25, 35, and 45 °C. The experimental devices were maintained at a desired temperature with an accuracy of ± 1 °C. The samples of tartaric acid + water were mixed with varying amounts of tributyl phosphate + dodecane by shaking in glass-stoppered separatory funnels and thermostated for 2 h. After decan-

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Table II. Ternary System Water (A) + Tartaric Acid (B) + (Tributyl Phosphate (75 vol %) + Dodecane (25 vol %)) (S) at 35 °C

Binodal Curve Results for the Organic-Rich Side (E)						
100w _{AE}	100w _{BE}	100w _{SE}	100w _{AE}	100w _{BE}	100w _{SE}	
3.5	0.0	96.5	3.0	5.0	92.0	
3.3	0.5	96.2	2.8	6.9	90.3	
3.2	1.3	95.5	2.8	8.1	89.1	
3.2	2.8	94.0	2.8	9.5	87.7	
3.1	4.2	92.7	2.7	10.2	87.1	

Binodal Curve Results for the Aqueous-Rich Side (R)						
100w _{AR}	100w _{BR}	100w _{SR}	100w _{AR}	100w _{BR}	100w _{SR}	
38.5	59.5	2.0	87.9	11.3	0.8	
45.8	52.7	1.5	91.2	8.2	0.6	
51.9	46.4	1.7	93.6	5.8	0.6	
58.7	39.8	1.5	97.7	1.9	0.4	
71.9	27.0	1.1	98.9	0.6	0.5	
79.6	19.5	0.9	99.6	0.0	0.4	
83.3	15.3	0.4				

Mutual Solubility Data						
100w _A	100w _B	100w _S	100w _A	100w _B	100w _S	
39.9	61.1	0.0	0.7	10.7	88.6	
2.1	11.6	86.3	0.0	10.8	89.2	
1.2	10.7	88.1				

Tie-Line Data						
aqueous phase (R)			organic phase (E)			
100w _{AR}	100w _{BR}	100w _{SR}	100w _{AE}	100w _{BE}	100w _{SE}	m
98.7	0.9	0.4	3.3	0.3	96.4	0.31
96.3	3.2	0.5	3.3	0.8	95.9	0.26
93.1	6.3	0.6	3.2	1.5	95.3	0.24
90.1	9.3	0.6	3.2	2.2	94.6	0.23
86.4	12.9	0.7	3.2	2.7	94.1	0.21
82.7	16.5	0.8	3.1	3.4	93.5	0.20
75.6	23.4	1.0	3.1	4.5	92.4	0.19
68.6	30.2	1.2	3.0	5.5	91.5	0.18
62.2	36.4	1.4	2.8	6.4	90.8	0.18
53.9	44.5	1.6	2.8	8.4	88.8	0.19
49.3	49.0	1.7	2.8	9.4	87.8	0.19
44.2	53.8	1.9	2.7	10.2	87.1	0.19
38.5	59.5	2.0	2.7	12.7	84.6	0.21

tation over a period of 1 h, the aqueous phase and organic phase in each of the tunnels were separated from each other. Tartaric acid, being present in each phase in equilibrium, was neutralized with standard sodium hydroxide (0.1 or 1.0 mol dm⁻³), and phenolphthalein was used as the indicator. The error induced from titrating and weighing was less than 1%. Water contained in each phase was determined by the Karl-Fischer method. The cloud-point method based on turbidimetric titration from mixtures of fixed composition was used to determine liquid-liquid solubility isotherms at a fixed temperature. Mutual solubility data were obtained with a relative accuracy of 1% from saturated solutions. Tartaric acid was titrated with standard sodium hydroxide (1.0 mol dm⁻³).

Results and Discussion

Tables I-III present the binodal curve results, mutual solubility data, and tie-line results of the pseudoternary system water + tartaric acid + tributyl phosphate at 25, 35, and 45 °C, respectively. Solubility isotherms and tie lines at each temperature are shown in Figures 1-3. There is a zone of solid phase for this ternary system which might belong to the type 4 classification proposed by Treybal (6). The standard deviation of each value mentioned in Tables I-III was estimated to be about 0.1.

The partition coefficients defined as the ratio of acid concentration in mass percent in the organic phase to that

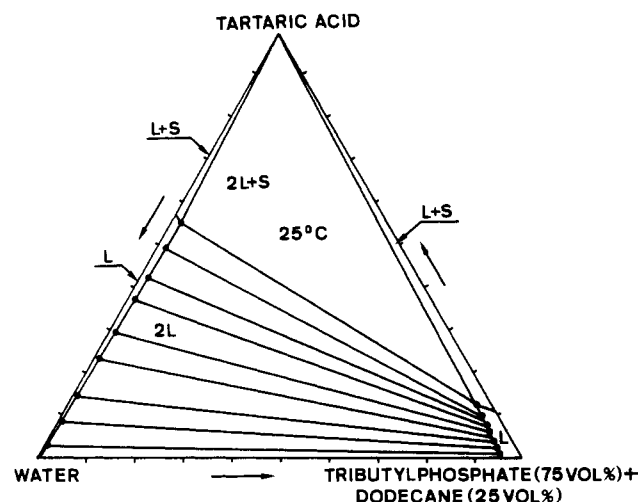
Table III. Ternary System Water (A) + Tartaric Acid (B) + (Tributyl Phosphate (75 vol %) + Dodecane (25 vol %)) (S) at 45 °C

Binodal Curve Results for the Organic-Rich Side (E)						
100w _{AE}	100w _{BE}	100w _{SE}	100w _{AE}	100w _{BE}	100w _{SE}	
2.8	0.0	97.2	2.3	6.9	90.8	
2.6	0.5	96.9	2.3	8.4	89.3	
2.3	1.5	96.2	2.6	9.6	87.8	
2.2	3.4	94.4	2.7	10.4	86.9	
2.0	5.5	92.5	2.7	11.9	85.3	

Binodal Curve Results for the Aqueous-Rich Side (R)						
100w _{AR}	100w _{BR}	100w _{SR}	100w _{AR}	100w _{BR}	100w _{SR}	
35.7	62.3	2.0	85.7	13.6	0.7	
43.5	52.0	1.5	89.2	10.3	0.5	
52.8	45.7	1.5	91.1	8.3	0.6	
61.7	37.2	1.1	94.6	4.9	0.5	
69.2	29.9	0.9	97.7	1.6	0.7	
79.1	20.1	0.8	98.8	0.7	0.5	
83.8	15.5	0.7	99.6	0.0	0.4	

Mutual Solubility Data						
100w _A	100w _B	100w _S	100w _A	100w _B	100w _S	
36.2	63.8	0.0	0.7	10.5	88.8	
1.9	11.3	86.8	0.0	10.8	89.2	
1.1	11.0	87.9				

Tie-Line Data						
aqueous phase (R)			organic phase (E)			
100w _{AR}	100w _{BR}	100w _{SR}	100w _{AE}	100w _{BE}	100w _{SE}	m
98.7	0.9	0.4	2.8	0.2	97.0	0.30
96.4	3.2	0.4	2.5	0.8	96.7	0.24
98.2	6.3	0.5	2.4	1.3	96.3	0.20
89.6	9.9	0.5	2.3	1.9	95.8	0.20
86.7	12.7	0.6	2.2	2.5	95.3	0.19
83.2	16.1	0.7	2.2	3.2	94.6	0.20
79.7	19.5	0.8	2.2	3.8	94.0	0.19
76.4	22.8	0.8	2.1	4.2	93.7	0.18
71.9	27.2	0.9	2.0	4.9	93.1	0.18
66.7	32.3	1.0	2.0	5.7	92.3	0.18
59.1	39.7	1.2	2.3	7.2	90.5	0.18
51.3	48.1	1.6	2.4	8.6	89.0	0.18
43.5	54.8	1.7	2.7	10.3	87.0	0.19
35.7	62.2	2.1	2.7	11.9	85.4	0.19

**Figure 1.** Equilibrium diagram of water + tartaric acid + tributyl phosphate at 25 °C.

in the aqueous phase are also included in Tables I-III. The distribution curves (Figure 4) show that the temperature has little influence on the extraction of tartaric acid by tributyl phosphate.

The selectivity curves at each temperature are shown in Figure 5. The tributyl phosphate is a very selective solvent

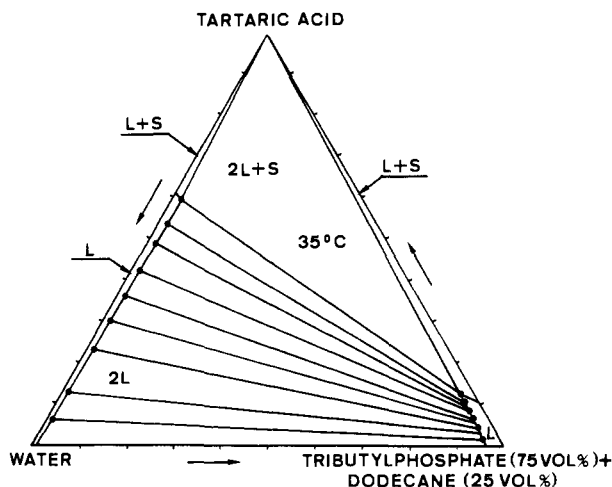


Figure 2. Equilibrium diagram of water + tartaric acid + tributyl phosphate at 35 °C.

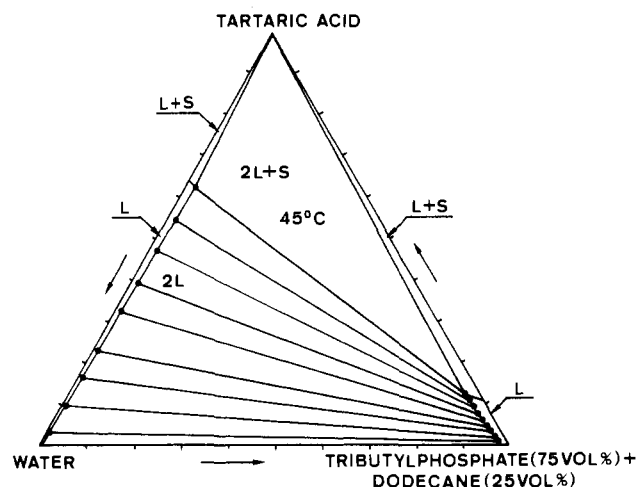


Figure 3. Equilibrium diagram of water + tartaric acid + tributyl phosphate at 45 °C.

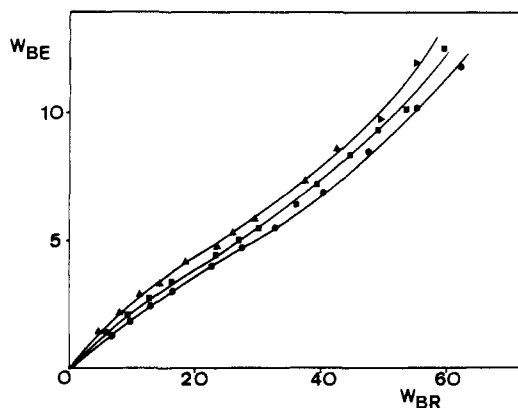


Figure 4. Distribution curves at different temperatures: (▲) 25 °C, (■) 35 °C, (●) 45 °C. The ordinate represents the mass fraction of tartaric acid in the organic phase. The abscissa represents the mass fraction of tartaric acid in the aqueous phase.

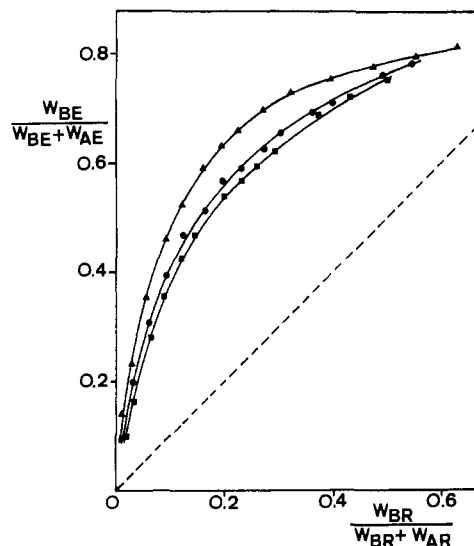


Figure 5. Selectivity curves at different temperatures: (■) 25 °C, (●) 35 °C, (▲) 45 °C. The ordinate represents the ratio of acid to (acid + water) in the solvent phase. The abscissa represents the ratio of acid to (acid + water) in the water phase.

in relation to tartaric acid because the curves are located well above the bisectrix which represents unity.

Compared with conventional solvents such as 4-methyl-2-pentanone, 3-methyl-1-butanol, and 2-methyl-1-propanol (5), the mixture composed of tributyl phosphate (75 vol %) + dodecane (25 vol %) can be considered as a solvent more attractive for extraction of tartaric acid from distillery wastewater.

Glossary

w_A	mass fraction of water
w_B	mass fraction of tartaric acid
w_S	mass fraction of solvent
w_{AR}	mass fraction of water in the aqueous phase
w_{BR}	mass fraction of tartaric acid in the aqueous phase
w_{SR}	mass fraction of solvent in the aqueous phase
w_{AE}	mass fraction of water in the organic phase
w_{BE}	mass fraction of tartaric acid in the organic phase
w_{SE}	mass fraction of solvent in the organic phase
m	partition coefficient w_{BE}/w_{BR}
s	solid phase
l	liquid phase

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Received for review February 24, 1992. Accepted July 10, 1992.