Intensification of Propionic Acid Separation from Aqueous Solution using Reactive Extraction with Tri-n-butyl Phosphate (TBP) Dissolved in n-Decane and 1-Decanol

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Abstract

Over the last three 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. Propionic acid is widely used in the food, pharmaceutical and chemical industries. Fermentation technology for the production of this acid in particular has been known for more than a century. The importance to recover propionic acid effectively from fermentation broth and aqueous waste effluents has got more attention recently. Generally, the aqueous solutions, such as fermentation broth or wastewater stream has very low concentration of propionic acid (less than 10% (w/w). Also, these aqueous solutions have various impurities. Many separation processes in chemical industries have been employed to recover the organic acids from aqueous solutions. 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. Among the all alternate, reactive extraction is found to be more efficient separation process, because of its high selectivity for desired compounds and low waste production. So, Separation of propionic acid from aqueous solutions (fermentation broth or wastewater stream) can be intensified through reactive extraction using phosphorus bonded oxygen bearing extractant (TBP) with diluents. The reactive extraction of propionic acid by tri-n-butylphospahte (TBP) in inert diluent (n-decane) and a modifier (1-decanol) is studied. The equilibrium experiments are carried out to investigate the effects of modifier composition (1-decanol), extractant (TBP) concentration, and initial acid concentration on extraction efficiency. The extraction efficiency is defined by distribution coefficient and degree of extraction. The extraction efficiency is found to be increased with increasing modifier composition and TBP composition, and decreased with increasing initial acid concentration. Mathematical modeling using mass action law approach is used to determine the number of extractant

(TBP) molecules (n) involved in the acid:TBP complex formation. The extraction equilibrium constants (K_E) is also estimated using same modeling approach.

Keywords: Intensification, Reactive Extraction, Diluent, Modifier, Extraction Efficiency.

Introduction

The importance to recover propionic acid effectively from fermentation broths and aqueous effluents has got more and more attention from the research point of view. Propionic acid has a large use in the chemical, pharmaceutical and food industries as food preservative, herbicides, polymers, etc. Generally, the aqueous solutions, such as fermentation broth or wastewater stream has very low concentration of propionic acid (less than 10% (w/w). Also, these aqueous solutions have various impurities. So there is a need of finding out an economic separation method which can compete with the synthetic process [1].

Many separation processes in chemical industries have been employed to recover the organic acids from aqueous solutions [2]. But, reactive extraction is found to be more efficient process, because of its high selectivity for desired compounds [3-4]. In this regard, the organophosphorous compounds and long-chain aliphatic amines act as better extractants to separate out carboxylic acids from dilute aqueous solutions. A phosphoryl group and a strong Lewis basicity make these compounds a better extractant. Again, they co-extract small amounts of water, and show low solubility in water [5].

These phosphorous based, oxygen bonded extractants are dissolved in a diluent to attain appropriate physical properties for extraction. Polar diluents are found suitable than non-polar diluents [10].

Literature cited out the extraction equilibrium study of various organic acids (propionic, nicotinic, formic, acetic, etc.) with different extractants (tri-n-butyl phosphate, tri-*n*-octyl phosphine oxide, etc.) dissolved in various diluents [6-7]. The studies are aimed to investigate the initial acid concentration, extractant type, the extractant composition, and effect of different diluents on equilibrium parameters such as distribution coefficients, degree of extraction and equilibrium complexation constants [3, 7, 10].

The effect of a modifier (1-decanol), an active reagent for the extraction of tartaric and lactic acids by tri-*n*-octylamine (TOA) dissolved in 1-decanol and *n*-dodecane has been studied [8-9].

To intensify the reactive extraction process, it is very important to understand the influence of different physical and operating parameters. To do that, a study has been carried out to analyze the effect of most crucial parameters such as concentration of inactive and active (modifier) diluents, initial acid concentration and extractant concentration on the separation of propionic acid. Also, equilibrium extraction constant (K_E) and the number of extractant molecules per acid molecule (n) have been calculated by graphical method to have a better understanding of the process.

Materials and method

The organic phase was prepared by taking Tri-*n*-butyl phosphate (TBP) as the extractant dissolved in n-decane (an inert diluent) and 1-decanol (an active diluents and modifier), to recover propionic acid from aqueous solution. TBP was supplied by Spectrochem. Pvt. Ltd., India having molar mass of 266.32 g mol^{-1} and density of 0.975 g mL^{-1}. *n*-Decane and 1-decanol were supplied by Sd. Fine Chem. Ltd., India. Propionic acid, a colorless liquid with a pungent odor was delivered by Sigma-Aldrich Co., USA. The aqueous solution of propionic acid was prepared using de-ionized water. Sodium hydroxide (NaOH) of 0.015N, used for titration, was supplied by Merck Pvt. Ltd., Germany. For the standardization of the NaOH solution, oxalic acid was obtained from Sd. Fine Chem. Ltd., India. Phenolphthalein solution (pH range 8.2 to 10.0) used as an indicator for titration was obtained from Ranbaxy, India. All chemicals were used without any pretreatment and of analytical reagents grade with more than 98% of purity.

The extraction equilibrium experiments were carried out at constant temperature (298 K) with equal volumes (16 m*L* of each phase) of the aqueous and organic solutions shaken at 100 rpm for 8 hours in conical flasks of 100 m*L* on a temperature controlled reciprocal shaking machine (HS 250 basic REMI labs). Our preliminary studies had shown that 8 h of mixing time is sufficient to reach equilibrium. After attaining equilibrium, the phases were brought into contact with each other for separation. The effect of extractant (TBP) composition (0.913-2.923 mol L^{-1}) in the organic phase was studied for different aqueous phase acid concentrations (0.337-1.35 mol L^{-1}). The initial and equilibrium pH values of aqueous solutions were measured using a digital pH-meter of ArmField Instruments (PCT 40, Basic Process Module) which were varied in the range of 2.45 to 2.92 and 2.74 to 3.42 respectively.

The equilibrium acid concentration in the aqueous phase was determined by potentiometric titration and that in the organic phase was calculated by mass balance. The reproducibility was checked by carrying out the experiments twice in some selected cases with an accuracy of ±5%.

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

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

where, C_{org} is total (analytical) concentration of propionic acid in all its forms (by partition, dimmers, and as complexes) in organic phase and C_{aq} is total (analytical) concentration of all its existing forms (dissociated and undissociated) 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 and is given by Eq. 2.

$$E = \frac{K_D}{1 + K_D} \times 100 \qquad (2)$$

Results and discussions

The chemical stability of organophosphorous compounds makes them an efficient extractant with excellent separation efficiency. TBP, an organophosphorous compound, contains a phosphoryl group (>P=O) which serves as a stronger Lewis base for its high polarity, which leads to a high degree of extraction. TBP is selected because of its low water co-extraction (4.67% by weight at 20^0C) and very low solubility in the aqueous phase (0.04% by weight at 20^0C). Due to the presence of both electron donor and electron acceptor groups in >P(O)OH grouping, it undergoes specific interactions like self-association and molecular complex formation with diluents or other solutes.

From the Figure 1, the degree of extraction increases with an increase of 1-decanol concentration for 0.913 mol L^{-1} of TBP (25%). The increased 1-decanol concentration enhances the solubility of propionic acid in the organic phase.

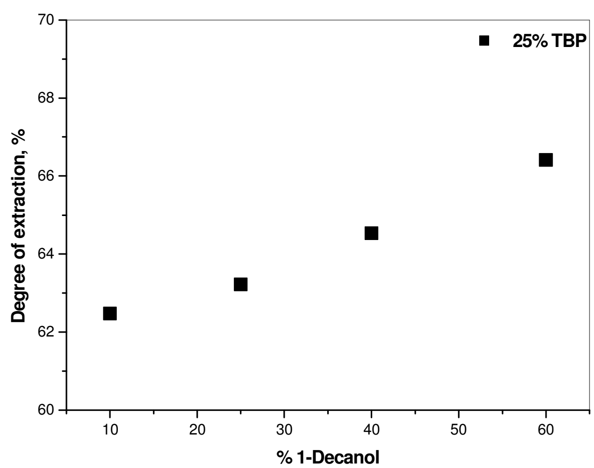

Figure 1: Effect of modifier (1-decanol) on degree of extraction with 0.913 mol L^{-1} TBP and 0.405 mol L^{-1} initial propionic acid concentration

In the figure 2, the equilibrium isotherms have been shown for five different acid concentration by considering four different TBP concentrations with *n*-decane and 1-decanol (1:1 vol %). From the figure it is obvious that high TBP concentration favors extraction of acid in the organic phase. At low acid concentration, there is a linear relationship between acid concentrations in the two phases validating Henry's law.

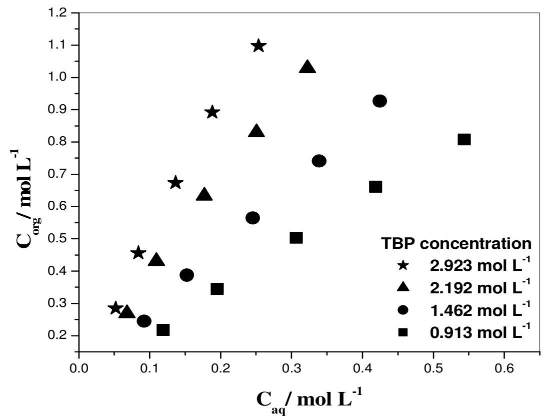

Figure 2: Equilibrium isotherms of propionic acid for different TBP concentration dissolved in n-decane/1-decanol (1:1 vol %)

Figure 3 visualizes the effect of initial acid concentration on the degree of extraction (%) and distribution coefficient. Distribution coefficients significantly decrease as the concentration of propionic acid is increased from 0.337 to 1.35 mol L^{-1}.

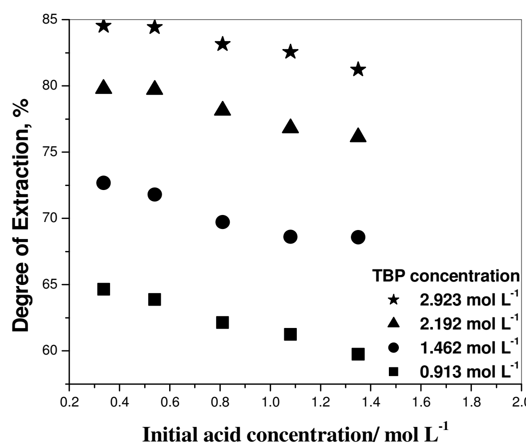

Figure 3: Effect of initial acid concentration on extraction efficiency with variable TBP concentration in n-decane/1-decanol (1:1 vol%)

The effect of TBP on the degree of extraction (E) is shown in the figure 4. It is observed that an increase in the extractant concentration increases the degree of extraction from 59.76% to 84.44% at 0.337 mol L^{-1} acid concentration, which signifies extractant's capability to recover propionic acid at low acid concentration.

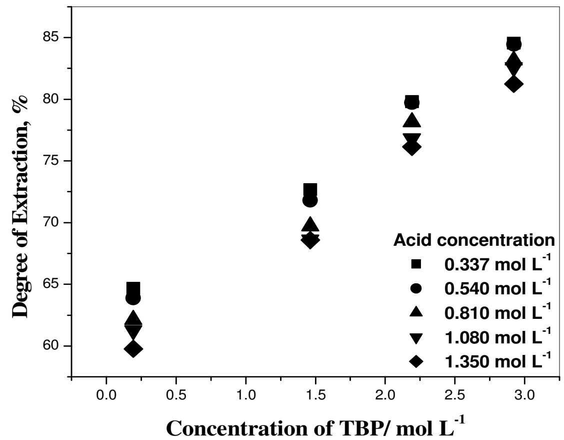

Figure 4: Effect of TBP concentration on extraction efficiency at various propionic acid concentration with n-decane/1-decanol (1:1 vol%)

The extraction mechanism of propionic acid (*HA*) with extractant (TBP) can be described by Eq. (3). This shows interfacial equilibrium between acid (*HA*) and extractant ($\overline{P}_{org}$) with formation of their complexes.

$$HA_{aq} + n\overline{P}_{org} \Leftrightarrow \overline{HAP}_{n(org)} \quad (3)$$

The extraction equilibrium constant, K_E, can be calculated using the Eq. (4).

$$K_E = \frac{[\overline{HAP}_{n(org)}]}{[HA_{aq}][P_{org}]^n} \quad (4)$$

Propionic acid also dissociates under equilibrium in aqueous phase as given by Eq. (5).

$$HA \Leftrightarrow A^- + H^+ \quad (5)$$

The corresponding dissociation constant, K_a is determined with the relationship as given by Eq. (6):

$$K_a = \frac{[A^-{}_{aq}][H^+]}{[HA_{aq}]} \quad (6)$$

Using Eqs. (1) and (6) the following relation can be found out and given by Eq. (7).

$$K_D = \frac{K_E[\overline{P}_{org}]^n}{\left(1 + \frac{K_a}{[H^+]}\right)} \quad (7)$$

Linearization of Eq. 7 is done by taking logarithm on both sides of the equation to get Eq. (8).

$$\log K_D + \log\left(1 + \frac{K_a}{[H^+]}\right) = \log K_E + \log[\overline{P}_{org}] \quad (8)$$

where, [$\overline{P}_{org}$] is the free TBP concentration in the organic phase, represented as:

$$[\overline{P}_{org}] = [\overline{P}_{org}]_{in} - n[\overline{HAP}_{n(org)}] \quad (9)$$

Putting the value of $[\overline{P}_{org}]$ from Eq. (9) in the Eq. (8) gives in Eq. (10).

$$\log K_D + \log\left(1 + \frac{K_a}{[H^+]}\right) = \log K_E + n\log\left([\overline{P}_{org}]_{in} - n[\overline{HAP_{n(org)}}]\right) \quad (10)$$

The Eq. (10) can be simplified by making an assumption that $[\overline{P}_{org}]_{in} >> n[\overline{HAP_{n(org)}}]$. In this case the initial extractant concentration $[\overline{P}_{org}]_{in}$ can also be used to determine the parameters n and K_E in the Eq. (10).

A plot of equation (10) by taking, $\log K_D + \log\left(1 + \frac{K_a}{[H^+]}\right)$ on y-axis and $[\overline{P}_{org}]_{in}$ on x-axis yields the straight line with slope of n and intercepts of $\log K_E$ as shown in Figure 5. For the extraction equilibrium with TBP, the slopes of the straight lines suggest in all cases of acid concentration the formation of solvates between one molecule each of both the reactants. The slope, n and the values of equilibrium constants K_E for different initial acid concentrations are given in Table 1.

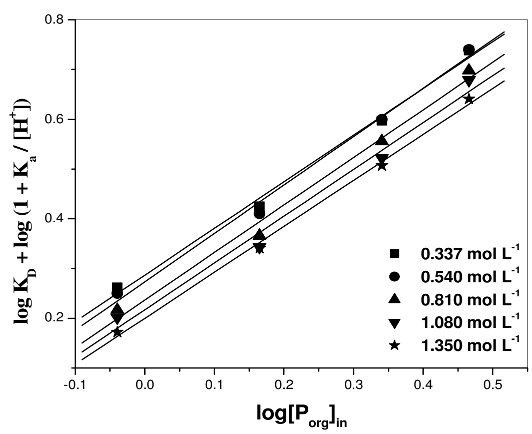

Figure 5: Graphical representation of Eq. (3) for determination of extraction constants (K_E) and apparent number of reacting molecule (n) using TBP dissolved in n-decane/1-decanol (1:1 vol%) with different initial acid concentration

Table 1: Values of Equilibrium extraction constant (K_E) and the number of reacting extractant molecules (n) from graphical method (with TBP dissolved in n decane/ 1-decanol of 1:1 vol%) at different concentration of propionic acid

C_{in} /mol L^{-1}	n	$\log K_E$	R^2	SD
0.337	0.9385±0.0498	0.2868±0.0149	0.997	0.0189
0.540	0.9736±0.0588	0.2731±0.0177	0.996	0.0224
0.810	0.9561±0.0703	0.2365±0.0212	0.995	0.0267
1.080	0.9412±0.0854	0.2169±0.0257	0.992	0.0325
1.350	0.9244±0.0361	0.1998±0.0109	0.998	0.0137

The value of stoichiometric coefficients (n) less than one indicate that active diluents, 1-decanol, having higher dielectric constant also contributed in the extraction of organic acid. Therefore, dielectric constant may be considered as an indicator of solvent–solute local interactions than of solute solvation by solvent or extractant.

The degree upto which the organic phase (extractant and diluents) may be loaded with acid is expressed by the loading ratio, Z (ratio of equilibrium total acid concentration in the organic phase to the total extractant, TBP concentration) and is given by Eq. (11).

$$Z = \frac{C_{org}}{[\overline{P}_{org}]_{in}} \tag{11}$$

The loading ratio (Z) is an important factor which determines the stoichiometry of the overall extraction of the acid in the organic phase. 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 TBP is formed. A plot of $Z/(1\text{-}Z)$ versus $[HA]$ yields a straight line with a slope of complexation constant (K_{E1}) as given by Eq. (12).

$$\frac{Z}{1-Z} = K_{E1}[HA] \tag{12}$$

Since propionic acid is used in the concentration range of 0.337-1.35 mol L^{-1} and TBP is diluted in the range of 0.913-2.923 mol L^{-1}, the loading ratio is found to be low, ($Z < 0.5$). 1:1 complexes of acid and TBP are formed and $Z/ (1 - Z)$ versus $[HA]$ for the respective TBP concentrations are plotted to obtain the value of equilibrium complexation constant (K_{E1}) as shown in Figure 6. Equilibrium extraction constant (K_{E1}) for 1:1 complex of propionic acid and TBP at 298 K for the extraction of acid in entire concentration ranges of TBP (0.913 – 2.923 mol L^{-1}) and acid (0.337 – 1.35 mol L^{-1}) is found to be 2.31 $mol^{-1}\cdot m^3$.

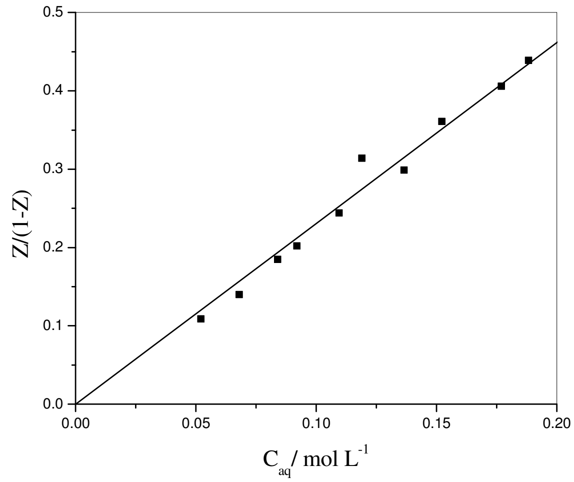

Figure 6. Plot of $Z / (1 - Z)$ versus [HA] for the estimation of (1:1) propionic acid-TBP equilibrium complexation constant (K_{E1}) in the entire range of TBP concentrations

Table 2. Equilibrium extraction constant (K_{E1}) for the extraction of propionic acid (0.337 – 1.35 mol L^{-1}) in the entire range (0.913 - 2.923 mol L^{-1}) of TBP from Figure 6

Extractant system	K_{E1} ($mol^{-1}\cdot m^3$)	R^2	*SD*
TBP + decane + 1-decanol	2.31 ± 0.043	0.99	0.0169

Conclusions

The studies on reactive extraction of propionic acid with TBP dissolved in inert and active diluents with various extractant and acid concentrations provide the useful data for designing the extraction system to recover propionic acid from aqueous streams as well as fermentation broth. The extraction efficiency of TBP increases with the concentration of active diluent, 1-decanol. The values of distribution coefficient (K_D) and degree of extraction (E) also depend upon initial concentration of propionic acid. Low acid concentration favors extraction even at any extractant concentration. The extraction efficiency is found to be increase with increasing TBP concentration significantly. The values of the equilibrium parameters K_E and n are determined using graphical method (mass action law modeling approach). The maximum values of K_E and n are found to be 1.94 and 0.94, respectively, at 0.337 mol L^{-1} propionic acid concentration. Since, the loading ratio was less than 0.5 in most of the cases, no significant overloading was obtained. The value of K_{E1} is found to be 2.31 for the entire range of propionic acid and TBP concentrations. The values of n, near about one, show formation of 1:1 complexes of acid and TBP at the equilibrium.

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