

Separation Characteristics of Lactic Acid in Reactive Extraction and Stripping

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Abstract—Lactic acid has recently been drawing much interest as a raw material for biodegradable polymer. Various extractants for lactic acid separation were tested and TOA (triethylamine) was found the most effective one. Lactic acid was separated by reactive extraction with TOA dissolved in various diluents. The effect of temperature on the extraction efficiency was smaller than that of composition for the system studied in this work.

Key words: Lactic Acid, Amine, Diluent, Stripping, TSR, DSR

INTRODUCTION

Recently, lactic acid fermentation has received much attention because of the demand for biodegradable lactide polymer and the high cost of petroleum, which is usually used as feed stock for production of lactic acid by chemical synthetic process [Kaiming et al., 1996; Han and Hong, 1998a; Seo et al., 1999; Hong and Hong, 1999]. High purity and heat stable lactic acid, which was mainly available from synthetic manufacture, is now being produced by fermentation. However, the fermentation process needs an economic separation method to compete with the synthetic process because the fermentation broth contains various impurities [Kertes and King, 1986].

Several possible alternatives exist for the recovery of lactic acid from fermentation broth. Among these, reactive extraction is considered to be an effective primary separation step for the recovery of lactic acid from fermentation broth. Reactive extraction is the separation process using reaction between extractant and material extracted [Tamada et al., 1990; Tamada and King 1990a; Fahim et al., 1992; Prochazka et al., 1994; Han and Hong, 1996, 1998b; Matsumoto et al., 1998]. The extractant in the organic phase reacts with material of aqueous phase and the reaction complex formed is solubilized into the organic phase.

There are three categories in extractants used in reactive extraction [Kertes and King, 1986]. These are the acid extraction by solvation with carbon-bonded oxygen-bearing extractants, by solvation with phosphorous-bonded oxygen-bearing extractants, and by proton transfer or by ion-pair formation with high molecular weight aliphatic amines.

The first two categories involve the solvation of the acid by donor bonds. The distinction between the first two categories is based on the strength of the solvation bonds and the specificity of solvation. Solvation with alcohols, ethers, and ketones, which are typical carbon-bonded oxygen donor extractants, is not regarded as being specific [Schuegerl, 1994]. The significantly more basic donor pro-

perties of the phosphorous-bonded oxygen cause a specific solvation process and the number of solvating molecules per extracted acid is accessible experimentally. In the third category, ionic interactions, i.e., reactions are involved.

Extraction of proton-bearing organic and inorganic compounds from aqueous media by long-chain aliphatic amines dissolved in water-immiscible organic solvents is one of the newest developments in extraction technology. The extractability of acids, in contrast to that of anionic acidic metal complexes, depends more on the composition of the organic phase, the amine, and the diluent than on the aqueous phase conditions. The requirements for practical extraction applications are rather general for both strong and weak acids and are fairly well described in the literature [Schuegerl, 1994].

In general, there are primary, secondary, and tertiary amines in amine-type extractants. Among these amines, the tertiary amine have been widely used in reactive extraction because the primary and secondary amines tend to react irreversibly with carboxylic acid and the stripping of solvent becomes difficult [Hong et al., 1999].

In reactive extraction, a stripping step is needed for the recovery of extractant and extracted material. In reactive extraction of lactic acid, the stripping step is carried out by diluent-swing-regeneration (DSR) and temperature-swing-regeneration (TSR). DSR is the recovery method using the shift of equilibrium curve with diluent composition in organic phase and TSR is the method using the shift of equilibrium curve with temperature [Tamada and King, 1990b; Hong et al., 2000].

In this study, the extractabilities of various extractant systems were investigated. The effect of operating temperature and diluent composition on extraction efficiency was also studied. Regeneration of lactic acid in the extract was carried out in simple distillation equipment by varying diluent composition at proper operating temperature.

EXPERIMENTAL

1. Materials

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To compare extractabilities of various amines, triamylamine (TAA), tributylamine (TBA), tripentylamine (TPA) and trioctylamine (TOA) were used. The high purity amines are used without further purification. Trioctylamine, a C₈ straight-chain tertiary amine, was obtained from Acros Co. Tributylamine and tripentylamine were purchased from Aldrich Co. Triamylamine was obtained from Junsei Co.

Diluents were used in reactive extraction of lactic acid due to the high boiling point, high viscosity, and corrosive property of tertiary amines. Diluents can be classified into active and inactive diluent. Active diluents have functional groups that enable greater solvation of the acid-amine complex. In this study, methylene chloride, tributylphosphate (TBP), chloroform, 1-octanol, iso-butyl alcohol, 1-chlorobutane, methylisobutylketone (MIBK) and n-decanol were used as active diluents. Inactive diluents give a very low distribution of the acid into the solvent phase [Tamada and King, 1990]. Their property is nonpolar. Hexane, cyclohexane, isooctane, n-heptane, kerosene, pentane and chlorobenzene were used as inactive diluents. All reagents were GR grade.

Lactic acid, 20 wt% obtained from Acros, was diluted to various concentrations.

2. Experimental Procedures

The initial concentration of lactic acid was varied from 0.1 M to 0.22 M by considering the concentration of lactic acid obtained from fermentation. The concentrations of TOA tested in this work were 0.4, 0.6, and 0.8 M of the basis of diluent.

Experiments were performed using 25 ml vials, each equipped with a magnetic stirrer and thermostatted at various temperature. Equal volumes (10 ml) of initial aqueous and organic phases were agitated for 15 min. To maintain constant temperature, a water bath was used. In order to separate mixed phase into aqueous phase and organic phase they were centrifuged at 5,000 rpm for 15 min.

The concentration of lactic acid in aqueous phase was determined by 0.1 N NaOH by using the phenolphthalein indicator. The acid concentration in organic phase was calculated by mass balance. The lactic acid concentration in the organic phase was periodically checked by contacting it with 0.1 N NaOH [Hong and Hong, 1999].

In the stripping, extraction was first performed with 100 ml of both phases. After extraction the 100 ml of extracted organic phase and the 100 ml stripping water were mixed and distilled at 50 °C. Active diluent was obtained from the condenser and stripped lactic acid as recovered in the reboiler.

RESULTS AND DISCUSSION

1. Comparison Between Amine Type Extractant and Phosphorous Type Extractant

In this study, we compared the extractability between phosphorous type extractant (TBP) and amine type extractant. Tributylphosphate (TBP), Dibutylphosphate (DBP) and Trioctylphosphine oxide (TOPO) are involved in phosphorous type extractants. In the reactive extraction of organic acids, TBP and TOPO have been mainly used due to their high extractability. TBP is relatively low viscous and low cost in comparison with TOPO, so we selected TBP as phosphorous type extractants.

Phosphorus type extractant and amine type extractant have good extractabilities in the reactive extraction. However, extractants must

Table 1. Reactive extraction of lactic acid using tributylphosphate (TBP)

| Extractants | Extraction efficiency (%) | Distribution coefficient |
|-------------------|-----------------------------|--------------------------|
| TBP1 | 47.99 | 0.92 |
| TBP2 | 46.64 | 0.87 |
| TBP3 | 46.48 | 0.87 |
| TBP4 | 47.15 | 0.89 |
| TBP5 | 48.81 | 0.95 |
| Stripping of TBP5 | Efficiency of stripping (%) | 43.73 |

not only have good extractability but also good property for the stripping.

Table 1 shows the distribution coefficient (D) and the extraction efficiency (E) in reactive extraction of lactic acid in TBP.

$$D = \frac{C_{LA}^{org}}{C_{LA}^{raff}} \quad (1)$$

$$E(\%) = \frac{C_{LA,i}^{org} - C_{LA,i}^{raff}}{C_{LA,i}^{org}} \times 100 = \frac{D}{1+D} \times 100 \quad (2)$$

where $C_{LA,i}^{org}$ is the initial concentration of lactic acid in the aqueous phase and $C_{LA,i}^{raff}$ is the concentration of lactic acid in the raffinate phase, respectively. C_{LA}^{org} is the concentration of lactic acid in organic phase.

As seen in Table 1, the extractability of TBP was about 47%. In the case of TBP, lactic acid extracted was stripped at the efficiency of ca. 43%. Table 2 shows the reactive extraction of lactic acid using various amines in chloroform. In this study loading is defined as follows:

$$\text{Loading}(Z) = \frac{C_{amine}^{org}}{C_{amine,i}} \quad (3)$$

where $C_{amine,i}$ is the initial concentration of amine extractants. As shown in Table 2, the extractability of amine was higher than that of TBP. As the number of carbons in the tertiary amine increases, the extractability is increased. This is due to the fact that the basicity and the polarity of amines increase with their chain length. The same tendency has been reported in the case of tertiary amine dissolved in active diluent [Hong and Hong, 1999, 2000a, b]. In general, it appears that the tertiary amine having more than eight carbons per chain is not effective in reactive extraction due to its steric interference. However, in Table 3, the extraction efficiency of amine was lower than that of TBP. This is due to the low solubility of kerosene for amine-acid complex and its nonpolar properties.

Table 2. Reactive extraction of lactic acid using various amines in chloroform (CF)

| Extractant/ active diluent | Extraction efficiency (%) | Distribution coefficient | Loading (Z) |
|-------------------------------|------------------------------|-----------------------------|----------------|
| TBA/CF | 60.11 | 1.51 | 0.608 |
| TPA/CF | 70.74 | 2.42 | 0.73 |
| TOA/CF | 90.40 | 9.44 | 0.94 |

TBA: Tributylamine, TPA: Tripentylamine, TOA: Trioctylamine

Table 3. Reactive extraction of lactic acid using various amines in kerosene

| Extractant/active diluent | Extraction efficiency (%) | Distribution coefficient | Loading (Z) |
|---------------------------|---------------------------|--------------------------|-------------|
| TAA/kerosene | 12.33 | 0.14 | 0.118 |
| TBA/kerosene | 19.44 | 0.24 | 0.186 |
| TPA/kerosene | 13.56 | 0.16 | 0.129 |

TAA: Triamylamine

Table 4. Reactive extraction of lactic acid using various amines in a tributylphosphate diluent

| Extractant/active diluent | Extraction efficiency (%) | Distribution coefficient | Loading (Z) |
|---------------------------|---------------------------|--------------------------|-------------|
| TBA/TBP | 16.28 | 0.19 | 0.16 |
| TPA/TBP | 38.40 | 0.62 | 0.39 |
| TOA/TBP | 88.12 | 7.42 | 0.90 |

In Table 4 the reactive extraction of lactic acid using various amines in a TBP diluent is shown. As can be seen in Table 4, TOA/TBP system has the similar efficiency of reactive extraction as that of TOA/CF system. However, as the boiling point of TBP is much higher than that of CF, the operating cost of TOA/TBP is very high.

2. Effect of Type of Active Diluents

Long chain amine extractants used in this experiment have high boiling point and viscosity. Therefore, the appropriate selection of active diluent can effectively help the reactive extraction and the stripping process. Table 5 shows the effect of active diluent on the reactive extraction of lactic acid. As seen there, methylene chloride and chloroform have large solubilities for acid-amine complex among active diluents used in this study. Most active diluents except for MIBK have larger solubilities than those of phosphorus type active diluents because of the properties of active diluents. The affinity of active diluent on the reaction complex has a strong influence on the efficiency of reactive extraction.

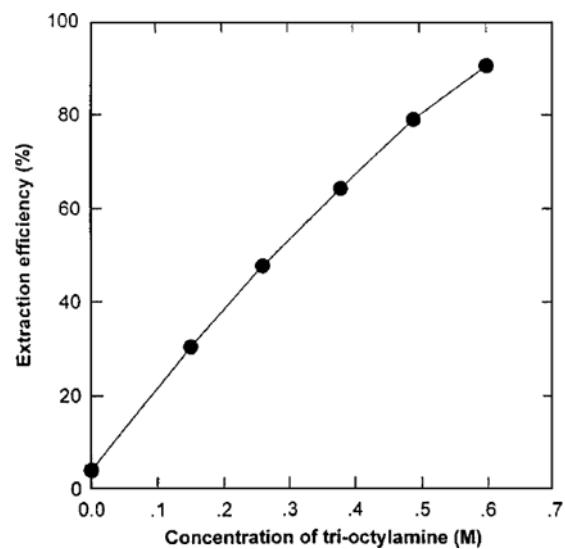
3. Effect of Temperature and Diluent Composition

Temperature and diluent composition are important factors influencing the extraction and stripping efficiency. The variation of temperature and diluent composition induces a shift of the equilibrium curve, thereby acid extracted into organic phase moves into aqueous phase.

Table 5. Effect of active diluent type on the reactive extraction of lactic acid using TBA

| Extractant/active diluent | Extraction efficiency (%) | Distribution coefficient | Loading |
|---------------------------|---------------------------|--------------------------|---------|
| | | | (Z) |
| TBA/MC | 61.11 | 1.53 | 0.62 |
| TBA/CF | 60.11 | 1.51 | 0.61 |
| TBA/IA | 50.07 | 1.00 | 0.51 |
| TBA/IB | 57.35 | 1.35 | 0.58 |
| TBA/MIBK | 17.00 | 0.21 | 0.17 |

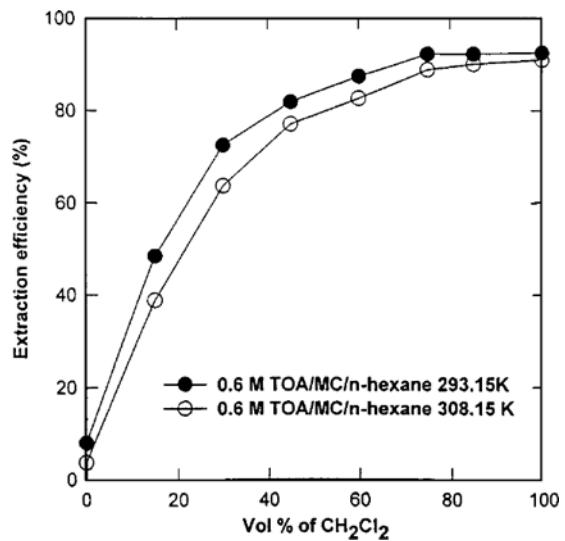
MC: methylene chloride, IA: iso-amyl alcohol, IB: iso-butyl alcohol, MIBK: methyl ether butyl ketone

**Fig. 1. Effect of concentration of TOA on the reactive extraction (Trioctylamine/methylene chloride system).**

Amines are very corrosive in certain range of concentration; therefore, the use of appropriate concentration of amine is important to effective extraction as well as to avoiding corrosivity.

In Fig. 1, the concentration of amine (TOA) is varied from 0 M to 0.6 M. The initial concentration of lactic acid is 10 wt%, which is based on the concentration of lactic acid produced from fermentation. As can be seen from Fig. 1, the increase of amine concentration brings about gradual increase of extraction efficiency. Near 0.6 M, most of the lactic acid is extracted. In this study, we selected 0.6 M TOA solution at extraction and stripping.

Active diluent solubilizes reaction complexes into the organic phase in the reactive extraction. In this study, methylene chloride was used as an active diluent due to its low boiling point, excellent extractability, low toxicity, and low cost. Methylene chloride has a low boiling point, about 40 °C at atmospheric pressure.

**Fig. 2. Effect of composition of active diluent on the reactive extraction of lactic acid.**

The concentration of methylene chloride as an active diluent was varied to measure the stripping power by diluent-swing-regeneration (DSR). As can be seen in Fig. 2, the extraction efficiencies are increased with the composition of methylene chloride. Therefore, the solubility of reaction complex in the active diluent as well as the extractability of amine is an important factor in the reactive extraction of lactic acid. The differences of solubilities to the variation of composition are adequately large for the stripping of lactic acid. Variation of inactive diluent has little influence on the extraction efficiencies except the polar chlorobenzene.

The complexation reactions in the organic phase involve proton transfer or hydrogen-bonding formation and are expected to be exothermic. Formation of a complex makes the system more ordered and thus decreases the entropy. Therefore, as the temperature is increased, the amount of lactic acid extracted decreases [Tamada and King, 1990b]. Experiments were performed at 20 °C and 35 °C be-

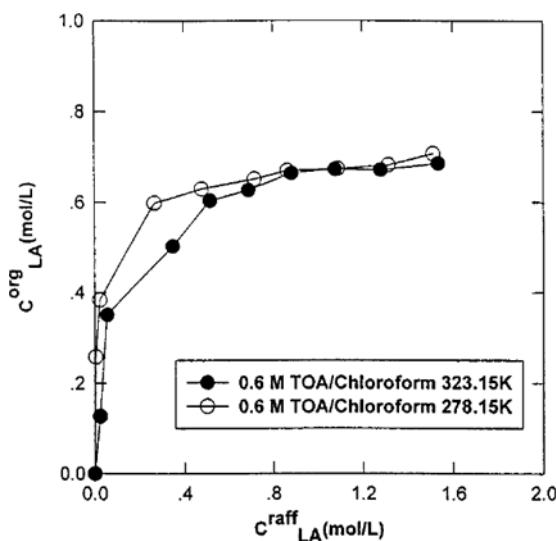


Fig. 3. Effect of temperature on the reactive extraction of lactic acid.

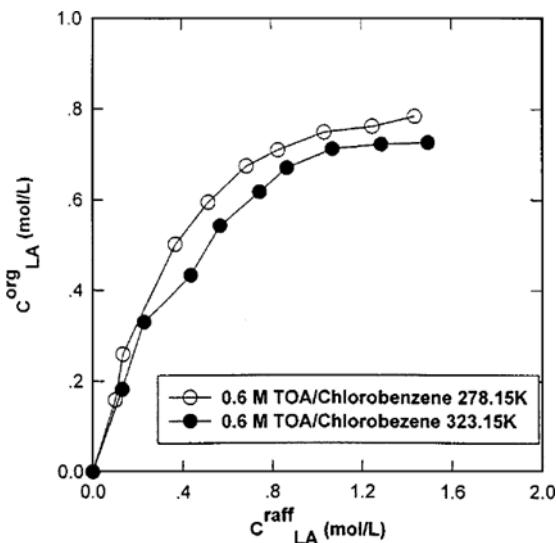


Fig. 4. Effect of temperature on the reactive extraction of lactic acid in TOA/chlorobenzene system.

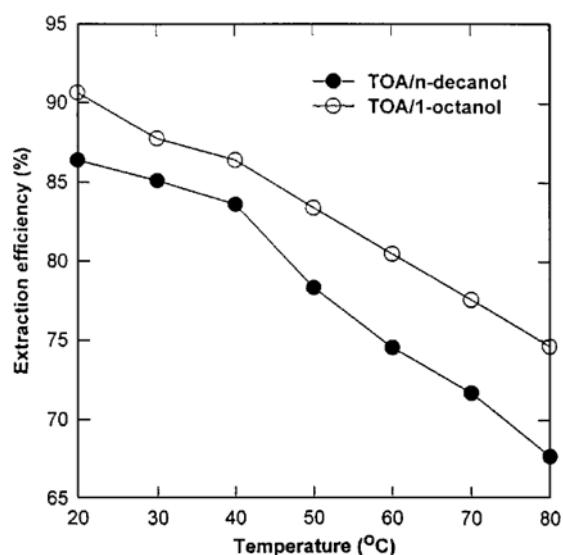


Fig. 5. Effect of temperature on extraction efficiency of lactic acid.

cause of the boiling point of the active diluent. As seen in Fig. 3 and 4, the effect of temperature is smaller than that of composition. However, in 0.6 M TOA/1-decanol and 0.6 M TOA/1-octanol system (Fig. 5), the effect of temperature is not large in comparison with the effect of composition in spite of a large variation of temperature.

The effect of temperature is the phenomenon that the efficiency of extraction decreases with an increase of temperature. As a result of experiment, temperature effect is changed with variation of active diluent. As can be seen from Fig. 6, the sensitivity with variation of temperature decreases with an increase of polarity of active diluent.

In this study, n-hexane, cyclohexane, chlorobenzene, isooctane and n-heptane were used as inactive diluents. As seen in Fig. 7, the

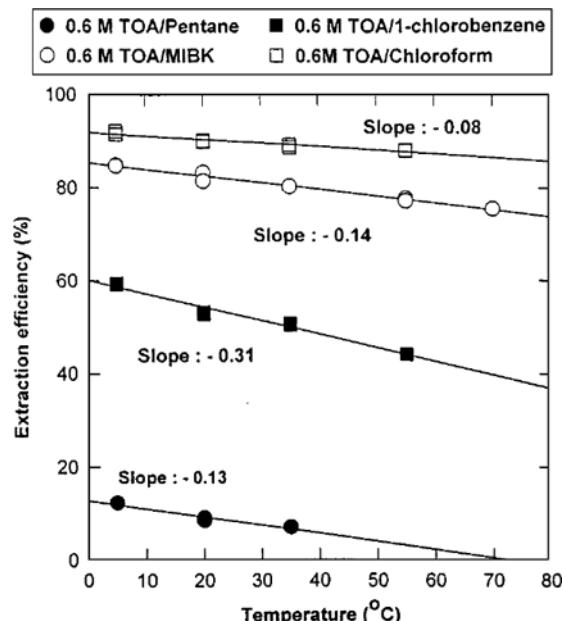


Fig. 6. Effect of type of active diluent on extraction efficiency of lactic acid.

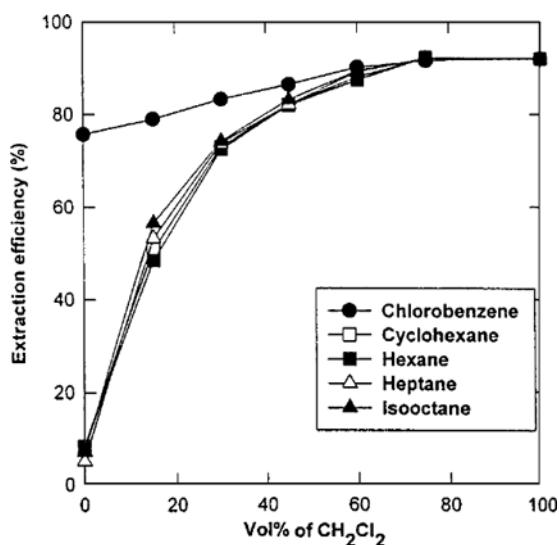


Fig. 7. Effect of concentration of methylene chloride on extraction efficiency of lactic acid at 298.15 K.

variation of inactive diluent has a large influence on the efficiency of extraction. If a polar diluent is used as an inactive diluent, the efficiency of extraction has a different trend with that of other diluents. DSR is the regeneration method with the equilibrium curve shift as the variation of diluent composition. As the composition of inactive diluent is increased, the extraction efficiency is decreased. After reactive extraction, the extracted lactic acid is moved into stripping water by the variation of diluent composition in the stripping process. In the stripping process with simple distillation, methylene chloride is distilled and collected in a condenser. As methylene chloride is collected, the composition of methylene chloride in mixed diluent, methylene chloride/inactive diluent, is decreased, and then extracted lactic acid is moved into flash water (stripping water).

4. Stripping of Lactic Acid by Simple Distillation

The lactic acid extracted should be stripped for the final production of lactic acid. The stripping of lactic acid was generally performed by TSR or DSR. However, in stripping by simple distillation, TSR and DSR were both used because a change in the composition of the active diluent is related to an increase in temperature. In this study the lactic acid in the organic phase was stripped by a simple distillation process at 50 °C. Lactic acid was stripped in the reboiler, and methylene chloride was condensed and recovered from the condenser for reuse. As can be seen from Table 6, the stripping efficiencies are about 70% and do not change with the variation of inactive diluent except for polar chlorobenzene.

CONCLUSION

Trioctylamine (TOA) was selected as an extraction agent for the reactive extraction of lactic acid. The appropriate selection of ac-

tive diluent could help the reactive extraction and the stripping step due to the affinity of reaction complex. Extraction efficiencies were increased with an increase of composition of active diluent. However, the variation of inactive diluent had a large influence on extraction efficiency, except polar chlorobenzene. The effect of temperature was small in comparison with the effect of composition.

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Table 6. Effect of various inactive diluents on the stripping efficiencies. Extractant: 0.6 M TOA/Methylene chloride

| Inactive diluent | Hexane | Cyclohexane | Heptane | Isooctane | Chlorobenzene |
|--------------------------|--------|-------------|---------|-----------|---------------|
| Stripping efficiency (%) | 71.2 | 68.7 | 68.2 | 71.1 | 16.7 |

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