

Equilibrium Studies on Reactive Extraction of Lactic Acid using Tri-butyl amine in Chloroform

Shalini Basetty⁺ and Basava Rao V. V

University College of Technology (A), Osmania University, Hyderabad-07, India

Abstract. Lactic acid is an important commercial product and separating it out of aqueous solution is a growing requirement in fermentation based industrial waste streams. Separation of Lactic acid extraction from aqueous phase by conventional methods is very much difficult. Reactive extraction is a promising method to achieve high distribution coefficients with good selectivity. In the present work, equilibrium studies in extraction and reactive extraction of lactic acid from aqueous solutions were carried out with tertiary amine i.e., tri-butyl amine, dissolved in chloroform at various concentrations. The extraction efficiency is found to increasing with increase in amine concentration. Parameters such as distribution coefficients, loading ratio, and degree of extraction and equilibrium constants were estimated.

Keywords: Reactive Extraction, Lactic Acid, Tri-butyl Amine, Chloroform, Distribution Coefficient, Selectivity, Extraction Efficiency, Loading Ratio

1. Introduction

Lactic acid, (2-hydroxypropionic acid, $\text{CH}_3\text{CHOHCOOH}$, is a colorless, organic liquid) is the simplest hydroxyl acid and is predominantly produced by fermentation in the industry. It is utilized in many fields especially in food and pharmaceutical industries. Lactic acid can be converted to ethanol, propylene glycol, acrylic polymers and polyesters. Lactic acid undergoes self-esterification resulting in the formation of lactoyl and it is not useful for many industrial purposes. Lactic acid is a raw material for the production of biodegradable polylactic acid. A growing demand for biodegradable polymers in manufacturing new materials of specific uses such as controlled drug delivery draws attention to improved conventional processes for lactic acid production [1].

Fermentation processes for the production of organic acids produce multi component aqueous solutions with production of acid concentrations below 10% w/w. The classical product separation method for lactic acid from fermentation broth is based on the precipitation of calcium lactate with the addition of calcium hydroxide to the aqueous fermentation broth. The solid is filtered off and treated with sulphuric acid leading to the precipitation of calcium sulphate. The lactic acid in the filtrate is then purified using activated carbon, evaporation and crystallization to yield crystals of the lactic acid. These separation and final purification stages account for approximately fifty percent of the production costs. Consequently they are undesirable and also not eco-friendly due to the consumption of lime and sulphuric acid. The production of large quantities of calcium sulphate sludge as a solid waste is another problem. Lactic acid is non-volatile and hence distillation is also not useful. There are many other methods to separate lactic acid from aqueous solutions such as Ion Exchange Chromatography, Adsorption, Capillary Zone Electrophoresis, Electro dialysis and Anion Exchange. All these methods are not economically viable. The literature survey shows that the reactive extraction of lactic acid using TBA, chloroform has not been reported for liquid-liquid reactive extraction.

⁺ Corresponding author. Tel.: + (91-40-27098901; fax: +(91-40-2098472).
E-mail address: (profbasavarao_1964@yahoo.com).

Among these methods, reactive extraction has been proposed to be a promising method with its high distribution coefficient, simplicity, low energy demand, and ineffectuality to thermal stability of the products. Reactive extraction is a solvent or liquid-liquid extraction system with a chemical reaction that occurs between the extracted solute and the extractant present in the organic phase. The process is named as complex extraction as well as dissociation extraction by some researchers [2].

2. Theory

2.1 Reactive Extraction

Reactive extraction strongly depends on various parameters such as the distribution coefficient, degree of extraction, loading ratio, complexation equilibrium constant, types of complexes (1:1, 2:1, etc.), rate constant of lactic acid-extractant reaction, properties of the solvent (extractant and diluents). The extraction of lactic acids is categorized into three groups:

- acid extraction by solvation with carbon-bonded oxygen-bearing extractants
- acid extraction by solvation with phosphorus-bonded oxygen-bearing extractants and
- acid extraction by proton transfer or by ion pair formation, the extractant being high-molecular weight aliphatic amines

The most suitable extractants are the phosphorous-based oxygen extractants and amine based extractants. Aliphatic amines are effective and relatively inexpensive extractants that have been used successfully to extract lactic acid [3]. In general, there is primary, secondary, tertiary and quaternary amine in amine class. Primary amines are too soluble in water to be used with aqueous solution. Quaternary amines such as Aliquat 336 and secondary amines such as Adogen 283 are more toxic to microorganisms than tertiary amines. Tertiary amine extractants are effective, with KD strongly dependent upon the nature of the diluents used and the concentration of amine in that diluent. Tertiary amines are found to be effective in extracting lactic acid and alcohols are among the best diluents, with the additional advantage that a lactic acid ester can be produced after the extraction process is completed. Tertiary amines with C7 to C10/12 alkyl groups (TAA) have been proposed as suitable extractants for lactic acid [4].

The number in the tertiary amine increases the extractability increases this is due to the fact that basicity and polarity of amine increases with chain length. The amine extractants are dissolved in a diluent that dilutes the extractants to desired composition and controls the viscosity and density of solvent phase. It has been found that, in extraction of acid by amine, the type of diluent and the composition of solvent diluent mixture affect the equilibrium. Polar diluents have been shown to be more effective diluents than non polar ones due to high partitioning coefficients [5]. Polar and proton diluents such as alcohols have been shown to be most suitable for amines because they give highest distribution coefficients resulting from formation of solvents through specific hydrogen bonding between the proton of diluent and acid amine complex. It has been found that diluents especially those with functional group can significantly affect the extraction behavior of amines. The stoichiometry of solute-amine complex and the loading of amines as well as the third phase formation are affected by diluent [6]. Third phase formation is not desired in extraction processes. The effect of diluents can be understood in terms of its ability to solvate to organic phase species, therefore it is necessary to distinguish general solvation from electrostatic, dispersion or other forces and specific solvation due to hydrogen bonding. The structure of the acid amine complex in the diluents was determined by Wennersten [7]. He proposed that the first acid interacts with the amine directly to form an ion pair and the [OH] of carboxyl of second acid forms a hydrogen bond with the conjugate [CO] of the carboxylate of the first acid to form a complex. The diluted extractant gives much higher KD values than the pure extractant [8].

2.1. Extraction Equilibrium

In reactive extraction, the solute reacts with the amine in the organic phase, and the resulting acid-amine complexes are supposed to be stabilized due to the hydrogen bonding with the diluent. Because of its hydrophobic nature, the complex formation enhances the extraction of solute from aqueous to organic phase. The extraction of lactic acid with amine can be described by the set of reactions involving the formation of complexes with n acid molecules and one amine molecule

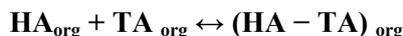
- The ionization of carboxylic acid in the aqueous solution.



- The partition of undissociated acid between the two phases.



- The complex formation between carboxylic acid and tertiary amine in the organic phase during reactive extraction



Where HA represents the undissociated carboxylic acid, and TA denotes the tertiary amine. According to the ammonium salt is formed by the tertiary amine and undissociated carboxylic acid in the organic phase.

The extraction process is analyzed by means of the degree of extraction and distribution coefficient. The distribution coefficient, K_D , is calculated using Eq. 1.

$$K_d = \frac{C_{\text{org}}^*}{C_{\text{aqu}}} \quad (1)$$

Where, C_{org}^* is the total concentration of carboxylic acid in organic phase and is the C_{aqu} total acid concentration (dissociated and un-dissociated) in aqueous phase at equilibrium.

The degree of extraction is defined as the ratio of acid concentration in the extracted phase to the initial acid concentration in aqueous solution by assuming no change in volume at equilibrium as given by Equation 2.

$$E = \frac{K_d}{(1+K_d)} * 100 \quad (2)$$

The extraction equilibrium constant K_{En} and the number of molecules of extractant are computed by applying law of mass action that is the ratio between concentrations of reactant molecules and the concentration of product species, according to the general equation of interaction between the extractant and the extracted species is given by Equation 3

$$K_{\text{En}} = \frac{[\text{HA-TA}]_{\text{org}}}{[\text{TA}]_{\text{org}} * [\text{HA}]_{\text{n.org}}} \quad (3)$$

K_{En} is expected to be depending on the properties of the acid and the solvation efficiency of diluent used.

The extent to which the organic phase (extractant and diluents) may be loaded with acid is expressed by the loading ratio, Z (ratio of total acid concentration in the organic phase to the total extractant concentration) as given by Equation 4.

$$Z = \frac{[\text{HA}]_{\text{org}}}{[\text{TA}]_{\text{org}}} \quad (4)$$

The value of Z depends on the extractability of the acid (strength of the acid base interaction) and its aqueous concentration. The stoichiometry of the overall extraction equilibrium depends on the loading ratio in organic phase (Z). If the organic phase is not highly concentrated by acid, i.e., at very low loading ratios ($Z < 0.5$), 1:1 complex of acid and extractant is formed. A plot of $Z/(1-Z)$ versus $[\text{HA}]$ yields a straight line passing through origin with a slope of complexation constant (K_{E1}) as given by Eq. 5, for higher loading ratios at least ($Z > 0.5$) 2:1 complex of acid and extractants is formed and plot between $Z/(2-Z)$ versus $[\text{HA}]^2$ yields a straight line passing through origin with a slope K_{E2} .

3. Experimental

3.1. Materials

All the chemicals lactic acid (88% pure), tri-butyl amine (99% pure), chloroform (extra pure) and sodium hydroxide of reagent grade are used supplied by M/S. s d fine- chem. limited (SDFCL). All solutions of lactic acid were prepared by dissolving lactic acid of analytical purity in distilled water. The organic solutions are prepared by dissolving TBA in chloroform. The volumetric titrations are carried out using NaOH 0.5N and phenolphthalein is used as an indicator.

3.2. Procedure

Lactic acid is dissolved in distilled water to prepare the aqueous solutions with initial concentration of acid in the range of 0.10 to 0.43M. The organic solutions are prepared by dissolving TBA in chloroform as (20%, 40%, 60%, and 80%) solution in chloroform. Equal volumes of the aqueous and organic solution (50 ml of each phase) are contacted in temperature controlled shaker batch for 60-70 minutes at 25^oC (RIVOTEK). After attaining equilibrium, both the phases are separated in 125 ml separating funnel. After separation, the aqueous phase is analyzed to determine the concentration of acid by titration using fresh 0.5N NaOH solution and phenolphthalein as an indicator. The acid concentration in the organic phase is calculated by mass balance. For selected data points reproducibility is checked and found that the experimental data are reproducible within $\pm 5\%$ of accuracy.

4. Results and Discussion

The chemical equilibrium isotherms, for (20%, 40%, 60%, and 80%) tri-butyl amine in chloroform, for the distribution of lactic acid between water and organic phase (in 1:1 volume ratio) within the range of 0.09M to 0.43M initial lactic acid concentrations were determined at 30^oC and are shown in Figure 1. It can be inferred from figure 1 that the distribution of lactic acid increased with the increase of concentration of tri-n-butylamine in chloroform.

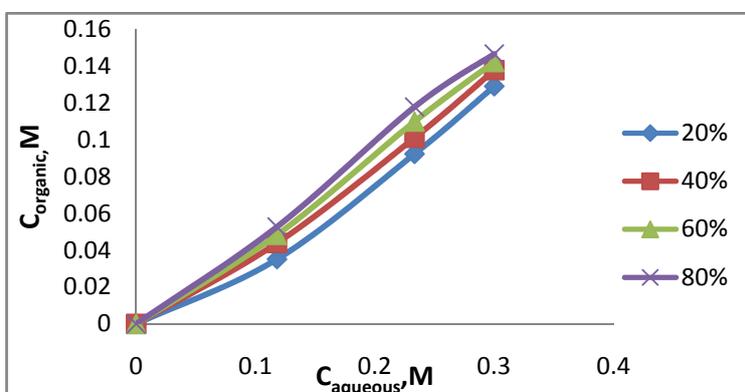


Fig. 1: Equilibrium isotherm for reactive extraction of lactic acid with % soln of tributylamine in chloroform soln

4.1. Distribution Coefficient, K_d

The effect of tri-butyl amine in chloroform on the extraction is evident. The amount of acid extracted from aqueous solutions at any initial acid concentration increased with increasing amine concentration. The values of distribution coefficient, K_d , is given in Fig.2

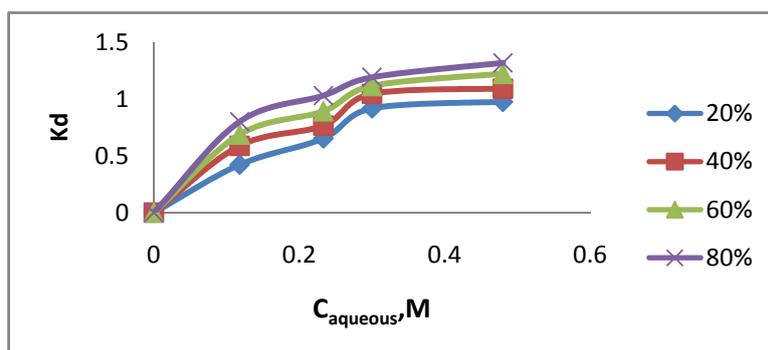


Fig. 2: Distribution Coefficient for reactive extraction of lactic acid with % soln of tri-butyl amine in chloroform

4.2. Loading and Equilibrium Complexation Constants, K_{E1} and K_{E2}

The stoichiometry of the overall extraction reaction depends on the loading ratio in the organic phase, z . The equilibrium concentration of lactic acid in aqueous phase for different concentrations of tri-butylamine in chloroform was plotted against loading of amine, z , it is observed that the loading ratio decreased with increase in concentrations of tri-butyl amine. This happens only when complexes involving more acid molecules are formed at lower concentration of tri-butylamine. Since there is decrease in loading with

increasing tri-butylamine concentration, it is clear that complexes involving only one amine are formed. The 1:1 complex is formed if the organic phase is not highly loaded with acid, i.e., at low acid concentrations.

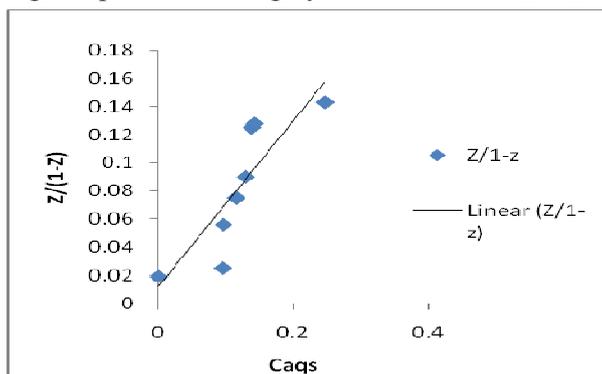


Fig. 3: Plot $Z/(1-Z)$ vs $Caqs$ for estimation of (1:1) lactic acid amine equilibrium complexation constant

The 2:1 complex is formed if the organic phase is highly loaded, i.e., at low TBA concentrations and high acid concentrations, so to confirm the formation of 2:1 complex, the values of $z/2-z$ were plotted against $CAaq^2$ for tri-butylamine in Figure 4, giving a straight line with a slope of Hence it is concluded that lactic acid forms a 2:1 complex with TBA for high concentrations while being extracted from aqueous solutions with a Complexation constant, K_{E2} . The same type of complexes have also been observed by earlier workers [4].

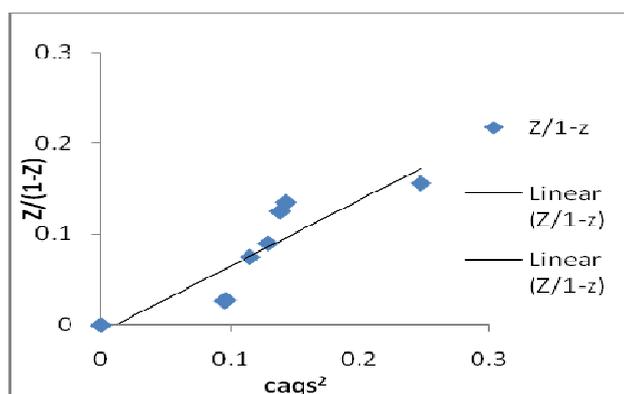


Fig. 4: Plot $Z/(1-Z)$ vs $Caqs^2$ for (2:1) equilibrium complexation const of acid amine

5. Conclusions

The extraction of lactic acid from aqueous solutions by TBA dissolved in chloroform was studied. Physical and chemical equilibrium for lactic acid extraction by TBA in chloroform as a diluent was determined. The extent to which the organic phase (amine + diluent) may be loaded with lactic acid is expressed as a loading ratio. Calculations based on the stoichiometry of the reactive extraction and the equilibrium involved indicated that more lactic acid is transferred to the organic phase than would be expected from a 1:1 stoichiometry of the reaction. The extraction equilibrium was interpreted as a result of consecutive formation of two acid- amine species with stoichiometry of 1:1 and 2:1. Equilibrium complexation constants for (1:1) and (2:1) were estimated.

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7. References

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