Effect of Chloride Salt on Extraction of Lactic Acid with n-Butanol

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ABSTRACT

Extraction of lactic acid from its aqueous solution using n-butanol containing inorganic salt was studied. Effect of changing process variables (salt type and concentration, initial lactic acid concentration and extraction temperature) on extraction efficiency was investigated. Three chloride salts, i.e. NaCl, $MgCl_2$ and $CaCl_2$ were used. Degree of extraction was represented by value of distribution coefficient of lactic acid in each system. The result was compared with salt-free system of the same extracting conditions. Salting-in and salting-out effects were clearly observed for all the salts within the studied concentration range. When the salt concentration was sufficiently high, the distribution coefficient increased with increasing salt concentration. Among these three salts, NaCl demonstrated the highest degree of lactic acid extraction using n-butanol. The distribution coefficient was found to decrease with increasing temperature in the range of 30-50 °C.

***Keyword**: Lactic acid, Liquid-Liquid extraction, n-Butanol, chloride salt*

1 INTRODUCTION

Lactic acid or 2-hydroxypropanoic acid is an acid that contains both hydroxyl and carboxylic group in its molecule. The acid is used as biologically produced acidulates and preservatives in food industry. It is also widely used as a starting material for chemical synthesis, because of its optical activity and its hydroxyl and carboxyl moieties. In addition, the acid has a potential of becoming a very large volume chemical intermediate, produced from renewable resources for use as a feedstock for biodegradable plastics and other environmental-friendly green compounds. But until now, the extensive use of lactic acid in chemical industry is hampered by the high production costs of optically pure lactic acid [1], which is strictly required in the production of the biodegradable poly (lactic acid) polymers, especially those to be used in biomedical applications and drug delivery [2].

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 [3]. Unfortunately, fermentation comes with several disadvantages. For example, this process can produce rather dilute solution of lactic acid due to inhibitory nature of the acid to the microorganism. Furthermore, the fermentation broth always contains several 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 [4] – [7]. The method provides high selectivity and enhances the recovery by utilizing a combination of an extractant (also known as carrier) and diluents to intensify the separation through simultaneous reaction and extraction [3]. 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 forms 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. Examples are quaternary ammonium salts such as the commercial extractant Aliquat 336 or tri-(C_8C_{10}) methylammonium chloride, where chloride anion is replaced by the anion of the acid during the extraction [9].

Despite the high distribution coefficient obtained from the extraction with specified solvents, some of the extractants are expensive and might inherit some toxicity. As a result, recovery of lactic acid by extraction with more economical and environmental friendly solvents is still needed. Extraction of lactic acid from aqueous solution using n-butanol was explored [10]. It was reported that the process efficiency was significantly dependent on pH of the aqueous solution, 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, therefore, higher in the extraction of more concentrated lactic acid solution. Disadvantage of lactic acid extraction with n-butanol, however, is the fact that this alcohol is partially miscible in water, which, consequently, leads to incomplete solvent recovery after the operation.

This work was aim to investigate extraction of lactic acid from its aqueous solution using n-butanol when different chloride salts were added. Effects of salt type and concentration, initial lactic acid concentration, as well as extraction temperature on distribution coefficient of the acid in these systems were studied. Loss of n-butanol after the extraction was also observed.

2 RESEARCH METHODOLOGY

2.1 Material and Equipments

Lactic acid with concentration of 88 %wt and n-butanol with 99.9% purity were purchased from Acros. Sodium hydroxide (NaOH), sodium chloride (NaCl) and Sulfuric acid (H_2SO_4) were of reagent grade and were both purchased from Sigma. Calcium chloride ($CaCl_2$) and Magnesium chloride hexahydrate ($MgCl_2$. $6H_2O$) were obtain from CARLO ERBA.

2.2 Procedure

Aqueous lactic acid solution was prepared from the commercial lactic acid to the desired concentration. Weighed quantity of chloride salt was added into the 20 ml of lactic acid solution. Equal volume of n-butanol was then mixed with the prepared solution, and the mixture was shaken in a temperature-controlled shaking bath for 3 hr. The two phases were separated after the mixture was left to settle for 1 h. Concentration of lactic acid in both phases were determined by HPLC using Hypersil BDS C_{18}-column 4.0×100 mm, 3-Micro (Agilent). Sulfuric acid solution with concentration of 0.005 M H_2SO_4 and flow rate of 0.7 mL/min was used as a mobile phase. The UV wavelength was set at 210 nm, and the injection volume was 10 μL. All samples were diluted.

3 RESULTS AND DISCUSSION

The concentration of lactic acid used in the present work ranged from 0.1 to 1 M. Chloride salts with quantities between 0.5 to 5 g were added into 20 ml lactic acid solution. Effect of salt concentration, initial lactic acid concentration and temperature were studied. Efficiency of lactic acid extraction in each system was represented by the distribution coefficient (D) and the degree of extraction (%E),

$$D = \frac{C_{org}}{C_{aq}} \tag{1}$$

$$\%E = \frac{V_0 C_0 - V_{eq} C_{aq}}{V_0 C_0} \tag{2}$$

where C_0 is the concentration of lactic acid in the starting solution, C_{org} and C_{aq} are equilibrium concentration of lactic acid in the organic and aqueous phase, respectively. V_0 is the volume of starting solution and V_{eq} is volume of the aqueous phase after extraction. Distribution coefficient is an indicator of degree of extraction, i.e. the higher the distribution coefficient, the more lactic acid is extracted into the organic phase.

3.1 Effect of salt concentration on lactic acid distribution coefficient and degree of extraction

It is known that addition of a salt or a non-volatile solute in a solvent mixture can significantly change tow-phase equilibrium. Specifically, adding salt to an aqueous solution of addition of salt to an aqueous solution of an organic acid can result in either decrease or increase in solubility of the acid in the solution [11]. If the acid solubility is increased upon addition of salt, the effect is called “salting in”. On the other hand, if its solubility is diminished when the salt is added, the effect is called “salting out”. In addition to the behavior of a particular solute in aqueous solution, ability to induce salting in and salting out of a solute in aqueous solution depends on type and concentration of the salts as well as the ions presenting in the solution after ionization of the salts.

Research by Franz Hofmeister in the early 20th century organized various anion and cation by their ability to salting out. The cations are arranged as follows.

$$NH_4^+ \rangle K^+ \rangle Na^+ \rangle Li^+ \rangle Mg^{2+} \rangle Ca^{2+}$$

The arrangement, which is called “Hofmeister series”, indicates that, among the cations shown in the series, NH_4^+ has the highest ability of salting out, and Ca^{2+} has the lowest ability.

Distribution coefficient (D) and degree of lactic acid extraction (%E) with n-butanol containing different chloride salts are shown in Table 1. Extractions without addition of salt is used as controlled experiments.

It should be noted that, in extraction where no salt was added into the system, D and %E increased with increasing initial lactic acid concentration in its aqueous solution. This observation agrees with the result of previous study, where larger distribution coefficient was obtained at higher acid concentration in the starting aqueous solution [10].

It can be seen from Table 1 that, in all the extraction systems, both D and %E were decreased when 0.5 g of the salt was added. This observation signified that lactic acid preferred to be in the aqueous phase rather than the organic phase. In other word, the acid was more soluble in the aqueous phase when 0.5 g of salts was added, which could be considered as “salting-in” effect of the chloride salts in the process.

Table 1 *Distribution coefficient (D) and degree of lactic acid extraction (%E) with n-butanol containing different chloride salt*

gram of salt added	0.1 M Lactic acid					
	NaCl		$MgCl_2$		$CaCl_2$	
	D	%E	D	%E	D	%E
0	0.72	33.34	0.72	33.34	0.72	33.34
0.5	0.52	30.42	0.61	33.32	0.59	32.44
1.0	0.60	33.49	0.60	34.69	0.60	33.41
3.0	0.69	38.45	0.78	41.78	0.57	32.77
5.0	0.76	41.28	0.90	45.53	0.57	32.99
gram of salt added	0.3 M Lactic acid					
	NaCl		$MgCl_2$		$CaCl_2$	
	D	%E	D	%E	D	%E
0	0.72	35.60	0.72	35.60	0.72	35.60
0.5	0.65	34.05	0.67	35.55	0.61	33.45
1.0	0.72	36.14	0.72	37.41	0.63	34.02
3.0	0.85	42.22	0.80	40.87	0.58	33.53
5.0	1.11	49.04	0.92	46.58	0.61	35.79
gram of salt added	0.5 M Lactic acid					
	NaCl		$MgCl_2$		$CaCl_2$	
	D	%E	D	%E	D	%E
0	0.84	37.95	0.84	37.95	0.84	37.95
0.5	0.76	36.42	0.75	35.77	0.68	34.73
1.0	0.76	37.08	0.78	37.50	0.66	34.82
3.0	0.87	43.03	0.84	41.21	0.68	37.39
5.0	1.02	47.13	0.98	46.19	0.71	39.28
gram of salt added	0.7 M Lactic acid					
	NaCl		$MgCl_2$		$CaCl_2$	
	D	%E	D	%E	D	%E
0	1.01	40.26	1.01	40.26	1.01	40.26
0.5	0.68	31.35	0.68	33.41	0.65	30.52
1.0	0.71	33.13	0.74	35.44	0.65	32.03
3.0	0.88	41.27	0.85	40.90	0.63	34.02
5.0	1.06	47.86	1.10	47.40	0.62	34.77
gram of salt added	1.0 M Lactic acid					
	NaCl		$MgCl_2$		$CaCl_2$	
	D	%E	D	%E	D	%E
0	1.14	41.59	1.14	41.59	1.14	41.59
0.5	0.70	31.21	0.73	32.70	0.69	32.27
1.0	0.72	33.70	0.80	37.29	0.69	33.27
3.0	0.91	40.64	0.98	43.89	0.74	35.72
5.0	1.13	46.13	1.12	48.56	0.76	36.38

When quantities of chloride salts were increased from 1 to 5 g, "salting-out" effect was observed in extraction with NaCl and $MgCl_2$, where both D and %E increased with the salt concentration. However, in extraction with addition of $CaCl_2$, these parameters appeared to be quite unvaried with increasing salt concentration.

Salting-in and salting-out effect of each salt are more apparent when D was plotted against the ionic strength of aqueous solution in each system. Ionic strength (I) is a measure of the concentration of ions in the solution and can be calculated from

$$I = \frac{1}{2}\sum_{i=1}^{n} C_i Z_i^2 \qquad (3)$$

where C_i is molar concentration of the i^{th} ion, Z_i is the charge of the ion and n is the number of ions presented in the solution. The plots are shown in Fig. 1, 2, 3, 4 and 5 for the system with initial lactic acid concentration of 0.1, 0.3, 0.5, 0.7 and 1 M.

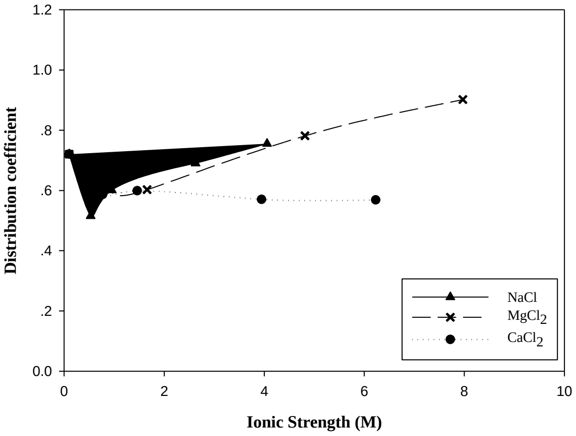

Fig. 1 *Effect of ionic strength on distribution coefficient of lactic acid for extraction with Initial acid concentration 0.1 M*

Result in Table 1 shows that NaCl and $MgCl_2$ pose similar effect on lactic acid extraction using n-butanol, i.e. values of D and %E obtained from the system when equal amount of these salts were added are quite similar. However, the plots in Fig. 1-5 indicate that NaCl might be more powerful to induce salting out of lactic acid since higher D was achieved in system with NaCl than the system with $MgCl_2$ of equal ionic strength. Furthermore, the value of D is in the order of $NaCl>MgCl_2>CaCl_2$, which is the same arrangement of these salts in Hofmeister series as previously shown.

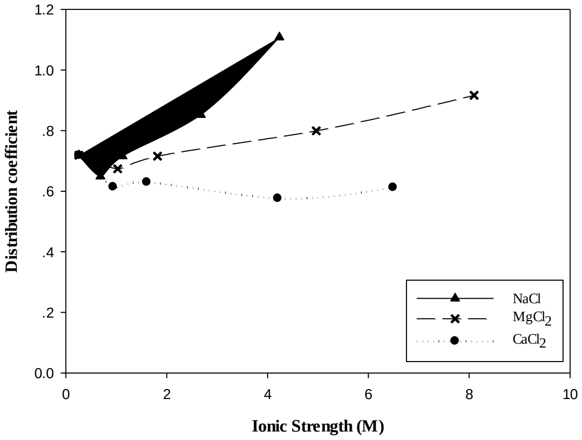

Fig. 2 *Effect of ionic strength on distribution coefficient of lactic acid for extraction with initial acid concentration 0.3 M*

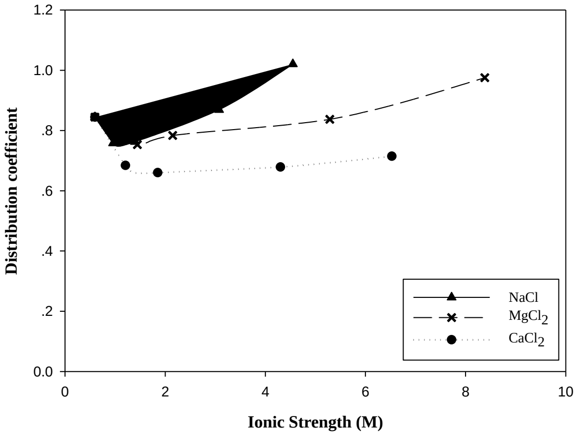

Fig. 3 *Effect of ionic strength on distribution coefficient of lactic acid for extraction with initial acid concentration 0.5 M*

3.2 Effect of temperature on lactic acid distribution coefficient and degree of extraction

Three temperatures (30, 40 and 50˚C) and two chloride salts (NaCl, $MgCl_2$) were selected to study the effect of temperature for the extraction of lactic acid system. The mass of salt in aqueous solution was maintained at the same level (5 g chloride salt in 20 ml of 0.1, 0.5 and 1 M lactic acid).

***Table 2** Distribution coefficient (D) and degree of lactic acid extraction (%E) with n-butanol containing 5 g of chloride salt in different initial lactic concentration.*

Lactic acid	NaCl					
concentration	30˚C		40˚C		50˚C	
[M]	D	%E	D	%E	D	%E
0.1	0.76	41.28	0.52	33.70	0.47	30.98
0.5	1.02	47.13	1.00	45.41	0.99	44.87
1	1.13	46.13	1.12	45.79	1.08	45.05
Lactic acid	$MgCl_2$					
concentration	30˚C		40˚C		50˚C	
[M]	D	%E	D	%E	D	%E
0.1	0.90	45.53	0.64	36.54	0.62	35.59
0.5	0.98	46.19	0.95	45.43	0.92	42.86
1	1.12	48.56	1.03	45.70	1.00	44.84

Distribution coefficients in extraction with NaCl and $MgCl_2$ as function of extraction temperature are shown in Fig. 6 and 7, respectively. In both systems, D was found to be lower when the temperature was increased. Result in Table 2 also illustrates the same effect of extraction temperature on degree of lactic acid extraction. The temperature effect was more pronounced in the system with dilute concentration of lactic acid. The reason for this observation could be the higher solubility of lactic acid in aqueous solution at higher temperature, i.e. lactic acid was more soluble in aqueous solution at higher temperature so it was extracted into the organic phase less than the system with lower temperature.

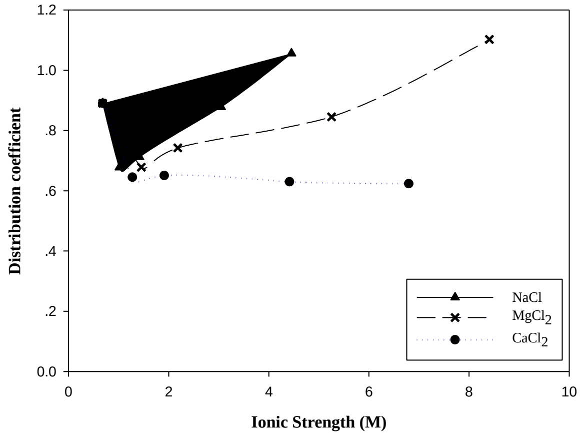

***Fig. 4** Effect of ionic strength on distribution coefficient for extraction with initial acid concentration 0.7 M*

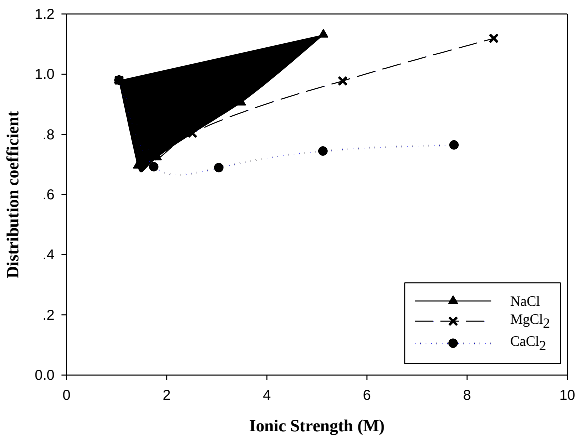

***Fig. 5** Effect of ionic strength on distribution coefficient of lactic acid for extraction with initial acid concentration 1.0 M*

4 CONCLUSION

Extraction of lactic acid using n-butanol with addition of chloride salts was studied. The results show that NaCl was the most powerful in enhancing the extraction of this acid under the experimental conditions used in this study. Ability of the salts in increasing the distribution coefficient and degree of lactic acid extraction is in the order of NaCl $>MgCl_2>CaCl_2$, which is the same arrangement of these salts in Hofmeister series. Effect of temperature on distribution coefficient indicated that, in the temperature range 30-50 ˚C, higher degree of extraction would be achieved if the process were carried out at lower temperature.

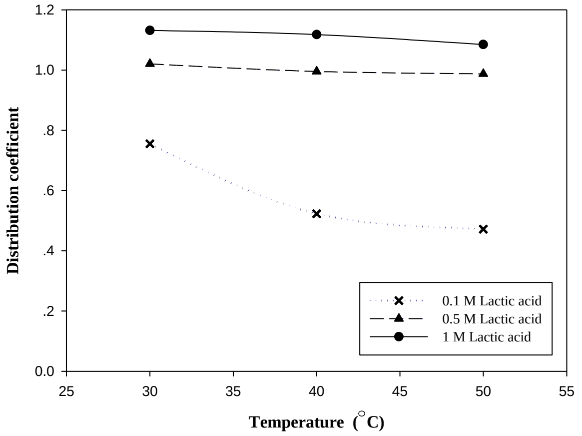

Fig. 6 *Effect of temperature on distribution coefficient of lactic acid for extraction with addition of 5g NaCl*

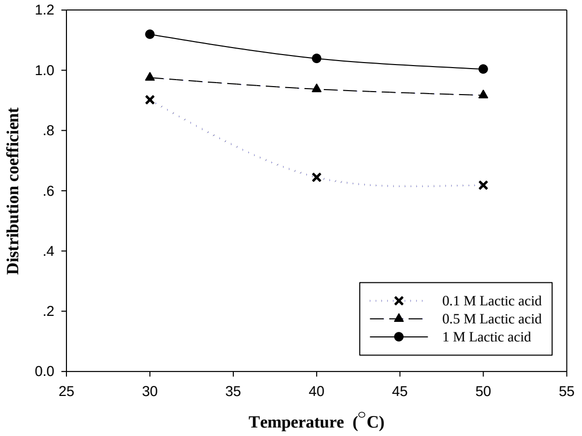

Fig. 7 *Effect of temperature on distribution coefficient of lactic acid for extraction with addition of 5g* $MgCl_2$

5. ACKNOWLEDGEMENTS

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