n-Butanol as an Extractant for Lactic Acid Recovery

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Abstract—Extraction of lactic acid from aqueous solution using n-butanol as an extractant was studied. Effect of mixing time, pH of the aqueous solution, initial lactic acid concentration, and volume ratio between the organic and the aqueous phase were investigated. Distribution coefficient and degree of lactic acid extraction was found to increase when the pH of aqueous solution was decreased. The pH Effect was substantially pronounced at pH of the aqueous solution less than 1. Initial lactic acid concentration and organic-to-aqueous volume ratio appeared to have positive effect on the distribution coefficient and the degree of extraction. Due to the nature of n-butanol that is partially miscible in water, incorporation of aqueous solution into organic phase was observed in the extraction with large organic-to-aqueous volume ratio.

Keywords—Lactic acid, liquid-liquid extraction, n-Butanol, Solvating extractant.

I. Introduction

LACTIC acid or 2-hydroxypropanoic acid is a carboxylic acid that contains both hydroxyl and carboxyl group in its molecule. The acid is widely used in food, chemical and pharmaceutical industries. It also has been used in production of polylactate, a biodegradable polymeric material. As a result, high purity lactic acid has been constantly in high demand.

Lactic acid can be produced by either chemical synthesis or by fermentation. The latter has proven to be the better alternative as it is more energy efficient and can produce stereospecific acid [1]. Unfortunately, the disadvantage of fermentation is that it can produce rather dilute solution of lactic acid due to inhibitory nature of the acid to the microorganism. In addition, the fermentation broth always contains many impurities including cell biomass, other organic acids, and unconsumed nutrients. Recovery and purification of lactic acid from dilute media requires many steps and unit operations, which consequently contribute to high cost of production.

Reactive extraction has been one of the attractive methods for lactic acid recovery and has been studied by several researchers [2-6]. The method provides high selectivity and enhances the recovery by utilizing a combination of an

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extractant (also known as carrier) and diluents to intensify the separation through simultaneous reaction and extraction [1]. Depending on the extraction mechanism, two categories of the extractants have been studied. The first category is solvating extractants, which extraction mechanism is by competing with water in interaction with the solute of interest and convey it into the organic phase. Examples of solvating extractants include tertiary amine, such as tri-*n*-octylamin (TOA), which form a water-insoluble complex with lactic acid and, therefore, selective extract the acid from the aqueous to the organic phase [7]. Other solvating extractants that have been reportedly used include alkyl phosphate esters, such as tributyl phosphate (TBP) and trioctyl phosphine oxide (TOPO) as well as neutral extractants with oxygen-containing polar groups such as ketones (e.g. methyl isobutyl ketone), alkyl sulfoxides, or esters (e.g., tri-*n*-butyl phosphate and trioctylphosphine oxide).[8].

The second category is the extractants that function as the ion exchangers. Example is quaternary ammonium salts such as the commercial extractant Aliquat 336 or tri-(C_8C_{10}) methylammonium chloride, where the chloride anion is replaced by the anion of the acid during the extraction [9].

This work studied the extraction of lactic acid with n-butanol as a single solvent. The objective is to determine apparent equilibrium constant and to elucidate influence of different variables on extraction of this acid.

II. Materials and Method

A. Chemicals

Lactic acid with concentration of 88 wt% and n-Butanol with 99.9 wt% % purity were purchased from Acros. Sodium hydroxide (NaOH) and hydrochloric acid (HCl) were of reagent grade and were both purchased from Sigma.

B. Preparation of lactic acid aqueous solution

Aqueous lactic acid solution was prepared by dissolving lactic acid solution in deionized water until the desired concentration was achieved. The pH of the solutions was adjusted prior to extraction by addition of concentrated HCl.

C. Procedure

n-Butanol was used as a single solvent for extraction of lactic acid in this study. Every experiment was carried out in 50 ml separatory funnels. The initial pH and lactic acid concentration of the aqueous phase were firstly determined. Equal volumes (10 ml each) of aqueous and organic phase were then mixed and shaken at ambient temperature and

settling for 1 hr for a complete phase separation, although preliminary study had shown that mixing time of 45 minutes was sufficient to reach the equilibrium of the process. After the phase separation, pH and volume of the aqueous phase were measured. Lactic acid content in the aqueous solution was determined by titration with a standard NaOH solution. Acid content in the organic phase was obtained by material balance of the species. For the extraction of lactic acid from fermentation broth, the acid content was determined with Shimadzu GC-14B, equipped with flame ionization detector (FID) using a DB-1HT capillary column, (30 m length, 0.25 mm internal diameter and 0.10 μm film thickness). The injector and detector temperature were set at 300 and 350oC, respectively. The column temperature was increased stepwise from 40oC to 140oC and from 140oC to the final temperature of 220oC. Finally, heating to 340oC at 10.0oC/min and holding for 5.0 min. Helium was used as a carrier gas. All samples were diluted with methanol before the analysis.

III. RESULTS AND DISCUSSION

n-Butanol was used as a solvent for extraction of lactic acid from aqueous solution. Effect of mixing time, pH of the aqueous solution and initial lactic concentration on the extraction efficiency were studied. The efficiency of extraction was represented by two parameters: degree of extraction (%E) and the distribution coefficient (D), where

$$\%E = \frac{V_0 C_0 - V_{eq} C_{eq}}{V_0 C_0} \qquad (1)$$

and

$$D = \frac{\overline{C_{eq}}}{C_{eq}} \qquad (2)$$

V is the volume of aqueous phase, C and $\overline{C}$ is concentration of lactic acid in aqueous and organic phase, respectively. Subscript 0 refers to the initial condition, while eq to the condition at equilibrium.

The first stage of this study is to observe the kinetic of extraction and determine the proper mixing time for this process. As seen in Fig. 1, the distribution coefficient of the acid increases with the mixing time. The equilibrium was reached at about 45 min, and both the distribution coefficient and the extraction efficiency did not further increase when the mixing time was longer than 45 min.

Several studies had demonstrated the significance of acidity or pH of the aqueous solution on the distribution coefficient degree of lactic acid extraction [10-11]. However, the effect of this variable depends on the mechanism of extraction. With amines and other solvating extractant, the extraction of lactic acid decreases upon an increase of the pH of the aqueous phase at fixed concentrations of the extractant and the acid. Therefore, extraction with this group of extractants is normally more efficient at low pH value of the aqueous solution [9]. On
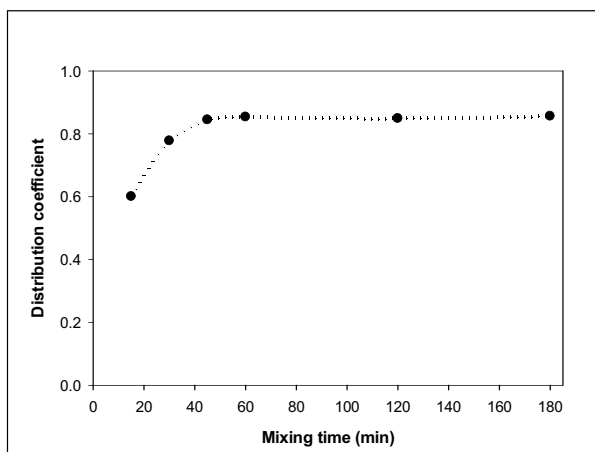

Fig. 1 Effect of mixing time on distribution coefficient.

the contrary, in extraction with anion exchanging extractant like quaternary ammonium salts, the increase in pH of the aqueous phase favors the dissociation of lactic acid, and thus the anionic form is increasingly extracted into the organic phase [8].

Effect of pH of starting aqueous solution on the distribution coefficient of the acid in extraction with n-butanol was elucidated in this study by carrying out the experiments at almost constant lactic acid concentration at 0.17 M. Since n-butanol is of solvating extractant type, the extraction of lactic acid was conducted at low pH ranging from 0.27 to 1.21. Adjustment of the initial pH of the aqueous solution was adjusted to the desired value by addition of concentrated hydrochloric acid. The distribution coefficients are graphically presented as function of the pH in Fig. 2. At the initial pH of the aqueous phase as low as 0.27, distribution coefficient of 13.8 was achieved. As the pH increased, values of the distribution ratio drastically reduced. This phenomenon is commonly observed in the extraction of lactic acid with solvating extractant. Higher distribution coefficient at low pH could be from the availability of unassociated form of lactic acid, which presents largely when the pH of the solution was reduced, and this form is favored in extraction with solvating mechanism as mentioned previously. It should be noted, additionally, that dependence of distribution coefficient on pH is more crucial when the pH of the aqueous solution is lower than 1.

Effect of pH on the degree of extraction was similar to that on the distribution coefficient. At pH of the aqueous solution of 0.27, close to 95% of the acid was extracted into the organic phase. The degree of extraction was reduced to 57.60% and 51.62% when the pH of aqueous solution was increased to 0.96 and 1.21, respectively.

Effect of initial concentration of lactic acid in the aqueous solution on distribution coefficient and degree of lactic acid extraction were investigated in the extraction where the pH was not controlled and in the extraction where the pH was fixed at 2.4. The results are illustrated in Fig. 3 and Table II
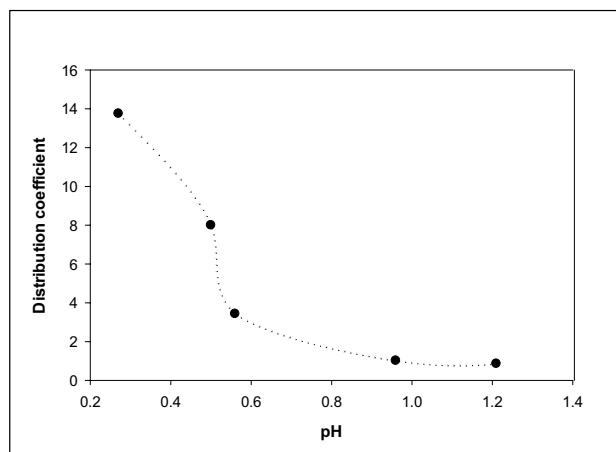
Fig. 2 Effect of initial pH of aqueous phase on distribution coefficient.

Fig. 3 Effect of lactic acid concentration

TABLE I
DEGREE OF EXTRACTION AS A FUNCTION OF PH

pH	Degree of extraction
0.27	94.95
0.50	90.61
0.56	82.77
0.96	57.60
1.21	51.62

TABLE II
DEGREE OF EXTRACTION AS A FUNCTION OF INITIAL LACTIC ACID CONCENTRATION IN AQUEOUS PHASE.

Initial lactic acid concentration in aqueous phase (M)	pH	Equilibrium lactic acid solution in aqueous phase (M)	Degree of extraction
0.10	2.4	0.06	48.64
0.19	2.2	0.10	54.74
0.43	2.1	0.21	59.89
0.65	2.0	0.31	62.15
0.79	1.9	0.36	62.61
1.01	1.8	0.45	64.51
0.10	2.4	0.06	53.52
0.18	2.4	0.09	56.15
0.43	2.4	0.21	57.45
0.62	2.4	0.30	59.85
0.78	2.4	0.38	58.94
0.99	2.4	0.47	61.76

TABLE III
DEGREE OF LACTIC ACID EXTRACTION AS A FUNCTION OF ORGANIC-TO-AQUEOUS VOLUME RATIO

Initial phase volume (ml)		Equilibrium phase volume (ml)		Equilibrium concentration (M)		Degree of extraction
aqueous	butanol	aqueous	butanol	aqueous	butanol	
10	10	9.0	11.0	0.051	0.043	51.01
10	20	6.4	23.1	0.034	0.031	77.13
10	30	4.0	35.6	0.026	0.023	88.92
10	40	1.3	48.5	0.023	0.019	96.97

for the distribution coefficient and the degree of lactic acid extraction, respectively. It can be seen that both parameters increased with increasing initial acid concentration in both systems. However, slightly lower distribution coefficients were obtained in the extraction where the pH was fixed at 2.4 due to the higher pH than the natural value of the same lactic acid concentration. It is expectable that the distribution coefficient at each initial lactic acid concentration should be higher if the pH of aqueous solutions were fixed at the lower values. This result further emphasizes the impact of pH of aqueous solution on extraction of lactic acid with n-butanol that the variable should be kept low in order to maximize the acid recovery.

Effect of the volume ratio between n-butanol and starting aqueous solution on degree of lactic acid extraction was also studied. In every experiment, the volume of aqueous solution was fixed at 10 ml, while volume of n-butanol was changed to achieve organic-to-aqueous volume ratio of 4:1, 3:1, 2:1 and 1:1. Equilibrium volume and concentration of lactic acid inboth phase, as well as the degree of extraction, are given in Table III. Degree of lactic acid extraction was found to increase significantly when the higher volume ratio between n-butanol and starting aqueous solution was used in the process. At the volume ratio of 4:1, nearly 97% of lactic acid was presented in the organic phase after the extraction. The problem arouse in extraction with large volume of organic solvent, especially the one that is partially miscible with water like n-butanol, is the incorporation of the two phases during the process. Due to a larger volume, n-butanol acted as a solvent and part of the aqueous solution was embodied into the
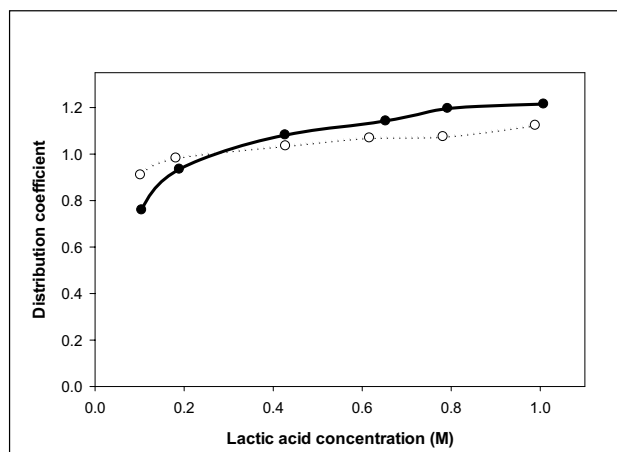
organic phase. The result was the larger volume of the organic and the reduced volume of the aqueous after the system reached equilibrium as seen in Table III. The phenomenon was more pronounced when the organic-aqueous volume ratio was increased.

The incorporation between organic and aqueous phase as observed in this study leads to a suspicion that conveying of lactic acid into the organic phase might be due to two mechanisms. The first one is by a direct solvation between lactic acid and n-butanol, and the second is by partially dissolution of aqueous solution, which contained lactic acid, into the organic phase. Even though both mechanisms led to large degree of extraction, it should be note that incorporation

between the two phases might complicate in steps following the extraction, for example, the stripping of lactic acid from loaded organic phase. Consequently, extraction of lactic acid with n-butanol should be carried out with properly selected organic-to-aqueous volume ratio. For this study, extraction of lactic acid at low pH of the aqueous solution using the equal volume between organic and aqueous phase had given a satisfactory result.

IV. Conclusion

Extraction of lactic acid from aqueous solution using n-butanol was explored. Among the process variables investigated in this study, pH of the aqueous solution appeared to have substantial effect on the distribution coefficient and degree of lactic acid extraction, especially in the pH range less than 1, where the degree of extraction decreased considerably with the increase of pH in that range. Degree of extraction was also enhanced by increasing lactic acid concentration in the aqueous phase and volume ration between the aqueous and the organic. However, since n-butanol is partially miscible in water, proper organic-to-aqueous volume ratio must be used in order to avoid the incorporation between both phases, which might lead to a complexity in steps following the extraction.

Acknowledgment

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