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Equilibrium Studies for Extraction of Propionic Acid Using Tri-*n*-Butyl Phosphate in Different Solvents

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Propionic acid extraction from the aqueous phase is important in view of its number of uses. The recovery technique should provide high selectivity and yield. A number of techniques like distillation, membrane, dialysis, electrodialysis, and reactive extraction are available. The profound success of reactive extraction has been noted in the recovery of carboxylic acids from dilute solutions. In the present paper, equilibrium with propionic acid using tri-*n*-butyl phosphate, an organophosphorous compound, in eight different diluents (1-dodecanol, benzene, toluene, heptane, hexane, butyl acetate, petroleum ether, and paraffin liquid) has been studied. Equilibrium parameters such as distribution coefficients, loading ratio, degree of extraction, and equilibrium complexation constants have been presented. The data obtained are useful in understanding the equilibrium characteristics and efficient design of the recovery process of propionic acid by reactive extraction.

Introduction

A number of carboxylic acids are obtained by bioprocessing of natural products such as by fermentation. A problem posed in fermentation is the recovery of the product acid. The recovery of these valuable products is always a challenge for both pharmaceutical and food industries, which are their major users. A number of methods are available such as precipitation, adsorption, membranes, dialysis, distillation, ion exchange, or reactive extraction to recover carboxylic acids from fermentation broths.[1] Conventionally, precipitation by calcium hydroxide was employed to extract carboxylic acids, but the method is expensive as it employs a large amount of chemicals and is environmentally unfriendly as it produces a large amount of waste sludge. Alternative methods have always been discussed to recover the acid.

Reactive extraction is an important recovery technique, which has received increasing attention over the past decade, particularly for recovery of carboxylic acids.[2–5] Reactive extraction employs an extractant to remove the acid. Extractants are usually classified as: (i) anion exchange extractants (e.g., aliphatic primary, secondary, and tertiary amines), which form ion pairs (salts) in acidic medium; (ii) cation exchange extractants (e.g., phosphine and phosphoric acid), which exchange the proton against the cation; (iii) solvating extractants (e.g., phosphoric and phosphinic acid, esters, and phosphinoxides), which are Lewis bases and form nonstoichiometric compounds with neutral solutes; and (iv) chelate-forming extractants (e.g., aliphatic and aromatic hydroxyines), which exchange the cation and form coordinate binding.

Extractants are generally viscous liquids or solids, so they are dissolved in diluents, which improve their physical properties like surface tension and viscosity. Diluents provide the solution of the extractants and also general and specific solvation to the extractant−acid complexes formed. Polar diluents are more favorable than low polarity, low dielectric constant, aliphatic, or aromatic hydrocarbons. The solvation of the whole extractant−acid complex is based on dipole−dipole interaction and has been found to play an important role in the neutralization reaction between acid and extractant, which is promoted by increasing the polarity of the diluent.

Propionic acid is an important carboxylic acid used in food industries, manufacture of fungicides, herbicides, plasticizers, and pharmaceuticals.[6] Propionic acid salts are used primarily for animal feed preservation, including hay, silage, and grains, and in human foods, mainly in baked goods and cheeses. Propionic acid is also used as an intermediate in the synthesis of herbicides, cellulose acetate−propionate plastics, and pharmaceuticals and in alkyl propionate esters for solvents. Very small volumes of propionate esters are used as flavors and fragrances. Propionic acid inhibits the growth of mold and some bacteria. Accordingly, most propionic acid produced is used as a preservative for both animal feed and food for human consumption. For animal feed, it is used either directly or as its ammonium salt. In human foods, especially bread and other baked goods, it is used as its sodium or calcium salt. It can be used to modify synthetic cellulose fibers. Specific uses of propionic acid draw attention toward a better recovery process, which will increase the productivity and reduce the overall production cost.

Industrial production of propionic acid is by a petrochemical route which includes carbonylation of ethylene with carbon monoxide and water, oxidation of propanal, and direct oxidation of hydrocarbons.[7] Since the price of petrochemical products is increasing, the production by fermentation route is gaining interest. Propionic acid is produced biologically by its coenzyme A-ester, propionyl-CoA, from the metabolic breakdown of fatty acids containing odd numbers of carbon atoms, and also it is the product of the breakdown of some amino acids. Bacteria of the genus *Propionibacterium* produce propionic acid as the end product of their anaerobic metabolism.

Conventional fermentation technologies for propionic acid production from glucose or lactose are limited by low reactor productivity ($<1\ \mathrm{g\cdot L^{-1}\cdot h^{-1}}$), low product mass fraction yield

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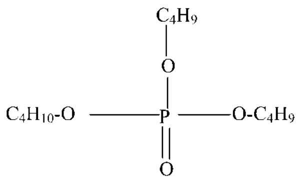
($w < 0.50$), and low product concentration ($<40\ \mathrm{g{\cdot}L^{-1}}$). The low productivity and low product concentration in the conventional propionic acid fermentations can be attributed to the fact that propionic acid bacteria are strongly inhibited by propionic acid, especially when the pH is below 6.[8,9] Extractive fermentation is a relatively new technology that has been shown to be advantageous for alcohol and organic acid fermentations.[10] The advantages for extractive fermentation 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. Extractive fermentation also may allow the process to produce and recover the fermentation product in one continuous step and reduce the downstream processing load and the recovery costs. However, to date, only limited success in organic acid extractive fermentation has been achieved with carboxylic acid fermentation.[11,12] Very little has been done with propionic acid extractive fermentation.[13,4] Furthermore, no extractive fermentation process has been demonstrated for its long-term use to produce an organic acid.

Zhong et al.[14] studied the reactive extraction of propionic acid using Alamine 304-1 in 2-octanol, 1-dodecanol, and Withohol 85 NF as diluents at various amine volume fractions from (0 to 100) % and found extraction to be maximum at the amine volume fraction between (20 and 40) %. Diluents significantly effect the extraction power of the extractant, with 2-octanol providing the highest distribution coefficient of the three. Extraction of different carboxylic acids using tri-*n*-butyl phosphate (TBP), tri-*n*-octylamine, and their mixtures was investigated by Matsumato et al.,[12] and the synergistic effect was highlighted in improving the extraction. Studies on the propionic acid reactive extraction using trioctylamine in various diluents (hexanol, butyl acetate, and petroleum ether) show the positive effect of the different diluents on the extraction.[4] Uslu et al.[15] 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. However a study on the same acid with the tertiary amine (Alamine 336) diluted in toluene at 298.15 K indicated more propionic acid to be transferred to the organic phase than would be expected from the 1:1 stoichiometry of the reaction, thus 2:1 and 3:1 acid−amine complexes were considered.[16] This indicates that complexation depends on the extractant−diluent system chosen.

In the present work, reactive extraction of propionic acid was studied using TBP, an organophosphorous compound, in eight different categories of diluents: 1-dodecanol (alcohol); benzene, toluene (aromatic hydrocarbons); heptane, hexane (inert), butyl acetate (ester); petroleum ether (ether) and paraffin liquid (mixture of hydrocarbons). A comparison of the type of diluents on extraction was investigated. Physical extraction using these diluents and chemical extraction using TBP with a volume fraction of (10 to 40) % in respective diluents were performed and compared. Extraction mechanism, distribution coefficient, and equilibrium complexation constants were determined. The difference in degree of extraction is discussed.

Experimental

Chemicals. Tri-*n*-butyl phosphate (volume fraction of 99 %) (Himedia, India), a phosphorus-bonded oxygen donor, is a light colorless liquid with the molar mass of $266.32\ \mathrm{g{\cdot}mol^{-1}}$ and density of $0.92\ \mathrm{g{\cdot}cm^{-3}}$. The chemical structure is as below



Propionic acid (volume fraction of 99 %) (Himedia, India) and the diluents: heptane (Ranbaxy Ltd., India), toluene (Nice Ltd., India), hexane (Ranbaxy Ltd., India), butyl acetate (SRL Ltd., India), 1-dodecanol (Acros, USA), benzene (Ranbaxy Ltd., India), petroleum ether (SD. Fine Chem. Ltd., India), and paraffin liquid (RFCL Ltd., India) are of technical grade and were used as supplied by suppliers. These diluents were used to see the effect of alcohol (1-dodecanol), ether (petroleum ether), aromatic hydrocarbons (benzene, toluene), inert (hexane, heptane), mixed aliphatic hydrocarbons (paraffin liquid), and ester (butyl acetate) on the solvation of the complex in the reactive extraction of propionic acid. Distilled water was used to prepare the solutions of various concentrations of propionic acid. NaOH used for titration is of analytical grade and was supplied by Ranbaxy, India. For the standardization of the NaOH, oxalic acid (99.8 %) was obtained from S.D. Fine-Chem Ltd., India. Phenolphthalein solution (pH range 8.2 to 10.0) was used as an indicator for titration and was obtained from Ranbaxy, India. The initial TBP concentrations in the range of $(0.37\ \text{to}\ 1.65)\ \mathrm{mol{\cdot}L^{-1}}$ and the initial aqueous acid concentration range ($[\mathrm{HA}]^{\circ}$) of $(0.05\ \text{to}\ 0.4)\ \mathrm{mol{\cdot}L^{-1}}$ were used (where superscript "o" signifies the initial). Low concentration was used because propionic acid concentration in the fermentation broth is not greater than $0.5\ \mathrm{mol{\cdot}L^{-1}}$.[17]

Procedure. The extraction experiments were performed using a temperature-controlled water bath shaker (Remi Equipment Pvt. Ltd., India) at constant temperature (305 K). Equal volumes ($25\ \mathrm{cm^3}$) of aqueous and organic phases were taken in a 100 mL conical flask and were shaken for 12 h. This could be considered as the appropriate time for attaining equilibrium. The solutions were then made to settle for at least 2 h at a fixed temperature (305 K) and atmospheric pressure in a separating funnel.[2] The lower phase was taken for analysis after filtration through the MILLEX GV filter unit ($0.22\ \mu\mathrm{m}$).

Analysis Method. Aqueous phase pH was measured by an Orion 3 star pH benchtop (Thermo Electro Corporation). The aqueous phase acid concentration was determined by titration with NaOH and by HPLC. The wavelength of operation ($\lambda = 230$) in HPLC was measured by a UV spectrophotometer. The HPLC system (Waters 1523) was composed of a binary pump, refractive index detector (Waters 2414), and dual λ absorbance detector (Waters 2487). The column used was C-18. Table 1 shows the comparison of typical results obtained by titration and HPLC for propionic acid solutions. The results of the above methods were comparable (with an uncertainity of less than 2 %) provided that NaOH is prepared fresh every time before titration was to be carried out. So, remaining acid measurements were made by the HPLC system only, and the results of experiments by HPLC were reported in the present work. The acid content in the organic phase was determined by mass balance.

Table 1. Comparison of Analysis Methods Used for Extraction of Propionic Acid

	$[HA]°/mol \cdot L^{-1}$		% deviation	% deviation
actual	by titration	by HPLC	in titration	in HPLC
0.0500	0.0510	0.0501	2.00	0.24
0.1000	0.0982	0.1012	1.80	1.20
0.1500	0.1520	0.1512	1.33	0.80
0.2000	0.1996	0.2046	0.20	2.30
0.3000	0.3050	0.3028	1.67	0.93
0.4000	0.4105	0.3998	2.62	0.05

Results and Discussion

Extractants employed for reactive extraction of carboxylic acids are classified by King et al.[18] as conventional carbon bonded oxygen bearing extractants, organophosphorous extractants, and higher molar mass aliphatic amines, on the basis of extraction mechanism involved. In the category of carbon bonded oxygen bearing diluents like alcohols, ethers, ketones, etc., the extracting ability results from the solvating characteristics of the oxygen donor. The extraction commonly called physical extraction involves the solvation of acid molecules by donor bonds. The physical extraction of propionic acid using 1-dodecanol, benzene, toluene, heptane, hexane, butyl acetate, petroleum ether, and paraffin liquid was performed and shown in Figure 1. Except for butyl acetate and 1-dodecanol, the extraction was poor.

Table 2 shows the values of partition (distribution) coefficient (ratio of organic to aqueous phase concentration of acid) and dimerization constants of the extraction of propionic acid in the respective solvents determined as according to the work of King et al.[2] The values of distribution coefficients were found to follow the trend ester (butyl acetate) > alcohol (1-dodecanol) > aromatic hydrocarbon with side group (toluene) > ether (petroleum ether) > aromatic hydrocarbon without any side group (benzene) > inerts (hexane, heptane, and paraffin liquid). Propionic acid has a high affinity to water and low relative volatility that renders it difficult to separate. The low activity of propionic acid toward these diluents, i.e., its higher solubility in water than in organic solvents, is the cause of the low distribution coefficient (<1). Further, since these solvents are relatively soluble in water, the back recovery of them proves to be costly. The conventional extraction techniques are thus unprofitable. Better possibilities are offered by the reactive extraction technique by employing organophosphorous compounds and amines which have proved to be effective in the recovery of carboxylic acids.[18]

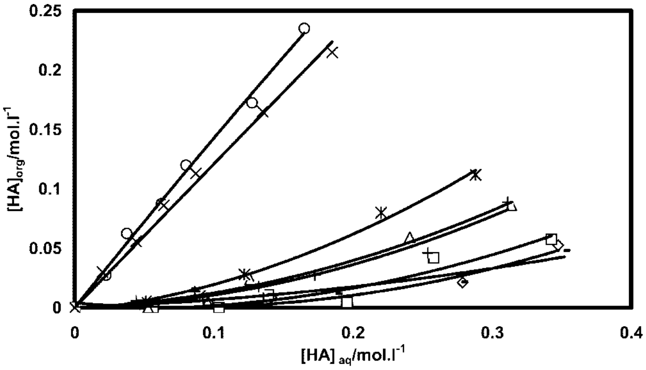


Figure 1. Physical extraction of propionic acid in different diluents. ◇, paraffin liquid; Δ, petroleum ether; +, benzene; ×, 1-dodecanol; □, heptane; $*$, toluene; −, hexane; ○, butyl acetate.

Table 2. Partition and Dimerization Coefficients for Propionic Acid Extracted from Water into Organic Solvents at 305 K[a]

diluent	partition coefficient (A)	dimerization coefficient (B)
heptane	0.0052	0.5058
petroleum ether	0.0504	0.7414
hexane	0.045	0.2179
butyl acetate	1.4681	–
1-dodecanol	1.4059	–
toluene	0.0858	1.1009
benzene	0.0307	0.7542
paraffin liquid light	0.0031	0.5454

[a] $[HA]_{org} = A[HA]_{aq} + B[HA]_{aq}^2$.

Table 3. Extraction Equilibrium Results for the Propionic Acid + TBP + *n*-Butyl Acetate System at 305 K for Various Concentrations of TBP and Acid

$S_{org}^{initial}$ $mol \cdot L^{-1}$	$[HA]°$ $mol \cdot L^{-1}$	$[HA]_{aq}$ $mol \cdot L^{-1}$	$[HA]_{org}$ $mol \cdot L^{-1}$	K_D	E	pH_{aq}	Z_t
0.37	0.05	0.02	0.04	2.33	70.00	3.46	0.09
	0.10	0.03	0.07	2.08	67.50	3.25	0.18
	0.15	0.04	0.11	2.75	73.33	3.20	0.30
	0.20	0.06	0.14	2.33	70.00	3.09	0.38
	0.30	0.10	0.21	2.16	68.33	2.98	0.55
	0.40	0.14	0.26	1.91	65.63	2.89	0.71
0.74	0.05	0.02	0.04	2.33	70.00	3.46	0.05
	0.10	0.02	0.08	3.44	77.50	3.35	0.10
	0.15	0.05	0.11	2.33	70.00	3.17	0.14
	0.20	0.06	0.15	2.64	72.50	3.11	0.20
	0.30	0.08	0.22	2.75	73.33	3.02	0.30
	0.40	0.11	0.29	2.64	72.50	2.95	0.39
1.10	0.05	0.01	0.04	3.00	75.00	3.51	0.03
	0.10	0.02	0.08	3.44	77.50	3.35	0.07
	0.15	0.03	0.12	4.45	81.67	3.29	0.11
	0.20	0.05	0.15	3.00	75.00	3.14	0.14
	0.30	0.06	0.25	4.45	81.67	3.11	0.22
	0.40	0.08	0.33	4.33	81.25	3.04	0.30
1.65	0.05	0.02	0.03	2.00	66.72	3.43	0.02
	0.10	0.06	0.04	0.67	40.20	3.09	0.05
	0.15	0.04	0.11	2.39	70.53	3.17	0.07
	0.20	0.05	0.15	3.09	75.56	3.14	0.09
	0.30	0.08	0.22	2.95	74.69	3.03	0.14
	0.40	0.10	0.30	3.01	75.04	2.97	0.18

Table 4. Extraction Equilibrium Results for the Propionic Acid + TBP + 1-Dodecanol System at 305 K for Various Concentrations of TBP and Acid

$S_{org}^{initial}$ $mol \cdot L^{-1}$	$[HA]°$ $mol \cdot L^{-1}$	$[HA]_{aq}$ $mol \cdot L^{-1}$	$[HA]_{org}$ $mol \cdot L^{-1}$	K_D	E	pH_{aq}	Z_t
0.37	0.05	0.02	0.03	1.78	64.00	3.41	0.09
	0.10	0.04	0.06	1.56	61.00	3.20	0.16
	0.15	0.06	0.10	1.73	63.33	3.11	0.26
	0.30	0.13	0.17	1.38	58.00	2.91	0.47
	0.40	0.17	0.23	1.34	57.25	2.84	0.62
0.74	0.05	0.02	0.03	1.63	62.00	3.39	0.04
	0.10	0.04	0.07	1.86	65.00	3.23	0.09
	0.15	0.06	0.09	1.59	61.33	3.10	0.12
	0.30	0.12	0.18	1.50	60.00	2.92	0.24
	0.40	0.15	0.25	1.67	62.50	2.87	0.34
1.10	0.05	0.02	0.04	2.33	70.00	3.46	0.03
	0.10	0.03	0.07	1.94	66.00	3.24	0.06
	0.15	0.05	0.10	2.00	66.67	3.14	0.09
	0.30	0.14	0.16	1.14	53.33	2.89	0.15
	0.40	0.13	0.27	2.01	66.75	2.90	0.24
1.65	0.05	0.01	0.04	2.57	72.00	3.48	0.02
	0.10	0.03	0.07	2.57	72.00	3.29	0.04
	0.15	0.05	0.11	2.33	70.00	3.17	0.06
	0.30	0.09	0.21	2.33	70.00	2.99	0.13
	0.40	0.12	0.28	2.45	71.00	2.93	0.17

Organophosphorous compounds are effective extractants and provide higher distribution coefficients than carbon bonded oxygen bearing extractants. The chemical stability of organophosphorous compounds plays an important role in the possibility of its use as an efficient extracting solution with good

Table 5. Extraction Equilibrium Results for the Propionic Acid + TBP + Hexane System at 305 K for Various Concentrations of TBP and Acid

$S_{\text{org}}^{\text{initial}}$ mol·L^{-1}	$[\text{HA}]^{\circ}$ mol·L^{-1}	$[\text{HA}]_{\text{aq}}$ mol·L^{-1}	$[\text{HA}]_{\text{org}}$ mol·L^{-1}	K_D	E	pH_{aq}	Z_t
0.37	0.05	0.02	0.03	1.08	52.00	3.33	0.07
	0.10	0.06	0.04	0.79	44.00	3.11	0.12
	0.15	0.08	0.08	1.00	50.00	3.04	0.20
	0.20	0.11	0.09	0.87	46.50	2.95	0.25
	0.30	0.17	0.13	0.79	44.00	2.85	0.36
	0.40	0.24	0.16	0.69	41.00	2.77	0.44
0.74	0.05	0.02	0.03	1.63	62.00	3.39	0.04
	0.10	0.04	0.06	1.70	63.00	3.22	0.09
	0.15	0.07	0.08	1.05	51.33	3.04	0.10
	0.20	0.09	0.11	1.25	55.50	3.00	0.15
	0.30	0.11	0.19	1.78	64.00	2.95	0.26
	0.40	0.16	0.24	1.45	59.25	2.85	0.32
1.10	0.05	0.01	0.04	2.57	72.00	3.48	0.03
	0.10	0.03	0.07	2.45	71.00	3.28	0.06
	0.15	0.04	0.11	2.85	74.00	3.20	0.10
	0.20	0.06	0.14	2.57	72.00	3.11	0.13
	0.30	0.09	0.22	2.53	71.67	3.01	0.20
	0.40	0.13	0.27	2.05	67.25	2.90	0.24
1.65	0.05	0.01	0.04	3.55	78.00	3.55	0.02
	0.10	0.02	0.08	3.17	76.00	3.33	0.05
	0.15	0.03	0.12	3.55	78.00	3.25	0.07
	0.20	0.05	0.15	3.35	77.00	3.16	0.09
	0.30	0.07	0.23	3.35	77.00	3.06	0.14
	0.40	0.10	0.30	2.92	74.50	2.96	0.18

Table 6. Extraction Equilibrium Results for the Propionic Acid + TBP + Toluene System at 305 K for Various Concentrations of TBP and Acid

$S_{\text{org}}^{\text{initial}}$ mol·L^{-1}	$[\text{HA}]^{\circ}$ mol·L^{-1}	$[\text{HA}]_{\text{aq}}$ mol·L^{-1}	$[\text{HA}]_{\text{org}}$ mol·L^{-1}	K_D	E	pH_{aq}	Z_t
0.37	0.05	0.03	0.03	1.00	50.00	3.32	0.07
	0.10	0.05	0.05	0.98	49.50	3.14	0.13
	0.15	0.08	0.07	0.92	48.00	3.03	0.19
	0.20	0.11	0.09	0.89	47.00	2.95	0.25
	0.30	0.17	0.13	0.78	43.67	2.84	0.35
	0.40	0.22	0.18	0.84	45.63	2.79	0.49
0.74	0.05	0.02	0.03	1.78	64.00	3.41	0.04
	0.10	0.04	0.06	1.78	64.00	3.22	0.09
	0.15	0.05	0.10	1.78	64.00	3.12	0.13
	0.20	0.07	0.13	1.78	64.00	3.05	0.17
	0.30	0.12	0.18	1.59	61.33	2.93	0.25
	0.40	0.15	0.25	1.61	61.75	2.87	0.33
1.10	0.05	0.01	0.04	2.57	72.00	3.48	0.03
	0.10	0.03	0.07	2.57	72.00	3.29	0.07
	0.15	0.04	0.11	2.66	72.67	3.19	0.10
	0.20	0.06	0.14	2.51	71.50	3.11	0.13
	0.30	0.09	0.21	2.45	71.00	3.00	0.19
	0.40	0.12	0.28	2.45	71.00	2.93	0.26
1.65	0.05	0.01	0.04	3.55	78.00	3.55	0.02
	0.10	0.02	0.08	3.35	77.00	3.34	0.05
	0.15	0.03	0.12	3.41	77.33	3.24	0.07
	0.20	0.05	0.16	3.44	77.50	3.17	0.09
	0.30	0.07	0.23	3.11	75.67	3.04	0.14
	0.40	0.09	0.31	3.26	76.50	2.98	0.19

Table 7. Extraction Equilibrium Results for the Propionic Acid + TBP + Benzene System at 305 K for Various Concentrations of TBP and Acid

$S_{\text{org}}^{\text{initial}}$ mol·L^{-1}	$[\text{HA}]^{\circ}$ mol·L^{-1}	$[\text{HA}]_{\text{aq}}$ mol·L^{-1}	$[\text{HA}]_{\text{org}}$ mol·L^{-1}	K_D	E	pH_{aq}	Z_t
0.37	0.05	0.02	0.03	1.89	65.45	3.42	0.09
	0.10	0.03	0.07	2.06	67.27	3.25	0.18
	0.15	0.04	0.11	2.37	70.30	3.17	0.29
	0.20	0.07	0.13	2.06	67.27	3.07	0.36
	0.30	0.09	0.21	2.44	70.91	3.00	0.57
	0.40	0.13	0.27	2.19	68.64	2.91	0.74
0.74	0.05	0.03	0.02	0.79	44.00	3.29	0.03
	0.10	0.05	0.05	1.13	53.00	3.15	0.07
	0.15	0.06	0.09	1.34	57.33	3.08	0.12
	0.20	0.10	0.11	1.11	52.50	2.98	0.14
	0.30	0.13	0.17	1.29	56.33	2.90	0.23
	0.40	0.18	0.22	1.27	56.00	2.84	0.30
1.10	0.05	0.02	0.03	1.75	63.64	3.41	0.03
	0.10	0.03	0.07	2.79	73.64	3.31	0.07
	0.15	0.04	0.11	2.67	72.73	3.19	0.10
	0.20	0.06	0.14	2.61	72.27	3.11	0.13
	0.30	0.09	0.21	2.51	71.52	3.01	0.20
	0.40	0.11	0.29	2.49	71.36	2.94	0.26
1.65	0.05	0.01	0.04	2.67	72.73	3.49	0.02
	0.10	0.02	0.08	3.40	77.27	3.34	0.05
	0.15	0.03	0.12	3.34	76.97	3.23	0.07
	0.20	0.05	0.15	3.23	76.36	3.15	0.09
	0.30	0.07	0.23	3.07	75.45	3.04	0.14
	0.40	0.10	0.30	3.19	76.14	2.98	0.18

separation effect with 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 is selected because of its low water coextraction (mass fraction is 4.67 %) and very low solubility in the aqueous phase (mass fraction is 0.039 %). TBP contains the =P(O)OH group, which has a marked tendency toward 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 knowledge of these factors is necessary for understanding the mechanism of extraction, the effect of diluents, and the role of additional reagents.

Since TBP has a relatively high viscosity ($3.56 \cdot 10^{-3}$ Pa·s) and density close to unity (0.98 g·cm^{-3}), it is used along with low viscosity and low density diluents, which could facilitate good phase separation in the continuous extraction process. Diluents chosen in the study were chosen from different chemical classes to examine the effect of diluent−complex interactions. These interactions were found to affect the stoichiometry of reaction and magnitude of the corresponding equilibrium constants.

The chemical extraction data for propionic acid extraction using TBP in different diluents are presented in Tables 3 to 10. The data clearly show that chemical extraction is far better than physical extraction. The K_D values (defined as the ratio of total (analytical) concentration of acid in all its forms (by partition, dimmers, and as complexes) in the organic phase and total (analytical) concentration of all its existing forms (dissociated and undissociated) in aqueous raffinate) were found to increase with an increase in TBP concentration in different diluents. However, as stated earlier, TBP being viscous was used only up to a volume fraction of 40 % in different diluents. K_D variation with initial acid concentration was found to first increase and then decrease on increasing the acid concentration from (0.05 to 0.4) mol·L^{-1}. The similar trend was found for degree of extraction (E) defined as

$$E = \frac{K_D \cdot 100}{1 + K_D} \tag{1}$$

It is well-known that carboxylic acid dissociates in aqueous solution. Under the experimental condition where the pH of the aqueous solution was smaller than the pK_a of the acid (4.67), the effect of the acid dissociation was negligibly small. Thus, only the undissociated form of the acid was expected to exist in the aqueous phase. The mass law equilibria describing the

Table 8. Extraction Equilibrium Results for the Propionic Acid + TBP + Heptane System at 305 K for Various Concentrations of TBP and Acid

$S^{\text{initial}}_{\text{org}}$ / mol·L^{-1}	$[\text{HA}]^{\circ}$ / mol·L^{-1}	$[\text{HA}]_{\text{aq}}$ / mol·L^{-1}	$[\text{HA}]_{\text{org}}$ / mol·L^{-1}	K_D	E	pH_{aq}	Z_t
0.37	0.05	0.03	0.02	0.79	44.00	3.29	0.06
	0.10	0.05	0.05	0.85	46.00	3.12	0.12
	0.15	0.09	0.06	0.70	41.33	3.00	0.17
	0.20	0.12	0.08	0.67	40.00	2.92	0.22
	0.30	0.19	0.11	0.55	35.67	2.81	0.29
	0.40	0.26	0.14	0.57	36.13	2.75	0.39
0.74	0.05	0.03	0.03	1.00	50.00	3.32	0.03
	0.10	0.04	0.06	1.50	60.00	3.20	0.08
	0.15	0.06	0.09	1.42	58.67	3.08	0.12
	0.20	0.09	0.11	1.29	56.25	3.00	0.15
	0.30	0.14	0.16	1.16	53.67	2.89	0.22
	0.40	0.18	0.22	1.23	55.25	2.83	0.30
1.10	0.05	0.02	0.03	1.78	64.00	3.41	0.03
	0.10	0.03	0.07	2.08	67.50	3.25	0.06
	0.15	0.05	0.10	2.00	66.67	3.14	0.09
	0.20	0.07	0.13	1.94	66.00	3.06	0.12
	0.30	0.11	0.20	1.86	65.00	2.96	0.18
	0.40	0.14	0.26	1.86	65.00	2.89	0.24
1.65	0.05	0.02	0.03	1.78	64.00	3.41	0.02
	0.10	0.02	0.08	3.17	76.00	3.33	0.04
	0.15	0.05	0.10	2.13	68.00	3.15	0.06
	0.20	0.06	0.14	2.51	71.50	3.11	0.08
	0.30	0.09	0.21	2.49	71.33	3.00	0.12
	0.40	0.11	0.29	2.54	71.75	2.94	0.16

Table 9. Extraction Equilibrium Results for the Propionic Acid + TBP + Paraffin Liquid System at 305 K for Various Concentrations of TBP and Acid

$S^{\text{initial}}_{\text{org}}$ / mol·L^{-1}	$[\text{HA}]^{\circ}$ / mol·L^{-1}	$[\text{HA}]_{\text{aq}}$ / mol·L^{-1}	$[\text{HA}]_{\text{org}}$ / mol·L^{-1}	K_D	E	pH_{aq}	Z_t
0.37	0.05	0.04	0.01	0.38	27.27	3.22	0.04
	0.10	0.07	0.03	0.45	30.91	3.06	0.08
	0.15	0.09	0.06	0.61	37.88	2.98	0.15
	0.20	0.14	0.07	0.48	32.50	2.90	0.18
	0.30	0.18	0.12	0.65	39.24	2.83	0.32
	0.40	0.26	0.14	0.57	36.14	2.75	0.39
0.74	0.05	0.03	0.02	0.96	49.09	3.31	0.03
	0.10	0.05	0.05	1.08	51.82	3.15	0.07
	0.15	0.07	0.08	1.26	55.76	3.07	0.11
	0.20	0.10	0.10	1.08	51.82	2.98	0.14
	0.30	0.13	0.17	1.28	56.06	2.90	0.23
	0.40	0.18	0.22	1.17	53.86	2.82	0.29
1.65	0.05	0.02	0.03	2.13	68.00	3.44	0.02
	0.10	0.03	0.07	2.17	68.50	3.26	0.04
	0.15	0.04	0.10	2.24	69.21	3.18	0.06
	0.20	0.06	0.14	2.39	70.50	3.10	0.09
	0.30	0.08	0.22	2.85	74.00	3.03	0.13
	0.40	0.11	0.29	2.67	72.75	2.95	0.18

Table 10. Extraction Equilibrium Results for the Propionic Acid + TBP + Petroleum Ether System at 305 K for Various Concentrations of TBP and Acid

$S^{\text{initial}}_{\text{org}}$ / mol·L^{-1}	$[\text{HA}]^{\circ}$ / mol·L^{-1}	$[\text{HA}]_{\text{aq}}$ / mol·L^{-1}	$[\text{HA}]_{\text{org}}$ / mol·L^{-1}	K_D	E	pH_{aq}	Z_t
0.37	0.05	0.03	0.02	0.67	40.00	3.27	0.05
	0.10	0.06	0.04	0.68	40.50	3.09	0.11
	0.15	0.08	0.07	0.88	46.67	3.02	0.19
	0.20	0.12	0.08	0.69	41.00	2.93	0.22
	0.30	0.16	0.14	0.85	46.00	2.85	0.37
	0.40	0.22	0.18	0.79	44.00	2.78	0.48
0.74	0.05	0.02	0.03	1.38	58.00	3.37	0.04
	0.10	0.04	0.06	1.56	61.00	3.20	0.08
	0.15	0.06	0.09	1.36	57.67	3.08	0.12
	0.20	0.09	0.12	1.35	57.50	3.01	0.16
	0.30	0.14	0.16	1.21	54.67	2.90	0.22
	0.40	0.18	0.22	1.25	55.63	2.83	0.30
1.10	0.05	0.02	0.03	1.56	61.00	3.39	0.03
	0.10	0.03	0.07	2.17	68.50	3.26	0.06
	0.15	0.05	0.10	2.00	66.67	3.14	0.09
	0.20	0.07	0.13	1.99	66.50	3.07	0.12
	0.30	0.11	0.20	1.86	65.00	2.96	0.18
	0.40	0.14	0.26	1.84	64.75	2.89	0.24
1.65	0.05	0.02	0.03	1.78	64.00	3.41	0.02
	0.10	0.03	0.07	2.51	71.50	3.28	0.04
	0.15	0.04	0.11	2.49	71.33	3.18	0.06
	0.20	0.06	0.14	2.51	71.50	3.11	0.09
	0.30	0.09	0.22	2.53	71.67	3.01	0.13
	0.40	0.12	0.28	2.25	69.25	2.92	0.17

extraction of propionic acid by TBP in different diluents can be represented as

$$\text{HA}_{\text{aq}} + p\text{S}_{\text{org}} \leftrightarrow (\text{HA.S}_p)_{\text{org}} \tag{2}$$

where subscripts "aq" and "org" stand for aqueous and organic phases and p is solvation number of TBP. As the propionic acid−TBP complex is formed, it is rapidly extracted into the organic phase. The extraction equilibrium constant (K_S) and the number of reacting molecules of extractant are computed by applying the law of mass action that is the ratio between concentrations of reactant molecules and the concentration of the product species, according to the general equation of interaction between the extractant and the extracted species

$$K_S = [(\text{HA}).(\text{S})_p]_{\text{org}}/[\text{HA}]_{\text{aq}}[\text{S}]^p{}_{\text{org}} \tag{3}$$

where $[\text{HA}]_{\text{aq}}$, $[\text{S}]_{\text{org}}$, and $[(\text{HA.S})]_{\text{org}}$ represent acid, extractants, and complex concentration in the respective phases. K_S is expected to depend on the properties of the acid and the solvation efficiency of the diluent used. The dissociation of the acid in the aqueous phase is given as

$$\text{HA} \leftrightarrow \text{H}^+ + \text{A}^- \qquad K_{\text{HA}} = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \tag{4}$$

$[\text{H}^+]$ and $[\text{A}^-]$ are concentrations of the proton and anion of acid, and K_{HA} is the dissociation constant with value $1.413 \cdot 10^{-5}$ mol·L^{-1} for propionic acid.[18] The overall distribution coefficient is evaluated as the function of extraction constant and the number of reacting species as

$$K_D = \frac{[\text{HA.S}_p]_{\text{org}}}{[\text{HA}]_{\text{aq}} + [\text{A}^-]_{\text{aq}}} = \frac{K_S[\text{HA}]_{\text{aq}}[\text{S}]^p{}_{\text{org}}}{[\text{HA}]_{\text{aq}} + K_{\text{HA}}[\text{HA}]_{\text{aq}}/[\text{H}^+]_{\text{aq}}} = \frac{K_S[\text{S}]^p{}_{\text{org}}}{1 + K_{\text{HA}}/[\text{H}^+]_{\text{aq}}} \tag{5}$$

Since the effect of the acid dissociation was negligibly small, eq 5 can be modified and then solved to get

$$\log(K_D) = \log(K_S) + p \log[\text{S}]_{\text{org}} \tag{6}$$

where $[\text{S}]_{\text{org}}$ can be expressed as

$$[\text{S}]_{\text{org}} = [\text{S}]^{\text{initial}}_{\text{org}} - p[\text{HA}]_{\text{org}} \tag{7}$$

thus the plot of log (K_D) versus log $[\text{S}]_{\text{org}}$ would yield a straight line with the slope of p (solvation number) and the intercept of log (K_S), from where K_S can be obtained.

Niitsu and Sekine[19] have reported that the solvation number of the aliphatic carboxylic acids was 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 association between the individual phosphoryl group and individual acid group and displays the strong effect of acid concentration on the experimentally determined distribution ratio.

Figure 2 shows the plot of eq 6 for a few systems, and it can be found that the fit of eq 6 was obtained. In other systems (TBP in hexane, butyl acetate, 1-dodecanol, benzene, and petroleum ether, respectively), also a straight line with unit slope was obtained. The slope, standard deviation, and the values of equilibrium complexation constants are given in Table 11.

In some cases, at low TBP (volume fraction of 10 % TBP in 1-dodecanol, butyl acetate, and benzene, respectively) and high acid concentrations ($[HA]^{\circ}_{aq} \geq 0.3\ mol \cdot L^{-1}$), the loading ratio defined as

$$Z_t = \frac{[HA]_{org}}{[S]_{org}^{initial}} \tag{8}$$

was found to be greater than 0.5. In those cases, the mechanism departs from that implied in eqs 2 to 6. The extraction mechanism can be proposed to be that involving the formation of (2:1) or (3:1) acid−extractant complexes. In such cases, the equilibrium constants can be obtained by the plot of the following equations

$$\frac{Z_t}{1 - Z_t} = K_{S1}[HA]_{aq} \quad \text{for (1:1) acid−extractant complex and } Z_t < 0.5 \tag{9}$$

$$\frac{Z_t}{2 - Z_t} = K_{S2}[HA]^2_{aq} \quad \text{for (2:1) acid−extractant complex and } Z_t > 0.5 \tag{10}$$

$$\frac{Z_t}{3 - Z_t} = K_{S3}[HA]^3_{aq} \quad \text{for (3:1) acid−extractant complex and } Z_t \gg 0.5 \tag{11}$$

Since propionic acid was used in the dilute concentration range in almost all the cases, only (1:1) propionic acid−TBP complexes were found, and the plots of $Z_t/1 - Z_t$ versus $[HA]_{aq}$ for the respective TBP−diluent combinations were plotted to obtain the value of equilibrium complexation constant K_{S1}. The large difference among K_{S1} values for the same acid in different diluents indicates that solvation by the diluent is a critical factor in the extraction of acid. Inert diluents give very low distribution of the acid into the solvent phase.

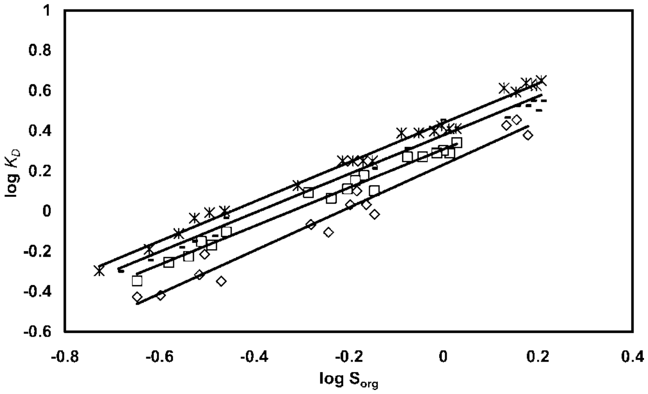


Figure 2. Estimation of equilibrium complexation constant of the extraction of propionic acid using TBP dissolved in various diluents. □, heptane; ◇, paraffin liquid; *, toluene; −, hexane.

Table 11. Standard Deviation σ, Slope, and Equilibrium Complexation Constants K_S for Extraction of Propionic Acid Using TBP in Different Diluents

diluent	σ (standard deviation)	slope	K_S/L·mol^{-1}
heptane	0.384	0.98	2.03
petroleum ether	0.635	0.98	2.12
hexane	0.523	0.98	2.39
butyl acetate	2.004	0.98	4.34
1-dodecanol	2.415	0.99	2.18
toluene	0.496	0.99	2.75
benzene	2.303	0.96	2.79
paraffin liquid	0.434	0.96	1.7

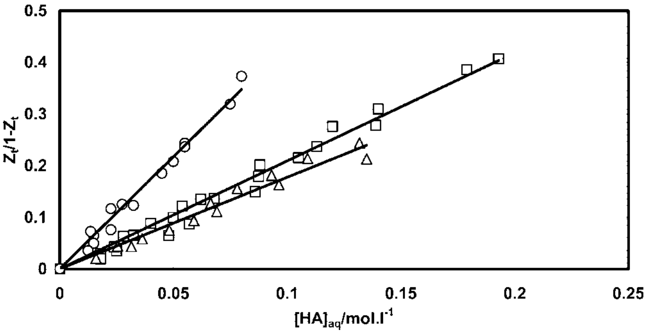


Figure 3. $Z_t/1 - Z_t$ vs $[HA]_{aq}$ for the estimation of the (1:1) propionic acid−TBP complexation constant in different diluents. □, *n*-heptane; Δ, petroleum ether; ○, butyl acetate.

The values of equilibrium complexation constants obtained by these plots were in agreement with that obtained by the fit of eq 6 (Figure 3). For a loading ratio greater than 0.5, the fit of $Z_t/(2 - Z_t)$ versus $[HA]^2_{aq}$ when plotted gives the values of K_{S2} for a system involving such cases. The following are the values of K_{S2} for such systems

$$\text{TBP} + \text{Benzene} \quad K_{S2} = 1.46 \tag{12}$$

$$\text{TBP} + \text{Butyl acetate} \quad K_{S2} = 0.3 \tag{13}$$

$$\text{TBP} + \text{1-dodecanol} \quad K_{S2} = 1.34 \tag{14}$$

(3:1) complexes were not formed as the concentration of propionic acid is not sufficiently high for this type of association.

The value of Z_t was found to increase with an increase in acid concentration for all cases. Further, at given aqueous activity, loading decreases with increasing TBP concentration in all diluents.

Different approaches have been used to quantify the effect of diluents on the (1:1) complexation. Both partition and self-association constants are strongly dependent on the nature of the diluents; i.e., the thermodynamic activity of the species taking part in the organic phase equilibria is changed when one diluent is replaced by another. The effect of diluent on partition and self-association constants was explained by specific interactions only between the TBP and the diluents. Attempts have been made to correlate the extraction efficency in terms of K_S values with solvent properties like molecular mass, boiling point, density, refractive index, dielectric constant, dipole moment, and E_T parameter. While no reasonable correlation with molar mass, specific gravity, density, dielectric constant, and refractive index could be obtained, K_S values could be correlated well with solvent dipole moment μ and the E_T parameter[20] which is based on the absorption spectrum of pyridinium-*N*-phenol-betaine. The greater the μ and E_T values, the greater the solvating power of solvent. However, since values of μ and E_T cannot be predicted for all the diluents, no significant correlation exists for all systems. For butyl acetate ($\mu = 1.84$; $E_T = 38.5$), toluene ($\mu = 0.36$; $E_T = 33.9$), and hexane ($\mu = 0.08$; $E_T = 30.9$), the following equation can predict the K_S value from the μ and E_T values

$$K_S = 1.2 \cdot 10^{-6} \mu^{-0.02266} E_T^{\ 4.14} \tag{15}$$

Dependence on μ indicates that the extraction probably occurs via solvation of the complex based on dipole−dipole interaction, an observation identical to that reported for amine extraction of citric acid.[21] However, for diluents of similar type, e.g., inerts (hexane and heptane) or aromatics (benzene and toluene), the dependence on molar mass, boiling point, and specific gravity can be made. An increase in molar mass, boiling point, and specific gravity hinders the dissolution of the acid−TBP complex and hence lowers the equilibrium extraction coefficient.

Conclusion

The extraction of propionic acid using TBP was studied in the presence of 1-dodecanol, benzene, toluene, heptane, hexane, butyl acetate, petroleum ether, and paraffin liquid as diluents. TBP is viscous and is thus used in different diluents. The work was to determine the effectiveness of the respective diluents in extraction of propionic acid using TBP. Both physical and chemical extractions were studied, and the better performances of extractant−diluent combination over the diluent alone were observed. Different parameters like distribution coefficient, degree of extraction, loading ratio, and equilibrium complexation constants were determined. Since the loading ratio was less than 0.5 in most of the cases, no overloading was obtained and only a (1:1) acid−TBP complex was formed. However, in a few systems, in dilute concentrations of acid, (2:1) acid−TBP complexes were also formed, and the values of equilibrium complexation constants for those cases were also estimated. The attempts were made to correlate the extraction constants with the physical constants of diluents. The successful relationship was obtained using dipole moment and E_T parameter. However, for diluents of similar type, e.g., inerts (hexane and *n*-heptane) or aromatics (benzene and toluene), the increase in molar mass, boiling point, and specific gravity results in lowering of the equilibrium extraction coefficient.

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