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Optimization of Process Parameters for Reactive Lactic Acid Extraction

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The reactive extraction method was used to separate lactic acid from its aqueous solutions. In this method, the amine in the solvent phase reacts with the lactic acid in the aqueous phase, resulting in the extraction of acid into the organic phase. In this study, Alamine 336 diluted with oleyl alcohol was used as the solvent. The effects of initial lactic acid concentration, pH, temperature, extraction time, stirring rate, the amount of Alamine 336 in oleyl alcohol and the ratio of organic phase volume to aqueous phase volume, V_{org}/V_{aq}, on the distribution coefficient of the lactic acid, K_D, were investigated. K_D increased with increasing stirring rate, extraction time and amount of Alamine 336 and V_{org}/V_{aq}, and decreased with increasing temperature and initial lactic acid concentration. Optimum conditions for reactive extraction of the lactic acid were determined by using the Linear Box-Wilson experimental design method. The optimum conditions were found as follows: initial lactic acid concentration: 21 g/L, pH: 2.0, temperature: 32°C, stirring rate: 120 rpm, amount of Alamine 336 in oleyl alcohol: 41% and V_{org}/V_{aq}:1/1.

Key Words: Reactive extraction, lactic acid, separation of lactic acid, amine extraction, two-phase system, Box-Wilson method

Introduction

Organic acids, widely used in the food, pharmaceutical and chemical industries, are important chemicals. Fermentation technology for the production of organic acids in particular has been known for more than a century and acids have been produced in aqueous solutions. They have severe inhibiting effects on the rate of conversion and thus several separation methods, such as liquid extraction, chromatographic methods, evaporation, ultrafiltration, reverse osmosis, dialysis, crystallization, precipitation and drying, have been practised to remove acids from reactants[1]. Reactive liquid-liquid extraction of the organic acids by a suitable extractant has been found to be a promising alternative to the conventional processes[2,3,4]. Tertiary and quaternary amines such as Alamine 336 and Aliquat 336 form ion pairs with the undissociated carboxylic acids, which result in higher extraction efficiencies. The solvation of the whole amine:acid complex is based on dipole-dipole interaction and has been found to play an important role in the neutralization reaction between acid and amine. In order to improve the amine's solvation power, diluents such as oleyl alcohol, chloroform, methyl isobutyl ketone and 1-octanol have been tested[3,5,6]. The diluents affect the basicity of the amine, the stability of the acid:amine complex formed and its solvation power. The pH of the aqueous phase is an important parameter for the reactive extraction of organic acids. Yang et al.[7] reported that lower pH values result in good separation of lactic acid by long chain tertiary amines. In the intermediate pH range (3-5), K_D decreased with increasing equilibrium pH of the aqueous phase. However, in the extremely high and low pH ranges, K_D remained insensitive to pH values. Similarly, Choudhury et al.[8] reported that the distribution coefficient of lactic acid was high at pH 2.0. In addition, these authors pointed out that the amount of amine in diluents affects the reactive extraction of organic acids. K_D increased with increasing amount of Aliquat 336 in their studies. They reported that increasing amine concentration might have a toxic effect on microorganisms in the in-situ extractive fermentation.

Temperature and initial organic acid concentration are also important parameters for the extraction of organic acids. Yabannavar and Wang[9] investigated the extraction of aqueous lactic acid by trioctylphosphineoxide in dodecane and Alamine 336 in oleyl alcohol. In their study, K_D decreased with increasing initial lactic acid concentration and increased with increasing percent Alamine 336 in oleyl alcohol. Martin et al.[10] studied the extraction of lactic acid from aqueous solutions by Alamine 336 dissolved in toluene. They observed that the extraction of lactic acid decreased with increasing temperature.

In the present study, the reactive extraction of aqueous lactic acid by Alamine 336 in oleyl alcohol was investigated systematically. The Linear Box-Wilson experimental design method was used to find the optimum conditions for a lactic acid extraction process. To this end, the effects of initial lactic acid concentration, pH, temperature, extraction time, stirring rate, amount of Alamine 336 in oleyl alcohol and V_{org}/V_{aq} were investigated.

Experimental

Materials

In the experiments, Alamine 336 (Hoechst Corporation Co.), lactic acid (Merck Co.) and oleyl alcohol (Merck Co.) were used.

Reactive Extraction

Aqueous lactic acid solution of the required concentration was prepared by diluting the lactic acid with distilled water. Amine organic solutions were prepared by diluting 15-50% Alamine 336 with oleyl alcohol. Experiments were carried out in 250 ml shake flasks with a working volume of 50 ml in the reciprocal shaker. Stirring rate, extraction time, temperature and pH varied from 50 to 150 rpm, 5 to 30 min, 25 to 40°C and 2 to 4, respectively. The initial pH of the lactic acid solution was adjusted by NaOH and HCl solutions. After attaining equilibrium, the phases were brought into contact for separation.

Product Recovery

After extraction, the lactic acid in the solvent was recovered by using concentrated NaOH solution (2N). 1 ml NaOH solution was added to 10 ml of organic phase. In the backward extraction, lactic acid was converted to sodium lactate and 10 times concentrated.

Analytical Methods

Lactic acid concentration in the aqueous phase was determined by potentiometric titration using 0.1 N NaOH. The amount of lactic acid in the organic phase was obtained by mass balance. The calculated distribution coefficient, K_D, was defined as

$$K_D = \frac{\text{Lactic acid in the organic phase } (\frac{g}{L})}{\text{Lactic acid in the aqueous phase}(\frac{g}{L})}$$

Results and Discussion

Reactive extraction of lactic acid with Alamine 336 in oleyl alcohol was studied. Experiments were carried out in a reciprocal shaker. Each experiment was performed three times and the results were given as the calculated mean value. The Linear Box-Wilson design method was used to define the optimum conditions. The experiments were carried out at the maximum and minimum points of these parameters.

Effect of Acid Concentration

In the lactic acid extraction with Alamine 336, the variation of K_D with initial lactic acid concentration is given in Figure 1. With 15% Alamine 336 in oleyl alcohol and unit V_{org} to V_{aq} ratio, K_D decreased from 10.5 to 0.5 upon increasing initial lactic acid concentration from 10 to 100 g/L. With 50 % Alamine 336 in oleyl alcohol and unit V_{org} to V_{aq} ratio, K_D decreased from 13 to 4 upon increasing initial lactic acid concentration from 10 to 100 g/L. At higher initial lactic acid concentrations, the amount of Alamine may be the limiting factor for the amine:acid reaction. Similar results were reported by Yabannavar and Wang[9].

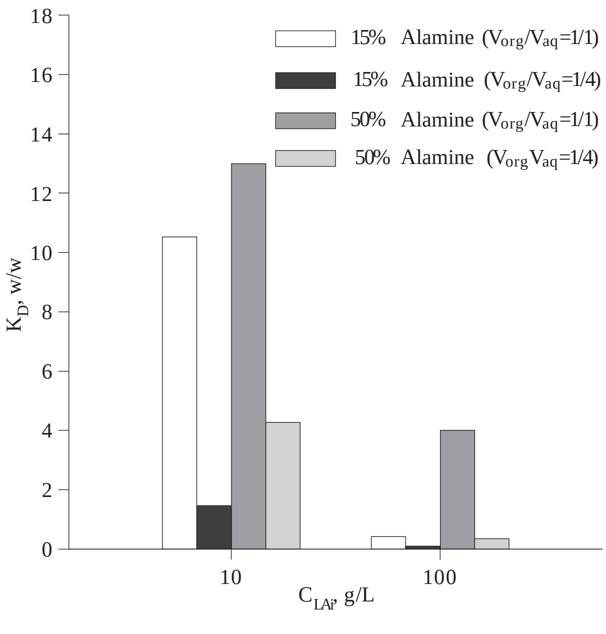

Figure 1. Variaton of distribution coefficient with initial lactic acid concentration. N=150 rpm, pH=2.0, t=30 min, T=25°C

Effect of pH

pH strongly affects the ionization of carboxylic acids. Most carboxylic acids are weak acids. They partially ionize in the aqueous solution according to

$$HA \rightleftharpoons H^+ + A^-$$

The concentrations of dissociated (A^-) and undissociated acids (HA) are affected by the concentration of the hydrogen ion (H^+) or pH. At extremely low pH values, the acid is mainly in undissociated form. Most aliphatic amines extract undissociated acids from the aqueous phase by forming an acid-base complex[7]. The dissociation coefficient of the lactic acid is 1.38×10^{-4} (for pK=3.86 and 25°C). The concentration of the dissociated acid was calculated using the dissociation coefficient. The amount of dissociation was found to be 2.27% and 1.17% for 10 and 100 g/L lactic acid concentration, respectively. As shown in Figure 2, K_D values decreased with increasing pH, from 2 to 4 at the 10 g/L initial lactic acid concentration for all V_{org} to V_{aq} ratios and Alamine percentages.

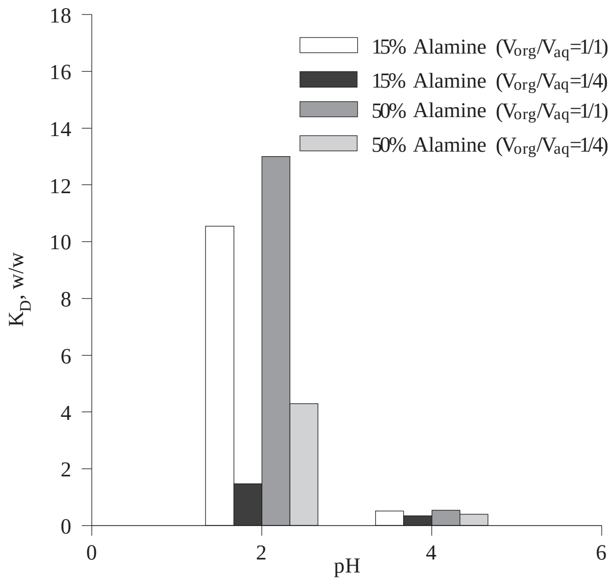

Figure 2. Variation of distribution coefficient with pH. C_{LAi}=10 g/L, N=150 rpm, t=30 min, T=25°C

Effect of Temperature

It is known that the distribution coefficient, K_D, depends on the temperature. Experiments were carried out with 15 and 50% Alamine in oleyl alcohol in the temperature range of 25-40°C at 10 g/L lactic acid concentration and at a pH of 2.0. The results are presented in Figure 3. K_D decreased with increasing temperature at all V_{org}/V_{aq} ratios and Alamine percentages, but only slightly. This can be attributed to the reversible complexation reactions between the organic acid and the amine. The complexation reactions in the organic phase involve a proton transfer reaction or hydrogen bond formation, and are mildly exothermic[10,11].

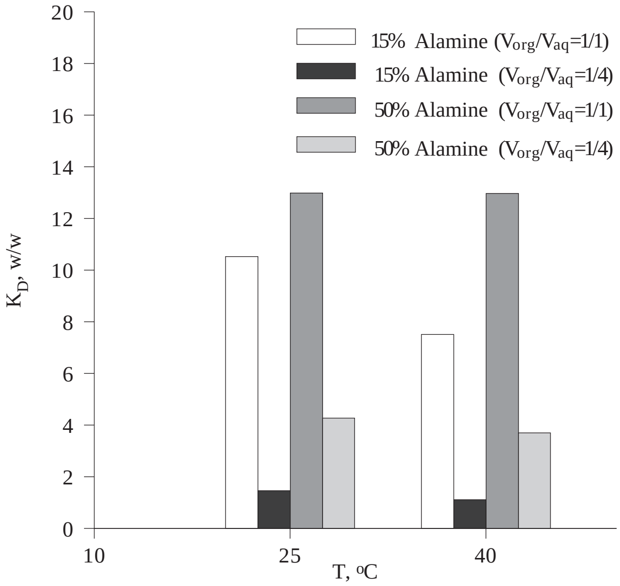

Figure 3. Variation of distribution coefficient with temperature. C_{LAi}=10 g/L, N=150 rpm, pH=2.0, t=30 min

Effect of extraction time

Before Box-Wilson experiments were carried out, the effect of extraction time on K_D was investigated. K_D did not change with the extraction time increasing from 20 min to 30 min. Therefore, the experiment was conducted at 5 and 30 min extraction times. The variation of K_D with extraction time at a pH of 2.0, a temperature of 40°C and 10 g/L lactic acid concentration is given in Figure 4. As can be seen, K_D increases with increasing extraction time for all Alamine % and all V_{org}/V_{aq} ratios. The extraction time affects the attainment of equilibrium conditions. Because of the low reaction rate, the reactive extraction of lactic acid increases with increasing extraction time. In the literature, the effect of the extraction time on lactic acid extraction has not been investigated.

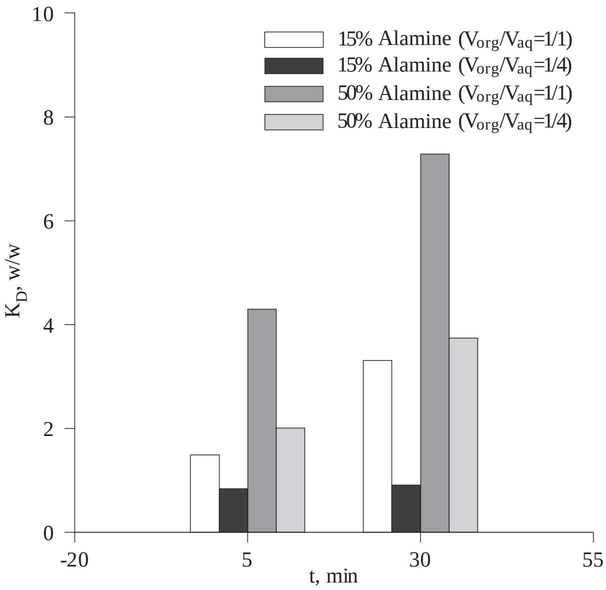

Figure 4. Variation of distribution coefficient with extraction time. C_{LAi}=10 g/L, N=150 rpm, T=40°C, pH=2.0

Effect of stirring rate

In the study of reactive extraction, stirring rate and type of stirring are highly important due to the mass transfer limitations. As seen in Figure 5, K_D increased by about a factor of 6 by increasing the stirring rate from 50 to 150 rpm.

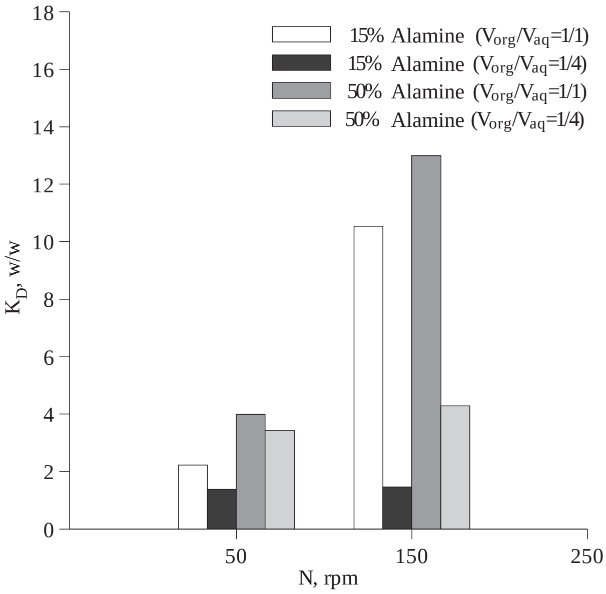

Figure 5. Variation of distribution coefficient with stirring rate. C_{LAi}=100 g/L, N=150 rpm, t=30 min, T=25°C, pH=2.0

Effect of Alamine 336 concentration and ratio of organic phase to aqueous phase

Experiments were carried out at Alamine 336 concentrations of 15% - 50%, and V_{org}/V_{aq} ratios of 1/1 - 1/4. As can be seen in Figures 1-5, the value of K_D increased with increasing Alamine concentration in oleyl alcohol and V_{org}/V_{aq} ratio. The high extraction power of Alamine 336 can be attributed to its strong Lewis-base nature. The function of Alamine 336 with oleyl alcohol is to form the acid-amine complex in the extraction. The complexation reaction rate increases in the organic phase at higher Alamine concentrations. Consequently, mass transfer between aqueous phase and organic phase increases and K_D also increases. Yabannavar and Wang[9] and Martin et al.[12] obtained similar results in reactive extraction studies.

Experimental design and optimization by the Box-Wilson experimental design method

The Linear Box-Wilson method is an experimental design method that determines the effect of parameters on each other in a multi-parameter system by performing a minimum number of experiments[13]. In this study, the experimental design was made with seven independent variables. Thus, the total number of experiments is $2^n = 2^7 = 128$. These independent variables are initial lactic acid concentration (U_1), pH (U_2), temperature (U_3), extraction time (U_4), stirring rate (U_5), Alamine 336 concentration (U_6) and V_{org}/V_{aq} ratio (U_7); the dependent variable (Y_{KD}) is the distribution coefficient of lactic acid. Maximum and minimum values for the initial lactic acid concentration, pH, temperature, extraction time, stirring rate, Alamine 336 concentration and V_{org}/V_{aq} were selected to be 10 and 100 g/L, 2.0 and 4.0, 25 and 40°C, 5 and 30 min, 50 and 150 rpm, 15 and 50%, 1/4 and 1/1, respectively.

The experimental data were evaluated on a personal computer and the equation formed is as follows:

$$Y_{KD} = 1.68 - 0.11Z_1 + 0.18Z_2 + 0.52Z_3 - 1.36Z_4 + 0.70Z_5 - 1.02Z_6 + 0.92Z_7 - 0.06Z_1Z_2 + 0.02Z_1Z_3 + 0.10Z_1Z_4 - 0.03Z_1Z_5 + 0.09Z_1Z_6 - 0.08Z_1Z_7 - 0.18Z_2Z_3 - 0.16Z_2Z_4 + 0.11Z_2Z_5 - 0.09Z_2Z_6 + 0.12Z_2Z_7 - 0.46Z_3Z_4 + 0.02Z_3Z_5 - 0.43Z_3Z_6 + 0.39Z_3Z_7 - 0.64Z_4Z_5 + 1.00Z_4Z_6 - 0.83Z_4Z_7 - 0.23Z_5Z_6 + 0.32Z_5Z_7 - 0.43Z_6Z_7(1) \tag{1}$$

Regression coefficient: $r^2 = 0.9289041$

Where

$$Z_i = \frac{U_i - U_{i,ave}}{\Delta U_i}, \quad U_{i,ave} = \frac{U_i^+ + U_i^-}{2}, \quad \Delta U_i = \frac{U_i^+ - U_i^-}{2}$$

The optimum conditions obtained from this equation were initial lactic acid concentration: 21 g/L, pH: 2.0, temperature: 32°C, stirring rate: 120 rpm, amount of Alamine 336 in oleyl alcohol: 41% and V_{org}/V_{aq}: 1/1.

Conclusions

Carboxylic acids are poorly extractable by common organic solvent due to their hydrophilic nature. Therefore, reactive extraction has been considered for their recovery from aqueous solutions. There are reversible complexation reactions between the organic acid and the solvent phase. Because of the two phases in this system, the aqueous and organic, mass transfer is important. Consequently, the reactive extraction system is rather complex. In order to investigate the effects of all parameters on the distribution coefficient of lactic acid, the Linear Box-Wilson experimental design method was used. In this study the distribution coefficient, K_D, increased with increasing stirring rate, extraction time, Alamine concentration and V_{org}/V_{aq} and with decreasing temperature and initial lactic acid concentration. Some parameters, such as initial lactic acid, pH and V_{org}/V_{aq}, affected the reactive extraction of lactic acid much more than the other parameters.

Studies on lactic acid reactive extraction from fermentation broth are currently being carried out.

Acknowledgements

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Nomenclature

C_{Lai}	Initial lactic acid concentration, gL^{-1}
K_D	Lactic acid distribution coefficient, gL^{-1}/ gL^{-1}
N	Stirring rate, rpm
T	Temperature,°C
t	Time, min
V_{aq}	Volume of aqueous phase, cm^3
V_{org}	Volume of organic phase, cm^3
Y_{KD}	Predicted lactic acid distribution coefficient, gL^{-1}/ gL^{-1}

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