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Extraction of Propionic Acid From Model Solutions: Effect of pH, Salts, Substrate, and Temperature

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Propionic acid can be successfully produced from fermentation broth once an efficient recovery method is available for the produced acid. Reactive extraction in this regard is a promising recovery method. pH, salt, substrate, and temperature studies are crucial in the extraction of propionic acid, because these parameters varied in actual fermentation broth. With this regard, effects of these were studied. Extraction from model solutions and salt or substrate containing systems is lower than what was obtained from normal aqueous solutions. Reason of this is the varying degree of hindrances of the salts on extraction of the acid. pH has very large effect on extraction efficiency of the extracting system. At pH > pK$_a$ of acid, very low extraction was obtained. Temperature was found to have no effect on the extraction from model solutions used. © 2009 American Institute of Chemical Engineers *AIChE J,* 55: 1705–1711, 2009
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Introduction

Recently, there has been wide interest in carboxylic acids extraction from fermentation broths. Till date, most of carboxylic acids are produced by synthesis from petrochemical feed stocks. The high cost of substrate and strict environmental regulations lead manufactures to look for a clean mode of production of different carboxylic acids. Propionic acid is an important carboxylic acid and is used in numerous processes such as in the production of cellulose plastics (used in textile, lacquer formulations, and moulding plastics), in the manufacture of ester solvents, perfume bases, and butyl rubber to improve processability and scorching resistance.[1] Isolation of propionic acid from dilute waste water and fermentation broths is an economic problem. The separation, purification, and preconcentration of propionic acid are rather difficult because of its strong affinity to water. The high solubility in water renders traditional solvents such as alcohols, ethers, esters, and inert diluents (hexane, *n*-heptane) to be successfully used for the acid extraction. The conventional method of recovery of propionic acid from fermentation broth is calcium hydroxide precipitation method. The approach includes addition of calcium hydroxide to form calcium salt of propionic acid, to which sulphuric acid is added to liberate the free propionic acid.[2] This method of recovery is expensive and unfriendly to environment because it consumes lot of lime and sulphuric acid and also produces a large quantity of calcium sulphate sludge as solid waste. Consequently, this method is falling out of favour. Therefore, it is reasonable to look for other methods of recovery for carboxylic acid.

Solvent extraction, membrane bioreactor, liquid surfactant membrane extraction, adsorption, direct distillation, electrodialysis, reactive extraction, reverse osmosis, anion exchange, etc., are some of the techniques that can be used for propionic acid recovery.[2] All of these processes have their own advantages and disadvantages. Adsorption or ion-exchange process requires regeneration of ion-exchange resin and adjustment of feed pH to increase the sorption efficiency requiring large amount of chemicals. Electrodialysis and dialysis have good potential and advantage of simultaneous separation and concentration. Yet, they suffer from problems

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of membrane fouling that requires frequent cleaning of the dialyzer. Distillation is the well-established and reliable technology, but it has drawback that there is formation of high-boiling esters and dimmers. In hollow fiber membrane extraction process, membrane has tendency to form emulsion but has advantage of large interfacial surface area for mass transfer in a compact unit. The drawbacks of reverse osmosis are potential formation of emulsion and complexity of operation. Interest in liquid surfactant membranes for biochemical separations has focused on their potential advantages. The main advantage of liquid surfactant membranes over other separation techniques is the large surface area available for mass transfer, which results in a fast rate of separation. Despite apparent advantages, very few industrial applications have been reported so far. Several drawbacks were shown to hinder implementation, mainly complexity of operation and swelling in liquid surfactant membrane. The use of supported liquid membranes for the recovery of propionic acid offers unique advantages. Some of the advantages are lower energy consumption, higher separation factors in a single stage, and the ability to concentrate propionic acid during the separation. However, supported liquid membrane often suffers from membrane instability.

Membrane bioreactors can be used to avoid toxicity due to extractant by immobilization of biocatalyst in membrane for the production and recovery of carboxylic acid. The major drawback of the membrane bioreactor is difficulties in cleaning and sterilization.[3] Reactive extraction has emerged as a promising recovery method to obtain the carboxylic acids from the bioreactor. It provides numerous advantages like high yield, higher conversions of the substrate than the usual fermentation without product removal, constant pH maintenance without base addition, and continual plant operation. Extensive works on reactive extraction of different carboxylic acids are found in the literature.[2–21] Most of these studies are on the effect of diluents, extractants, acid concentrations, and some on pH and salts. Some of these are given.

Uslu and Inci[6] studied the extraction of propionic acid with Aliquat 336 using five single solvents and three binary solvents. The obtained results and the observed phenomenon were discussed in the view of extraction mechanism. Extractions using mixed diluents were found to be higher. Use of mixed extractants is another emerging technique for reactive extraction. Keshav et al.[8] studied the extraction of propionic acid using tri-*n*-butyl phosphate in eight different diluents (1-dodecanol, benzene, toluene, heptane, hexane, butyl acetate, petroleum ether, and paraffin liquid). Equilibrium parameters such as distribution coefficients, loading ratio, degree of extraction, and equilibrium complexation constants have been presented. Zhong et al.[12] studied the reactive extraction of propionic acid using Alamine 304-1 in 2-octanol, 1-dodecanol, and withcohol 85 NF as diluents at various amine concentrations (0-100%) and found extraction to be maximum at the amine concentration between 20 and 40%. Diluent effects the extraction power of the extractant with 2-octanol providing the highest ability to solvate the acid–extractants complexes. Extraction of glycolic, malic, and citric acids by Alamine 336 and tri-*n*-octylamine dissolved in iso-butyl methyl ketone (MIBK)/toluene mixture (1:1 volume ratio) were presented by Inci and Aydin.[13] The effects of amine type and the concentration on extraction of hydroxycarboxylic acids by amines were investigated. Formation of acid–amine complexes is a dominating factor in the system under consideration. The distribution coefficients and loading factors are calculated and reported.

Effect of pH on the extraction of pyruvic acid using tri-*n*-octylamine (TOA) was studied by Ma et al.[14] Distribution coefficient (K_D), degree of extraction ($E\%$), and loading ratios (z) decreased with increase in pH. Equilibrium complexation constants (K_S) were evaluated upto a certain pH only. Above certain pH, complex extraction hinders K_S determination. Harington and Hossain[15] studied the effect of feed pH for various combinations of TOA and Aliquat for extraction of lactic acid by sunflower oil. At all pH, Aliquat provides greater K_D. Synergistic effect was observed at low pH, and extraction using mixed extractants was found to be higher than that using them as single. However, at higher pH, no substantial difference was observed and very low extractions were obtained in all cases.

The effects of pH, salts, and contaminated acid on the intrinsic reaction kinetics were studied by Jun et al.[16] Extraction rates were found to steeply decrease at pH > 3 due to the dissociation of carboxylic group. Salts (NaCl, $MgCO_3$, K_2HPO_4, and $(NH_4)_2SO_4$) and contaminated acid (pyruvic acid) had negative influence on the extraction process of succinic acid and thus extraction was decreased. Influence of NaCl and lactose on the extraction of lactic acid at room temperature was studied by San-Martin et al.[17] Lowering of extraction by NaCl and no effect on extraction by lactose were found on the extraction of lactic acid. Effect of pH (2.0 and 2.5) and inorganic salts (Na_2SO_4 and NaCl) on extraction of different carboxylic acids (acetic acid, propionic acid, butyric acid, valeric acid, and caproic acid) using tributylphosphate was studied by Ingale and Mahajini.[18] The effect of salts were studied for solutions with ionic strength of 2.112 kion m^{-3} obtained by respective salts addition. It was found that decreasing pH from 2.5 to 2 lowers the extraction. Different chemical (H_2SO_4 and HCl) used for pH adjustment have different effects on the distribution of acid obtained. Presence of salts alone (absence of mineral acid) was found to increase the value of K_D, and extractions by HCl–NaCl system were higher than Na_2SO_4–H_2SO_4 system. K_D was observed to decrease in the presence of mineral acids when pH of the system was decreased from 2.5 to 2.0.

Different types of salts and carbon sources are found in fermentation broths owing to the impurities. Till date, most of the research has been focused on the reactive extraction of carboxylic acids from aqueous solutions. Establishment of reactive extraction on commercial scale requires knowledge of effect of impurities such as NaCl, $(NH_4)_2SO_4$, and K_2HPO_4 on extraction. Hence, reactive extraction of propionic acid from model solutions was studied using TOA in MIBK. The concentrations of different chemicals were chosen to closely represent the actual concentration found in the fermentation broth.[22–25]

Materials and Methods

Chemicals

TOA ($C_{24}H_{51}N$; 98%, ACROS, India), a tertiary amine was used as an extractant. Propionic acid (CH_3CH_2COOH;

99% purity; molar mass 74.08; density 992 kg m^3; Himedia, India) and diluent (MIBK; 99% purity; molar mass 100.16; density 799–802 kg m^3; Ranbaxy India Ltd.) are of technical grade and were used without pretreatment. Distilled water was used to prepare the solutions of various concentrations of propionic acid. Salts such as sodium chloride (Qualigens India Ltd.), sodium sulphate (S.D Fine Chem. India Ltd.), and potassium phosphate (Ranbaxy India Ltd.) and carbon sources such as lactose (SISCO Research Lab. Pvt. Ltd.) and dextrose (Ranbaxy India Ltd.) were used as obtained. Mobile phase for high-pressure liquid chromatography (HPLC) was composed of ammonium dihydrogen phosphate (RFCL India Ltd.) solution in millipore water (RFCL India Ltd.). Sodium hydroxide (Ranbaxy India Ltd.) and orthophosphoric acid (Ranbaxy India Ltd.) were used for pH adjustment of aqueous solution of propionic acid and mobile phase of HPLC, respectively.

Extraction method

Extraction experiments involved shaking equal volumes (20×10^{-6} m^3) of aqueous and organic phases for 12 h in a water bath at constant temperature, followed by settling of the mixture for at least 2 h at a same temperature in an incubator. Aqueous-phase pH was measured by an Orion 3 star pH benchtop (Thermo Electro Corporation). Aqueous-phase acid concentration was determined by an HPLC system (Waters 1523) consisting of a binary pump, refractive index detector (Waters 2414), and dual λ absorbance detector (Waters 2487). The sample was eluted by 0.25 kmol m^{-3} aqueous ammonium dihydrogen phosphate solution adjusted to pH 2.2 by an aqueous phosphoric acid solution endowing at a rate of 0.002 L min^{-1} in a reverse phase C-18 column (4 mm internal diameter × 150 mm length). Propionic acid was detected at 236 nm. The acid content in the organic phase was determined with a mass balance. Few experiments were carried out in duplicate and consistency was found within ±2%.

Results and Discussion

Extraction equilibria

Physical (only MIBK) and chemical extractions (TOA (40%) + MIBK) were compared in Figure 1. Clearly, it can be seen that higher distribution of acid was obtained in TOA + MIBK. This is because of the higher uptake of acid by chemical complexation between acid and TOA according to the following reactions:

$$[\mathrm{HA}]_{\mathrm{aq}} + [\mathrm{T}]_{\mathrm{org}} \overset{K_{\mathrm{E}(1:1)}}{\longleftrightarrow} [\mathrm{T}:\mathrm{HA}]_{\mathrm{org}} \tag{1}$$

$$[\mathrm{HA}]_{\mathrm{aq}} + [\mathrm{T}:\mathrm{HA}]_{\mathrm{org}} \overset{K_{\mathrm{E}}(2:1)}{\longleftrightarrow} [\mathrm{T}:(\mathrm{HA})_2]_{\mathrm{org}} \tag{2}$$

$$[\mathrm{HA}]_{\mathrm{aq}} + [\mathrm{T}:(\mathrm{HA})_{\mathrm{n}-1}]_{\mathrm{org}} \overset{K_{\mathrm{E}(\mathrm{n}:1)}}{\longleftrightarrow} [\mathrm{T}:(\mathrm{HA})_n]_{\mathrm{org}} \tag{3}$$

The uptake of acid by TOA decides which type of acid–TOA complex, i.e. (1:1), (2:1), or (3:1), is formed and which decides the equilibrium complexation constant. In general, for (n:1) complexation:

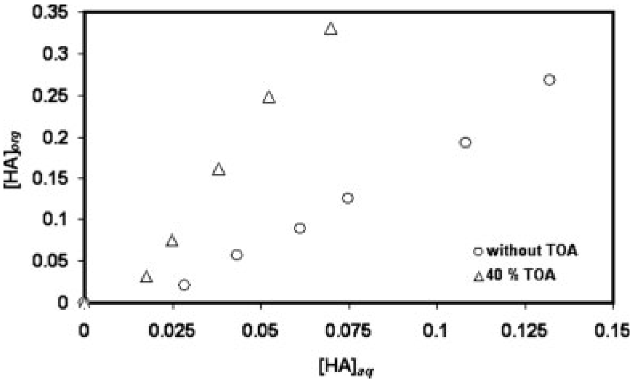

Figure 1. Extraction of propionic acid from aqueous solutions of propionic acid ($[\mathrm{HA}]_o$ = 0.05–0.4 kmol m^{-3}) with and without TOA in MIBK.

○, Without TOA; △, 40% TOA.

$$K_{\mathrm{E}(n:1)} = \frac{[\mathrm{T}:(\mathrm{HA})_n]_{\mathrm{org}}}{[\mathrm{T}]_{\mathrm{org}}[\mathrm{HA}]_{\mathrm{aq}}^n} \tag{4}$$

$K_{\mathrm{E}(n:1)}$ is expected to depend on the properties of the acid and the solvation efficiency of the diluent used. The most important factor associated with the characteristics of acids which affect their equilibrium complexation should be identified with the number of carboxylic groups and their acid strength, the nature and number of additional functional groups (keto acids, hydroxyl acids, etc.) on the molecule, and the size and hydration of the anion. Because only the undissociated acid is extractable, the experimental $K_{\mathrm{E}(n:1)}$ value depends much on the acid strength. The experimentally accessible distribution ratio K_{D} is given as:

$$K_{\mathrm{D}} = \frac{[\mathrm{HA}]_{\mathrm{org}}}{[\mathrm{HA}]_{\mathrm{aq}}} \tag{5}$$

Degree of extraction is defined in terms of K_{D} as

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

Influence of only 30 and 40% TOA in MIBK was studied here. This is because the extraction is maximum at this optimum range of TOA. Below and above this range, lower extractions were obtained. Since the nonpolar TOA by itself is a relatively poor solvating medium for the polar complexes, loading decreases with increasing TOA concentration in diluents, as the solvent becomes a less favorable solvating agent. $E\%$ was found to increase from 58 to 78% by the addition of TOA. Extraction using 40% TOA ($E\%$ = 78%) was slightly higher than 30% TOA ($E\%$ = 77%) in MIBK. The TOA/diluent system favors the formation of not overloaded polar acid–TOA structures corresponding to the loading ratio restricted mainly between 0.03-0.40. Loading ratio is defined as the ratio of acid concentration in organic phase after equilibrium to the initial concentration of TOA. The values of loading factor less than 0.5 depicts no overloading and only (1:1) acid–amine complexes to be formed in all cases.[2] Thus, for $n = 1$, Eq. 4 can be rearranged to get

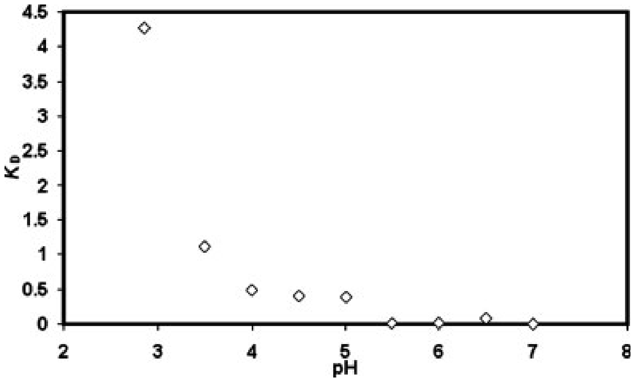

Figure 2. Effect of pH on reactive extraction of propionic acid ($[HA]_o$ = 0.2 kmol m^{-3}) using 40% TOA in MIBK.

$$K_{E(1:1)}[HA]_{aq} = \frac{[T:HA]_{org}}{[T]^{o}_{org} - [T:HA]_{org}} = \frac{[HA]^{total}_{org}}{[T]^{o}_{org} - [HA]^{total}_{org}} = \frac{z}{1-z} \qquad (7)$$

where $[T]_{org}$ was substituted as:

$$[T]_{org} = [T]^{o}_{org} - [T:HA]_{org} \qquad (8)$$

and

$$z = \frac{[HA]^{total}_{org}}{[T]^{o}_{org}} \qquad (9)$$

is the loading ratio. $z/1 - z$ was plotted versus $[HA]_{aq}$ and a straight line passing through the origin was obtained. The value of $K_{E(n:1)}$ was obtained as 3.80 m^3 $kmol^{-1}$.

Effect of pH

Results shown in Figure 1 are at normal (natural) pH of the systems. However, since pH of fermentation broth varies as acid is produced, it becomes important to study the influence of pH of extraction on propionic acid. Figure 2 shows extraction of 0.2 kmol m^{-3} propionic acid using TOA + MIBK when pH was varied from 2.8 to 7. Sodium hydroxide was used for pH adjustment of aqueous solution of propionic acid. Initially, as the pH is increased from natural pH (2.8–3.5), there is a gradual decrease in the extraction and at pH greater than 5.5, very low K_D (<0.02) was observed. Thus, at pH $> pK_a$ of acid, extraction is very low. This is because, at higher pH, most of acid is present in its dissociated from and since TOA extracts only the undissociated form of acid, very low K_D was obtained.

Effect of salts

Fermentation broths contain various salts. With this aim, effect of salts such as NaCl, $(NH_4)_2SO_4$, and K_2HPO_4 on reactive extraction of propionic acid using TOA (40%) in MIBK was studied. The results are presented in Table 1. In studies involving NaCl and $(NH_4)_2SO_4$, ionic strength (I) of the solution varied from 0.05 to 1.5. The values of ionic strengths of system used were as observed in actual fermentation broths.[23,24] With the addition of NaCl, K_D was found to increase with increase in the ionic strength of solution from 0.05 to 0.1; however, decrease in K_D was observed with ionic strength >0.1. An instantaneous fall in K_D was found even when a small amount of NaCl is present in the aqueous system. $(NH_4)_2SO_4$ addition shows similar type of results as observed in the case of NaCl.

Extraction of 0.2 kmol m^{-3} propionic acid was studied by varying K_2HPO_4 from $I = 0.0025$ to 0.02. Again the choice of selection of I values were close to that in actual fermentation systems.[22–25] Similar to NaCl and $(NH_4)_2SO_4$, it was found that with increase in K_2HPO_4 concentration, in the system, K_D was found to first increase and then decrease. The highest K_D values were obtained at $I = 0.005$.

Each salt has different hindrance effects on extraction of the acid. NaCl has great effect whereas effects of $(NH_4)_2SO_4$ and K_2HPO_4 were less significant. Lowest K_D value for propionic acid solutions containing NaCl, $(NH_4)_2SO_4$, and K_2HPO_4, respectively, were found to be 1.56, 3.00, and 3.05. Addition of salt affects the pH of the system; however, Jun et al.[16] reported that they have negligible effect on interfacial concentrations of the succinic acid and TOA. Formation of acids by the anions of salts and H^+ of the acid provides lowering of extraction of propionic acid, because these acids also compete with the acid present in the system for extraction. Presence of propionic acid and NaCl, Na_2SO_4, and K_2HPO_4 in system leads to the formation of acids such as HCl, H_2SO_4, and H_3PO_4 in the aqueous phase, which were extracted by TOA into the organic phase. This also proves that some propionic acid is converted into sodium propionate in the case of NaCl and Na_2SO_4 and potassium propionate in the case of K_2HPO_4. Schunk and Maurer[26] explained the effect on the basis of water coextraction. They found that in the extraction of acetic acid using TOA in MIBK in the presence of NaCl, the stoichiometric molality of water in organic phase increases with increasing stoichiometric molality of both acids in that organic phase. Salting out of MIBK was also pointed out.

Presence of salt should cause the salting out of propionic acid. Thus an increase in distribution coefficient should be

Table 1. Effect of Salts on the Extraction of 0.2 kmol m^{-3} Propionic Acid Using 40% TOA in MIBK

Salt	Ionic strength (I) (kion m^{-3})	pH_o	$[HA]_{org}$ (kmol m^{-3})	K_D	E%
NaCl	0.05	3.21	0.136	2.14	68.13
	0.1	3.10	0.143	2.51	71.54
	0.5	2.92	0.122	1.56	60.98
	1	2.85	0.124	1.62	61.82
	1.5	2.80	0.123	1.59	61.34
Na_2SO_4	0.05	3.39	0.150	2.98	74.88
	0.1	3.57	0.154	3.34	76.97
	0.5	3.66	0.150	2.98	74.90
	1	3.77	0.150	3.02	75.15
	1.5	3.83	0.149	3.04	75.23
K_2HPO_4	0.0025	3.62	0.147	3.07	75.43
	0.005	3.73	0.156	3.53	77.92
	0.01	3.84	0.154	3.31	76.82
	0.015	4.03	0.155	3.26	76.53
	0.02	4.11	0.150	3.05	75.33

Table 2. Effect of Substrate Concentration of Reactive Extraction of 0.2 kmol m^{-3} Propionic Acid Using 40% TOA in MIBK

Salt	Concentration (kg^{-1})	pH$_o$	$[HA]_{org}$ (kmol m^{-3})	K_D	E%
Lactose	0.01	3.55	0.174	6.55	86.76
	0.02	3.60	0.167	5.11	83.63
	0.03	3.63	0.162	4.30	81.14
	0.04	3.65	0.165	4.22	80.84
	0.06	3.60	0.161	4.23	80.88
Dextrose	0.01	3.60	0.166	4.80	82.75
	0.02	3.53	0.166	4.85	82.90
	0.03	3.50	0.165	4.67	82.35
	0.04	3.49	0.164	4.49	81.79
	0.06	3.48	0.157	3.68	78.64

obtained. However, in contrary to it a decrease in the distribution coefficient was found. The reason of this may be that the Cl^-, SO_4^{-2}, HPO_4^{-2} ions of NaCl, Na_2SO_4, and K_2HPO_4, respectively, interact with the hydrogen ion of propionic acid to yield HCl, H_2SO_4, and H_3PO_4 in the aqueous phase. The acid in return converts into sodium propionate and potassium propionate. The salting out effect occurs as the result of the formation of salt–liquid phase complexes with water more than the different acids, respectively. The formation of these complexes reduces the activity of the more attracted component in the solution and increases the activity of the less attracted component that results in expelling or salting out the later from the liquid solution. Thus, salting out occurs but of HCl, H_2SO_4, and H_3PO_4 more than propionic acid. The salted out acid react with amine to form complexes in the organic phase. This effect is different for different salts. Banat et al.[27] suggested that there is a correlation between the ionic radius salting out effect; salting out effect increases with decreasing atomic radius. The smaller ion allows a closer approach to its charge center, which in turn exerts a stronger attractive force for molecular association in solution. Further, it is expected that salting out effect increases with increasing salt concentration owing to increase in intermolecular forces between the salt and the polar component, water in the mixture. The influence of sodium chloride, sodium nitrate, and sodium sulfate was discussed by Schunk and Maurer,[26,28] for extraction of citric acid and acetic acid where similar differences in extraction in presence of respective salts were highlighted. It was explained that when equal volume of an aqueous feed of H_2SO_4 and HCl, respectively, and an organic 1.24 molal feed solution of TOA in MIBK are equilibrated at 298 K, the maximum number for partition coefficient of H_2SO_4 was about 500, whereas it was about 200 for HCl. Thus, this could be another reason for lower K_D value in NaCl system.

Effect of substrate sources

Because there is no 100% conversion of feed material in the fermentation broth, it was decided to study the influence of feed material (lactose and dextrose) on reactive extraction of propionic acid. Concentrations of these sources varied from 0.01 to 0.06 kg L^{-1} as they are normally in this range in a commercial fermentation broth.[24,25] Table 2 shows the extraction of 0.2 kmol m^{-3} using TOA + MIBK, in presence of lactose and dextrose. It can be seen that lower concentrations of both lactose and dextrose in the system resulted K_D values even higher than that obtained without them. However, as their concentration approached 0.04 kg L^{-1}, which is their usual concentration in the fermentation broth, K_D dropped to a value close to that obtained without them. Since, we are interested in studies of recovery of acid from fermentation broths that usually contains substrate source around 0.04 kg L^{-1}, it can be concluded that the presence of substrate does not have any effect on the extraction of acid. Thus, the different feed material does not interfere with the complexation of propionic acid to TOA. However, the marginal reduction in K_D value can be caused by the increased viscosity of the aqueous phase that could have yielded changes in the surface tension at the interface leading to lower complexation and hence lower extraction. However, if conversion of substrate of bioreactor is low, i.e. more of substrate is left unconverted (>0.04 kg L^{-1}) lower K_D would be expected.

Extraction from model solutions

Extraction of propionic acid from model solutions constituting salt and substrate sources was also studied. Six model solutions were prepared as given in Table 3. Concentrations of different component (salts and substrate) were taken as usually found in fermentation broths.[22–25] Concentration of substrate source (0.02 kg L^{-1} each) and NaCl were fixed in all model systems. Two concentrations of Na_2SO_4 and three concentrations of K_2HPO_4 were chosen. Table 4 shows equilibrium data for extraction of 0.2 kmol m^{-3} propionic acid from different model solution. Difference in behavior of the different system can be accounted as due to Na_2SO_4 and K_2HPO_4 as other constituents are fixed.

Physical extraction was nearly uninfluenced by the presence of salts and substrates. Values of K_D were nearly constant for respective acid concentrations (0.1, 0.2, and 0.4 kmol m^{-3}, respectively). Chemical extraction in all cases gives higher K_D values in comparison with physical extractions. At lower concentrations of both salts (system 2), extraction was higher among all systems for acid concentration for 0.2 and 0.4 kmol m^{-3} aqueous acid concentrations. The probable reason for that may be the acid was always in

Table 3. Description of Model Solutions Used in the Study

System	NaCl (kmol m^{-3})	Na_2SO_4 (kmol m^{-3})	K_2HPO_4 (kg^{-1})	Lactose (kg^{-1})	Dextrose (kg^{-1})	pH$_o$
Model 1	0.05	0.033	0.000145	0.02	0.02	3.54
Model 2	0.05	0.017	0.000145	0.02	0.02	3.45
Model 3	0.05	0.017	0.000290	0.02	0.02	3.50
Model 4	0.05	0.033	0.000290	0.02	0.02	3.57
Model 5	0.05	0.033	0.000871	0.02	0.02	3.81
Model 6	0.05	0.017	0.000871	0.02	0.02	3.80

Table 4. Effect of Model Solutions on Reactive Extraction of Propionic Acid Using 40% TOA in MIBK

			Without TOA		With TOA	
$[HA]_o$ kmol/m^3	Model	pH$_o$	$[HA]_{org}$ (kmol m^{-3})	K_D	$[HA]_{org}$ (kmol m^{-3})	K_D
0.1	1	3.70	0.0518	1.339	0.0578	1.371
	2	3.62	0.0569	1.320	0.0631	1.709
	3	3.69	0.0606	1.539	0.0609	1.559
	4	3.77	0.0567	1.308	0.0604	1.526
	5	4.06	0.0573	1.339	0.0656	1.905
	6	4.03	0.0579	1.377	0.0665	1.987
0.2	1	3.54	0.1305	1.877	0.1426	2.484
	2	3.45	0.1307	1.885	0.1447	2.617
	3	3.50	0.1315	1.921	0.1473	2.794
	4	3.57	0.1345	2.053	0.1440	2.573
	5	3.81	0.1343	2.042	0.1434	2.532
	6	3.80	0.1258	1.697	0.1444	2.600
0.4	1	3.54	0.2887	2.595	0.2999	2.996
	2	3.45	0.2728	2.145	0.3187	3.921
	3	3.50	0.2761	2.227	0.3176	3.852
	4	3.57	0.2775	2.266	0.3158	3.751
	5	3.81	0.2772	2.257	0.3143	3.469
	6	3.80	0.2737	2.166	0.3091	3.500

excess above that is converted to H_2SO_4 and H_3PO_4, thus yielding higher K_D values. However, this cannot be accounted for lower concentration of the acid (0.1 kmol m^{-3}), where it was found that higher K_D is obtained for systems 5 and 6 (highest concentration of K_2HPO_4). For acid concentrations of 0.2 and 0.4 kmol m^{-3} and Na_2SO_4 concentration of 0.017 kmol m^{-3}, K_D was found to be higher at K_2HPO_4 concentration of less than 0.29, whereas for 0.1 kmol m^{-3} propionic acid solution and for both concentrations of Na_2SO_4, higher K_D was found to be at higher K_2HPO_4 concentration. The trend is similar to that obtained when only K_2HPO_4 was present in the system. For fixed K_2HPO_4 concentration, K_D was found to decrease with increase in Na_2SO_4 concentration for all acid concentrations studied. The best extraction systems giving higher extractions were model solutions 2 and 3 where either both Na_2SO_4 and K_2HPO_4 are present in low concentration (0.017 and 0.145 kmol m^{-3} respectively) (Model 2) or where Na_2SO_4 is in low concentration (0.017 kmol m^{-3}) and K_2HPO_4 of 0.290 kmol m^{-3} is present (Model 3).

Effect of temperature on extraction from model solutions

Usually bioreactors operate at temperature close to 313 K.[15] With this regard, effect of temperature on reactive extraction of propionic acid was studied and presented in Table 5. Model systems 1, 2, and 3 were considered for the study. Varying results were obtained. In Model system 1, extraction was found to increase with increase in temperature, whereas for Model system 3, the trend was reverse. For Model system 2, K_D decreases with increase in temperature from 305 to 313 K, whereas it increases as temperature increased from 313 to 333 K. Although some variation on K_D was observed for the three model solutions, overall there is only slight effect of temperature on extraction of propionic acid from all the broths. This concludes that temperature variation from 305 to 333 K have had negligible effect on reactive extraction of propionic acid from model solutions.

Conclusions

Reactive extraction of propionic acid was carried out to study the effects of pH, salts, substrate sources, model solutions, and temperature using TOA (40%) + MIBK. Increase in pH brought an abrupt decrease in the extraction of propionic acid (0.2 kmol m^{-3}) by TOA (40%) + MIBK, with nearly no extraction at pH > pK_a of the acid. Different salts have different effects on the propionic acid extraction from aqueous solution containing them. Greater reduction in K_D was found for propionic acid aqueous solution containing NaCl, whereas $(NH_4)_2SO_4$ and K_2HPO_4 containing solutions have little effect on extraction by TOA (40%) + MIBK. Different model solutions (with $[HA]_o = 0.1$, 0.2, and 0.4 kmol m^{-3}) were prepared containing salt and substrate mixtures in various proportions and extraction of acid by TOA in MIBK

Table 5. Effect of Temperature on Reactive Extraction of 0.2 kmol m^{-3} Propionic Acid From Model Solutions

Temperature (K)	Model	pH$_o$	$[HA]_{aq}$ (kmol m^{-3})	$[HA]_{org}$ (kmol m^{-3})	K_D	E %
305	1	3.54	0.057	0.143	2.48	71.30
	2	3.45	0.055	0.145	2.62	72.35
	3	3.50	0.053	0.147	2.79	73.64
313	1	3.54	0.061	0.152	2.50	71.41
	2	3.45	0.059	0.141	2.39	70.50
	3	3.50	0.057	0.143	2.54	71.73
333	1	3.54	0.055	0.145	2.66	72.65
	2	3.45	0.055	0.145	2.63	72.47
	3	3.50	0.058	0.142	2.43	70.87

was carried out. Concentration of substrate source and NaCl was fixed and Na_2SO_4 and K_2HPO_4 concentrations were varied. The trend was found to be same as was obtained when Na_2SO_4 and K_2HPO_4 were present alone in the propionic acid aqueous system. However, lower values of K_D were obtained in comparison with aqueous solutions containing no salts or substrate. Temperature was found to have negligible effect on extractions from model solutions.

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Notation

K_D = distribution coefficient
$K_{E(1:1)}$ = extraction equilibrium constant for (1:1) acid–extractant complex $(\text{kmol m}^{-3})^{-1}$
$K_{E(2,1)}$ = extraction equilibrium constant for (2:1) acid–extractant complex $(\text{kmol m}^{-3})^{-2}$
$K_{E(n:1)}$ = extraction equilibrium constant for (n:1) acid–extractant complex $(\text{kmol m}^{-3})^{-n}$
[HA] = concentration of acid (kmol m^{-3})
[T] = concentration of extractant (kmol m^{-3})
[T:HA] = concentration of acid–amine complex (kmol m^{-3})
$E\%$ = degree of extraction
z = loading ratio
$[HA]_{org}^{total}$ = total acid extracted into organic phase (kmol m^{-3})

Subscripts

aq = aqueous phase
org = organic phase
o = initial

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