Extraction of Caproic Acid Using Tri-*n*-butyl Phosphate in Benzene and Toluene at 301 K

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The recovery of caproic acid from the aqueous stream is of practical relevance due to its market value and the stringent environmental standards. 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, reactive extraction equilibrium of caproic acid using tri-*n*-butyl phosphate (TBP, extractant), an organophosphorous compound, in benzene and toluene (diluents) 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 reactive extraction process for the recovery of caproic acid.

Introduction

Caproic acid (*n*-hexanoic acid) is a light colorless transparent oily liquid with a pungent smell, found in oils and animal fats and used in organic synthesis, manufacturing of perfume, medicine, lubricating grease, rubber, and dyes. The market for caproic acid would be expanded greatly if it could be produced from inexpensive starting materials and if it is to be converted to alkane fuels.[1−3]

Caproic acid can be produced commercially by various routes such as carbonylation of ethylene with carbon monoxide and water, oxidation of propanal, and direct oxidation of hydrocarbons. Although the petrochemical route promises good yield, because of its high cost, it is generally not preferred. Because of the rise in petroleum costs, fermentation is the most preferred way of producing caproic acid.[4]

The separation of caproic acid from aqueous streams is of great importance and essential from the points of view of its use and environmental concern. The easiest way to recover the carboxylic acids is to neutralize them with inorganic acids such as H_2SO_4 and HCl, followed by solvent extraction. If sulfuric acid is used to neutralize the waste, it is possible to recover caustic value through Na_2SO_4 which can be a useful byproduct.[5] A number of methods are available such as precipitation, adsorption, membranes, dialysis, distillation, ion exchange, reactive extraction, and so forth to recover carboxylic acids from fermentation broths or aqueous streams. Conventionally, precipitation by calcium hydroxide was employed to extract carboxylic acids, but the method is expensive as it employs large amount of chemicals and is environmental unfriendly as it produces large amount of waste sludge. Alternative methods have always been discussed in the literature to recover the acid.

Reactive extraction is an important alternative recovery technique, which has received increasing attention over the past decade particularly, for recovery of various carboxylic acids.[6−9] In reactive extraction, an extractant is used to remove the acid from aqueous phase. Extractants are usually classified as the following: (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 a 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 a higher solubility of extractants by specific solvation in which acid complexes are formed. Polar diluents are more favorable than low polarity, low dielectric constant aliphatic or aromatic hydrocarbons in some cases. Reactive extraction depends on the interaction between extractant and acid, diluent and acid, and diluent and extractant. In some cases the extractant in nonpolar diluent is more favorable than the polar diluent. 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.[10] Wasewar and his group have extensively worked on the reactive extraction of propionic acid, lactic acid, acrylic acid, and other carboxylic acids.[11−20]

Wang et al.[21] 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.

Tri-*n*-butyl phosphate (TBP) was used to separate caproic acid from an aqueous waste stream at pH 2 to 2.5.[5] The distribution coefficient K_D was measured for the extraction of caproic acid from aqueous waste stream and also studied for the effect of the presence of salts such as sodium sulfate and sodium chloride.

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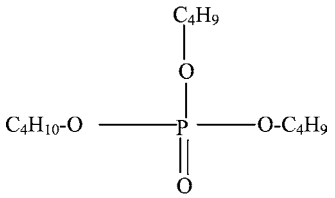

Figure 1. Structure of TBP.

Kencaly et al.[4] used a novel method of caproic acid synthesis. They used ruminal bacteria *Ruminococcus flavefaciens* and nonruminal bacterium *Clostridium ckluyveri* which are grown together on cellulose and ethanol. Succinate and acetate produced 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 high cost of production. The method also paves the way for extraction from waste streams which have low concentrations of caproic acid, using *C. ckluyveri*.

Senol[22] studied the liquid−liquid equilibrium of [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 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.

It was found from the literature that very little work has been done until now on the recovery of caproic acid by reactive extraction. Hence, it has been thought desirable to study the reactive extraction of caproic acid. In present work, TBP (extractant) in benzene and toluene (diluents) were used for the extraction of caproic acid from aqueous phase. To study the effect of various aromatic diluents on the extraction, benzene and toluene were selected. Physical extraction using these diluents and chemical extraction using TBP with volume fractions of (20 and 40) % in respective diluents were performed and compared. The extraction mechanism, distribution coefficient, and equilibrium complexation constants were determined. The difference in the degree of extraction is discussed.

Materials and Methods

Materials. TBP (volume fraction of 99 %) (CDH Laboratory Reagent, India), a phosphorus-bonded oxygen donor, is a light colorless liquid with the molar mass of 266.32 $g \cdot mol^{-1}$ and density of 0.975 $g \cdot cm^{-3}$. The chemical structure is given in Figure 1.

Caproic acid (volume fraction of 97 %) (SD Fine Chem. Ltd., India) and the diluents, toluene (Qualigens Fine Chemicals, India) and benzene (Qualigens Fine Chemicals, India), are of technical grade and were used as supplied by suppliers. Distilled water was used to prepare the solutions of various concentrations of caproic acid. NaOH used for titration is of laboratory grade and was supplied by SD Fine Chem. Ltd., India. For the standardization of the NaOH, oxalic acid (volume 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 initial TBP concentrations of (0.7322 and 1.466) $mol \cdot L^{-1}$ and the initial aqueous acid concentration range of (0.005 to 0.057) $mol \cdot L^{-1}$ were used. A low concentration was used because caproic acid concentration in the fermentation broth is not greater than 0.057 $mol \cdot L^{-1}$.

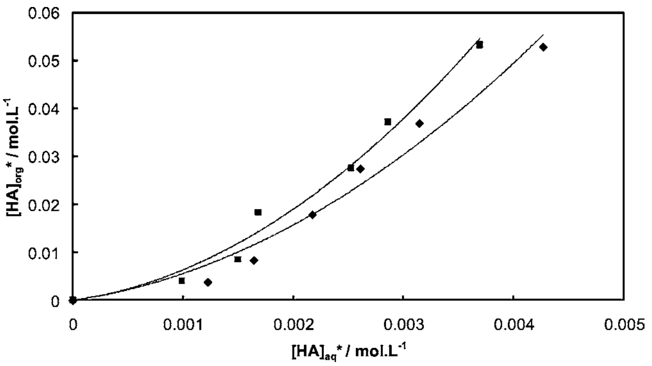

Figure 2. Equilibrium isotherm for the extraction of caproic acid from benzene and toluene at 301 K. Initial concentration range of caproic acid = (0 to 0.057) $mol \cdot L^{-1}$. ■, benzene; ◆, toluene.

Methods. The extraction experiments were performed using a temperature-controlled water bath shaker (model RSB-12, Remi Equipment Pvt. Ltd., India) at constant temperature (301 K ± 1 K). The temperature was measured by a Pt100 sensor-thermocouple with a digital display of accuracy within ± 0.4 K. Equal volumes (15 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 (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).

Aqueous phase pH was measured by a digital pH meter (model R/594, Superfit, India). It was assumed that there was no change in phase volumes after extraction. 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 the titration was to be carried out. The weighing balance of Shimadzu make (model AW220 with accuracy up to 0.1 mg) was used to weigh the solid NaOH for the preparation of NaOH solution. The concentration of acid in the organic phase was determined by mass balance as the initial concentration of acid in the aqueous phase minus the final acid concentration in the aqueous phase. The experiments were repeated several times to check the consistency, and the error found was within the limit of ± 2 % of concentration.

Results and Discussion

Extractants employed for the reactive extraction of carboxylic acids are classified by Kertes and King[23] as conventional carbon-bonded oxygen-bearing extractants, organophosphorous extractants, and higher molar mass aliphatic amines, on the basis of the extraction mechanism involved. In the category of carbon-bonded oxygen-bearing diluents like alcohols, ethers, ketones, and so forth, 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 caproic acid using benzene and toluene was performed and shown in Figure 2.

Extraction of caproic acid by diluent alone was accounted for due to three phenomenona: (i) ionization of acid in the aqueous phase (K_{HA}); (ii) partition of the undissociated acid in organic phase (P), and (iii) dimerization of acid in organic phase (D).[23] These have been described as:

Table 1. Partition and Dimerization Coefficients, Distribution Coefficient, and Degree of Extraction for Caproic Acid Extracted from Water into Organic Solvents at 301 K

	$[HA]_{org} = P[HA]_{aq} + D[HA]^2_{aq}$					
diluent	partition coefficient (P)	dimerization coefficient (D)	range of K_D	average K_D	range of %E	average %E
benzene	3.375	1963	0 to 12.5	7.28	75 to 92.5	87.4
toluene	3.280	2910	0 to 14.5	8.41	80 to 93.5	89.1

1. Ionization of the acid in the aqueous solution:

$$[HA]_{aq} \leftrightarrow H^+ + A^- \qquad (1)$$

$$K_{HA} = [H^+][A^-]/[HA] \qquad (2)$$

2. Partition of the undissociated molecular acid between the two phases, aqueous (aq) and organic (org):

$$[HA]_{aq} \leftrightarrow [HA]_{org} \qquad (3)$$

$$P = [HA]_{org}/[HA]_{aq} \qquad (4)$$

3. Dimerization of the acid in the organic phase:

$$2[HA]_{org} \leftrightarrow [HA]^2_{org} \qquad (5)$$

$$D = [HA]_{2,org}/[HA]^2_{org} \qquad (6)$$

The overall distribution coefficient for physical extraction ($K_D^{diluent}$) can be written in terms of these parameters as:

$$K_D^{diluent} = \frac{[HA]_{org,total}}{[HA]_{aq,total}} = \frac{[HA]_{org} + 2[HA]_2}{[HA]_{aq} + [A^-]} = \frac{P + 2P^2D[HA]_{aq}}{1 + K_{HA}/[H^+]_{aq}} \qquad (7)$$

For the dilute concentration of acid (used in the study), it can fairly be assumed that second term in the denominator of above equation can be neglected, thus

$$K_D^{diluent} = P + 2P^2D[HA]_{aq} \qquad (8)$$

Or it can written in other form as

$$[HA]_{org} = P[HA]_{aq} + D[HA]^2_{aq} \qquad (9)$$

The degree of extraction (E %) of caproic acid in the respective diluents is expressed as:

$$E\,\% = K_D^{overall}\cdot 100/(1 + K_D^{overall}) \qquad (10)$$

Equation 9 was fitted to the experimental value (Figure 2) to yield the values of P and D. The values of partition coefficient, dimerization constant, distribution coefficient, and degree of extraction are given in Table 1. The values of P and D are found as 3.375 and 1963 for benzene and 3.28 and 2910 for toluene. The $K_D^{diluent}$ values for benzene and toluene lies between 0 to 12.5 and 0 to 14.5 with average value of 7.28 and 8.41, respectively.

The values of distribution coefficients were found to be higher in toluene than benzene. Caproic acid has a high affinity to water and low relative volatility that renders it difficult to separate. The low activity of caproic acid toward these diluents, that is, 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 reactive extraction technique by employing organophosphorous compounds and amines which have proved to be effective in the recovery of carboxylic acids.[23]

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 the carbonyl group. This leads to higher distribution coefficient. TBP is selected because of its low water coextraction (mass fraction is 4.67 %) and very low solubility in aqueous phase (mass fraction is 0.039 %).[10] 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 ═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.[10]

Since TBP has a relatively high viscosity ($3.56\cdot10^{-3}$ Pa·s) and density close to unity (0.975 g·cm^{-3}), it is used along with low viscosity and low density diluents, which could facilitate good phase separation in continuous extraction process. The chemical extraction data for caproic acid extraction using TBP in different diluents are presented in Tables 2 and 3. 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, dimers and as complexes) in the organic phase and total (analytical) concentration of all its existing forms (dissociated and undissociated) in aqueous phase) was found to increase with the 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 increase on increasing the acid concentration from (0.005 to 0.057) mol·L^{-1}. The similar trend was found for the degree of extraction (E).

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 pK_a of the acid (4.84), the

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

$S_{\mathrm{org}}^{\mathrm{initial}}$ mol·L^{-1}	[HA]$^{\mathrm{o}}$ mol·L^{-1}	$[\mathrm{HA}]_{\mathrm{aq}}$ mol·L^{-1}	$[\mathrm{HA}]_{\mathrm{org}}$ mol·L^{-1}	K_{D}	%E	Z_{t}	K_{S}
0.7322	0.057	0.00127	0.05573	43.8	97.8	0.076	43.5
	0.04	0.00083	0.03917	47.2	97.93	0.053	
	0.03	0.00072	0.02926	39.6	97.5	0.040	
	0.02	0.00066	0.01934	29.5	96.7	0.026	
	0.01	0.00068	0.00932	13.7	93.2	0.013	
	0.005	0.00056	0.00444	7.9	88.7	0.006	
1.4644	0.057	0.00138	0.05562	40.2	97.6	0.038	14.9
	0.04	0.00115	0.03885	33.8	97.3	0.026	
	0.03	0.00122	0.02878	23.6	95.9	0.020	
	0.02	0.00115	0.01885	16.4	94.3	0.013	
	0.01	0.00105	0.00895	8.48	89.5	0.006	
	0.005	0.00082	0.00418	5.10	83.6	0.003	

Table 3. Extraction Equilibrium Results for the Caproic Acid + TBP + Toluene System at 301 K for Various Concentrations of TBP and Caproic Acid

$S_{\mathrm{org}}^{\mathrm{initial}}$ mol·L^{-1}	[HA]$^{\mathrm{o}}$ mol·L^{-1}	$[\mathrm{HA}]_{\mathrm{aq}}$ mol·L^{-1}	$[\mathrm{HA}]_{\mathrm{org}}$ mol·L^{-1}	K_{D}	E	Z_{t}	K_{S}
0.7322	0.057	0.0016591	0.0553409	33.4	97.1	0.076	25.9
	0.04	0.0015377	0.0384623	25.0	96.2	0.053	
	0.03	0.0013893	0.02861067	20.6	95.4	0.039	
	0.02	0.0013219	0.01867812	14.2	93.4	0.026	
	0.01	0.0008902	0.00910975	10.2	91.1	0.012	
	0.005	0.0008363	0.00416371	5.0	83.3	0.006	
1.4644	0.057	0.0014703	0.05552974	37.8	97.4	0.038	14.9
	0.04	0.0013758	0.03862416	28.1	96.6	0.026	
	0.03	0.0011803	0.02881975	24.4	96.1	0.020	
	0.02	0.0009037	0.01909626	21.1	95.5	0.013	
	0.01	0.0008228	0.0091772	11.2	91.8	0.006	
	0.005	0.0008093	0.00419068	5.2	83.8	0.003	

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

$$\mathrm{HA}_{\mathrm{aq}} + p\mathrm{S}_{\mathrm{org}} \leftrightarrow (\mathrm{HA}\cdot\mathrm{S}_p)_{\mathrm{org}} \tag{11}$$

where subscript "aq" and "org" stands for aqueous and organic phases and p is the solvation number of TBP. As the caproic 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

$$K_{\mathrm{S}} = [\mathrm{HA}\cdot\mathrm{S}_p]_{\mathrm{org}}/[\mathrm{HA}]_{\mathrm{aq}}[\mathrm{S}]_{\mathrm{org}}^p \tag{12}$$

where $[\mathrm{HA}]_{\mathrm{aq}}$, $[\mathrm{S}]_{\mathrm{org}}$, and $[(\mathrm{HA}\cdot\mathrm{S}_p)]_{\mathrm{org}}$ 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:

$$\mathrm{HA} \leftrightarrow \mathrm{H}^+ + \mathrm{A}^- \qquad K_{\mathrm{HA}} = \frac{[\mathrm{H}^+][\mathrm{A}^-]}{[\mathrm{HA}]} \tag{13}$$

$[\mathrm{H}^+]$ and $[\mathrm{A}^-]$ are concentrations of proton and anion of acid, and K_{HA} is the dissociation constant with a value of $1.57\cdot10^{-5}$ mol·L^{-1} for caproic acid. The overall distribution coefficient is evaluated as the function of extraction constant and the number of reacting species as:

$$K_{\mathrm{D}} = \frac{[\mathrm{HA}\cdot\mathrm{S}_p]_{\mathrm{org}}}{[\mathrm{HA}]_{\mathrm{aq}} + [\mathrm{A}^-]_{\mathrm{aq}}} = \frac{K_{\mathrm{S}}[\mathrm{HA}]_{\mathrm{aq}}[\mathrm{S}]_{\mathrm{org}}^p}{[\mathrm{HA}]_{\mathrm{aq}} + K_{\mathrm{HA}}[\mathrm{HA}]_{\mathrm{aq}}/[\mathrm{H}^+]_{\mathrm{aq}}} = \frac{K_{\mathrm{S}}[\mathrm{S}]_{\mathrm{org}}^p}{1 + K_{\mathrm{HA}}/[\mathrm{H}^+]_{\mathrm{aq}}} \tag{14}$$

Since the effect of the acid dissociation was negligibly small, eq 14 can be modified and then solved to get,

$$\log(K_{\mathrm{D}}) = \log(K_{\mathrm{S}}) + p\log[\mathrm{S}]_{\mathrm{org}} \tag{15}$$

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

$$[\mathrm{S}]_{\mathrm{org}} = [\mathrm{S}]_{\mathrm{org}}^{\mathrm{initial}} - p[\mathrm{HA}]_{\mathrm{org}} \tag{16}$$

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

Niitsu and Sekine[24] have reported that the solvation number of the aliphatic carboxylic acids were the same as the numbers of carboxyl groups on each acid; thus, the value of p for caproic acid can be taken as one. This indicated a stoichiometric association between individual phosphoryl group and individual acid group and displays the strong effect of acid concentration on the experimentally determined distribution ratio. The value of equilibrium complexation constants (K_{S}) is given in Tables 2 and 3 for benzene and toluene in TBP.

The value of Z_{t} (loading ratio = total acid in organic phase/total extractant on organic phase) was found to increase with the increase in acid concentration for all cases. Furthermore, 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 complexation. Both partition and self-association constants are strongly dependent on the nature of the diluents; that is, the thermodynamic activity of the species taking part in the organic phase equilibria is changed when one diluent is replaced by other. The effect of diluent on partition and self-association constants was explained by specific interactions only between the TBP and the diluents. An attempt has been made to correlate the extraction efficiency in terms of K_{S} values with solvent properties like molecular mass, boiling point, density, refractive index, dielectric constant, dipole moment, and E_T parameter. For benzene and toluene, the increase in molar mass, boiling point, and specific gravity results in the lowering of the equilibrium extraction coefficient. The values of K_{S} were found to be 43.5 and 14.9 for (20 and 40) % TBP in benzene, respectively, and 25.9 and 14.9 for (20 and 40) % TBP in toluene, respectively. It can be seen that the benzene has the higher K_{S} value than the toluene for 20 % TBP and the same for 40 % TBP. Hence, benzene is more preferable than toluene for the extraction of caproic acid using TBP for low concentrations of TBP.

Conclusion

The extraction of caproic acid using TBP was studied in the presence of benzene and toluene as diluents. TBP is viscous and is thus used in different diluents. The purpose of this work was to determine the effectiveness of the respective diluents in extraction of caproic acid using TBP. Both physical and chemical extractions were studied, and the better performances of extractant−diluent combinations 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. The values of partition coefficient (P) and dimerization constants (D) are found as 3.375 and 1963 for benzene and 3.28 and 2910 for toluene. The K_D^{diluent} values for benzene and toluene lie between 0 to 12.5 and 0 to 14.5 with average values of 7.28 and 8.41, respectively. The values of the caproic acid−TBP equilibrium complexation constant (K_S) were found to be 43.5 and 14.9 for (20 and 40) % TBP in benzene, respectively, and 25.9 and 14.9 for (20 and 40) % TBP in toluene, respectively. Benzene is more preferable than toluene for the extraction of caproic acid using TBP for low concentrations of TBP.

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