Reactive Extraction of Caproic Acid Using Tri-*n*-butyl Phosphate in Hexanol, Octanol, and Decanol

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Reactive extraction is an alternative method for recovery of caproic acid as compared to other processes such as distillation, membrane, dialysis, electrodialysis, and so forth. The profound success of reactive extraction has been noted in the recovery of carboxylic acids from dilute solutions. In present paper, reactive extraction of caproic acid using tri-*n*-butyl phosphate (TBP) (extractant), an organophosphorous compound, in hexanol, octanol, and decanol (diluents) has been studied. Results were presented in terms of distribution coefficients, loading ratio, degree of extraction, and equilibrium complexation constants. Four different models, relative basicity, mass action law, Langmuir, and linear solvation energy relationship (LSER) models, were used to represent the reactive extraction equilibrium for caproic acid−TBP−diluent. The data obtained are useful in understanding the equilibrium characteristics and efficient design of reactive extraction process for the recovery of caproic acid.

Introduction

Caproic acid (hexanoic acid) is a yellowish transparent oily carboxylic acid with a pungent smell. It is used in 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 converted to alkane fuels.[1−3] Caproic acid can be produced commercially by 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] Because of environmental concerns, the separation of caproic acid from aqueous streams is of great importance and essential from the points of view of its wide uses. The neutralization followed by extraction is the easiest way to recover the carboxylic acids. In this, it is neutralized with inorganic acids such as H_2SO_4 and HCl, followed by solvent extraction using a suitable extractant. If sulfuric acid is used to neutralize the waste, it is possible to recover caustic 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 to recover the carboxylic acid.[6] Reactive extraction is an important alternative recovery method, which has received increasing attention over the past decade particularly, for the recovery of various carboxylic acids, lactic acid,[6−11] propionic acid,[12−22] caproic acid,[23] itaconic acid,[24] citric acid,[25] acrylic acid,[22,26] nicotinic acid,[27] levulinic acid,[28] phenyl acetic acid,[29] butyric acid,[22] and so forth. Wasewar and his group have extensively worked on the reactive extraction of propionic acid, lactic acid, acrylic acid, and other carboxylic acids.[6−40] In reactive extraction, an extractant is used to remove the acid from the aqueous phase. 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. Reactive extraction depends on the interaction between extractant and acid, diluent and acid, and diluent and extractant.

Wang et al.[41] used trialkylphosphine oxide in kerosene to recover caproic acid. Reactive extraction of caproic acid using tri-*n*-butyl phosphate (TBP) in xylene and toluene was studied.[23] TBP was used to separate caproic acid from an aqueous waste stream.[5] It was found from the literature that very few works have 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 hexanol, octanol, and decanol (diluents) were used for the extraction of caproic acid from aqueous phase. To show the effect of various diluents which have different structures on the extraction, hexanol, octanol, and decanol were selected. Physical extraction using these diluents and chemical extraction using TBP with volume fractions of (20 and 40) % at a 301 K temperature and atmospheric pressure in respective diluents were performed and compared. The extraction mechanism, distribution coefficients, and equilibrium complexation constants were determined. The difference in degree of extraction is discussed. Four different kinds of models, relative basicity, mass action law, Langmuir, and linear solvation energy relationship (LSER) models, were used to represent the reactive extraction equilibrium for caproic acid−TBP−diluent.

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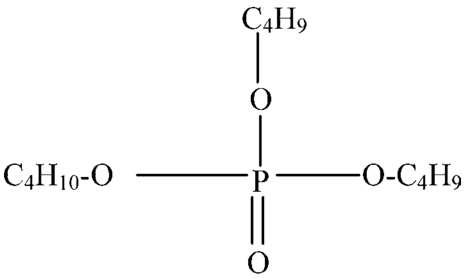

Figure 1. Structure of TBP.

Materials and Methods

Materials. TBP (mass 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·mol^{-1} and density of 0.975 g·cm^{-3}. The chemical structure is given in Figure 1. Caproic acid (mass fraction of 97 %) and the diluents, hexanol (mass fraction of 98 %), octanol (mass fraction of 99 %), and decanol (mass fraction of 99 %), 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. For the standardization of the NaOH, oxalic acid (mass fraction of 99.8 %) was used. Phenolphthalein solution (pH range 8.2 to 10.0) was used as an indicator. All of the chemicals except for TBP were supplied by S.D. Fine-Chem Ltd., India. The initial TBP concentrations of (0.7322 and 1.466) mol·L^{-1} and the initial aqueous acid concentration range of (0.005 to 0.057) mol·L^{-1} were used. A low concentration was used because caproic acid concentration in the fermentation broth is not greater than 0.057 mol·L^{-1}.

Methods. The extraction experiments were performed using a temperature-controlled water bath shaker (model RSB-12, Remi Equipment Pvt. Ltd., India) at a constant temperature (301 K ± 1 K) and atmospheric pressure. The temperature was measured by a PT100 sensor-thermocouple with 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 an appropriate time for attaining equilibrium. The solutions were then allowed 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 was prepared fresh every time before titration was to be carried out. The weighing balance of Shimadzu make (model AW220 with an 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 a material balance. The few experiments were repeated to check the consistency, and the error found was within the limit of ± 2 % of concentration.

The distribution coefficient (K_D) was calculated as the ratio of total acid in the organic phase to the total acid in the aqueous phase. The degree of extraction (E %) of caproic acid in respective extractants is expressed as:

$$E\,\% = \frac{100K_D}{1 + K_D} \qquad (1)$$

The caproic acid concentration in the organic phase at equilibrium depends on the degree of extraction. In present work, a large degree of caproic acid extraction was observed; therefore, all of the caproic acid with half the molar concentration of the extractant can be extracted into the organic phase. Hence, the relative basicity (pK_B) was calculated as twice the pH of equilibrium aqueous phase.[42] For caproic acid, log P is taken as 1.99.[43]

Results and Discussion

Physical Extraction. Extraction of caproic acid by diluent alone (physical extraction) was basically accounted by three steps:[44] ionization of acid in the aqueous phase (K_a), partition of the undissociated acid in organic phase (P), and dimerization of acid in organic phase (D), and it can be described as:

Ionization of the acid in the aqueous solution:

$$\mathrm{HA_{aq}} \leftrightarrow \mathrm{H^+} + \mathrm{A^-} \qquad (2)$$

$$K_a = \frac{[\mathrm{H^+}][\mathrm{A^-}]}{[\mathrm{HA}]} \qquad (\mathrm{p}K_a = 4.85) \qquad (3)$$

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

$$\mathrm{HA_{aq}} \leftrightarrow \mathrm{HA_{org}} \qquad (4)$$

$$P = \frac{[\mathrm{HA}]_{\mathrm{org}}}{[\mathrm{HA}]_{\mathrm{aq}}} \qquad (5)$$

Dimerization of the acid in the organic phase:

$$2\mathrm{HA_{org}} \leftrightarrow \mathrm{HA^2_{org}} \qquad (6)$$

$$D = \frac{[\mathrm{HA}]_{2,\mathrm{org}}}{[\mathrm{HA}]^2_{\mathrm{org}}} \qquad (7)$$

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

$$K_D^{\mathrm{diluent}} = \frac{[\mathrm{HA}]_{\mathrm{org,Total}}}{[\mathrm{HA}]_{\mathrm{aq,Total}}} = \frac{[\mathrm{HA}]_{\mathrm{org}} + 2[\mathrm{HA}]_2}{[\mathrm{HA}]_{\mathrm{aq}} + [\mathrm{A^-}]} = \frac{P + 2P^2D[\mathrm{HA}]_{\mathrm{aq}}}{1 + K_a/[\mathrm{H^+}]_{\mathrm{aq}}} \qquad (8)$$

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

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

Or it can be written in another form as

$$[\text{HA}]_{\text{org}} = P[\text{HA}]_{\text{aq}} + D[\text{HA}]_{\text{aq}}^{2} \qquad (10)$$

The physical extraction experiments of caproic acid were carried out using three diluents of alcohol category such as hexanol, octanol, and decanol. Equation 10 was fitted to the experimental data to yield the values of P and D. The values of partition coefficient, dimerization constant, distribution coefficient, and degree of extraction is given in Table 1.

The values of P (partition coefficient) for caproic acid in hexanol, decanol, and octanol was found to be 15.23, 18.22, and 7.78, respectively. The $K_{\text{D}}^{\text{diluent}}$ values for caproic acid in hexanol, decanol, and octanol were obtained as 16.7 to 71.8, 13.4 to 73.7, and 8.9 to 57.1, respectively. The values of distribution coefficients were found to be higher in octanol than hexanol and decanol.

Chemical Extraction. 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 extractant with a 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 a higher distribution coefficient.[13] TBP is selected because of low water coextraction (mass fraction is 4.67 %) and very low solubility in aqueous phase (mass fraction is 0.039 %).[13] 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.[13]

Since TBP has a relatively high viscosity ($3.56 \cdot 10^{-3}$ Pa·s) and density close to unity ($0.975\ \text{g}\cdot\text{cm}^{-3}$), 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 hexanol, octanol, and decanol is presented in Tables 2, 3, and 4, respectively. 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) were found to decrease 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 % at a constant temperature of 301 K and atmospheric pressure 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) $\text{mol}\cdot\text{L}^{-1}$. The similar trend was found for the degree of extraction (E). The value of Z (loading ratio = total acid in organic phase/total extractant in 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.

The mechanism of reactive extraction and its behavior can be represented with the help of various models such as the relative basicity model, mass action law model, linear solvation energy relationship model, Langmuir model, and so forth. The attempts were made in the next sections to describe the reactive extraction of caproic acid using TBP in hexanol, octanol, and decanol by these models.

Relative Basicity Model. Shan[45] proposed the relative basicity model to relate the 1:1 equilibirum complexation constant with relative basicity. It was found that the apparent extraction equilibrium constant of a 1:1 complex, K_{11}, mainly depended on the nature of solute and extractant, that is, log P and pK_{a} of the acid, and the apparent basicity of extractant to HCl, pK_{B}. A model equation is in the following form:

$$\log K_{11} = C_1(\text{p}K_{\text{B}} - \text{p}K_{\text{a}}) + \log(C_2P) \qquad (11)$$

Equation 11 can be used to predict the extraction equilibrium behavior of carboxylic acids with extractant/diluent. K_{11} in eq 11 represents the extraction capacity of the acid by forming the complex of ion-pair, H-bond association, and solvating power of the complex. The solvating power is a complicated H-bonding association between the complex and the diluent, which depends on the nature of the solute, extractant, and diluent. Furthermore, pK_{B} in eq 11 is the relative basicity of the extractant mixture to HCl, excluding the nature of solute. If the basicity of the extractant mixture is relative to the solute, this relative basicity of the extractant can represent all of the nature of the solute, diluent and extractant, as well as special associations, for example, solvating power.[42] The model eq 11 was fitted for experimental data, and following relations were obtained.

20 % TBP + 80 % hexanol:

$$\log K_{11} = -0.671(\text{p}K_{\text{B}} - \text{p}K_{\text{a}}) + \log(0.147P) \qquad (12)$$

40 % TBP + 60 % hexanol:

$$\log K_{11} = -0.986(\text{p}K_{\text{B}} - \text{p}K_{\text{a}}) + \log(0.046P) \qquad (13)$$

20 % TBP + 80 % octanol:

$$\log K_{11} = -1.548(\text{p}K_{\text{B}} - \text{p}K_{\text{a}}) + \log(1.714P) \qquad (14)$$

40 % TBP + 60 % octanol:

Table 1. Partition and Dimerization Coefficients, Distribution Coefficient, and Degree of Extraction for Caproic Acid Extracted from Water into Organic Solvents at 301 K ($[\text{HA}]_{\text{aq,initial}} = (0.005\ \text{to}\ 0.057)\ \text{mol}\cdot\text{L}^{-}$)

	$[\text{HA}]_{\text{org}} = P\,[\text{HA}]_{\text{aq}} + D\,[\text{HA}]_{\text{aq}}^{2}$					
diluent	partition coefficient (P)	dimerization coefficient (D)	range of K_{D}	average K_{D}	range of %E	average %E
hexanol	15.23	70008	16.7 to 71.8	43.5	94.4 to 98.6	97.2
octanol	18.22	57749	13.4 to 73.7	48.1	93.1 to 98.7	97.1
decanol	7.78	40139	8.9 to 57.1	36.4	89.9 to 98.3	95.8

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

$S_{\mathrm{org}}^{\mathrm{initial}}$	$[\mathrm{HA}]^{\mathrm{o}}$	$[\mathrm{HA}]_{\mathrm{aq}}$	$[\mathrm{HA}]_{\mathrm{org}}$														
$\mathrm{mol \cdot L^{-1}}$	$\mathrm{mol \cdot L^{-1}}$	$\mathrm{mol \cdot L^{-1}}$	$\mathrm{mol \cdot L^{-1}}$	K_D	$\%E$	Z	$\mathrm{pH_{eq}}$	$\mathrm{p}K_B$	K_{11} (exp)	K_{11} basicity model	K_{11} Langmuir model	K_{11} LSER model	K_{11} (exp) (avg)	K_{11} basicity model (avg)	K_{11} Langmuir model (avg)	K_{11} LSER model (avg)	K_{11} mass action law model (avg)
0.7322	0.057	0.0047	0.0522	11.05	91.7	0.071	2.43	4.87	16.25	13.85	12.65	14.23	9.91	9.84	11.22	9.98	9.37
	0.04	0.0044	0.0355	8.07	88.9	0.048	2.45	4.90	11.59	13.20	12.88	13.76					
	0.03	0.0034	0.0265	7.58	88.3	0.036	2.50	5.00	10.75	11.25	14.01	11.35					
	0.02	0.0026	0.0173	6.59	86.8	0.023	2.56	5.13	9.22	9.21	13.68	9.45					
	0.01	0.0016	0.0083	4.90	83.0	0.011	2.67	5.34	6.77	6.68	9.35	6.12					
	0.005	0.0011	0.0039	3.53	77.9	0.005	2.77	5.55	4.85	4.82	4.72	4.98					
1.4644	0.057	0.0051	0.0518	10.15	90.9	0.035	2.41	4.83	7.15	4.62	4.26	7.29	3.69	3.43	3.69	3.82	3.21
	0.04	0.0048	0.0351	7.27	87.9	0.024	2.43	4.86	5.08	4.35	4.14	4.67					
	0.03	0.0044	0.0255	5.76	85.2	0.017	2.45	4.90	4.00	3.99	4.02	4.11					
	0.02	0.0041	0.0158	3.80	79.1	0.010	2.46	4.92	2.62	3.75	3.91	3.12					
	0.01	0.0029	0.0070	2.41	70.7	0.004	2.54	5.08	1.65	2.61	3.40	2.32					
	0.005	0.0014	0.0035	2.38	70.4	0.002	2.70	5.41	1.63	1.25	2.42	1.45					

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

$S_{\mathrm{org}}^{\mathrm{initial}}$	$[\mathrm{HA}]^{\mathrm{o}}$	$[\mathrm{HA}]_{\mathrm{aq}}$	$[\mathrm{HA}]_{\mathrm{org}}$														
$\mathrm{mol \cdot L^{-1}}$	$\mathrm{mol \cdot L^{-1}}$	$\mathrm{mol \cdot L^{-1}}$	$\mathrm{mol \cdot L^{-1}}$	K_D	$\%E$	Z	$\mathrm{pH_{eq}}$	$\mathrm{p}K_B$	K_{11}(exp)	K_{11} basicity model	K_{11} Langmuir model	K_{11} LSER model	K_{11} (exp) (avg)	K_{11} basicity model (avg)	K_{11} Langmuir model (avg)	K_{11} LSER model (avg)	K_{11} mass action law model (avg)
0.7322	0.057	0.0021	0.0548	25.87	96.2	0.074	2.61	5.23	38.19	41.99	39.34	40.37	22.64	22.55	27.5	22.12	22.21
	0.04	0.0019	0.0380	19.95	95.2	0.052	2.64	5.28	28.74	35.15	35.46	32.79					
	0.03	0.0013	0.0286	21.09	95.4	0.039	2.72	5.45	29.98	19.54	26.69	22.34					
	0.02	0.0012	0.0187	14.45	93.5	0.025	2.73	5.47	20.26	17.96	25.30	19.12					
	0.01	0.0010	0.0089	8.62	89.6	0.012	2.79	5.58	11.91	12.17	20.80	12.12					
	0.005	0.0008	0.0041	4.89	83.0	0.005	2.84	5.68	6.72	8.43	17.39	5.98					
1.4644	0.057	0.0060	0.0509	8.39	89.3	0.034	2.38	4.76	5.94	5.61	5.46	5.21	4.25	4.23	3.16	4.04	4.15
	0.04	0.0049	0.0350	7.10	87.6	0.023	2.42	4.85	4.96	5.15	4.66	5.34					
	0.03	0.0039	0.0260	6.67	86.9	0.017	2.47	4.95	4.64	4.67	3.76	4.35					
	0.02	0.0027	0.0172	6.19	86.1	0.011	2.55	5.11	4.28	4.02	2.63	3.93					
	0.01	0.0018	0.0081	4.30	81.1	0.005	2.64	5.29	2.95	3.38	1.67	3.11					
	0.005	0.0010	0.0039	3.94	79.7	0.002	2.79	5.59	2.70	2.52	0.78	2.35					

Table 4. Extraction Equilibrium Results for Caproic Acid + TBP + Decanol System at 301 K for Various Concentrations of TBP and Caproic Acid

$S_{\text{org}}^{\text{initial}}$ mol·L^{-1}	[HA]° mol·L^{-1}	$[\text{HA}]_{\text{aq}}$ mol·L^{-1}	$[\text{HA}]_{\text{org}}$ mol·L^{-1}	K_D	%E	Z	pH_{eq}	$\text{p}K_{\text{B}}$	K_{11}(exp)	K_{11} basicity model	K_{11} Langmuir model	K_{11} LSER model	K_{11} (exp) (avg)	K_{11} basicity model (avg)	K_{11} Langmuir model (avg)	K_{11} LSER model (avg)	K_{11} mass action law model (avg)
0.7322	0.057	0.0018	0.0551	30.30	96.8	0.075	2.65	5.31	44.76	45.31	44.69	44.23	23.25	23.18	23.82	23.62	22.87
	0.04	0.0016	0.0383	22.72	95.7	0.052	2.67	5.34	32.75	35.29	36.23	36.45					
	0.03	0.0015	0.0284	18.77	94.9	0.038	2.69	5.39	26.67	24.98	26.64	25.87					
	0.02	0.0013	0.0186	13.83	93.2	0.025	2.72	5.45	19.38	16.91	18.15	18.12					
	0.01	0.0011	0.0088	7.47	88.1	0.012	2.76	5.52	10.33	10.82	11.37	11.45					
	0.005	0.0009	0.0040	4.10	80.3	0.005	2.80	5.61	5.63	5.765	5.81	5.63					
1.4644	0.057	0.0020	0.0549	27.17	96.4	0.037	2.63	5.26	19.28	20.99	19.53	21.87	10.45	10.35	10.18	10.74	10.12
	0.04	0.0017	0.0382	21.38	95.5	0.026	2.65	5.31	14.99	14.52	14.53	14.11					
	0.03	0.0015	0.0284	17.93	94.7	0.019	2.68	5.37	12.48	10.13	10.41	11.89					
	0.02	0.0014	0.0185	12.79	92.7	0.012	2.71	5.42	8.84	7.740	7.93	8.02					
	0.01	0.0013	0.0086	6.41	86.5	0.005	2.72	5.45	4.40	6.20	6.28	5.55					
	0.005	0.0010	0.0039	3.94	79.7	0.002	2.79	5.59	2.70	2.54	2.40	3.01					

$$\log K_{11} = -0.416(\text{p}K_{\text{B}} - \text{p}K_{\text{a}}) + \log(0.053P) \tag{15}$$

20 % TBP + 80 % decanol:

$$\log K_{11} = -2.943(\text{p}K_{\text{B}} - \text{p}K_{\text{a}}) + \log(10.591P) \tag{16}$$

40 % TBP + 60 % decanol:

$$\log K_{11} = -2.706(\text{p}K_{\text{B}} - \text{p}K_{\text{a}}) + \log(2.773P) \tag{17}$$

The percentage of TBP and hexanol, octanol, or decanol are given by volume at 301 K and atmospheric pressure. The model values for K_{11} for reactive extraction of caproic acid using TBP in hexanol, octanol, and decanol are presented in Tables 2, 3, and 4, respectively. It can be seen that model values are in very good agreement with the experimental values. The parity plot for the combined data of K_{11} is shown in Figure 2. It can be observed that all of the data is within ± 10 % except 2 to 3 data points. Hence this model can be used to describe the reactive extraction of caproic acid using TBP in various diluents.

Mass Action Law Model. In general, carboxylic acid dissociates in aqueous solution. Under the experimental conditions where the pH of the aqueous solution was smaller than pK_{a} of the caproic acid (4.85), the effect of the caproic acid dissociation was negligibly small. Thus, only the undissociated form of the acid was expected to exist in the aqueous phase. The mass action law for equilibria describing the extraction of caproic acid by TBP in different diluents (hexanol, octanol, and decanol) can be represented as:

$$\text{HA}_{\text{aq}} + p\text{S}_{\text{org}} \leftrightarrow (\text{HA}\cdot\text{S}_p)_{\text{org}} \tag{18}$$

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_{11}) 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

$$K_{11} = \frac{[(\text{HA})\cdot(\text{S})_p]_{\text{org}}}{[\text{HA}]_{\text{aq}}} \tag{19}$$

where $[\text{HA}]_{\text{aq}}$, $[\text{S}]_{\text{org}}$, and $[(\text{HA}\cdot\text{S})]_{\text{org}}$ represent acid, extractants, and complex concentration in the respective phases. K_{11} 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:

$$\text{HA} \leftrightarrow \text{H}^+ + \text{A}^- \qquad K_{\text{a}} = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \tag{20}$$

$[\text{H}^+]$ and $[\text{A}^-]$ 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

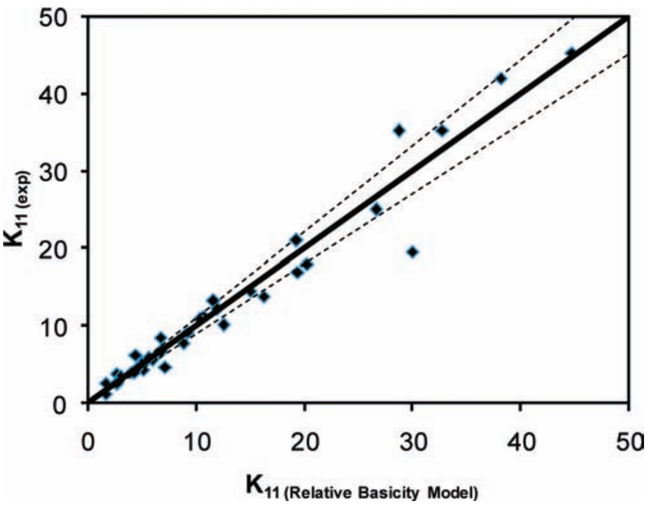

Figure 2. Parity plot for relative basicity model predicted K_{11} for extraction of caproic acid using TBP in various diluents. ◆, data points; —, parity line; ----, 10 % deviation.

is evaluated as the function of extraction constant and the number of reacting species as:

$$K_D = \frac{[HA \cdot S_p]_{org}}{[HA]_{aq} + [A^-]_{aq}} = \frac{K_S[HA]_{aq}[S]^p{}_{org}}{[HA]_{aq} + K_a[HA]_{aq}/[H^+]_{aq}} = \frac{K_S[S]^p{}_{org}}{1 + K_a/[H^+]_{aq}} \qquad (21)$$

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

$$\log(K_D) = \log(K_{11}) + p \log[S]_{org} \qquad (22)$$

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

$$[S]_{org} = [S]_{org}^{initial} - p[HA]_{org} \qquad (23)$$

thus the plot of $\log(K_D)$ versus $\log[S]_{org}$ would yield a straight line with the slope of p (solvation number) and the intercept of $\log(K_{11})$, from which K_{11} can be obtained.

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 caproic acid can be taken as 1.[46] This indicated a stoichiometric association between the individual phosphoryl group and the individual acid group and displays the strong effect of acid concentration on the experimentally determined distribution ratio. The values of equilibrium complexation constants (K_{11}) are given in Tables 2, 3, and 4 for hexanol, octanol, and decanol in TBP, respectively. It can be seen that model values are in very good agreement with the experimental values. The values of K_{11} was found to be 9.37 and 3.21 for (20 and 40) % TBP in hexanol, respectively, 22.21 and 4.15 for (20 and 40) % TBP in octanol, respectively, and 22.87 and 10.12 for (20 and 40) % TBP in decanol, respectively. It can be seen that the decanol has the higher K_{11} value than the hexanol and decanol; hence, decanol is more preferable than hexanol and octanol for the extraction of caproic acid using TBP.

Langmuir Model. Chemical interaction between the components of the acid−extractant complex are strong compared to the physical interactions in the system, so the equilibrium behaviors was modeled by postulating the formation of various stoichiometric complexes of acid and extractant. A Langmuir type of isotherm,[47,48] the individual complexes present in the organic phase, was identified, and their contributions to the overall extraction were determined as a function of relevant process parameters. The model is simple but practically useful to interpret the equilibrium data and is represented as:

$$\frac{[HA]_{org}}{[HA]_{org}^{max}} = \frac{K_E([HA]_{aq})^c}{1 + K_E([HA]_{aq})^c} \qquad (24)$$

where $c = ([HA]_{org}^{max})/([S]_{o;org})$ is assumed to be constant in the concentration range considered.

A modified Langmuir isotherm was fitted to the equilibrium data, and the best fitted model parameter relations were obtained as:

20 % TBP + 80 % hexanol:

$$[HA]_{org} = \frac{1.16 \cdot 10^7([HA]_{aq})^{3.04}}{1 + 8.81 \cdot 10^7([HA]_{aq})^{3.04}} \qquad (25)$$

40 % TBP + 60 % hexanol:

$$[HA]_{org} = \frac{230([HA]_{aq})^{1.6}}{1 + 1350([HA]_{aq})^{1.6}} \qquad (26)$$

20 % TBP + 80 % octanol:

$$[HA]_{org} = \frac{1440([HA]_{aq})^{1.88}}{1 + 8472([HA]_{aq})^{1.88}} \qquad (27)$$

40 % TBP + 60 % octanol:

$$[HA]_{org} = \frac{6000([HA]_{aq})^{2.24}}{1 + 3.54 \cdot 10^4([HA]_{aq})^{2.24}} \qquad (28)$$

20 % TBP + 80 % decanol:

$$[HA]_{org} = \frac{9.55 \cdot 10^{11}([HA]_{aq})^{4.77}}{1 + 5.62 \cdot 10^{12}([HA]_{aq})^{4.77}} \qquad (29)$$

40 % TBP + 60 % decanol:

$$[HA]_{org} = \frac{1.25 \cdot 10^{11}([HA]_{aq})^{4.52}}{1 + 7.41 \cdot 10^{11}([HA]_{aq})^{4.52}} \qquad (30)$$

The shown percentage of TBP and hexanol, octanol, or decanol are given by volume at a 301 K temperature and atmospheric pressure. The model predicted values of K_{11} were presented in Tables 2, 3, and 4. A parity plot for the comparison of experimental and model predicted values of K_D is given in

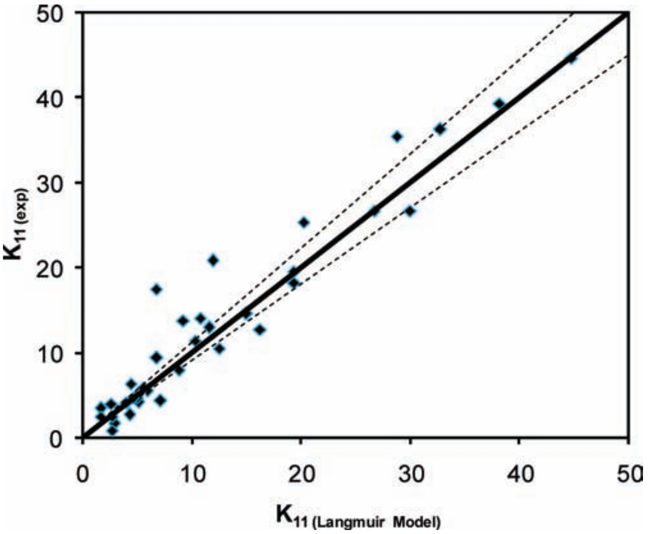

Figure 3. Parity plot for the Langmuir model predicted K_{11} for the extraction of caproic acid using TBP in various diluents. ◆, data points; —, parity line; ----, 10 % deviation.

Figure 3. It can be observed that many of the data points are not within ± 10 % except for a few data points. Hence, this model is not suitable to describe the reactive extraction of caproic acid using TBP in various diluents. Also the significant deviation in model K_{11} values was observed as compared with experimental values.

LSER Model. The ability of a diluent to donate a hydrogen atom toward the formation of a hydrogen bond is an important property. Protic diluents have these properties, but some protogenic, albeit aprotic diluents, have, more recently, shown having potential ability. The α parameter by Taft and Kamlet[49] is the most successful index that has been proposed to measure the hydrogen bond donor (HBD) ability. The LSER that measures property XYZ, in terms of diluent properties was defined as,[50]

$$\mathrm{XYZ} = \mathrm{XYZ}^0 + \text{solvent polarity/polarizability effect} + a\alpha + b\beta \quad (31)$$

where a and b are the susceptibilities of XYZ to changing solvent HBD acidity and hydrogen bond acceptance (HBA) basicity, respectively, and β is the HBA basicity of the solvent.[49] Values of α have been determined by the use of the solvatochromic comparison method.[49,51] In this method, indicator solutes are employed for which XYZ has a negligible susceptibility to the solvent HBA basicity ($b \approx 0$) but a high one for the solvent HBD acidity (large a). The $(\mathrm{XYZ})_0$ + solvent polarity/polarizability effect values are obtained for the indicator in solvents devoid of HBD abilities, so that $a\alpha$ for HBD solvents can be calculated from the values of XYZ in the latter kind of solvents. Finally, an averaging procedure for several indicator solutes and a normalization procedure are used to obtain values of α that are in the range of 0 to 1. Many linear solvation energy correlations involving the solvent HBD acidity scale have been reported, and the limitations of this scale have been discussed.[50,52]

Interactions of various types, dipole−dipole and/or dipole−induced dipole, hydrogen bonding, and so forth, are responsible for the extraction of carboxylic acid from aqueous solutions. The general LSER is a comprehensive tool to include the above-mentioned parameters of the diluents. Schmidt[53] presented a systematic study on the effect of diluents on amine extraction of acids. He distinguished among three types of solvation: solvation of acid anion, alkylammonium cation, or complex as a whole and found that the solvation of cation was not common in the case of tertiary amines. The solvation of the whole amine: acid complex is based on dipole−dipole interaction and was found to play an important role in the neutralization reactions between acid and amine, which are promoted by the increasing polarity of the diluent. An empirical parameter, DP^*, has been introduced to quantify this influence according to the equation based on the linear free energy principle

$$\ln K = \ln K^{\mathrm{o}} + aDP^* \quad (32)$$

where K^{o} and K are the extraction constants for standard and given diluent, respectively, and a is constant for a given extractant and solute. The values of DP^* were estimated for about 25 diluents.[53] The solvation of acid anion, which is based on specific interactions with the proton-donating diluent, is typical for the reaction of acid with alkylammonium salt. The hindering effect of the diluent can be explained as a competition between diluent and acid for the bonding with the amine salt. The other empirical parameter, DP, was introduced to quantify this type of solvation according to the following equation, similar to eq 32;

$$\ln K' = \ln K'^{\mathrm{o}} + a'DP \quad (33)$$

The DP values were estimated for about 30 diluents. If both types of solvation occur simultaneously, the combined equation is to be used in the form

$$\ln K = \ln K^{\mathrm{o}} + aDP^* + a'DP \quad (34)$$

Using this concept, Schmidt[53] described the effect of diluents on the extraction of mineral acids by various tertiary amines with a comparatively good fit. The attempts were also made to correlate the values of DP^* and DP with various physicochemical properties of the diluents. The main disadvantage lies in the fact that the parameters DP^* and DP were obtained on the basis of the same data set as the extraction constants, which were correlated with them. This seems to increase the empirical character of these parameters.

The LSER model by Kamlet et al.[50] was modified by Bizek et al.[54] and Uslu[55] to describe the effect of diluents on the values of distribution coefficients $K_{\mathrm{D}}^{\mathrm{overall}}$ in the form

$$\ln K_{\mathrm{D}}^{\mathrm{overall}} = \ln K_{\mathrm{D}}{}^{0} + P(\delta_{\mathrm{h}})^2/100 + s(\pi^* + d\delta) + b\beta + a\alpha \quad (35)$$

where δ_{h} is the Hildebrand's solubility parameter and π^*, d, and δ are the solvatochromic parameters that measure the solute + solvent, dipole + dipole, and dipole + induced dipole interactions, respectively. $K_{\mathrm{D}}{}^{0}$ represents the extraction constant for an "ideal inert" diluent. The solvatochromic parameter α scale of solvent HBA (hydrogen-bond donor) acidities describes the ability of the solvent to donate a proton in a solvent to solute hydrogen bond. The β scale of HBA (hydrogen-bond acceptor) basicities provides a measure of the solvent's ability to accept a proton (donate an electron pair) in a solute to solvent hydrogen bond, respectively. The coefficients p, s, d, a, and b include the properties of solute. Rather than p, s, d, and a are regression

Table 5. Solvatochromic Parameters: Hydrogen Bond Donor Acidity (π^*, δ) and Hydrogen Bond Acceptor Basicities (α, β) for Different Diluents Used

diluent	π^*	δ	β	α
hexanol	0.45	0	0.84	0.66
octanol	0.4	0	0.81	0.77
decanol	0.45	0	0.82	0.7

coefficients. The values of solvatochromic parameters π^*, δ, α, and β have been found for several hundreds of compounds. The second term of eq 31 which contains the solubility parameter δ_h does not affect the values of the objective function significantly. Thus, eq 31 reduces to

$$\ln K_D^{\text{overall}} = \ln K_D{}^0 + s(\pi^* + d\delta) + b\beta + a\alpha \tag{36}$$

The solvatochromic parameters, hydrogen bond donor acidity (π^*, δ) and hydrogen bond acceptor basicities (α, β) for different diluents used (hexanol, octanol, decanol), are given in Table 5. The LSER model has been fitted to the data, and the model K_{11} values have been reported in Tables 2, 3, and 4 for acid concentrations of (0.057, 0.04, 0.03, 0.02, 0.01, and 0.005) mol·L^{-1} for the extraction of caproic acid using TBP in different diluents. The parity plot for the combined data of K_{11} is shown in Figure 4. It can be observed that all of the data is within ± 10 % except 1 to 2 data points. Hence, this model can be used to describe the reactive extraction of caproic acid using TBP in various diluents.

Model Comparison. Different models (relative basicity model, mass action law model, Langmuir model, and LSER model) were used to represent the equilibrium behavior for reactive extraction of caproic acid using TBP in hexanol, octanol, and decanol. The comparison of model predicted values of K_{11} are shown in Tables 2, 3, and 4. These models have used different approaches as their name suggested. It can be observed that the trend of accuracy of model is: (1) relative basicity model, (2) LSER model (mass action law model), and (3) Langmuir model. The same can be found from the parity plots. Hence, the relative basicity model is the best suited model to explain the reactive extraction of caproic acid using TBP in hexanol, octanol, and decanol.

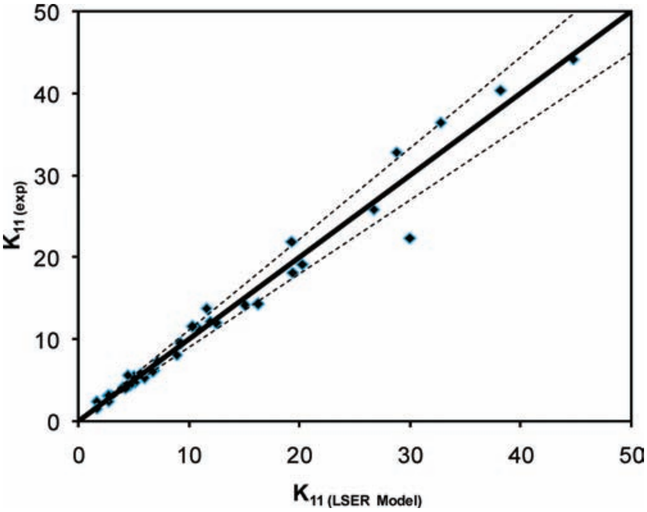

Figure 4. Parity plot for the LSER model predicted K_{11} for the extraction of caproic acid using TBP in various diluents. ◆, data points; —, parity line; ----, 10 % deviation.

Diluent Comparison. It was found that K_{11} increases in the order of hexanol < octanol < decanol. Hence decanol is the most suited diluents among the diluents used for the reactive extraction of caproic acid using TBP. 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 was made to correlate the experimental study with the physiochemical properties of diluents like molecular mass, boiling point, density, refractive index, dielectric constant, dipole moment, and E_T parameter, and so forth. The various physiochemical properties of diluents are given in Table 6. It can be seen that a systematic trend with respect to various properties for K_{11} were observed.

Conclusion

The recovery of caproic acid from the aqueous stream is of practical relevance due to mainly its market value and also environmental concerns. The extraction of caproic acid using TBP in hexanol, octanol, and decanol was studied. TBP is viscous and is thus used in different diluents. 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) were determined for various diluents. The experimental values of the caproic acid−TBP equilibrium complexation constant (K_{11}) were found to be 9.91 and 3.69 for (20 and 40) % TBP in hexanol, respectively, 22.64 and 4.25 for (20 and 40) % TBP in octanol, respectively, and 23.25 and 10.45 for (20 and 40) % TBP in decanol, respectively. Decanol is more preferable than hexanol and octanol for the extraction of caproic acid using TBP.

Different models (relative basicity model, mass action law model, Langmuir model, and LSER model) were used to represent the equilibrium behavior for reactive extraction of

Table 6. Various Physicochemical Properties of Diluents Chosen in the Extraction of Caproic Acid[a]

			BP	MP		ρ		μ				
solvent	MW	molecular structure	°C	°C	solubility in water	g·cm^{-3}	RI	cP	ε	log(P)	DM	E_T
hexanol	102.2	$C_6H_{14}O$	151.8	−52	0.59 g/100 mL	0.814	–	–	13.3	2.03	1.66	48.8
octanol	130.28	$CH_3(CH_2)_7OH$	195	−15.5	0.30 mg·L^{-1}	0.827	1.4295	8.925	10.3	3.00	1.71	48.3
decanol	158.29	$CH_3(CH_2)_9OH$	230	7	0.37 g/100 mL	0.827	1.4295	8.925	8.1	4.23	–	48.1

[a] BP: boiling point; MP: melting point; RI: refractive index; ρ: density of pure liquid; μ: viscosity; ε: dielectric constant; log(P): octanol water partition coefficient; DM: dipole moment.

caproic acid using TBP in hexanol, octanol, and decanol. The trend of accuracy of the model is: (1) relative basicity model, (2) LSER model (mass action law model), and (3) Langmuir model. The relative basicity model is the best suited model to explain the reactive extraction of caproic acid using TBP in hexanol, octanol, and decanol.

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