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Water-Enhanced Solubilities of Lactic Acid in Reactive Extraction Using Trioctylamine/Various Active Diluents Systems

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ABSTRACT

Trioctylamine (TOA) was used as the extraction agent for reactive extraction in various active diluents. Equilibrium and hydration data for various active diluents were obtained in 0.6 M TOA systems. From these data we divided the active diluents used into three classes: active diluents containing chlorine atoms, carbon-bonded oxygen donor active diluents, and phosphorus-bonded oxygen donor active diluents. This classification was based on the characteristic groups of active diluents. The amounts of lactic acid and water in the organic phase were strongly affected by physical extraction of the active diluents. The relationships between coextracted water and lactic acid extracted were represented by slopes in drawings. The sensitivity index, which is defined as the inverse of a slope, was introduced as the measure of the water-enhanced solubilities of lactic acid. Factors affecting the reactive extraction of lactic acid and water, such as the type of active diluents, the moles of amine used, and the bulkiness of the active diluents, were explained based on the characteristic groups of the active diluents.

INTRODUCTION

The recovery of lactic acid has recently received increasing attention due to its use as the monomer of biodegradable polymers. Long-chain aliphatic amines are known to be effective extractants for carboxylic acids and metal salts (1).

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Studies of reactive extraction using long-chain aliphatic amines have mainly concentrated upon selection of appropriate active diluents and the fitting of the equilibrium curve through interpretation of the reaction mechanism. The phenomena of water coextraction were reported by Forbes and Coolidge (2) and Herz and Lorents (3) but were not investigated systematically.

The coextraction effect of water was recently considered systematically by Starr and King (4) and Bizek et al. (5). Bizek et al. (5) interpreted the reactive extraction using thermodynamic concepts and predicted the concentration of water in the organic phase. Han and Hong (6) introduced water as the reaction species and predicted the equilibrium and the hydration curves. Starr and King (4) applied the effect of coextracted water on extraction to the stripping process of physical extraction. They found that water removal from the organic phase could decrease the solubility of carboxylic acid. This phenomenon was applied for the stripping method of carboxylic acid by the removal of water from the organic phase. Bizek et al. (7) studied the effect of active diluent on the reactive extraction of carboxylic acid using amines and the coextraction of water, but they did not consider the water-enhanced solubilities of carboxylic acids.

In this study we investigated the reactive extraction of lactic acid and the coextraction of water by the variation of active diluents in trioctylamine systems, and we explain the water-enhanced solubilities of lactic acid. In addition to these explanations, factors affecting the reactive extraction of lactic acid and water, such as the type of active diluents, the moles of amine used, and the bulkiness of active diluents, are discussed.

EXPERIMENTAL

Materials

Trioctylamine (TOA), a C_8 straight-chain tertiary amine, was obtained from Acros and was used as an extractant without further purification. Lactic acid (20 wt%), obtained from Acros, was diluted to various concentrations. The active diluents used can be classified into three groups (8):

1. The phosphorus-bonded oxygen donor active diluent: tributyl phosphate (TBP)
2. The carbon-bonded oxygen donor active diluents: 1-decanol, 1-octanol, and methyl isobutyl ketone
3. The active diluents containing chlorine atoms: 1-chlorobutane, chloroform, methylene chloride, and chlorobenzene

All reagents were GR grade. The initial concentration of lactic acid was varied from 0.1 to 2.22 M in order to obtain equilibrium data for the range of concentrations of lactic acid obtained from fermentation. TOA was used at 0.4, 0.6, 0.8, 1.0, and 1.2 M as the basis of active diluents in reactive extraction. The 0.6 M TOA/various active diluents systems were used to study the effect of active diluents on the water-enhanced solubilities of lactic acid.

Experimental Procedures

Lactic acid was extracted as follows. A 10-mL solution of lactic acid and a 10-mL TOA solution were transferred into a 25-mL vial. The vial was immersed in a circulator for 30 minutes and maintained at 20°C. Phase mixing was carried out by stirring with a magnetic bar at 1000 rpm and 20°C for 20 minutes.

Physical extraction by active diluents was also performed at the same conditions (1000 rpm, 20°C) for 60 minutes. The initial concentration of lactic acid was 10 wt% (1.11 mol/L) for physical extraction. To obtain the solubility of water for the trioctylamine solution, the trioctylamine solution was mixed with the pure water at 1000 rpm and 20°C for 20 minutes.

For the clear separation of two phases after each extraction, mixed phases were centrifuged at 5000 rpm and 20°C for 20 minutes. We took samples of each phase for analysis of the concentrations of water and lactic acid.

The concentration of lactic acid was analyzed by 0.1 N NaOH using phenolphthalein as the indicator. The water concentration in the organic phase was analyzed by a Coulometric Karl-Fisher Titrimeter.

RESULTS AND DISCUSSION

The Effect of the Moles of Trioctylamine on the Amount of Lactic Acid Extracted and Coextracted Water

Figures 1 and 2 show the effect of the moles of trioctylamine on the amount of extraction in 1-chlorobutane and methylene chloride/*n*-hexane, respectively. Due to stoichiometry, the amounts of coextracted water and lactic acid extracted were increased with an increase in the number of moles of trioctylamine.

As can be seen from Figs. 1 and 2, the slopes of the curves do not vary much with a change in the number of moles of trioctylamine. However, a change in the type of active diluent had a large effect on the values of the slopes as shown in Fig. 5. These results show that the type of active diluent is a more important factor than the number of moles of trioctylamine on the water-enhanced solubility of lactic acid.

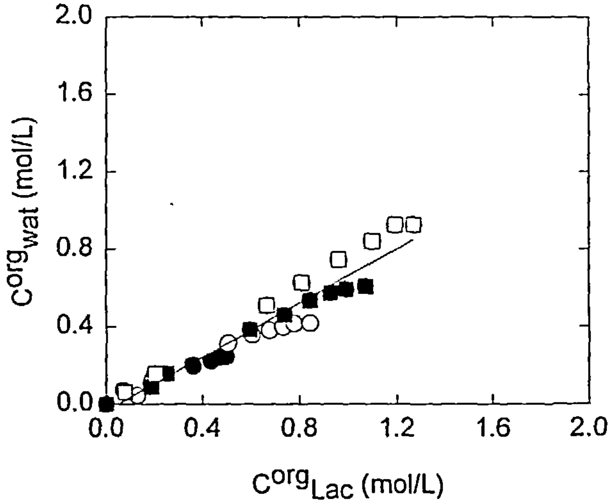

FIG. 1 The water-enhanced solubilities of lactic acid with the variation of the moles of trioctylamine in 1-chlorobutane at 20°C: (●) 0.4 M TOA/1-chlorobutane, (○) 0.6 M TOA/1-chlorobutane, (■) 0.8 M TOA/1-chlorobutane, (□) 1.0 M TOA/1-chlorobutane. Solid line: Regression line.

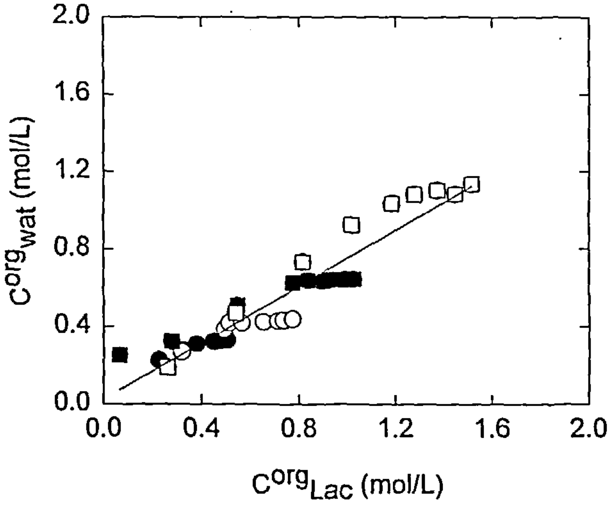

FIG. 2 The water-enhanced solubilities of lactic acid with the variation of the moles of trioctylamine in methylene chloride (MC)/*n*-hexane at 20°C: (●) 0.4 M TOA/MC/*n*-hexane, (○) 0.6 M TOA/MC/*n*-hexane, (■) 0.8 M TOA/MC/*n*-hexane, (□) 1.2 M TOA/MC/*n*-hexane. Solid line: Regression line.

The Variations of the Lactic Acid and the Water in the Organic Phase According to the Various Types of Active Diluents

In this experiment the active diluents used were mainly divided into three groups: phosphorus-bonded oxygen donor active diluents, carbon-bonded oxygen donor active diluents such as alcohols and ketones, and active diluents containing chlorine atoms.

Figures 3 and 4 show equilibrium and hydration data using these three groups of active diluents, respectively. These phenomena reported are due to the effects of the characteristic groups on the physical solubilities of lactic acid.

According to the equations of reactive extraction (6), the solubilities of lactic acid by the mixed solvents that were composed of the amine and the active diluent were divided into two classes. First, lactic acid was extracted by reaction with amines, as in Eq. (1). Second, as can be seen from Eq. (3), lactic acid was physically extracted by the characteristic groups of active diluents.

$$a \text{ Lactic acid} + \overline{\text{Amine}} + p\text{H}_2\text{O} \leftrightarrow \overline{\text{Lactic acid}_a\cdot\text{Amine}\cdot(\text{H}_2\text{O})_p} \quad (1)$$

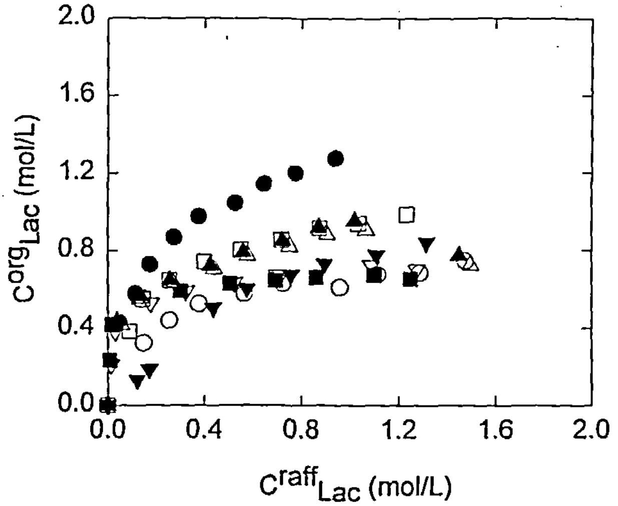

FIG. 3 The equilibrium data of lactic acid in 0.6 M trioctylamine/various active diluents systems at 20°C: (●) 0.6 M TOA/tributyl phosphate, (○) 0.6 M TOA/chlorobenzene, (■) 0.6 M TOA/chloroform, (□) 0.6 M TOA/MIBK, (▲) 0.6 M TOA/1-octanol, (△) 0.6 M TOA/1-decanol, (▼) 0.6 M TOA/1-chlorobutane, (▽) 0.6 M TOA/methylene chloride.

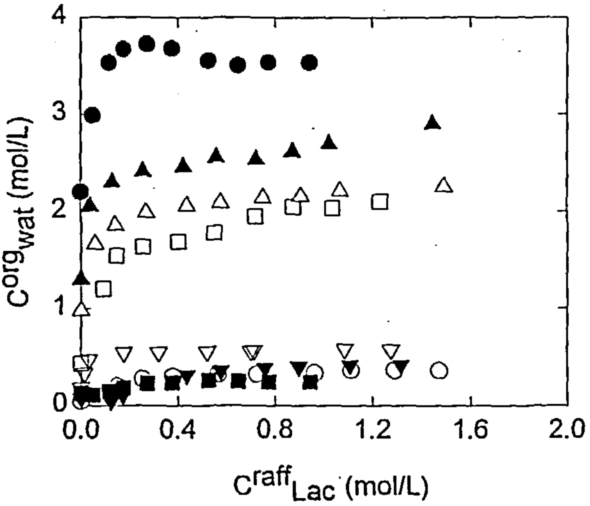

FIG. 4 The coextracted water in the organic phase in 0.6 M trioctylamine/various active diluents systems at 20°C: (●) 0.6 M TOA/tributyl phosphate, (○) 0.6 M TOA/chlorobenzene, (■) 0.6 M TOA/chloroform, (□) 0.6 M TOA/MIBK, (▲) 0.6 M TOA/1-octanol, (△) 0.6 M TOA/1-decanol, (▼) 0.6 M TOA/1-chlorobutane, (▽) 0.6 M TOA/methylene chloride.

$$\overline{\text{Amine}} + q\text{H}_2\text{O} \leftrightarrow \overline{\text{Amine}\cdot(\text{H}_2\text{O})_q} \qquad (2)$$

$$\text{Lactic acid} \leftrightarrow \overline{\text{Lactic acid}} \qquad (3)$$

First of all, the reaction of lactic acid with amines did not have large influence on the total solubility of lactic acid because the active diluents used in this experiment have good solubilities for the complex formed by the reaction. Second, the physical extraction of lactic acid has an important influence on the equilibrium and hydration curves because the physical extraction of lactic acid and water varies greatly with the type of characteristic group of active diluents. The distribution coefficients as determined by physical extraction are listed in Table 1.

As can be seen from Table 1, the phosphorus-bonded oxygen donor active diluent (tributyl phosphate) has a physical solubility for lactic acid as large as the solubility by reactive extraction. The phosphorus-bonded oxygen donor active diluents were also used as extractants without amines. Therefore, the equilibrium and hydration curves lie in the upper parts of Figs. 3 and 4 due to a combination of solubility by reaction and physical solubility.

TABLE 1
The Distribution Coefficients and the Water Contents Determined with and without Physical Extraction for Various Active Diluents

Active diluents	Distribution coefficient (*D*)	Water content with physical extraction (mol/L)	Water content without physical extraction (mol/L)
Chlorobenzene	No extraction	0.07	0.08
1-Chlorobutane	No extraction	0.09	0.05
Chloroform	No extraction	0.09	0.12
Methylene chloride	0.05	0.12	0.10
Methyl isobutyl ketone	0.01	1.08	0.43
1-Decanol	0.01	1.92	0.98
1-Octanol	0.15	2.55	1.30
Tributyl phosphate	0.71	3.54	2.20

The carbon-bonded oxygen donor active diluents such as alcohols and ketones (1-decanol, 1-octanol, and methyl isobutyl ketone) have good physical solubilities for lactic acid and water due to hydrogen bonds (4). In the physical extraction complex, the hydrogen of lactic acid was hydrogen bonded to the oxygen of water, and the oxygen atom of the active diluents was also hydrogen bonded to the hydrogen of water. As can be seen from Figs. 3 and 4, the equilibrium and hydration curves have moderate values.

In the active diluents containing chlorine atoms such as 1-chlorobutane, chloroform, methylene chloride, and chlorobenzene), the chlorine atom is so large that hydrogen bonds cannot be formed. The active diluents containing chlorine atoms have poor physical solubilities of lactic acid and water in the organic phase.

From a comparison of the data in Table 1, it was also inferred that less bulky active diluents in the same type of active diluents can have higher solubilities of lactic acid and water because of an increase of the dipole moment due to less bulkiness of the hydrocarbon groups.

The Effect of Various Types of Active Diluents on the Relation between the Lactic Acid and the Water in the Organic Phase

The slopes shown in Fig. 5 represent the water-enhanced solubilities of lactic acid in reactive extraction. The smaller slopes mean higher water-enhanced solubilities of lactic acid. The slope values for each active diluent are listed in Table 2. The sensitivity index, which is defined as the

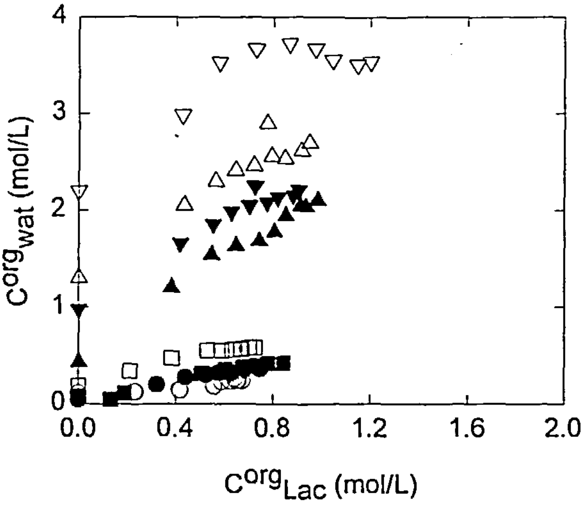

FIG. 5 The water-enhanced solubilities of lactic acid in the various active diluents: (●) 0.6 M TOA/chlorobenzene, (○) 0.6 M TOA/chloroform, (■) 0.6 M TOA/1-chlorobutane, (□) 0.6 M TOA/methylene chloride, (▲) 0.6 M TOA/MIBK, (△) 0.6 M TOA/1-octanol, (▼) 0.6 M TOA/1-decanol, (▽) 0.6 M TOA/tributyl phosphate.

TABLE 2
The Sensitivity Indices of Active Diluents Due to Water Removal from the Active Diluents

Types of active diluents	Active diluents	Slope	Sensitivity index (*S*)	Average of sensitivity index
Active diluents containing chlorine atoms	Methylene chloride	0.54	1.87	2.62
	1-Chlorobutane	0.49	2.04	
	Chlorobenzene	0.44	2.28	
	Chloroform	0.23	4.27	
Carbon-bonded oxygen donor active diluents	MIBK	1.65	0.61	0.68
	1-Octanol	1.48	0.68	
	1-Decanol	1.36	0.74	
Phosphorus-bonded oxygen donor active diluents	Tributyl phosphate	2.10	0.48	0.48

inverse of a slope, was introduced as the measure of the water-enhanced solubilities of each active diluent. These values indicate the increase of the solubility of lactic acid through an increase of the solubility of water in the organic phase ($\Delta C_{\mathrm{Lac}}^{\mathrm{org}}/\Delta C_{\mathrm{wat}}^{\mathrm{org}}$).

The sensitivity indices are the characteristics due to the characteristic groups of active diluents. As can be seen from Fig. 5, slopes of the same type of active diluents have similar values. For the three types of active diluents, the sensitivity index decreases in the order: active diluents containing chlorine atoms carbon-bonded oxygen donor active diluents such as alcohols and ketones phosphorus-bonded oxygen donor active diluents.

These results are explained as follows. Active diluents containing chlorine atoms have little physical extraction for the active diluents (Table 1). The lactic acids extracted primarily exist as a reaction complex form of lactic acid, amine, and water. Therefore, removal of water directly affects the stability of the complex. As can be seen from Fig. 5 and Table 2, the active diluents containing chlorine atoms have small slopes and large sensitivity indices.

As can be seen from Table 1, water was physically extracted without the extraction of lactic acid in carbon-bonded oxygen donor active diluents such as alcohols and ketones. Here, the removal of water has little influence on the stability of the complex formed because the physically extracted water was removed first. As shown in Fig. 5 and Table 2, the slopes are larger than those of the active diluents containing chlorine atoms. The sensitivity indices are contrary to the slopes.

The phosphorus-bonded oxygen donor active diluents also have good physical solubilities for lactic acid and water. The early removal of water affects the physically extracted water. Therefore, the effects of water removal do not directly affect the complexes formed by the amine. The sensitivity indices are relatively small (Table 2 and Fig. 5).

CONCLUSION

In this paper the water-enhanced solubilities of lactic acid were explained by the action of characteristic groups of active diluents. The water-enhanced solubilities did not vary greatly with a change in the number of moles of trioctylamine. The type of active diluents is a more important factor than the change in the number of moles of trioctylamine on the water-enhanced solubility of lactic acid.

The equilibrium and hydration data were classified into three divisions according to the type of active diluents. These phenomena were due to the effect of the characteristic groups on the physical solubilities of lactic acid in active diluents. It was also inferred that less bulky active diluents in the same type of active diluents can have higher solubilities for lactic acid and water due to an increase of the dipole moment due to the smaller bulkiness of the hydrocarbon groups.

The sensitivity index, which represents the amount of lactic acid extracted with the variation of water content in the organic phase, was defined as the inverse of the slope. For three types of active diluents the sensitivity index decreased in the order: active diluents containing chlorine atoms carbon-bonded oxygen donor active diluents such as alcohols and ketones phosphorus-bonded oxygen donor active diluents.

DEFINITIONS

Distribution coefficient (D)

$$= \frac{\text{concentration of lactic acid extracted in the organic phase}}{\text{concentration of lactic acid remaining in the aqueous phase}}$$

$$S = \frac{1}{\text{slope}} = \frac{\Delta C_{\text{Lac}}^{\text{org}}}{\Delta C_{\text{wat}}^{\text{org}}}$$

SYMBOLS

a	moles of lactic acid
p	moles of hydration in Reaction (1)
q	moles of hydration in Reaction (2)
C	molar concentration (mol/L)
Δ	difference

Superscripts

$\overline{\text{(overbar)}}$	species in the organic phase
org	organic phase
raff	aqueous raffinate phase

Subscripts

Lac	lactic acid
wat	water

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