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Equilibrium for the Reactive Extraction of Caproic Acid Using Tri-*n*-butyl Phosphate in Methyl Isobutyl Ketone and Xylene

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ABSTRACT: The recovery of caproic acid from the aqueous stream is of practical relevance due to its market value and the stringent environmental standards. The profound success of reactive extraction has been noted in the recovery of carboxylic acids from dilute solutions. In the present paper, the equilibrium of caproic acid with tri-*n*-butyl phosphate (TBP), an organophosphorous compound, in xylene and methyl isobutyl ketone (MIBK) has been studied. Equilibrium parameters such as the distribution coefficients, loading ratio, and degree of extraction have been presented. The data obtained are useful in understanding the equilibrium characteristics and efficient design of the recovery process of caproic acid by reactive extraction.

1. INTRODUCTION

The recovery of caproic acid from an aqueous stream is of considerable commercial importance from an environmental point of view. Caproic acid imparts finite chemical oxygen demand (COD) and biochemical oxygen demand (BOD) to the aqueous waste.[1] Caproic acid is formed during the air oxidation of cyclohexane in the manufacture of cyclohexanone/nol in a caprolactam plant. Caproic acid is a byproduct, and conventionally it can be separated from the reaction mixture by extraction with an aqueous caustic to form a water-soluble, sodium salt of respective acids.[2] The resulting aqueous stream (after extraction with aqueous caustic) is then neutralized with H_2SO_4 to liberate the caproic acid. Thus, this method of recovery is expensive and unfriendly to the environment as it consumes sodium hydroxide and sulfuric acid and also produces a large quantity of sodium sulfate sludge as solid waste.

Caproic acid is a carboxylic acid, and it can be produced by the fermentation route.[3] Carboxylic acids are promising intermediates, because the oxygen of the biomass is placed in a form that is useful for further reaction with many other products. Low concentrations of carboxylic acids (< 10 %) are achieved in fermentation. The chemical reaction combined with extraction can be considered as an alternative to the conventional calcium salt precipitation techniques for the recovery of carboxylic acids from aqueous stream. Reactive extraction with a specified extractant giving a higher distribution coefficient has been proposed as a promising technique for the recovery of carboxylic and hydroxycarboxylic acids.[4,5] Reactive liquid—liquid extraction has the advantage that caproic acid can be removed easily from the aqueous stream. Further, the caproic acid can be re-extracted and the extractant recycled to the process. When selecting an extractant, along with other considerations such as price, availability, ease of regeneration, very high distribution coefficients, and low toxicity, one must ensure that the extractant is environmentally friendly.[1] In other words, the extractant should have as low solubility in water as possible, so that it does not add substantially to COD of the aqueous raffinate. Tri-*n*-butyl phosphate (TBP) is one such solvent that process environmental engineers can use in their process.[1,6,7]

Strongly solvating extractants like organophosphorous compounds have primarily been used in inorganic analysis for the extraction and separation of inorganic acids or metal species.[8] Since phosphoryl can form hydrogen bonds to proton donors, strongly solvating extractants can also be used for the extraction of acidic organic compounds. Weak organic acids are extracted by organophosphorous compounds with a significantly higher distribution ratio. The high polarity of the phosphoryl group in TBP enables it to act as a strong Lewis base, and as a result it can form an acid—base complex when contacted with acid.[6] Diluent is usually added along with the extractant to enhance its physical properties by providing general solvation and affects the extraction power of the extractant by providing specific interaction. The diluent may consists of one or more components, inert or active. Various active polar and proton- or electron-donating diluents (halogenated aliphatic/aromatic hydrocarbons, ketones, nitrobenzenes, higher alcohols) enhance the extraction. On the other hand, inert diluents (long chain paraffins, benzene, etc.) limit the solvent capacity. Wasewar and his group have extensively worked on reactive extraction of various carboxylic acids.[9−18]

Wang et al.[19] suggested the use and importance of liquid—liquid extraction for recovery of caproic acid using trialkylphosphine oxide (TRPO). Equilibria of aqueous solutions of caproic acid with TRPO in kerosene were investigated. An extraction equilibrium model was used to describe the experimental data.

TBP was used to separate caproic acid from an aqueous waste stream at pH 2 to 2.5.[20] The distribution coefficient K_3 was measured for the extraction of caproic acid from aqueous waste stream, and also the effect of presence of salts such as sodium sulfate and sodium chloride was studied.

Kencaly et al.[3] used a novel method of caproic acid synthesis. They used ruminal bacteria *Ruminococcus flavefaciens* and non-ruminal bacterium *Clostridium ckluyveri* which are grown together on cellulose and ethanol. Succinate and acetate produced

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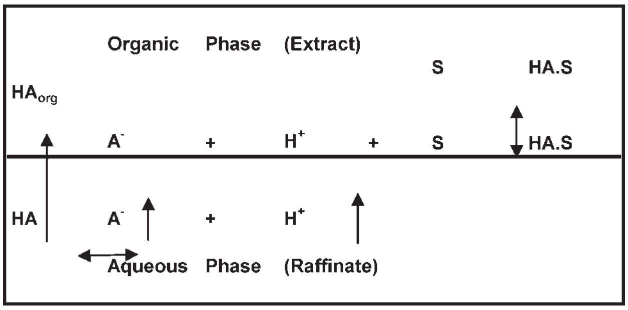

Figure 1. Mechanism for the reactive extraction of caproic acid (HA) using TBP(S).

by the cellulolytic organisms were converted to butyrate and caproate only when the culture medium was supplemented with ethanol. They suggested the use of ruminal and nonruminal bacteria, which are naturally produced and act as an inexpensive starting material, thereby preventing a high cost of production. The method also paves the way for extraction from waste streams which have low concentrations of caproic acid, using *Ckluyveri.*

Senol[21] studied the liquid−liquid equilibrium (water + caproic acid + 1-octanol) at 293.15 K and 101.3 ± 0.7 kPa. A log-basis approach SERLAS (solvation energy relation for liquid associated system) has been proposed to estimate the properties and liquid−liquid equilibria (LLE) of tertiary associated systems containing proton-donating and -accepting components capable of a physical interaction through hydrogen bonding. The reliability of the model has been analyzed against the LLE data with respect to the distribution ratio and separation factor.

A lot of work on the reactive extraction of different carboxylic acids using tertiary and quaternary amine has been done, but very little work on organophosphorous extractants for caproic acid extraction can be found. In view of this, attempts were made to study the extraction of caproic acid using TBP in methyl isobutyl ketone (MIBK) and xylene. The data on the distribution coefficient, equilibrium complexation constant, loading, and extraction efficiency were presented. The distribution of caproic acid between water and TBP dissolved in various diluents, and a comparison with the extraction capacity of pure diluent alone was studied at isothermal conditions.

2. THEORY

The recovery of caproic acid using TBP is by the formation of a complex via the interfacial reaction[20] and can be represented as:

$$\mathrm{HA_{aq}} + p\mathrm{S_{org}} \leftrightarrow (\mathrm{HA}\cdot\mathrm{S}_p)_{\mathrm{org}} \qquad (1)$$

As the acid−TBP complex is formed, it is rapidly extracted into the organic phase. The extraction mechanism is presented in Figure 1.

The extraction constant 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 concentration of the product species, according to the general equation of interaction between the extractant and the extracted species:

$$K_s = [(\mathrm{HA})\cdot(\mathrm{S})_p]_{\mathrm{org}}/[\mathrm{HA}]_{\mathrm{aq}}[\mathrm{S}]^p_{\mathrm{org}} \qquad (2)$$

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:

$$\mathrm{HA} \leftrightarrow \mathrm{H}^+ + \mathrm{A}^- \qquad K_{\mathrm{HA}} = \frac{[\mathrm{H}^+][\mathrm{A}^-]}{[\mathrm{HA}]} \qquad (3)$$

K_D is defined as the ratio of total (analytical) concentration of acid in all its forms (by partition, dimers, and as complexes) in the organic phase and total (analytical) concentration of all its existing forms (dissociated and undissociated) in aqueous raffinate. K_D includes the effects like ionic strength, nature of ion concentration of H$^+$, and so forth of solution constituents. The overall distribution coefficient is evaluated as the function of extraction constant and the number of reacting species as:

$$\begin{aligned} K_D &= \frac{[\mathrm{HA}\cdot\mathrm{S}_p]_{\mathrm{org}}}{[\mathrm{HA}]_{\mathrm{aq}} + [A^-]_{\mathrm{aq}}} \\ &= \frac{K_S[\mathrm{HA}]_{\mathrm{aq}}[\mathrm{S}]^p_{\mathrm{org}}}{[\mathrm{HA}]_{\mathrm{aq}} + K_{\mathrm{HA}}[\mathrm{HA}]_{\mathrm{aq}}/[\mathrm{H}^+]_{\mathrm{aq}}} \\ &= \frac{K_S[\mathrm{S}]^p_{\mathrm{org}}}{1 + K_{\mathrm{HA}}/[\mathrm{H}^+]_{\mathrm{aq}}} \end{aligned} \qquad (4)$$

It is well-known that carboxylic acid dissociates in aqueous solution. Under the experimental condition that pH of the aqueous solution was smaller than pK_a of the acid (4.85), the effect of the acid dissociation was negligibly small.

The equation set 1 and 3 is a simplified, though realistic, version of a more general and thermodynamically strict one that includes activity coefficient and/or allows for the simultaneous formation of two, or perhaps three, different solvates, depending on the organic phase loading.[8] When there is stoichiometric deficiency of the solvating agent S in the system, the distribution ratio (eq 4) requires the addition of appropriate terms to account for the acid extraction by the diluent alone and its dimerization. Kertes and King[22] have investigated extensively the evaluation of the eq 4 and found the constants of the equation. The solvation number of the acid was found to be the same as the number of −COOH group on the acid molecule. Caproic acid contains one −COOH group, and thus the solvation number (p) can be assumed to be unity.

The degree of extraction is calculated as,

$$E\% = K_D\cdot 100/(1 + K_D) \qquad (5)$$

The extent to which the organic phase can be loaded with caproic acid is expressed as the overall loading factor (Z_t) as,

$$Z_t = \frac{[\mathrm{HA}]_{\mathrm{org}}}{[\mathrm{S}]^{\mathrm{initial}}_{\mathrm{org}}} \qquad (6)$$

3. EXPERIMENTAL SECTION

3.1. Materials. TBP (mass fraction of 99 %) (CDH Laboratory Reagent, India), a phosphorus bonded oxygen donor, is a light colorless liquid with the molecular weight of 266.32 g·mol^{-1} and density of 975 g·L^{-1}. Caproic acid (mass fraction of 99 %) (SD Fine Chem. Ltd., India) and the diluents MIBK and xylene (supplied by Qualigens Fine Chemicals, India) are of technical grade and were used without pretreatment. Distilled water was used to prepare the solutions of various concentrations of caproic

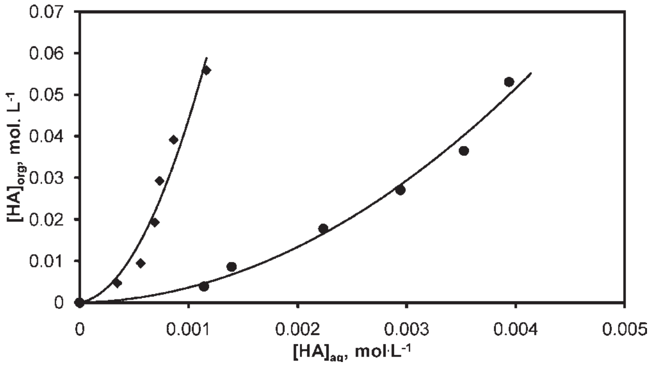

Figure 2. Physical extraction of caproic acid (HA) in xylene and MIBK. ◆, MIBK; ●, xylene.

acid solutions. NaOH used for the titration is of analytical grade and was supplied by SD Fine-Chem. Ltd., India. For the standardization of the NaOH, oxalic acid (mass fraction of 99.8 %) was obtained from SD Fine-Chem. Ltd., India. Phenolphthalein solution (pH range 8.2 to 10.0) was used as an indicator for titration and was obtained from SD Fine-Chem. Ltd., India. The range of pH for the experiment was (1.9 to 2.5) at the temperature 301 K. The initial TBP concentrations of (0.7322 and 1.466) $\mathrm{mol \cdot L^{-1}}$ and the initial aqueous acid concentration range of (0.005 to 0.057) $\mathrm{mol \cdot L^{-1}}$ were used. A low concentration was used because the caproic acid concentration in the fermentation broth is not greater than 0.057 $\mathrm{mol \cdot L^{-1}}$.

3.2. Methods. The extraction experiments were performed using a temperature-controlled water bath shaker (Remi Equipment Pvt. Ltd., India) at constant temperature (301 K). Equal volumes (15 mL) 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 (301 K) and atmospheric pressure in a separating funnel. The lower phase was taken for analysis after filtration through the MILLEX GV filter unit (0.22 μm). The aqueous phase pH was measured by a digital pH meter (Superfit, India). The aqueous phase acid concentration was determined by titration with NaOH. The results of the above methods were noted when NaOH is prepared fresh every time before titration was to be carried out. The acid content in the organic phase was determined by mass balance. The few experiments were repeated to check the consistency and found within limit of ± 2 %.

4. RESULTS AND DISCUSSION

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 separation effect with solutions containing chemically similar elements. TBP, an organophosphorous compound, contains a phosphoryl group which is a stronger Lewis base than carbonyl one. This leads to a high distribution coefficient. TBP was selected because of low water coextraction (4.67 mass %) and very low solubility in aqueous phase (0.039 mass %). TBP contains a =P(O) OH group, which has a marked tendency toward an intermolecular hydrogen bonding. Because of the presence of both electron donor and electron acceptor groups in the =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 role of additional reagents.

Table 1. Extraction Equilibrium Results for the TBP/Xylene/Caproic Acid System at 301 K for the Various Concentrations of TBP and Acid

$[\mathrm{HA}]^{\mathrm{o}}$ / $\mathrm{mol \cdot L^{-1}}$	$S_{\mathrm{org}}^{\mathrm{initial}}$ / $\mathrm{mol \cdot L^{-1}}$	$[\mathrm{HA}]_{\mathrm{aq}}$ / $\mathrm{mol \cdot L^{-1}}$	$[\mathrm{HA}]_{\mathrm{org}}$ / $\mathrm{mol \cdot L^{-1}}$	$\mathrm{pH_{initial}}$	$\mathrm{pH_{eq}}$	K_{D}	E (%)	Z_t
0.057	0.7322	0.0019	0.0550	2.46	2.64	28.72	96.63	0.075
	1.4644	0.0011	0.0558	2.52	2.76	47.42	97.93	0.038
0.04	0.7322	0.0014	0.0385	2.50	2.70	26.11	96.31	0.052
	1.4644	0.0010	0.0389	2.53	2.78	35.69	97.27	0.026
0.03	0.7322	0.0013	0.0286	2.51	2.73	21.38	95.53	0.039
	1.4644	0.0011	0.0289	2.53	2.78	26.52	96.36	0.019
0.02	0.7322	0.0010	0.0189	2.54	2.82	18.94	94.98	0.026
	1.4644	0.0009	0.0190	2.55	2.80	20.55	95.36	0.013
0.01	0.7322	0.0011	0.0089	2.54	2.79	8.43	89.39	0.012
	1.4644	0.0010	0.0089	2.54	2.79	8.69	89.68	0.006
0.005	0.7322	0.0016	0.0034	2.49	2.85	2.12	67.95	0.005
	1.4644	0.0008	0.0041	2.57	2.68	5.06	83.50	0.002

Since TBP has a relatively high viscosity ($3.56 \cdot 10^{-3}$ Pa·s) with specific gravity close to unity (0.975), it is used along with low viscosity and low density diluents, which could facilitate good phase separation in the continuous extraction process.

The extraction equilibria of caproic acid by xylene and MIBK (physical) and extractant—diluent combinations (chemical) were studied. The physical extraction using xylene and MIBK is shown in Figure 2. The regression equations for the physical extraction equilibrium of caproic acid in three diluents are represented as

$$[\mathrm{HA}]_{\mathrm{org}} = 3172[\mathrm{HA}]_{\mathrm{aq}}^{2} + 0.504[\mathrm{HA}]_{\mathrm{aq}} \text{ for xylene} \quad (7)$$

$$[\mathrm{HA}]_{\mathrm{org}} = 37506[\mathrm{HA}]_{\mathrm{aq}}^{2} + 4.209[\mathrm{HA}]_{\mathrm{aq}} \text{ for MIBK} \quad (8)$$

The coefficient of $[\mathrm{HA}]_{\mathrm{aq}}^{2}$ and $[\mathrm{HA}]_{\mathrm{aq}}$ provides the values of dimerization constant and distribution coefficient, respectively, for the respective extractions. In all of the cases the extraction was low with the K_{D} (ratio of total acid concentration in organic phase to total acid in aqueous phase) value lying between 3 to 13.5 and 13 to 48 for xylene and MIBK, respectively, for the various initial concentrations of caproic acid in aqueous phase. The degree of extraction is in the range of (77 to 93) % and (93 to 98)% in xylene and MIBK, respectively. The extraction of caproic acid in xylene is low as compared to MIBK.

Tables 1 and 2 demonstrate the influence of the organic solvent and the organic phase concentration of TBP on the distribution coefficient of caproic acid in xylene and MIBK, respectively. The TBP concentration (0.7322 and 1.4644) $\mathrm{mol \cdot L^{-1}}$ was used in diluents for the acid concentrations of (0.005, 0.01, 0.02, 0.03, 0.04, and 0.0572) $\mathrm{mol \cdot L^{-1}}$. The function of diluent is to dilute the extractant to the desired concentration and control the viscosity and density of the solvent phase. The TBP concentration was not used above 40 % because usually it was found that the K_{D} increase with the increase of the TBP content was accompanied with the viscosity increase of the system also,

Table 2. Extraction Equilibrium Results for the TBP/MIBK/Caproic Acid System at 301 K for the Various Concentrations of TBP and Acid

$[HA]^o$	$S_{org}^{initial}$	$[HA]_{aq}$	$[HA]_{org}$					
$mol \cdot L^{-1}$	$mol \cdot L^{-1}$	$mol \cdot L^{-1}$	$mol \cdot L^{-1}$	$pH_{initial}$	pH_{eq}	K_D	E (%)	Z_t
0.057	0.7322	0.0021	0.0548	2.45	2.61	25.06	96.16	0.074
	1.4644	0.0021	0.0548	2.45	2.61	25.32	96.20	0.037
0.04	0.7322	0.0018	0.0381	2.46	2.64	20.20	95.28	0.052
	1.4644	0.0018	0.0381	2.47	2.64	20.44	95.33	0.026
0.03	0.7322	0.0017	0.0282	2.47	2.66	15.85	94.06	0.038
	1.4644	0.0017	0.0282	2.47	2.66	16.06	94.14	0.019
0.02	0.7322	0.0014	0.0185	2.50	2.71	12.71	92.71	0.025
	1.4644	0.0014	0.0185	2.50	2.70	13.13	92.92	0.012
0.01	0.7322	0.0012	0.0087	2.52	2.75	7.32	87.99	0.012
	1.4644	0.0011	0.0088	2.53	2.77	7.80	88.63	0.006
0.005	0.7322	0.0011	0.0038	2.53	2.78	3.48	77.70	0.005
	1.4644	0.0010	0.0039	2.53	2.77	3.57	78.13	0.002

which causes the problem of TBP to disengage. Zhong et al.[23] found that the maximum K_D values were found for the extractant concentration of (20 to 40) %.

The K_D values for TBP in xylene lie in the range of 2 to 47.5 (Table 1). It was found that increasing the TBP concentration in the organic phase increases the equilibrium concentration of the acid in the organic phase and hence gives the higher distribution. The maximum removal of caproic acid was for 0.057 $mol \cdot L^{-1}$ caproic acid solution with 40 % (1.4644 $mol \cdot L^{-1}$) TBP in xylene. The chemical equilibrium can be obtained by a plot of organic versus aqueous concentrations for different concentrations of TBP in diluent.

The ideal behavior is observed due to the ability of diluent to solvate the complex effectively. However, if the diluent is a poor solvating medium for the species formed, the polar complexes tend to form clusters in the organic phase at higher phase loadings in the inert diluents.

Further, the results of reactive extraction of caproic acid using TBP in MIBK are given in Table 2. The K_D values for TBP in MIBK lie in the range of 3 to 25.5. It was found that this K_D values are less than the physical extraction (K_D = 13 to 48) of caproic acid using MIBK only. Here, the synergic effect of extractant was not observed.

On the basis of the overall extraction efficiency, MIBK is better solvent for reactive extraction of caproic acid using TBP. It may attributed to the solvating ability of MIBK with the extractant, TBP due to its distinct functional group >C=O, and the resultant steric effect.

5. CONCLUSION

The physical and reactive extraction of caproic acid using TBP in xylene and MIBK was studied, and the following conclusions were made:

- The distribution coefficient of caproic acid in xylene alone was low and lay between 3 and 13.5 with a degree of extraction in the range of (77 to 93) %.
- Reactive extraction using TBP in xylene shows a synergetic effect on the recovery of caproic acid and distribution coefficient lying between 2 and 47.5.
- The distribution coefficient of caproic acid in MIBK only was found in the range of 13 to 48 with a degree of extraction in the range of (93 to 98) %.
- The synergic effect was not observed when TBP was used in MIBK.
- MIBK is a better solvent than xylene for reactive extraction with TBP based on its overall extraction efficiency.
- Further the reactive extraction from model and actual fermentation broth will be carried out.

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NOMENCLATURE

K_D = distribution coefficient
K_S = extraction equilibrium constant [$L \cdot mol^{-1}$]
[HA] = concentration of acid [$mol \cdot L^{-1}$]
$[HA]^0$ = initial concentration of acid in aqueous phase [$mol \cdot L^{-1}$]
$[HA]_{aq}$ = equilibrium concentration of acid in aqueous phase [$mol \cdot L^{-1}$]
$[HA]_{org}$ = equilibrium concentration of acid in organic phase [$mol \cdot L^{-1}$]
$[S]_{org}^{initial}$ = initial concentration of extractant in organic phase [$mol \cdot L^{-1}$]
$[HA \cdot S]$ = concentration of acid−extractant complex [$mol \cdot L^{-1}$]
$[H^+]$ = concentration of hydroxyl ion [$mol \cdot L^{-1}$]
$[A^-]$ = concentration of anion [$mol \cdot L^{-1}$]
K_{HA} = dissociation constant [$L \cdot mol^{-1}$]
E = degree of extraction
Z_t = loading ratio

SUBSCRIPTS

aq = aqueous phase
org = organic phase
p = solvation number of TBP

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