Recovery of Propionic Acid using Reactive Extraction

Sushil Kumar[a1], B.V. Babu[a]* and K.L. Wasewar[b]

[a]Birla Institute of Technology and Science (BITS) Pilani- 333 031, India.
[1]Lecturer, Chemical Engineering Group, Email: skumar@bits-pilani.ac.in,
**Assistant Dean, Engineering Service Division and Head, Chemical Engineering Group.*
Email: bvbabu@bits-pilani.ac.in
[b]Assistant Professor, Chemical Engineering Department, Indian Institute of Technology (IIT), Roorkee – 247667 INDIA. Email: k_wasewar@rediffmail.com

ABSTRACT

Propionic acid is a carboxylic acid produced by fermentation and widely used in chemical, pharmaceutical and food industries. It is used primarily for animal feed preservation, including hay, silage, and grains, and in human foods (mainly in baked goods and cheeses). The growing demand of this acid draws attention towards a more economical energy efficient technology. The conventional methods for the recovery of propionic acid from fermentation broth are expensive and unfriendly to the environment. Reactive extraction with specified extractant giving a higher distribution coefficient has been emerged as a promising technique for the recovery of acids. For the design of extraction process, equilibrium data of extractant is required to select a proper extractant for reactive extraction. In the present work equilibrium study for the reactive extraction of propionic acid is carried out. Various diluents and extractants are used for equilibrium studies and data are presented in terms of distribution coefficient and equilibrium complexation constant. On the basis of higher distribution coefficient and equilibrium complexation constant, the best combination of diluent extractant is suggested. In physical equilibria, distribution coefficient (K_D = 2.14) with 1-octanol is maximum at concentration of 5% (v/v). Distribution coefficient(K_D = 2.3) is enhanced with Aliquat 336 (10%) in 1-octanol for the reactive extraction of propionic acid. Presented data can be used for the design of reactive extraction process for the recovery of propionic acid.

INTRODUCTION

Over the last 3 decades, there has been a resurgence of interest in large-scale production of fermentation chemicals due to the sharp increase in petroleum cost. So the potential role of a new energy efficient fermentation technology is receiving growing attention. The current economic impact of fermentation chemicals, however, is still limited, in large part because of difficulties of product recovery. Thus, for fermentation products to penetrate the organic chemicals industry, substantial improvements in the existing recovery technology are needed.

Organic acids are widely used in the food, pharmaceutical and chemical industries. 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. Propionic acid is used in the manufacture of herbicides, chemical intermediates, artificial fruit flavors, pharmaceuticals, cellulose acetate propionate, and preservatives for food, animal feed, and grain [1]. Commercial production of propionic acid is chiefly carried out by chemical synthesis from petroleum feedstocks [1], but fermentation is an attractive alternative to produce this acid from renewable resources. Several carbon sources have been used for this fermentation such as glucose [2], xylose [3], maltose [4], sucrose [5] and whey lac-tose [6]. The conventional method for the recovery of propionic acid from fermentation broth is the calcium hydroxide precipitation method. This method of recovery is expensive and unfriendly to the environment as it consumes lime and sulphuric acid and also produces a large quantity of calcium sulphate sludge as solid waste. Thus there is a need to look at other methods of producing propionic acid.

Reactive extraction with specified extractant giving a higher distribution coefficient has been proposed as a promising technique for the recovery of carboxylic and hydroxycarboxylic acids. This method is advantageous for alcohol and organic fermentations [7]. Some of the advantages include increased reactor productivity, ease in reactor pH control without requiring base addition, and use of a high-concentration substrate as the process feed to reduce process wastes and production costs. This method may also allow the process to produce and recover the fermentation product in one continuous step and reduce the down stream processing load and the recovery costs.

Long-chain, aliphatic amines are effective extractants for separation of carboxylic acids from dilute aqueous solution [8]. Generally, the amine extractants are dissolved in a diluent, an organic solvent that dilutes the extractant. It controls the viscosity and density of the solvent phase. In order to improve the amine's solvation power, diluents such as oleyl alcohol, chloroform, methyl isobutyl ketone and 1-octanol have been used. 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 [9]. In the present study, various pure diluents are used for extraction of propionic acid from aqueous solution. On the basis of distribution coefficients, reactive extraction is also carried out with amine extractant for the recovery of propionic acid.

EXPERIMENTAL

To carry out the equilibrium experiments, experimental set-up consists of temperature controlled shaker bath, conical flasks, separating funnels and burette for titration.

Materials

In the experiments, Aliqaut 336 (Merck Co.) and propionic acid (BDH Co.) were used. Various solvents, 1-octanol (Sd Fine Chemicals Co.), MIBK (Sd Fine Chemicals Co), heptane (SpectroChem Co.), xylene (Sd Fine Chemicals Co) and benzene (SpectroChem Co.) were also used.

Reactive Extraction

Aqueous propionic acid solution of the required concentration was prepared by diluting the propionic acid (99%v/v) with distilled water. The Aqueous acid solutions were prepared in the range of 1% to 10% v/v. Amine organic solutions (extractants) were prepared by diluting 10% Aliquat 336 (quaternary alkylammonium salt) with 1-octanol. Experiments were carried out in 150 ml shake flasks with a working volume of 50 ml in the temperature controlled reciprocal shaker bath with capacity of 12 flasks. Equal volumes (25 ml) of the aqueous phase and the organic phase in 150 ml. of flasks were shaken for 12 hrs. at room temperature.

Our preliminary studies had shown that 12 hrs. of mixing time is sufficient to reach equilibrium. The initial pH of the propionic acid solution was taken as such by initial concentration of solutions. After attaining equilibrium, the phases were brought into contact for separation.

Analytical Method

After settling, the phases were separated and the volume of each phase was determined. The propionic acid concentration in equilibrium aqueous phases was determined by potentiometric titration using 0.05N NaOH solution. The acid concentration in the organic phase was obtained by the mass balance. The extraction ability was represented by the distribution coefficient. The calculated distribution coefficient, K_D, is calculated with following relation as given by Eq. 1.

$$K_D = \frac{C_{org}}{C_{aq}} \qquad (1)$$

Where, C_{org} is the concentration of propionic acid in organic phase and C_{aq} is the concentration of propionic acid in aqeuous phase after reaching equilibrium.

RESULTS AND DISCUSSION

Experiments were carried out to describe the physical and chemical equilibria for propionic acid using pure diluents and Aliquat 336, a quaternary amine in 1-octanol.

Physical Equilibria

The physical equilibrium was studied for propionic acid using various solvents. 1-octanol, heptane, MIBK, xylene and benzene were used to find the distribution coefficient of propionic acid. Experiments were carried to know the effect of initial acid concentration on distribution coefficient for a particular solvent. The results are shown in Fig. 1 and 2.

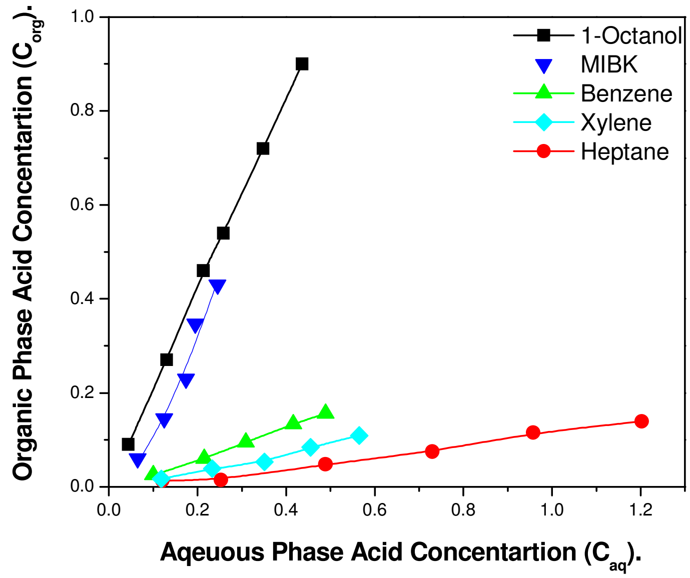

Fig. No. 1: Physical Equilibria for the Extraction of Propionic Acid with Pure Diluents

The equilibrium curves with 1-octanol and MIBK are much stripper from Fig. 1. So 1-octanol and MIBK solvents show better recovery of propionic acid in organic phase than benzene, xylene and heptane. Salvation strength is less for aromatic and hydrocarbon solvents. The values of equilibrium distribution coefficients using various solvents are summarized in Fig. 2. Conventional solvents such as 1-octanol, heptane, MIBK, xylene and benzene and aliphatic hydrocarbons are not efficient when applied to dilute, carboxylic acid solutions because of the low aqueous activity of carboxylic acids resulting in low distribution coefficients.

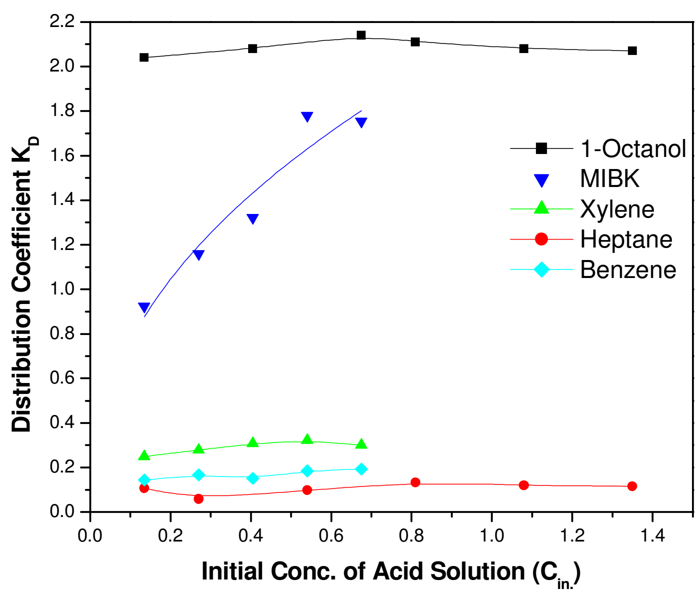

Fig. No. 2: Distribution Coefficient for Propionic acid with Initial Concentration of Acid using Diluents

The strength of solvation of the complex by the diluent decreases in the following order [10]: alcohol > nitrobenzene > proton-donating halogenated hydrocarbon (e.g. methylene chloride, chloroform, 1,2-dichloroethane) > ketone > halogenated aromatic > benzene > alkyl aromatic > aliphatic hydrocarbon. Our experimental studies show that there is maximum distribution coefficient (K_D = 2.14) of propionic acid with 1-octanol at concentration of 5% (v/v), as shown in Fig 2. At higher initial propionic acid concentration, the amount of solvent may be the limiting factor for the strength of solvation of the complex.

Chemical Equilibria

Long-chain, aliphatic amines are effective extractants for separation of carboxylic acids from dilute aqueous solution. In our experimental studies Aliquat 336, a quaternary amine is dissolved in a diluent, 1-octanol that dilutes the extractant. It controls the viscosity and density of the solvent phase. Chemical equilibria results for extraction of propionic acid are shown in Fig. 3.

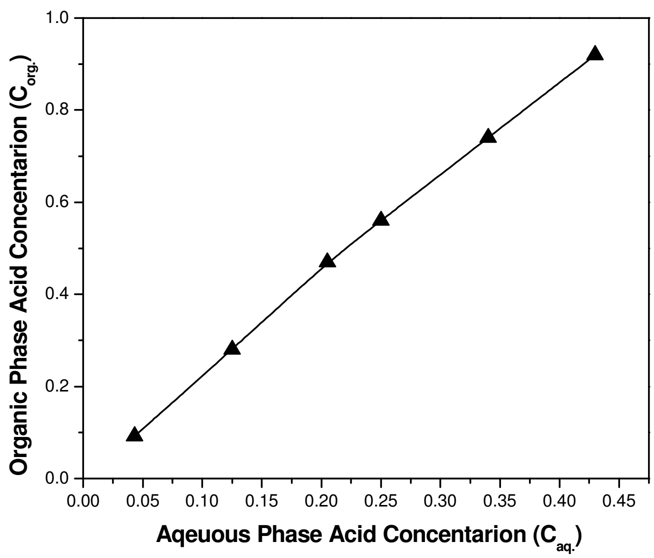

Fig. No. 3: Chemical Equilibria for the Extraction of Propionic Acid with Aliquat 336 (10%) in 1-Octanol.

In the propionic acid extraction with Aliquat 336, the variation of K_D with initial lactic acid concentration is given in Figure 4. With 10% Aliquat 336 in 1-octanol and unit V_{org} to V_{aq} ratio, K_D decreased from 2.3 to 2.14 upon increasing initial lactic acid concentration from 0.675 to 1.35gmol/L. At higher initial lactic acid concentrations, the amount of Aliquat 336 may be the limiting factor for the amine:acid reaction.

The differences among distribution coefficient and equilibrium values for the same acid in different diluents indicate that solvation of the complex by the diluent is a critical factor in the extraction of acid. The interactions between the complex and solvent can, somewhat arbitrarily, be divided into “general solvation” and “specific interaction” of the diluent with the complex. The polar diluents may be more effective with amine extractants. In Fig. 4, comparison of distribution coefficient (K_D) with or with out amine extractant (Aliquat 336) in 1-octanol is carried out. As can be seen that recovery of propionic acid from aqueous solution may be enhanced with quaternary amine (Aliquat 336) in 1-octanol.

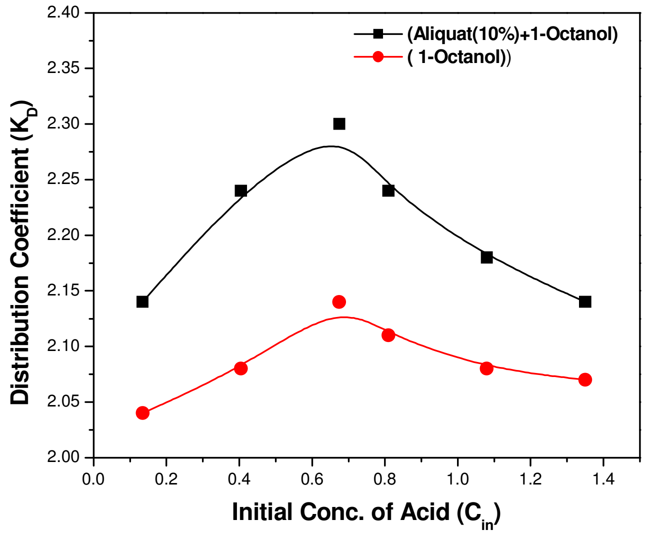

Fig. No.: 4 Distribution Coefficient for Propionic acid with Initial Concentration of Acid using Aliquat 336 (10%) in 1-Octanol.

Our experimental study shows that propionic acid is recovered from aqueous solution to organic solvent. Solvent can be regenerated to give pure acid. So an extractive separation and recovery process normally involves two steps: extraction and solvent regeneration. Extractant can be easily regenerated by stripping with a small volume of alkaline solution. There are various methods for back extraction such as temperature swing, diluent swing, and gas anti-solvent methods using NaOH, HCl, ammonia and trimethyl amine. Wasewar et al. (2004) have given the exhaustive discussion on these processes for the back extraction of carboxylic acids [11].

CONCLUSIONS

Conventional solvents such as 1-octanol, heptane, MIBK, xylene and benzene are not efficient when applied to dilute, propionic acid solutions because of the low aqueous activity of carboxylic acids resulting in low distribution coefficients. Physical and chemical equilibria for propionic acid extraction by Aliquat 336 dissolved in 1-decanol have been determined. It has been found that the combination of Aliquat 336 and solvent gave a higher distribution coefficient as compared to pure solvent. The polar diluents may be more effective with amine extractants. Distribution coefficient for extraction of propionic acid using Aliquat in 1-decanol was higher than pure solvents.

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