Reactive Extraction of Acrylic Acid Using Tri-*n*-butyl Phosphate in Different Diluents

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The increasing demand of carboxylic acid products is drawing great attention toward its recovery from waste streams/dilute solutions. With the above aim, the reactive extraction of acrylic acid from aqueous solutions using tri-*n*-butyl phosphate (TBP) in different diluents (paraffin liquid, toluene, and butyl acetate) was studied. The distribution coefficients and equilibrium extraction coefficients were obtained. Comparison was made on the basis of different physical properties of the solvents like molecular weight, dipole moment, dielectric constant, and E_T parameter. Results show that higher values of distribution coefficients by chemical extraction were obtained for TBP in inert diluents: paraffin liquid and toluene.

Introduction

Acrylic acid or prop-2-enoic acid ($CH_2{=}CHCOOH$) is the simplest unsaturated carboxylic acid with a vinyl group at the α-carbon position and a carboxylic acid terminus. In its pure form, acrylic acid is a clear, colorless liquid with a characteristic acrid odor. The estimated annual production capacity of acrylic acid is 4.2 million metric tons,[1] which ranks it at about position 25 in the list of organic chemical products. The major use of acrylic acid, and its salt and esters, is in polymeric flocculants, dispersants, coatings, paints, adhesives, and binders for leather, paper, and textile. Acrylic acid is conventionally produced from petrochemicals. Currently, most commercial acrylic acid is produced by partial oxidation of propene. In the so-called single-step process, the yield is at most (50 to 60) %, leading to large amounts of waste. A two-step process via acrolein is preferred, achieving about 90 % yield overall. There is a need for efficient one-step processes starting from cheap carbon sources. Unfortunately, petrochemical carbon sources are not renewable. This implies that their use adds to global CO_2 emissions and that they are expected to become more scarce and expensive in the future.

Production of acrylic acid by bioroute seems to be an attractive alternative.[2] Commercialization of the bioroute method poses a challenge of high cost of the recovery step in generation of the acid. Liquid−liquid extraction is one of the best methods for recovery of carboxylic acids from the bioreactor.[3−11] Reactive liquid−liquid extraction employs an extractant that can reversibly complex with acid in the broth. The reversible complexation provides high yield and high selectivity of acid over the nonacidic components in the broth. Extractants are generally viscous or solid, 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.

Equilibria of aqueous solutions of glyoxylic acid, glycolic acid, acrylic acid, and benzoic acid with trialkylphosphine oxide (TRPO) in kerosene were investigated by Li et al.[12] Equilibrium concentrations are given at 298 K. An extraction equilibrium model was used to describe the experimental data. The equilibrium constants were evaluated. Loading of TRPO was calculated. The separation and the purification of the acrylic acid produced from renewable sugars were studied using the liquid−liquid extraction process. Nonrandom two-liquids and universal quasichemical models and the prediction method universal quasichemical functional activity coefficients were used for generating liquid−liquid equilibrium diagrams for systems made up of acrylic acid, water, and solvents (diisopropyl ether, isopropyl acetate, 2-ethyl hexanol, and methyl isobutyl ketone), and the results were compared with available liquid−liquid equilibrium experimental data.[13]

Very little work on reactive extraction of acrylic acid can be found in the literature. In view of this reactive extraction, acrylic acid was studied using tri-*n*-butyl phosphate (TBP) in different diluents (paraffin liquid, toluene, and butyl acetate). The extraction mechanism and physical and chemical equilibria were studied. Extraction was explained on the basis of solvation ability of acid:TBP complexes by the diluent.

Experimental

Acrylic acid (molar mass 72.06 $kg\cdot mol^{-1}$; purity 99 %; density 1050 $kg\cdot m^{-3}$; Himedia India, Ltd.), paraffin liquid (density = (820 to 880) $kg\cdot m^{-3}$), toluene (molar mass 92.14 $kg\cdot mol^{-1}$; density 865 $kg\cdot m^{-3}$), and butyl acetate (molar mass 116.6 $kg\cdot mol^{-1}$; density 881 $kg\cdot m^{-3}$) are of technical grade and were used without pretreatment. Sodium hydroxide used for titration is of analytical grade and was supplied by Ranbaxy, India. For the standardization of the sodium hydroxide, 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 to 1.11) $kmol\cdot m^{-3}$ and the initial aqueous acid concentration range ($[HA]^o$) of (0.05 to 0.4) $kmol\cdot m^{-3}$ were used (where superscript "o" signifies the initial). Low concentration [(0.05 to 0.4)

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kmol·m^{-3}] was used because acrylic acid concentration in the fermentation broth is not greater than 0.5 kmol·m^{-3}.[14]

Extraction experiments involve shaking of equal volumes of aqueous and organic phases for 12 h at constant temperature (305 K) in an orbital shaking incubator (Metrex scientific instruments (P) Ltd., India) at 190 rpm, followed by settling of the mixture for at least 2 h at the same temperature in separating funnels maintained at the same temperature in the incubator. Aqueous phase acid concentration was determined by titration with sodium hydroxide solution (0.02 N). The acid content in the organic phase was determined with a mass balance. Few experiments were carried out in duplicate, and consistency was found within ± 2 %.

Results and Discussion

Physical extraction involves the extraction of solute into inert nonreacting hydrocarbons and substituted hydrocarbons and is relatively free of complexities. Two factors need to be accounted for to show the influence of diluents on the extraction: partial dissociation of the acids in the aqueous phase and dimerization in the hydrocarbon phase. The physical extraction of acrylic acid using paraffin liquid, toluene, and butyl acetate is described in terms of distribution coefficient (K_D^{diluent}) defined as

$$K_D^{\text{diluent}} = \frac{[\text{HA}]_{\text{org}}^{\text{diluent}}}{[\text{HA}]_{\text{aq}}} \quad (1)$$

where [HA] represents concentration of acid (kmol·m^{-3}) and subscripts "aq" and "org" refer to aqueous phase and organic phase, respectively. For the dilute concentration of acid (used in the study), Kertes and King[15] presented correlation of K_D^{diluent} in terms of dimerization constant (D) and partition coefficient as (P) as

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

or

$$[\text{HA}]_{\text{org}}=P[\text{HA}]_{\text{aq}}+2P^2D[\text{HA}]\text{aq}^2 \quad (3)$$

The physical extraction of acrylic acid using paraffin liquid, toluene, and butyl acetate was presented in Table 1. Except in butyl acetate, the extraction is low. "Classical extractants", such as aliphatic and aromatic hydrocarbons, are thus not able to fulfill the basic requirements of high distribution coefficient and high selectivity. The reason for this may be the higher affinity of acrylic acid for water. The higher K_D^{diluent} value for butyl acetate can be explained by its nature. Butyl acetate is a dipolar aprotic solvent and has a higher dipole moment (1.84) and E_T (38.5) value than paraffin liquid and toluene (dipole moment, 0.36; and E_T, 33.9) (E_T parameter[16] is an empirical parameter that should give assessment of solvation energy of the solute and is based on the absorption spectrum of pyridinium-*N*-phenol-betaine). It provides anion solvation by ion-dipole and ion-induced dipole forces. Partition coefficient values were obtained as 0.077, 0.182, and 2.281 for extractions using paraffin liquid, toluene, and butyl acetate, respectively, by fitting eq 3 to experimental data. As butyl acetate is an active diluent involving solvation of acid by ion pair interaction, no dimerization of acid was found in the organic phase. This was due to strong solute diluent interaction in comparison to solute−solute interaction which probably results in dimer formation. On the other hand, both paraffin liquid and toluene possess dimerization constant values (Table 1).

Table 1. Physical Equilibria for Extraction of Acrylic Acid Using Different Diluents

diluent	([HA]°) (kmol·m^{-3})	([HA]$_{\text{aq}}$) (kmol·m^{-3})	([HA]$_{\text{org}}$) (kmol·m^{-3})	K_D	P	(D) (m^3·kmol^{-1})
paraffin liquid	0.05	0.045	0.005	0.116	0.077	14.18
	0.10	0.094	0.006	0.068		
	0.15	0.140	0.010	0.071		
	0.20	0.180	0.020	0.111		
	0.30	0.253	0.047	0.184		
	0.40	0.350	0.050	0.143		
toluene	0.05	0.043	0.007	0.154	0.182	2.47
	0.10	0.090	0.010	0.111		
	0.15	0.119	0.031	0.261		
	0.20	0.173	0.027	0.156		
	0.30	0.236	0.064	0.271		
	0.40	0.327	0.073	0.223		
butyl acetate	0.05	0.017	0.033	1.885	2.281	–
	0.10	0.035	0.065	1.857		
	0.15	0.045	0.105	2.333		
	0.20	0.074	0.126	1.703		
	0.30	0.082	0.218	2.659		
	0.40	0.133	0.267	2.008		

Organophosphorous compounds like tri-*n*-butyl phosphate or tri-*n*-octyl phosphine oxide are strongly solvating extractants and have primarily been used in inorganic analysis for the extraction and separation of inorganic acids or metal species.[17] Since phosphoryl can form hydrogen bonds to proton donors, these organophosphorous compounds 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 tri-*n*-butyl phosphate (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.[18] The extraction reactions are ionic in nature. The recovery of acrylic acid using TBP (S) is by the formation of a complex via the interfacial reaction and can be represented as[15]

$$\text{HA}_{\text{aq}} + p\text{S}_{\text{org}} \leftrightarrow (\text{HA}\cdot\text{S}_p)_{\text{org}} \quad (4)$$

where p is the solvation number of TBP. As the acrylic acid−TBP complex is formed, it is rapidly extracted into the organic phase. The distribution coefficient of acid by chemical extraction (K_D^{Chem}) can be defined as

$$K_D^{\text{Chem}} = \frac{[\text{HA}]_{\text{org}}^{\text{total}} - \nu[\text{HA}]_{\text{org}}^{\text{diluent}}}{[\text{HA}]_{\text{aq}}} \quad (5)$$

where ν is volume fraction of diluent and $[\text{HA}]_{\text{org}}^{\text{diluent}}$ is the acid extracted into the organic phase by diluent alone. The overall distribution coefficient (K_D^{overall}) is obtained by summing up eqs 1 and 5.

$$K_D^{\text{overall}} = K_D^{\text{diluent}} + K_D^{\text{Chem}} \quad (6)$$

The degree of extraction (E %) is defined as

$$E\ \% = \frac{K_D^{\text{overall}}\cdot 100}{(1 + K_D^{\text{overall}})} \quad (7)$$

Table 2. Chemical Equilibria for Extraction of Acrylic Acid Using TBP in Paraffin Liquid

		experimental values						model values	
(S^{o}_{org}) (kmol·m^{-3})	([HA]°) (kmol·m^{-3})	([HA]$_{org}$) (kmol·m^{-3})	$K_D^{overall}$	*E* %	K_D^{Chem}	*z*	*m*	$K_D^{overall}$	*z*
0.37	0.05	0.015	0.411	29.11	0.279	0.039	0.014	0.772	0.074
	0.10	0.036	0.553	35.62	0.464	0.096	0.017	0.699	0.122
	0.15	0.060	0.672	40.20	0.572	0.163	0.027	0.685	0.166
	0.20	0.055	0.376	27.31	0.314	0.148	0.027	0.599	0.236
	0.30	0.101	0.511	33.82	0.457	0.274	0.032	0.553	0.297
	0.40	0.103	0.345	25.68	0.300	0.278	0.041	0.486	0.390
0.74	0.05	0.026	1.095	52.26	0.920	0.035	0.007	1.480	0.048
	0.10	0.053	1.143	53.35	1.034	0.072	0.009	1.365	0.086
	0.15	0.086	1.343	57.32	1.218	0.116	0.014	1.344	0.116
	0.20	0.111	1.248	55.52	1.158	0.150	0.014	1.261	0.152
	0.30	0.172	1.343	57.32	1.268	0.232	0.016	1.178	0.204
	0.40	0.216	1.169	53.89	1.104	0.291	0.020	1.082	0.270
1.1	0.05	0.030	1.560	60.94	1.374	0.028	0.005	2.142	0.038
	0.10	0.065	1.880	65.28	1.751	0.059	0.006	2.033	0.064
	0.15	0.102	2.142	68.17	1.995	0.093	0.009	2.009	0.087
	0.20	0.136	2.124	67.99	2.015	0.124	0.009	1.922	0.112
	0.30	0.215	2.545	71.79	2.446	0.196	0.011	1.852	0.142
	0.40	0.258	1.814	64.47	1.740	0.234	0.014	1.679	0.217

Table 3. Chemical Equilibria for Extraction of Acrylic Acid Using TBP in Toluene

		experimental values						model values	
(S^{o}_{org}) (kmol·m^{-3})	([HA]°) (kmol·m^{-3})	([HA]$_{org}$) (kmol·m^{-3})	$K_D^{overall}$	*E* %	K_D^{Chem}	*z*	*m*	$K_D^{overall}$	*z*
0.37	0.05	0.027	1.132	53.09	0.876	0.072	0.018	1.111	0.070
	0.10	0.052	1.065	51.57	0.879	0.139	0.027	0.994	0.130
	0.15	0.086	1.360	57.63	0.921	0.234	0.084	1.222	0.210
	0.20	0.105	1.098	52.33	0.843	0.283	0.073	0.988	0.255
	0.30	0.158	1.115	52.71	0.709	0.427	0.173	1.077	0.413
	0.40	0.181	0.826	45.24	0.526	0.489	0.197	0.889	0.526
0.74	0.05	0.033	2.004	66.71	1.683	0.045	0.009	2.058	0.046
	0.10	0.068	2.147	68.22	1.895	0.092	0.014	1.930	0.083
	0.15	0.106	2.418	70.74	1.853	0.143	0.042	2.198	0.130
	0.20	0.139	2.263	69.36	1.911	0.187	0.036	1.925	0.159
	0.30	0.208	2.263	69.36	1.706	0.281	0.086	2.033	0.253
	0.40	0.252	1.711	63.11	1.315	0.341	0.099	1.725	0.344
1.1	0.05	0.036	2.478	71.25	2.153	0.032	0.006	2.921	0.038
	0.10	0.074	2.776	73.52	2.512	0.067	0.009	2.789	0.067
	0.15	0.116	3.405	77.30	2.768	0.105	0.028	3.119	0.097
	0.20	0.151	3.098	75.60	2.711	0.137	0.025	2.789	0.124
	0.30	0.234	3.557	78.06	2.877	0.213	0.058	2.996	0.179
	0.40	0.294	2.789	73.61	2.305	0.268	0.066	2.621	0.252

Table 4. Chemical Equilibria for Extraction of Acrylic Acid Using TBP in Butyl Acetate

		experimental values						model values	
(S^{o}_{org}) (kmol·m^{-3})	([HA]°) (kmol·m^{-3})	([HA]$_{org}$) (kmol·m^{-3})	$K_D^{overall}$	*E* %	K_D^{Chem}	*z*	*m*	$K_D^{overall}$	*z*
0.37	0.05	0.033	2.017	66.86	0.243	0.090	0.088	1.928	0.086
	0.10	0.070	2.302	69.72	0.370	0.188	0.176	2.085	0.171
	0.15	0.109	2.646	72.57	0.349	0.294	0.284	2.450	0.272
	0.20	0.141	2.398	70.57	0.471	0.381	0.341	2.078	0.331
	0.30	0.218	2.672	72.76	0.270	0.590	0.589	2.551	0.563
	0.40	0.280	2.334	70.00	0.331	0.757	0.722	2.150	0.697
0.74	0.05	0.035	2.241	69.14	0.547	0.047	0.044	2.002	0.042
	0.10	0.074	2.889	74.29	0.867	0.100	0.088	2.329	0.081
	0.15	0.115	3.303	76.76	0.894	0.156	0.142	2.716	0.128
	0.20	0.151	3.118	75.72	1.042	0.205	0.170	2.380	0.156
	0.30	0.231	3.339	76.95	0.817	0.312	0.295	2.824	0.264
	0.40	0.299	2.955	74.72	0.843	0.404	0.361	2.410	0.329
1.1	0.05	0.035	2.366	70.29	0.826	0.032	0.030	1.998	0.027
	0.10	0.076	3.167	76.00	1.271	0.069	0.059	2.353	0.051
	0.15	0.119	3.773	79.05	1.434	0.108	0.095	2.794	0.080
	0.20	0.157	3.605	78.29	1.574	0.142	0.115	2.484	0.098
	0.30	0.242	4.198	80.76	1.554	0.220	0.198	3.095	0.162
	0.40	0.312	3.546	78.00	1.422	0.284	0.243	2.569	0.206

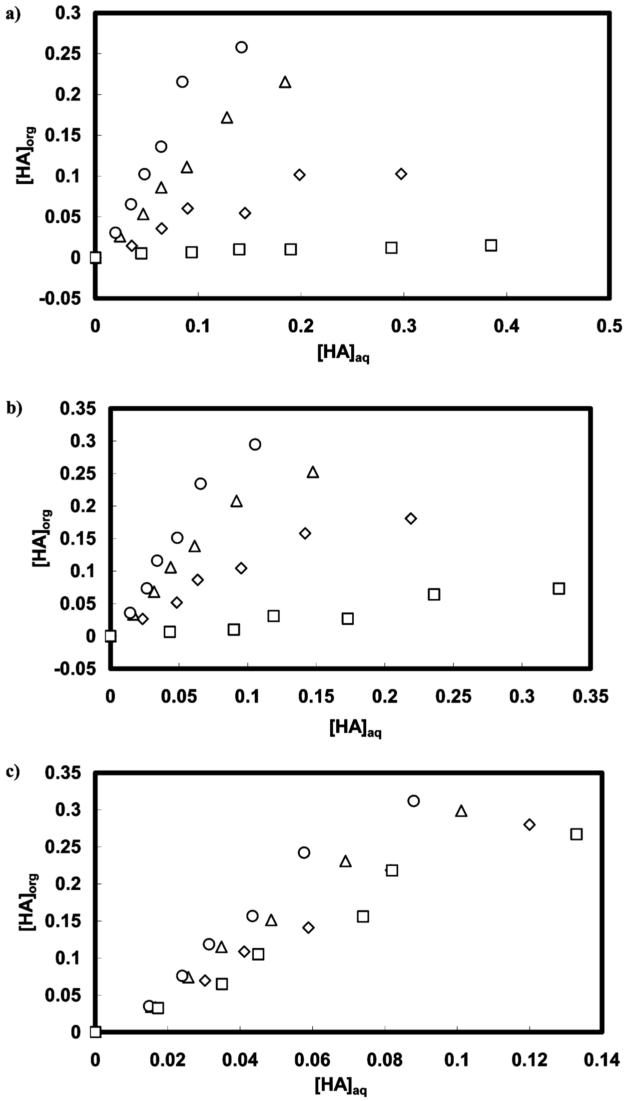

Figure 1. Physical and chemical extraction of acrylic acid [(0.05 to 0.4) kmol·m^{-3}] using TBP [(0.37 to 1.1) kmol·m^{-3}] in different diluents. (a) Paraffin liquid; (b) toluene, and (c) butyl acetate. ◇, 10 % TBP; Δ, 20 % TBP; ○, 30 % TBP; □, no TBP. [HA] = concentration of acid, kmol·m^{-3}. Subscripts: aq = aqueous phase, org = organic phase.

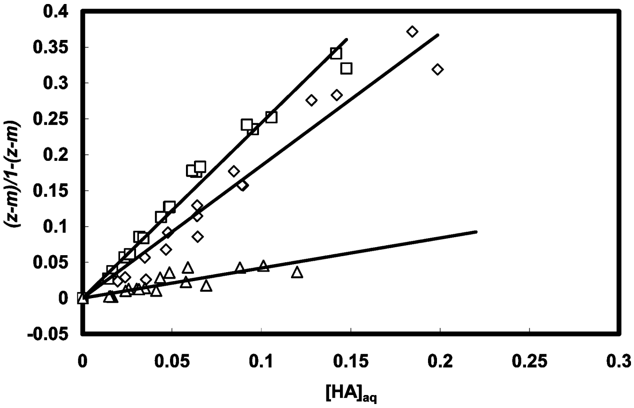

Figure 2. Equilibrium complexation constant determination for extraction of acrylic acid [(0.05 to 0.4) kmol·m^{-3}] using TBP [(0.37 to 1.1) kmol·m^{-3}] in different diluents. ◇, Paraffin liquid; □, toluene; Δ, butyl acetate; –, linear fit. z = loading ratio; m =($[HA]^{diluent}_{org}$)/($[S]^o_{org}$); [HA] = concentration of acid, kmol·m^{-3}; [S] = concentration of TBP, kmol·m^{-3}. Subscripts: aq = aqueous phase, org = organic phase. Superscript: o = initial.

Extraction equilibrium constant (K_S) is computed by applying the law of mass action as:

$$K_S = [(HA)\cdot(S)_p]_{org}/[HA]_{aq}[S]^p{}_{org} \qquad (8)$$

where $[HA]_{aq}$, $[S]_{org}$, $[(HA\cdot S)]_{org}$ represent acid, extractant, and complex concentrations and p is solvation number. Niitsu and Sekine[19] have reported that the solvation number of the aliphatic carboxylic acids was the same as the numbers of the carboxyl groups on each acid, thus the value of p for acrylic acid can be taken as one. This indicated a stoichiometric (1:1) 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. Substituting the value of $[S]_{org}$ as

$$[S]_{org} = [S]^o_{org} - [HA\cdot S]_{org} \qquad (9)$$

The overall distribution coefficient is evaluated as the function of extraction constant and the number of reacting species as

$$K_S[HA]_{aq} = \frac{[HA\cdot S]_{org}}{[S]^o_{org} - [HA\cdot S]_{org}} \qquad (10)$$

Usually the diluent removes the species by physical extraction. In this way, their concentration in the organic phase increases. On the other hand, the diluent can decrease the concentration of extracted species in the organic phase because it decreases the solubility of these in the organic phase or vice versa. In this case, the overall calculated distribution coefficient, which represents the ratio of the total acid concentration in the organic phase to that in the aqueous phase in all possible forms, could be obtained by including the term for physical extraction as

$$\begin{aligned} K_S[HA]_{aq} &= \frac{[HA\cdot S]_{org}}{[S]^o_{org} - [HA\cdot S]_{org}} \\ &= \frac{[HA]^{total}_{org} - \nu[HA]^{diluent}_{org}}{[S]^o_{org} - ([HA]^{total}_{org} - \nu[HA]^{diluent}_{org})} \\ &= \frac{(z - \nu m)}{1 - (z - \nu m)} \end{aligned} \qquad (11)$$

where z and m are defined as

$$z = \frac{[HA]^{total}_{org}}{[S]^o_{org}} \text{ and } m = \frac{[HA]^{diluent}_{org}}{[S]^o_{org}} \qquad (12)$$

z is the overall loading ratio and represents the extent to which the organic phase (extractant + diluent) can be loaded with acid. It depends on the extractability of the acid (strength of the acid–base interaction) and its aqueous concentration. The stoichiometry of the overall extraction reaction also depends on the loading ratio (z) in the organic phase.

The reactive extraction of acrylic acid with TBP [(10 to 30) %] in paraffin liquid, toluene, and butyl acetate has proved to be effective (Tables 2 to 4; Figure 1). Chemical extraction was compared with physical extraction, and it can be seen that for paraffin liquid (85.88, 94.57, and 96.55) %, for toluene (83.32,

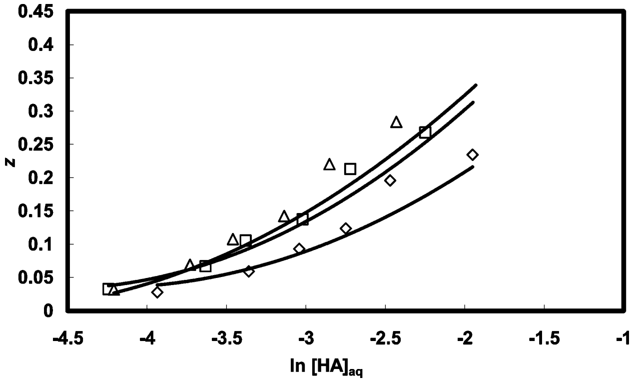

Figure 3. Loading curves or extraction of acrylic acid [(0.05 to 0.4) kmol·m^{-3}] using TBP (30 %) in different diluents. ◇, TBP + paraffin liquid; □, TBP + toluene; Δ, TBP + butyl acetate; −, model. z = loading ratio; [HA] = concentration of acid, kmol·m^{-3}. Subscripts: aq = aqueous phase.

91.557, and 94.16) %, and for butyl acetate (4.43, 22.78, and 32.87) % improvement in extraction could be obtained using (10, 20, and 30) % TBP in respective diluents over when these diluents were used alone. The higher value of distribution coefficients suggests that the acid−TBP complex has been formed, thus more acid is extracted than what has been physically. Higher complexation and thus high extraction were obtained at higher concentration of TBP (30 %). The function of solvents (diluent) is to act as the solvating medium for the complexes. K_D^{overall} follows the trends TOA + butyl acetate > TBP + toluene > TBP + paraffin liquid; however, K_D^{Chem} has a slight departure, TBP + toluene > TBP + paraffin liquid > TBP + butyl acetate. Thus, TBP is not an efficient extractant in butyl acetate, which may be due to poor solvation of TBP complexes in viscous butyl acetate.

Equilibrium complexation constants were evaluated by the plot of eq 11. Figure 2 shows the values of K_S as

$$\text{TBP + paraffin liquid} \qquad K_S = 1.85\ \text{m}^3\text{·kmol}^{-1} \tag{13}$$

$$\text{TBP + toluene} \qquad K_S = 2.44\ \text{m}^3\text{·kmol}^{-1} \tag{14}$$

$$\text{TBP + butyl acetate} \qquad K_S = 0.42\ \text{m}^3\text{·kmol}^{-1} \tag{15}$$

Higher values of K_S for TBP in paraffin liquid and toluene again confirm them as better solvation mediums.

Loading curves are represented as the plot of loading ratio against the log of acid concentration in the aqueous phase.[4] Figure 3 shows the loading curves for extraction of acrylic acid for 30 % TBP in different diluents. The solid curves show the calculated results of the "best" model, i.e., the simplest model that gave low error between the experimental and predicted results. The model values of the loading ratio were calculated using the model considering K_S values represented in eq 13 to eq 15. The model K_D^{overall} and z values were stated in Tables 2 to 4. If the error was not reduced significantly by inclusion of a particular complex, that complex was not considered to be part of the best model. Extraction of acrylic acid gives loading ratio values of less than 0.5. Thus, acid was expected to form 1:1 acid−TBP complexes. Further loading increases with an increase in acid concentration for all systems. In both cases, loading ratios were found to follow trend z for butyl acetate > z for toluene > z for paraffin liquid for nearly all acid concentrations.

Conclusion

Reactive extraction was employed for the recovery of acrylic acid from dilute aqueous streams. TBP, an organophosphorous compound, was used as extractant. TBP + butyl acetate was found to provide higher K_D^{overall} with E % as high as 80 %. The higher extraction in TBP + butyl acetate is due to chemical extraction using TBP + physical extraction by butyl acetate. However, TBP complexation with acid was poor in butyl acetate with $K_S = 0.42$ m^3·kmol^{-1}. Higher extraction using TBP as extractant was obtained in toluene and paraffin liquid.

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