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Recovery of propionic acid by reactive extraction — 1. Equilibrium, effect of pH and temperature, water coextraction

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ABSTRACT

Reactive extraction is a prominent technique for recovery of carboxylic acids for dilute aqueous stream and fermentation broth. In the present paper, the effect of acid concentration, extractant concentration and type of diluent on extraction of propionic acid using tri-n-butyl phosphate (TBP) in methyl isobutyl ketone and 1-decanol was studied. Physical and chemical extraction experiments were conducted to study the influence of TBP in the respective diluents. TBP + MIBK was found to be an effective system with more than 25% improvement in extraction in comparison to TBP + 1-decanol, where no significant effect was obtained. The difference in solvation of TBP:acid complexes in respective diluents was explained in terms of physical properties of the diluents. Effect of pH, temperature and water coextraction was also studied using TBP in MIBK. Higher acid extraction was found when solution pH was lower than 4. The effect of temperature was not so predominant at the ranges studied (305–333 K). This suggests that the TBP + MIBK system can advantageously be employed over wider temperature ranges found at different sources. Another advantage of the TBP + MIBK system was due to its lower water coextraction percentage values (<5).

Keywords: Reactive extraction; Propionic acid; TBP; Temperature; pH; Water coextraction

1. Introduction

Propionic acid finds wide applications in the chemical, food and pharmaceutical industries. The calcium, sodium and ammonium salts of propionic acid are used as preservatives attributed to their bactericidal, fungicidal, insecticidal and antiviral properties. Industrial production of propionic acid is by petrochemical route and most of production is via namely three processes: carbonylation of ethylene with carbon monoxide and water, oxidation of propanal and direct oxidation of hydrocarbons. The petrochemical route is facing the challenge of high prices of feed stocks. Production by fermentation is an attractive alternative for acid production since it is a cheap and clean process compared to the industrial substitutes. Yet, it suffers from two main disadvantages: high cost and low efficiency of the recovery technique of the generated acid. The bioroute for acid production from glucose and lactose as substrate sources was found to have low reactor productivity (<1 g/l h), low product yield (<50% /w) and low product concentration (40 g/l). The main reason behind it was the inhibition of the microorganisms by the product acid [1,2].

To commercialize the bioroute method for acid production, it is desireable that the acid be removed as soon as it is produced so that the problem of product inhibition can be removed. This can be achieved through an efficient recovery method. Reactive extraction is one of the states of art technology for the recovery of carboxylic acids. In

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reactive extraction, aliphatic amines and organo phosphorous compounds in diluents are used as reactive extractants that can provide higher recovery of acid in comparison to extraction techniques by employing conventional diluents like alcohols, ethers, esters or aliphatic and aromatic hydrocarbons [3–10]. For complete design of reactive extraction, equilibrium, kinetic, thermodynamic, pH and water coextraction data are required.

Studies on propionic acid reactive extraction using tri-n-octyl amine in various diluents (hexanol, butyl acetate and petroleum ether) show the positive effect reactive chemical extraction over physical extraction [4]. The acid was found to form (1:1) and (2:1) acid-amine complexes during the extraction. Ingale et al. [11] studied extraction of carboxylic acids (C_2–C_6) using TBP at pH 2–2.5. The pH was taken from an environment process engineering point of view. Extraction of five carboxylic acids (acetic, propionic, butyric, valeric, and caproic acid) was investigated using TBP and TOA in decanol + dodecane and extraction isotherms were obtained by Morales et al. [12]. Experimental data show that the estimated value of equilibrium extraction constant and apparent number of extracting molecules reacting with one molecule of monoacid depend not only on organic phase composition but also on how they are determined. Uslu et al. [13] studied reactive extraction of propionic acid using Aliquat 336 (quaternary amine) dissolved in five pure solvents (cyclohexane, hexane, toluene, methyl isobutyl ketone, and ethyl acetate) and binary solvents (hexane + MIBK, hexane + toluene, and MIBK + toluene) under various experimental conditions. Their results and the observed phenomena were discussed by taking into consideration the mechanism of extraction and the concentration of the interaction product in the aqueous phase. In all cases 1:1 acid-amine complexes were formed with no overloading.

The effect of temperature and water coextraction on extraction of succinic acid and lactic acid by Alamine 336 in different diluents was studied by Tamada et al. [14]. The amount of coextracted water and solubility of water in the diluents with amine present exhibited the same order. Enthalpy and entropies of complex formation were derived from results of effect of temperature. Wennersten [15] tested the temperature effect on the extraction of citric acid by various extractants. The focus of his work was on extractants that contain a phosphoryl group, e.g., *n*-tributyl phosphate and trioctyl phosphine oxide. In a later publication, Wennersten [16] examined the extraction of citric acid using C_8–C_{10} tertiary amine (Alamine-336, or A-336) in various diluents at 25 and 60°C. Wennersten concluded that the formation of the amine-acid complex is strongly dependent on temperature.

A sharp decrease of distribution of acid with temperature was observed for extraction of citric acid using tridecylamine in petroleum fractions with alcohol as modifier in xylene and in nitrobenzene by Baniel et al. [17]. Similar results were obtained by Wennersten [16] for the extraction of citric acid by Alamine 336 in a variety of diluents at 25 and 60°C where for the corresponding 35°C increase in temperature, distribution ratios decreased by as much as a factor of 6 and by Sato et al. [18] for the extraction of lactic, tartaric, succinic, and citric acids by trilaurylamine in xylene at 20, 30,40, and 50°C where for a 30°C temperature increase, distribution ratios decreased by factors between 2 and 10, depending upon the type of acid.

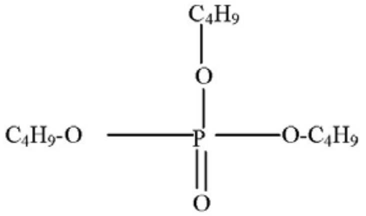
Based on the observations of effect of temperature on extraction, Baniel et al. [19] proposed a temperature-swing extraction/regeneration scheme. The extraction is carried out at a relatively low temperature, producing an acid-loaded organic extract and an aqueous raffinate waste stream containing the unwanted feed components. During regeneration, the extract is in contact with a fresh aqueous stream at a higher temperature to produce an acid-laden aqueous product stream and an acid-free organic phase. The concentration of the acid achievable in this stream depends upon the amount of change in the extraction equilibrium between temperatures and can be higher than that in the original aqueous feed stream. Thus temperature swing extraction/regeneration can be attractive for design of a completed reactive extraction process.

Much work on reactive extraction of propionic acid using different diluents like tri-n-octyl amine (TOA), Aliquat 336 and trioctyl phosphine oxide (TOPO) and TBP have been performed and are available in the literature [20–23]. However, no work could be found on the extraction of propionic acid using TBP in active diluents. In view of this, in the present paper, reactive extraction of propionic acid was studied using TBP in MIBK and 1-decanol. The effect of acid concentration, TBP concentration, and type of diluents is presented. An attempt has been made to differentiate the difference in extractions by TBP in the respective diluents on the physical properties of the diluents. Further very little work on effect of temperature, pH and water coextraction can be found in the literature for recovery of propionic acid from fermentation broths or water aqueous streams. So these parameters were also studied. The data obtained can form the basis for designing a propionic acid extraction system.

2. Material and methods

2.1. Chemicals

Tri-n-butyl phosphate (volume fraction of 99%) (Himedia, India), a phosphorous bonded oxygen donor, is a light colorless liquid with the molar mass of 266.32 g/mol and density of 0.92 g/cm^3. The chemical structure is:



Propionic acid (volume fraction of 99%) (Himedia, India) and the diluent, MIBK (Ranbaxy, India; molar mass: 100.16; density: 0.799–0.802 g/cm^3) and 1-decanol (Himedia India; molar mass: 158.29; density: 0.8297 g/cm^3) are of technical grade and were used as acquired from suppliers. Distilled water was used to prepare the solutions of various concentrations of propionic acid solutions. Analytical-grade NaOH used for titration and was supplied by Ranbaxy (India). For the standardization of the NaOH, oxalic acid (99.8%) was obtained from S.D. Fine Chem. (India). A phenolphthalein solution (pH range 8.2–10.0) was used as an indicator for titration and was obtained from Ranbaxy (India). The initial TBP concentrations in the range of 0.37 to 1.65 mol/l and the initial aqueous acid concentrations range ($[HA]_0$) of 0.1 to 0.4 mol/l were used where the superscript "0" signifies the initial. A low concentration (0.05–0.4 mol/l) was used because propionic acid concentration in the fermentation broth is not greater than 0.5 mol/l [2].

2.2. Procedure

The extraction experiments were performed using a temperature-controlled water bath shaker (Remi Equipment, India) at constant temperature. Equal volumes (25 cm^3) of aqueous and organic phases were taken in 100 ml conical flask and were shaken for 12 h. This could be considered as appropriate time for attaining equilibrium. The solutions were then made to settle for at least 2 h at a fixed temperature and atmospheric pressure in a separating funnel. The lower phase was taken for analysis after filtration through a Millex GV filter unit (0.22 μm). Aqueous phase acid concentration was determined by titration with NaOH. Fresh NaOH solution was prepared every time prior to use. The acid content in the organic phase was determined by mass balance. In experiments involving study of effect of temperature, the temperature was varied from 305 K to 333 K. The temperature of the shaker bath was maintained within ±2 K of the set-point. Usually in fermentation broth or in dilute waste aqueous streams temperature of medium is in the range of 303 K to 333 K. So it becomes important to test the effectiveness of the extractant–diluent system at working conditions.

In other experiments effect of pH was studied. Again the purpose was to find the effectiveness of extractant-diluent system to variable pH values of the source media. In experiments involving pH study, aqueous phase acid concentration was determined by a high-pressure liquid chromatography (HPLC) system (Waters 1523) consisting of a binary pump, refractive index detector (Waters 2414) and dual λ absorbance detector (Waters 2487). Organic-phase acid concentrations were corrected for extraction by the diluent alone at the appropriate temperature. Best-fit equilibrium constants for the complexes formed were determined. A few experiments were carried out in duplicate and consistency was found within ±2%.

3. Results and discussion

Organophosphorous compounds are effective extractants in separating acids from solutions containing chemically similar elements. TBP, an organophosphorous compound, contains a phosphoryl group which is a stronger Lewis base than the carbonyl group. This leads to a higher distribution coefficient. TBP contains =P (O)OH group, which has a marked tendency towards an intermolecular hydrogen bonding. 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. The relatively high viscosity (3.56×10^{-3} Pa·s) and density close to unity (0.98 g/cm^3), could not permit them to be used alone for extraction purposes. So they are mixed in low viscosity and low density diluents, which could facilitate good phase separation in a continuous extraction process. Active diluents (like alcohols, ketones, esters) have been found to provide better extraction in comparison to inert diluents (like aliphatic or aromatic hydrocarbons).

The mass law equilibria describing the extraction of propionic acid by TBP in diluent can be represented as:

$$HA_{aq} + pS_{org} \leftrightarrow (HA.\,S_p)_{org} \tag{1}$$

where subscripts "aq" and "org" stand for aqueous and organic phases and p is the solvation number of TBP.

The distribution of carboxylic acid between water and a non-reactive solvent is regarded to be a physical distribution. The physical distribution is accounted via existence of acid in partial dissociated and undissociated form in the aqueous phase and by transfer via partitioning and dimerization in the organic phase. The distribution coefficient can then be defined as [24]:

$$K_D^{\text{diluent}} = \frac{[HA]_{org}}{[HA]_{aq}} = \frac{[HA]_{(0)}P + 2[(HA)_2]_{(0)}}{[HA]_{(aq)} + [A^-]_{(aq)}} = \frac{P + 2P^2 D[HA]_{(aq)}}{1 + K_{HA}/[H^+]_{(aq)}} \tag{2}$$

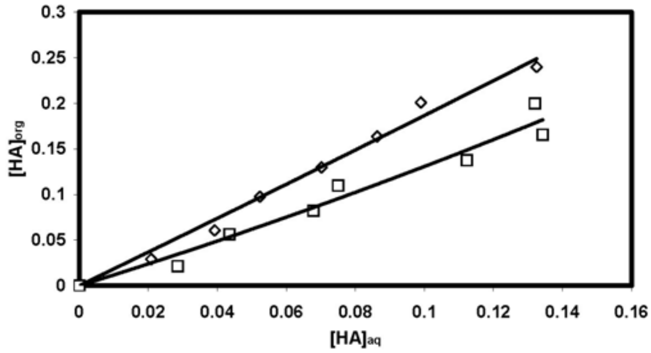


Fig. 1. Physical equilibria for the extraction of propionic acid (0.1–0.4 mol/l) using 1-decanol and MIBK. ◊ decanol; □ MIBK.

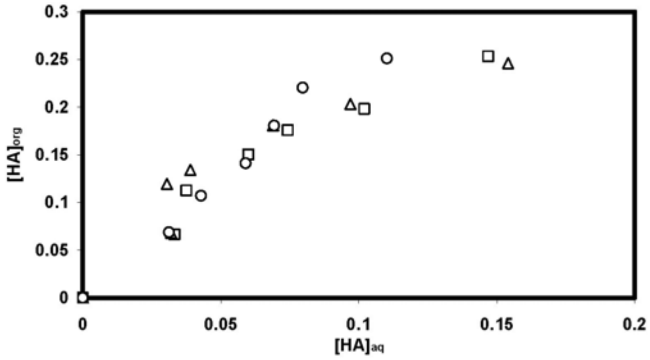


Fig. 2. Chemical equilibria for the extraction of propionic acid (0.1–0.4 mol/l) using 20–40% TBP in 1-decanol. □ 20% TBP; Δ 30% TBP; ○ 40% TBP.

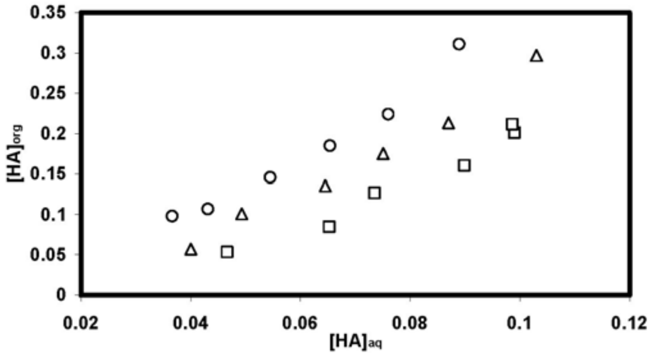


Fig. 3. Chemical equilibria for the extraction of propionic acid (0.1–0.4 mol/l) using 20–40% TBP in MIBK. □ 20% TBP; Δ 30% TBP; ○ 40% TBP.

where P is the partition and D is the dimerization constant. In the present study only dilute solutions of acid were taken, so the term $K_{\mathrm{HA}}/[\mathrm{H+}]_{(\mathrm{w})}$ can be presumed to be negligibly small and can be neglected to yield:

$$K_{\mathrm{D}}^{\mathrm{diluent}} = P + 2P^2 D[\mathrm{HA}]_{(\mathrm{aq})} \tag{3}$$

The physical equilibria for extraction of propionic acid using MIBK and 1-decanol are shown in Fig. 1. Eq. (3) was fitted to the experimental value to yield the values of P and D as 1.4 and 1.42 for 1-decanol and 0.89 and 3.44 for MIBK. The $K_{\mathrm{D}}^{\mathrm{diluent}}$ values for 1-decanol and MIBK lie between 1.39–2.02 and 0.75–2.04 respectively, which are not sufficiently high.

The low activity of propionic acid towards these diluents particularly in lower concentrations of acid, i.e., its higher solubility in water than in organic solvents is the cause of the low distribution coefficient. Thus extraction using conventional diluents is unprofitable. Better possibilities are offered by a reactive extraction technique by employing organophosphorous compounds and amines which have proven to be effective in the recovery of carboxylic acids [3,6,7].

The distribution coefficient of acid by chemical extraction can be defined as:

$$K_{\mathrm{D}}^{\mathrm{Chem}} = \frac{[\mathrm{HA}]_{\mathrm{org}} - \nu[\mathrm{HA}]_{\mathrm{org}}^{\mathrm{diluent}}}{[\mathrm{HA}]_{\mathrm{aq}}} \tag{4}$$

where ν is volume fraction of diluent and $[\mathrm{HA}]_{\mathrm{org}}^{\mathrm{diluent}}$ is the acid extracted into the organic phase by diluent alone. The overall distribution coefficient is obtained by summing up Eqs. (2) and (4).

$$K_{\mathrm{D}}^{\mathrm{overall}} = K_{\mathrm{D}}^{\mathrm{diluent}} + K_{\mathrm{D}}^{\mathrm{Chem}} \quad (5)$$

Figs. 2 and 3 show the chemical equilibria for propionic acid extraction using 20–40% TBP in respective diluents. TBP is not quite effective in 1-decanol whereas in MIBK, increase in percentage of TBP increases the $K_{\mathrm{D}}^{\mathrm{overall}}$ value. However, in all cases the extraction was significantly higher in case of chemical extraction in comparison to physical extraction. $E\%$ defined as

$$E\% = \frac{K_{\mathrm{D}} \times 100}{(1 + K_{\mathrm{D}})} \tag{6}$$

and was found to increase by 15% and 27% by employing chemical extraction in comparison to physical extraction.

The extraction equilibrium constant (K_{S}) is computed by applying the law of mass action as:

$$K_{\mathrm{s}} = [(\mathrm{HA}).(\mathrm{S})_p]_{\mathrm{org}}/[\mathrm{HA}]_{\mathrm{aq}}\,[\mathrm{S}]p_{\mathrm{org}} \tag{7}$$

where $[\mathrm{HA}]_{\mathrm{aq}}$, $[\mathrm{S}]_{\mathrm{org}}$, $[(\mathrm{HA.S})]_{\mathrm{org}}$ represent acid, extractants and complex concentration properties of the acid and the solvation efficiency of the diluent used. Niitsu and Sekine [25] reported that the solvation number of the aliphatic carboxylic acids were the same as the numbers of carboxyl groups on each acid, thus the value of p for propionic acid can be taken as one. This indicated a stoichiometric (1:1) association between the individual phosphoryl group and the individual acid group and displays the strong effect of acid concentration on the experimentally determined distribution ratio. Substituting the value of $[S]_{org}$ as:

$$[S]_{org} = [S]^{o}_{org} - [HA.S]_{org} \tag{8}$$

and rearranging

$$K_s[HA]_{aq} = \frac{[HA.S]_{org}}{[S]^{o}_{org} - [HA.S]_{org}} = \frac{[HA]^{total}_{org} - \nu[HA]^{diluent}_{org}}{[S]^{o}_{org} - \left([HA]^{total}_{org} - \nu[HA]^{diluent}_{org}\right)} = \frac{(z - \nu m)}{1 - (z - \nu m)} \tag{9}$$

where z and m are defined as:

$$z = \frac{[HA]^{total}_{org}}{[S]^{o}_{org}} \text{ and } m = \frac{[HA]^{diluent}_{org}}{[S]^{o}_{org}} \tag{10}$$

Fig. 4 shows the plot of Eq. 10 and the value of K_S was obtained as:

- For TBP + 1-decanol

$$K_S = 0.59 \text{ l/mol} \tag{11}$$

- For TBP + MIBK

$$K_S = 0.849 \text{ l/mol} \tag{12}$$

Higher $K_D^{overall}$ and K_S values for chemical extraction using TBP in MIBK, in comparison to TBP in 1-decanol, suggest it to be the better of the two. The differences in extraction by the above systems suggest that distribution of acid:TBP complexes are strongly dependent on the nature of the diluents. The effect of diluent on partition and self-association constants can be explained by specific interactions between TBP and the diluents. An attempt has been made to correlate the extraction efficiency in terms of K_S values with solvent properties like molecular mass, boiling point, density, refractive index, dielectric constant, dipole moment. MIBK has a lower molecular mass in comparison to 1-decanol. Thus it can be suggested that since TBP is itself relatively viscous, employing a lower molecular weight diluent can significantly improve the complexation ability of TBP with the acid. However, it can be stated here that it is not obvious that a lower molecular weight of solvent results in a better TBP+ diluent system since the lower the molecular weight, the higher the miscibility of the solvent with water. Thus, optimization should be made when selecting the diluent for TBP. Similarly, it can seen that MIBK higher extraction can be explained by its higher solvent dipole moment μ value (μ for MIBK = 4.2 D). Since the extraction probably occurs via solvation of the complex based on dipole–dipole interaction, a higher μ value of MIBK provides a higher ability to solvate the TBP:acid complexes.

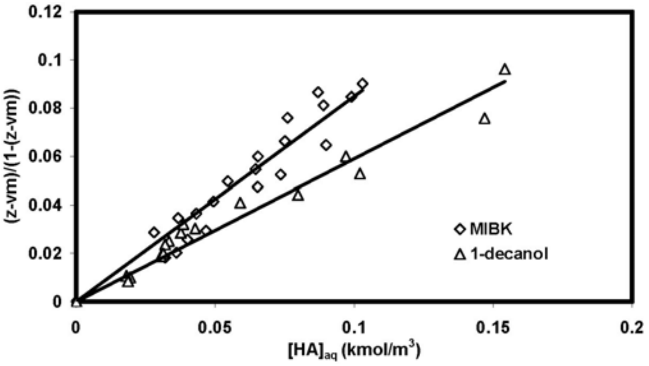


Fig. 4. Plot for the estimation of (1:1) propionic acid–TBP complexation constant in 1-decanol and MIBK respectively.

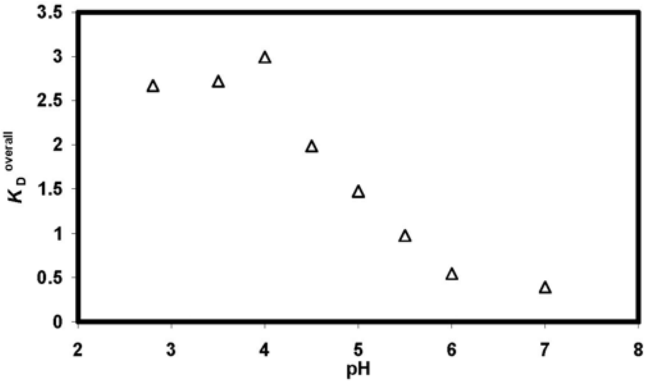


Fig. 5. Effect of pH on extraction of propionic acid 0.2 (mol/l) using 40% TBP in MIBK.

Due to higher extraction of propionic acid TBP + MIBK, it was decided to study the effect of pH, temperature and water coextraction on recovery of propionic acid. The study of effect of pH on reactive extraction is important since pH of fermentation broth varies as acid is produced and in aqueous streams pH was decided by the concentration of acid present. Fig. 5 shows extraction of 0.2 kmol/m^3 propionic acid using TBP in MIBK when pH was varied from 2.8 to 7. It can be seen that there is an increase in $K_D^{overall}$ as pH was varied from natural pH (2.8) to 4, whereupon it gradually decreases. At higher pH values (>6), nearly no extraction took place. The reason for this may be that TBP extract only the undissociated form of acid, and at higher pH, most of acid is present in dissociated form; thus lower extraction was obtained. As production of acid in the fermentation broth results in

Table 1
Effect of temperature on chemical equilibria for extraction of different concentration of propionic acid using 30%(1.1 mol/l) and 40% (1.65 mol/l) TBP in MIBK

T (K)	$[S]_o$ (mol/l)	$[HA]_o$ (mol/l)	pH_{aq}	K_D	E, %	$z_{overall}$	K_S (l/mol)
305	1.1	0.10	3.14	2.04	67.14	0.092	0.983
		0.15	3.20	2.75	73.33	0.100	
		0.20	3.07	2.10	67.75	0.123	
		0.25	3.04	2.33	69.98	0.159	
		0.30	3.00	2.45	71.00	0.194	
		0.40	2.96	2.88	74.25	0.270	
	1.65	0.10	3.18	2.48	71.24	0.065	
		0.15	3.22	3.09	75.56	0.069	
		0.20	3.12	2.67	72.75	0.088	
		0.25	3.07	2.82	73.85	0.112	
		0.30	3.03	2.95	74.67	0.136	
		0.40	3.00	3.50	77.76	0.189	
313	1.1	0.10	3.18	1.31	56.67	0.052	1.089
		0.15	3.13	1.86	65.05	0.089	
		0.20	3.07	2.03	67.00	0.122	
		0.25	3.03	2.18	68.54	0.156	
		0.30	3.01	2.61	72.33	0.197	
		0.40	2.95	2.70	73.00	0.265	
	1.65	0.10	3.21	1.68	62.67	0.038	
		0.15	3.17	2.36	70.24	0.064	
		0.20	3.11	2.51	71.50	0.087	
		0.25	3.06	2.71	73.07	0.111	
		0.30	3.05	3.29	76.67	0.139	
		0.40	2.98	3.26	76.50	0.185	
323	1.1	0.10	3.18	1.31	56.67	0.052	0.94
		0.15	3.21	2.93	74.56	0.102	
		0.20	3.06	1.90	65.50	0.119	
		0.25	3.00	1.82	64.48	0.147	
		0.30	3.00	2.41	70.67	0.193	
		0.40	2.79	0.83	45.50	0.165	
	1.65	0.10	3.20	1.54	60.67	0.037	
		0.15	3.15	2.08	67.53	0.061	
		0.20	3.08	2.23	69.00	0.084	
		0.25	3.04	2.42	70.80	0.107	
		0.30	3.03	2.90	74.33	0.135	
		0.40	2.97	3.00	75.00	0.182	
333	1.1	0.10	3.17	1.24	55.33	0.050	0.894
		0.15	3.06	1.20	54.50	0.074	
		0.20	2.97	1.04	51.00	0.093	
		0.25	2.98	1.63	62.00	0.141	
		0.30	3.00	2.41	70.67	0.193	
		0.40	2.94	2.57	72.00	0.262	
	1.65	0.10	3.19	1.46	59.33	0.036	
		0.15	3.14	2.07	67.44	0.061	

lowering of pH of the system, TBP could be used at that stage and can be quite effective for recovery of produced acid from the broth. Since results suggest that TBP is effective at pH values less than or equal to 4, it becomes important that pH of the source stream (from where acid is to be extracted) be lowered so that extraction of acid can be carried out effectively by TBP. Jarvinen et al. [26] suggested two methods for pH adjustment to optimal pH of extraction: either by using sulfuric acid or by strong cation exchanges. The second method was found to be better in comparison to first since the added H_2SO_4 competes with the acid to be extracted by extractant. So it can be proposed that some cation exchangers can be used if pH of the system from where propionic acid is to be extracted is at pH higher than 4, so that optimal and efficient use of TBP can be obtained.

Extraction of propionic acid by TBP is via intermolecular hydrogen bonding of the =P (O) OH group with the acid. The extraction of propionic acid by TBP:acid complex formation is expected to be exothermic and makes the system more ordered. Thus entropy decrease is expected.

The effect of temperature on reactive extraction of propionic acid using TBP in MIBK was studied in the present work with two aims: first to find the effect of temperature on extraction of the acid from fermentation broth or aqueous streams (where usually temperature vary in the range of 308 to 323 K) and second whether temperature swing extraction/regeneration can be used for recovery of the acid. Table 1 shows the equilibrium data for extraction of propionic acid by TBP (30–40%) + MIBK respectively when temperature was varied from 305 K to 333 K. It can be seen that, in general, both the $K_D^{overall}$ values and K_E values increase with an increase in temperature from 305 K to 313 K, whereupon they decrease. However, the overall decrease of K_E was not very large. This suggests that the extraction can be advantageously used for variable ranges of temperature without much drop in extraction efficiency. However, temperature swing regeneration could not be employed.

Water coextraction is the water that enters the organic phase with the solute. Apparently, forces that allow the diluent to solvate water molecules effectively also cause solvation of the water molecules surrounding or attached to a complex. It affects process economics because it may be necessary to recover pure acid from an aqueous solution produced from the extract during regeneration. Fig. 6 shows the plot of volume percentage of water co-extracted for various concentrations of acid for extraction of propionic acid using TBP in MIBK. Water coextraction was found to be maximum at the intermediate acid concentration. This is in agreement with the results of experiments where it was found that K_D values were higher at intermediate concentration of acid concentrations. Further, it can be seen that water coextraction increases with increase in concentration of TBP. 40% TBP in MIBK extracts more water in comparison to 30% TBP in MIBK. This suggests that water is extracted along with the complexes. Higher complexation was obtained in higher percentages of TBP, thus the water coextraction could be higher. However, in general, the selectivity of acid over water in the extraction by TBP is high relative to the results with conventional solvent, and in all cases the water coextraction is not above 5%, which has little effect upon process viability. Another probable reason for low water coextraction can be accounted of the nature of propionic acid. Propionic acid is mono-carboxylic acid and since water is co extracted with the carboxyate group, very low water coextraction could be expected.

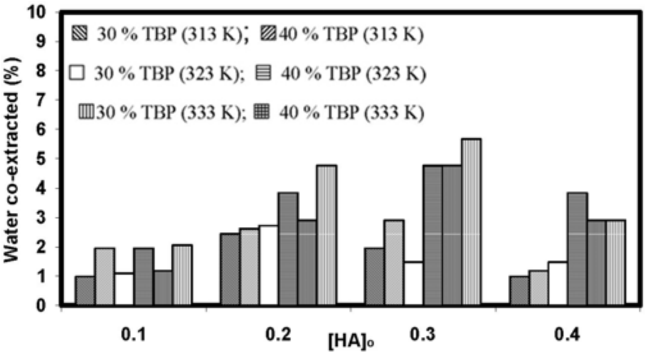


Fig. 6. Effect of water coextraction on extraction of propionic acid using TBP (30% and 40%) in MIBK.

4. Conclusions

TBP, an organophosphorous compound, was used for extraction of propionic acid using 1-decanol and MIBK as diluents. Comparison of physical extraction using 1-decanol and MIBK and chemical extraction using TBP in these diluents suggest that chemical extraction is better. The TBP + MIBK system provided higher recovery of acid in comparison to TBP + 1-decanol. K_S was obtained as 0.59 l/mol and $K_S = 0.85$ l/mol for TBP + 1-decanol and TBP + MIBK, respectively. Higher extraction of the TBP + MIBK system was explained by the better solvation ability of the TBP:acid complex ion MIBK. An effort was made to explain the extraction difference in terms of physical properties of solvent chosen. It was found that the lower molecular weight and higher dipole moment of MIBK can be the reason of its higher solvation ability of TBP:acid complexes.

The effect of pH on reactive extraction of propionic acid using TBP in MIBK was investigated to decide the optimum pH of operation for recovery of propionic acid, using TBP from aqueous streams or fermentation broths. TBP can be effectively employed for extraction of propionic acid when pH of the system is pH ≤ 4. The effect of temperature and water coextraction is important in respect to the process design. With this aim the effect of temperature and coextraction was studied for extraction of propionic acid using TBP in MIBK. The high $K_D^{overall}$ values and K_E at $T = 313$ K, which is the operating temperature of fermentation broths from where acid can be produced, suggest that TBP + MIBK can be successfully employed for recovery of the acid from fermentation broth. Low values of water coextraction are another advantage of the TBP + MIBK system.

5. Symbols

$[A]^-$ — Concentration of anion, mol/l
D — Dimerization coefficient, l/mol
$E\%$ — Degree of extraction
$[HA]$ — Acid concentration, mol/l
$[HA]_{org}^{diluent}$ — Concentration of acid extracted into the organic phase by diluent alone, mol/l
K_D^{chem} — Distribution coefficient of acid by chemical extraction
$K_D^{diluent}$ — Distribution coefficient of acid by diluent alone
$K_D^{overall}$ — Overall distribution coefficient
K_S — Equilibrium complexation constant, l/mol
p — Solvation number of TBP
P — Partition coefficient
pH_{aq} — pH of the aqueous phase in equilibrium with organic phase
$[S]$ — TBP concentration, mol/l
z — Loading ratio
ν — Volume fraction of diluent

Subscripts

aq — Aqueous phase
org — Organic phase

Superscript

0 — Initial

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References

[1] S.T. Hsu and S.T. Yang, Biotechnol. Bioeng., 38 (1991) 571–578.
[2] Z. Jin and S.T. Yang, Biotechnol. Prog., 14 (1998) 457–465.
[3] K.L. Wasewar, A.B.M. Heesink, G.F. Versteeg and V.G. Pangarkar, Chem. Eng. Sci., 59 (2004) 2315–2320.
[4] K.L. Wasewar and V.G. Pangarkar, Chem. Biochem. Eng., Q.20(3) (2006) 325–331.
[5] A. Keshav, K.L. Wasewar and S. Chand, Ind. Eng. Chem. Res., 47 (2008) 6192–6196.
[6] A. Keshav, K.L. Wasewar and S. Chand, Desalination, 244 (2009) 12–23.
[7] A. Keshav, K.L. Wasewar and S. Chand, J. Chem. Eng. Data, 53(7) (2008) 1424–1430.
[8] A. Keshav, K.L. Wasewar and S. Chand, Sep. Purif. Technol., 63 (2008) 179–183.
[9] A. Keshav, K.L. Wasewar and S. Chand, International Conference on Modeling and Simulation, CITICOMS 2007, Coimbatore Institute of Technology, Coimbatore, India, 2007.
[10] A. Keshav, K.L. Wasewar and S. Chand, International Symposium and 60th Annual Session of IIChE in association with International Partners (CHEMCON-2007), Calcutta, India, 2007.
[11] M.N. Ingale and V.V. Mahajani, Sep. Technol., 6 (1996) 1–7.
[12] A.F. Morales, J. Albet, G. Kyuchoukov, G. Malmary and J. Molinier, J. Chem. Eng. Data, 48 (2003) 874–886.
[13] H. Uslu and İ. İnci, J. Chem. Thermodyn., 39 (2007) 804–809.
[14] C.J. King and J.A. Tamada, Ind. Eng. Chem. Res., 29 (1990) 1327–1333.
[15] R. Wennersten, Proc., International Solvent Extraction Conference Liege University Press, Liege, Belgium, Vol. 2, 1980, pp. 63–68.
[16] R. Wennersten, J. Chem. Technol. Biotechnol., 33 (1983) 85–94.
[17] A.M. Baniel, R. Blumberg and K. Hajdu, US Patent 4,275,234, 1982.
[18] T. Sato, H. Watanabe and H. Nakamura, Bunseki Kagak, 34 (1985) 559–563.
[19] A.M. Baniel, R. Blumberg and K. Hajdu, UK Patent No. 1,426,018, 1973.
[20] A. Keshav, K.L. Wasewar and S. Chand, Chem. Biochem. Eng. Q., 22(4) (2008) 433–437.
[21] A. Keshav, K.L. Wasewar and S. Chand, AIChE J., AIChE J., in press.
[22] A. Keshav, K.L. Wasewar and S. Chand, J. Chem. Technol. Biotechnol., in press.
[23] A. Keshav, K.L. Wasewar and S. Chand, Ind. Eng. Chem. Res., 47(16) (2008) 6192–6196.
[24] A.S. Kertes and C.J. King, Biotechnol. Bioeng., 28 (1986) 269–282.
[25] M. Niitsu and T. Sekine, Bull. Chem. Soc. Japan, 51 (1978) 705–717.
[26] M. Järvinen, L. Myllykoski, R. Keiski and J. Sohlo, Bioseparation, 9 (2000) 163–166.