Liquid−Liquid Equilibria of Lactic Acid between Water and Tris(6-methylheptyl)amine and Tributyl Phosphate in Various Diluents

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Separation of an organic solute from dilute aqueous solution is difficult when the solute is not sufficiently volatile for distillation and furthermore is very soluble in the water phase. In this case, it is economically preferable to remove the solute by solvent extraction. In this work, the possibility of the extraction of lactic acid from agroindustrial aqueous effluent was studied. Two type of organic solvents such as organophosphorus extractant and a long-chain tertiary amine dissolved in various diluents of varying polarity were chosen for their abilities to extract lactic acid. Owing to their very low solubilities in the aqueous phase which limit the environmental pollution, the use of these solvents in biotechnology and food processing was reported in previous works (Yu-Ming, J.; Dao-Chen, L.; Yuan-Fu, S. *Proc. ISEC* **1980**, *II*, 517. Wennersten, R. J. *Proc. ISEC* **1980**, *II*, 63). The solubility of tris(6-methylheptyl)amine (triisooctylamine) in water (0.002 mass %) is less than the solubility of tributyl phosphate in water (0.039 mass %). Tie line data were determined at a temperature of 25 °C. For the selected solvents tributyl phosphate + dodecane, triisooctylamine + 1-octanol, and triisooctylamine + heptane + hexanol the partition coefficients defined as the ratio of lactic acid concentration (mass %) in the organic phase to lactic acid concentration (mass %) in the aqueous phase were found to be equal to average values of 0.77, 1.37, and 0.53, respectively.

Introduction

Lactic acid ($C_3H_6O_3$) is increasingly used in foods and in pharmaceutical products. As a food acidulant, lactic acid has a mild acidic taste in contrast with the sharp taste of some other food acids. Lactic acid is used widely to adjust pH and to improve flavor in food products. Lactic acid is also used in chemical synthesis as a reactive intermediate (*1−3*).

The possibility of recovery of carboxylic acids from dilute aqueous solutions such as fermentation broth and wastewater by the technique of liquid−liquid extraction has received increasing attention (*4−8*). In this work, the extraction of lactic acid from the aqueous effluent of wine distillery by a tertiary amine extractant or a phosphorus-bonded oxygen-bearing extractant was examined so as a compare the equilibrium behavior of both systems. Two solvents, tributyl phosphate dissolved in dodecane and tris(6-methylhepthyl)amine dissolved in two diluents such as 1-octanol and a mixture of heptane + hexanol, were investigated. Previous studies on extraction of lactic acid from dilute aqueous solution were made using solvents such as alcohols, ketones, ethers, and esters which are oxygenated carbon compounds. The extracting capacity of this latter type of solvent results from the solvation character of the oxygen group attached to a carbon atom which acts as a Lewis base. The partition coefficients are often small (*4*). Furthermore, the solubilities of these solvents in water are relatively high and hence involve a costly solvent recovery cycle and yield poor process economy. Tributyl phosphate contains a phosphoryl group which is a stronger Lewis base than the oxygenated carbon compounds. Since tributyl phosphate has a relatively high viscosity (3.56×10^{-3} Pa·s) and a specific gravity close to unity (0.98), it is necessary to mix it with a diluent of low viscosity and low density in order to facilitate good phase separation in a continuous extraction process. Dodecane was chosen because of its low viscosity (1.15×10^{-3} Pa·s), its low specific gravity (0.75 g·cm^{-3}), and its insolubility in water. Taking both the partition coefficient and phase separation into consideration, we have chosen the mixture of 70 vol % tributyl phosphate with 30 vol % dodecane as the organic solvent phase. When using tris(6-methylheptyl)amine as extractant, the strong amine interaction with the acid allows for the formation of acid−amine complexes. The long-chain tertiary amines have received the most attention principally owing to their low miscibility in the aqueous phase. Although water coextraction is less than with most conventional solvents, it is sufficient for clusters of water molecules to be associated with the complexation sites supporting ionization (*8*).

Two diluents, 1-octanol and a mixture of heptane + 1 hexanol, were investigated. Polar diluents increase the extracting capacity of amine by providing additional solvating power. The fundamental difference between oxygen- and nitrogen-bearing extractants is the behavior of the acid proton during the transfer of solute from an aqueous into an organic solution. With phosphorus-bonded oxygen-bearing extractants, the acid strength in the aqueous solution and the strength of the hydrogen bond in the organic phase permit the extracting power of the solvent to be estimated. With tertiary amine as extractant, the extent of cation−ion pair association between the alkylammonium cation and the acid radical provides a measure of the stability of the organic-phase complex. Further, the polarity of the diluent affects the basicity of the amine and consequently the stability in the ion pair complex formed. A change in the diluent accompanying the amine extractant

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Table 1. Ternary System Water (A) + Lactic Acid (B) + (Tributyl Phosphate (70 vol %) + Dodecane (30 vol %)) (S): Tie-Line Data at 25 °C[a]

aqueous phase (R)			organic phase (E)		
$100w_{AR}$	$100w_{BR}$	$100w_{SR}$	$100w_{AE}$	$100w_{BE}$	$100w_{SE}$
98.0	1.5	0.5	1.5	0.7	97.8
94.0	4.4	1.6	1.8	2.0	96.2
92.4	6.0	1.6	1.2	3.8	95.0
87.5	10.8	1.7	1.7	7.8	90.5
86.3	11.7	2.0	1.9	10.0	88.1
84.0	14.0	2.0	1.8	11.2	87.0
79.5	18.4	2.1	2.0	16.0	82.0
77.5	20.5	2.0	1.8	17.2	81.0
76.1	21.0	2.9	2.0	18.5	79.5
70.6	26.5	2.9	2.3	21.4	76.3
60.9	34.0	5.1	2.7	26.0	71.3
56.9	37.0	6.1	2.9	30.0	67.1
52.2	40.6	7.2	3.7	31.3	65.0
47.5	43.6	8.9	5.1	36.1	58.8
46.7	44.1	9.2	5.5	38.0	56.5
42.9	46.1	11.0	6.0	38.7	55.3
40.6	47.4	12.0	6.8	40.0	53.2
38.5	48.0	13.5	7.1	40.9	52.0

[a] w_{AR}, w_{BR}, and w_{SR}, represent, respectively, the mass fractions of A, B, and S in the aqueous phase. w_{AE}, w_{BE}, and w_{SE} represent, respectively, the mass fractions of A, B, and S in the organic phase.

can cause changes in both the complexation equilibrium constant and consequently the partition coefficient.

Experimental Section

Chemicals. Tributyl phosphate, dodecane, tris(6-methylheptyl)amine, the diluents, and lactic acid with a purity of 99% were obtained from Aldrich Chemical Corp. Analysis by high-performance liquid chromatography (HPLC) confirmed these purities.

Procedures. Tie line measurements for the systems water + lactic acid + solvent were determined by means of a device maintained at a constant temperature of 25 °C with an accuracy of ±1 °C. Several lactic acid solutions of different concentrations were mixed with varying amounts of solvent in glass-stoppered separatory funnels and thermostated for a time of 3 h. Normally, the concentration of acids in both phases does not change beyond about 2 h in the contacting device. After decantation over a period of 1.5 h, the aqueous and organic phases were analyzed. When tributyl phosphate (70 vol %) + dodecane (30 vol %) was used as solvent, the organic and aqueous phases were analyzed by titrating the acid with standard sodium hydroxide solutions (0.1 and 1.0 M) and phenolphthalein was used as the indicator.

When amine was employed as extractant, the analysis of acid concentration in the organic phase involves stripping of the lactic acid with a known excess amount of standard sodium hydroxide (0.1 M), and then the alkaline solution was back-titrated with hydrochloric acid solution (0.05 M). The error induced from titrating and weighing was less than 1%. Furthermore, a high-performance liquid chromatography method (HPLC) was used to confirm the results of dosage by the volumetric titration. According to the HPLC method, a stripping of the lactic acid from the organic phase with H_2SO_4 solution (0.5 M) was necessary before introducing samples into the apparatus. The HPLC system consisted of a pump (Spectra Physics Model SP 8800), an integrator (Chromjet SP 4400), a UV spectrophotometer (Spectra 100 UV–vis detector), and an analysis column (AMINEX HPX-87H) which worked at 40 °C. The eluent was 0.005 M H_2SO_4 at a flow rate of 0.4 cm^3/min. Water concentrations in each phase were determined by the Karl-Fisher method. The accuracy of the measurements was within ±2%. The solvent concentrations may be deduced by difference from the total concentration of the three compounds which equals 100%.

Table 2. Ternary System Water (A) + Lactic Acid (B) + (Triisoctylamine (20 vol %) + 1-Octanol (80 vol %)) (S): Tie-Line Data at 25 °C[a]

aqueous phase (R)			organic phase (E)		
$100w_{AR}$	$100w_{BR}$	$100w_{SR}$	$100w_{AE}$	$100w_{BE}$	$100w_{SE}$
98.0	1.9	0.1	1.9	2.0	96.1
94.8	4.2	1.0	2.1	8.0	89.9
91.4	6.6	2.0	3.0	11.8	85.2
90.0	8.0	2.0	3.2	15.5	81.3
88.9	9.0	2.1	3.0	17.6	79.4
86.6	11.0	2.4	3.2	18.0	78.8
85.6	11.8	2.6	3.5	19.1	77.4
82.0	15.0	3.0	3.8	20.2	76.0
79.0	17.4	3.6	4.3	23.1	72.6
78.1	18.0	3.9	4.5	25.0	70.5
75.4	20.3	4.3	4.9	25.5	69.6
70.9	24.2	4.9	5.4	28.8	65.8
69.0	25.4	5.6	6.3	31.3	62.4
65.3	28.5	6.2	6.4	31.8	61.8
61.4	31.5	7.1	7.9	36.1	56.0
54.0	36.9	9.1	11.6	43.0	45.4
50.0	39.2	10.8	13.1	45.1	41.8
46.1	41.7	12.2	14.0	46.5	39.5
45.5	42.2	12.3	14.8	47.2	38.0
44.2	41.0	14.8	20.0	48.0	32.0
34.1	47.8	18.1	19.3	49.0	31.7

[a] w_{AR}, w_{BR}, and w_{SR} represent, respectively, the mass fractions of A, B, and S in the aqueous phase. w_{AE}, w_{BE}, and w_{SE} represent, respectively, the mass fractions of A, B, and S in the organic phase.

Table 3. Ternary System Water (A) + Latic Acid (B) + (Triisoctylamine (20 vol %) + Heptane–Hexanol (1:1) (80 vol %)) (S): Tie-Line Data at 25 °C[a]

aqueous phase (R)			organic phase (E)		
$100w_{AR}$	$100w_{BR}$	$100w_{SR}$	$100w_{AE}$	$100w_{BE}$	$100w_{SE}$
96.5	2.0	1.5	1.1	1.1	97.8
87.8	9.8	2.4	1.5	3.3	95.2
82.3	14.2	3.5	1.8	5.8	92.4
77.7	18.0	4.3	1.8	8.0	90.2
73.9	20.8	5.3	2.0	9.2	88.8
70.8	23.1	6.1	2.2	11.6	86.2
67.7	25.2	7.1	2.6	12.4	85.0
62.1	28.9	9.0	2.8	14.2	83.0
60.2	30.2	9.6	2.8	13.8	83.4
50.5	36.3	13.2	3.0	17.2	79.8
45.0	39.2	15.8	3.3	17.7	79.0
40.9	41.0	18.1	5.0	24.3	70.7
39.5	41.0	19.5	5.1	24.9	70.0
37.6	41.8	20.6	6.0	26.4	67.6
33.9	43.0	23.1	7.1	29.1	63.6
30.0	43.0	27.0	9.0	32.3	58.7
27.2	43.0	29.8	9.1	33.2	57.1

[a] w_{AR}, w_{BR}, and w_{SR} represent, respectively, the mass fractions of A, B, and S in the aqueous phase. w_{AE}, w_{BE}, and w_{SE} represent, respectively, the mass fractions of A, B, and S in the organic phase.

Results and Discussion

From the liquid–liquid equilibrium data results in Tables 1–3, the configuration of phase diagrams belongs to the type 1 classification proposed by Treybal (*6*). In this case, there is only formation of one pair of partially miscible liquids. This type of binodal curve and the corresponding tie lines are a combination frequently encountered in the literature. The representation of the mass concentration of lactic acid in the organic phase against the mass concentration of lactic acid in the aqueous phase at equilibrium showed no significant difference between the partition coefficients when the acid was extracted by tributyl phosphate or extracted by tris(6-methylheptyl)amine extractant. Since 1-octanol is more polar than the mixture heptane + hexanol, the average value of the partition coefficient is relatively more important when the first diluent is used. The average values of the partition coefficient were found to be equal to 1.37 and 0.53, respectively. For extraction of lactic acid, the solvent triisooctylamine + 1-octanol provides a more favorable polar medium for the complex than one obtained with the diluent heptane + hexanol. A polar diluent such as 1-octanol favors complex formation through strong hydrogen bonding with the available oxygen accessible on the complexed carboxylic acid (*10*). The experimental fact that polar diluents are more favorable than nonpolar diluents is shown in the extraction of citric and lactic acids (*8*, *11*). Compared with conventional solvents such as carbon−oxygen compounds, tributyl phosphate and tris(6-methylheptyl)amine can be considered as selective solvents more attractive for extraction of lactic acid from agroindustrial effluent. Extraction with tertiary amines and regeneration of solvent according to a back-extraction by means of a basic aqueous solution is a process commonly used for recovery of carboxylic acids from aqueous media. Even though the capacity of the solvent is limited by the stoichiometry of complexation, tertiary amines which are slightly toxic tend to be the complexants of choice.

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