



## Recovery of propionic acid from aqueous phase by reactive extraction using quarternary amine (Aliquat 336) in various diluents

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### ABSTRACT

Propionic acid is an important carboxylic acid widely used in chemical, pharmaceutical, food and other industries. The growing importance of biological production (fermentation) expressed with new routes and increasing production rates, leads to look for technologies of downstream processing for product separation. Reactive extraction with specific extractant has been the promising technique for propionic acid recovery from fermentation broth. In present work, the extraction of propionic acid with Aliquat 336 (tri-(C<sub>8</sub>C<sub>10</sub>) methyl ammonium chloride) dissolved in *n*-heptane, petroleum ether, 1-decanol and 1-octanol respectively was investigated for various concentrations of acid. The overall distribution coefficient ( $K_D$ ), loading ratios, and equilibrium complexation constants were evaluated. The comparison with pure diluent at 305 K was also made and chemical extraction was found to be better than physical extraction. Alcohols (1-octanol and 1-decanol) when used as diluents with Aliquat 336, were found to give higher  $K_D$  values and also prevents the third phase formation which was found when Aliquat 336 was used with *n*-heptane and petroleum ether. Also the water co-extraction and back extraction/regeneration methods were discussed. The data obtained is useful in the designing of reactive extraction process for the recovery of propionic acid.

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### 1. Introduction

Propionic acid is one of the important carboxylic acid used in food industries; manufacture of fungicides, herbicides, plasticizers, pharmaceuticals, artificial fruit flavorings, perfumes, emulsifying agents, cellulose acetate propionate; used to produce thermoplastics, vinyl propionate; used as a basic monomer for dispersions and solvents for resins and paints; and additive in electroplating solutions [1]. Its market is growing at 4% annually. Specific uses of propionic acid draws attention towards better recovery processes which will increase the productivity and reduce overall production cost.

The conventional method of recovery is the calcium hydroxide precipitation method. The approach includes addition of calcium hydroxide to form calcium salt of propionic acid, to which sulphuric acid is added to liberate the free propionic acid [2]. This method of recovery is expensive and unfriendly to environment as it consumes lime and sulphuric acid and also produces a large quantity of calcium sulphate sludge as solid waste. Consequently, such methods are falling out of favor. It is therefore reasonable to look for other methods of recovery for carboxylic acid.

Extractive recovery of carboxylic acids from dilute aqueous solution such as fermentation broth and waste water, has been receiving increasing attention [2–4]. The acid content in these sources is less than 10% (w/w) [1]. Reactive extraction involves use of an extractant–diluent system to extract the acid. Organic solvents used for the extraction of carboxylic acids are categorized as: (i) conventional oxygen-bearing and hydrocarbon extractants; (ii) organophosphorous compounds; and (iii) high molecular weight aliphatic amines [5]. Conventional solvents like ketones, ethers, aliphatic hydrocarbons, etc. were found to be inefficient in the extraction of carboxylic acids from dilute solutions. The reason of this may be the low activity of these acids in these conventional solvents resulting in low distribution coefficients.

Different organophosphorous compounds like tri-*n*-butyl phosphate (TBP), tri-*n*-octyl phosphine oxide (TOPO) have provided higher distribution coefficient when used as extractants. Aliphatic amines have been found to be more effective and less expensive than the organophosphorous compounds. Aliphatic amines have been widely employed for the extraction of carboxylic acids like lactic, citric, nicotinic, butyric, valeric, glycolic, glyoxylic acids. The amine interacts with acid to form acid–amine complex and thus provide high distribution of acid. The high affinity of acid to the base provides an additional advantage of high selectivity over the non-acidic components in the mixture.

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## Nomenclature

$K_{D(\text{diluent})}$	distribution coefficient of acid in diluents
$K_{D(A^-)}$	distribution coefficient of acid anions in extractant–diluent system
$K_{D(HA)}$	distribution coefficient of undissociated acid in extractant–diluent system
$K_D$	overall distribution coefficient
$K_E$	extraction equilibrium constant ( $\text{m}^3/\text{kmol}$ )
$[R_4N^+Cl^-]$	Aliquat 336 concentration ( $\text{kmol}/\text{m}^3$ )
$[HA]$	acid concentration ( $\text{kmol}/\text{m}^3$ )
$K_a$	dissociation constant of the acid ( $\text{m}^3/\text{kmol}$ )
$z$	loading ratio
$[R_4N^+Cl^-:HA]$	acid–extractant complex concentration ( $\text{kmol}/\text{m}^3$ )

## Subscripts

aq	aqueous phase
org	organic phase
o	initial

Primary amines are excessively water soluble, secondary amine show the problem of gel formation, which interfere with the phase separation, tertiary amines having chain length less than six carbon atoms shows lower extraction [6]. Consequently, long chain tertiary amines and quaternary amines have received the most attention. Extensive work on the influence of type and concentration of extractants [7–9], nature of diluents [10–12], composition of the aqueous phase [3,13], the effect of pH [7,8,11,13], and the effect of temperature [14,15], has been found in literature.

Most of the work going on presently for production of propionic acid, involves the use of anaerobic bacteria. However, the production by these bacteria's in fermentation broth is limited by acid production of less than 5%, the reason of this being the strong inhibition of acid product [16]. Extractive fermentation involves in situ removal of acid product, thus increases the bioreactor productivity. However, most extractants work only at acidic pH, and the acidogenic anaerobes generally have poor growth rates at pH values below 6. Thus it becomes important to look for the extractant that works at high pH.

Kyouchoukov et al. [9] has studied the extraction of lactic acid with Aliquat 336 dissolved in dodecane and decanol at various experimental conditions. The effect of pH was also studied. Yang et al. [10] studied the extraction of carboxylic acids with tertiary and quaternary amines under various pH ranging from 2.0 to 8.5. Pure quaternary amine was found to provide higher distribution coefficient than tertiary amine. Extraction was conducted with two diluents, kerosene and 2-octanol. Neither of the two diluents was found to be active when used with Aliquat 336.

In present work, Aliquat 336 (quaternary amine) was used, to study its ability to extract propionic acid from aqueous phase. Four diluents, *n*-heptane, petroleum ether, 1-decanol, and 1-octanol were investigated for their ability to increase the extracting power of the extractant as well as to improve the physical properties of the recovery phase agent. Prior to this work, quaternary amines have not been studied for its ability to extract propionic acid in the presence of the respective diluents. Distribution coefficients, equilibrium extraction coefficients were presented and the comparison among the diluents and diluent–extractant systems was made. Also the extraction mechanism, water co-extraction, back extraction/regeneration were discussed.

## 2. Materials and methods

### 2.1. Materials

The commercial solvent Aliquat 336 (methyltricaprylammonium chloride), a mixture of  $C_8$ – $C_{10}$  with a minimum assay of 80% and with molecular weight of 404.17 and density of  $0.888 \text{ g}/\text{cm}^3$  was used for the extraction of acid. *n*-Heptane, petroleum ether, 1-decanol, and 1-octanol were used as diluents and were used without any purification. Propionic acid (Himedia, India) was used as received to prepare the organic acid solutions. Distilled water was used to prepare the aqueous solution of the acid. Aqueous phase acid concentration was determined by titration with NaOH and by HPLC. HPLC system (WATERS 1523) was composed of binary pump, refractive index detector (WATERS 2414) and dual  $\lambda$  absorbance detector (WATERS 2487). The column used was C-18. The results of the above methods were comparable.

### 2.2. Experimental methods

Equal volumes of aqueous solution containing acid and extractant were equilibrated in a temperature controlled water bath shaker (Metrex Scientific Instruments (P). Ltd. India) at 305 K for 12 h, followed by settling of the mixture for at least 2 h at the same temperature in separating funnels maintained at the same temperature in an incubator. 2 h was found to be sufficient for the complete phase disengagement. The aqueous phase was then separated and the acid concentration was determined by HPLC. The pH before and after equilibrium was measured by Orion 3 star pH meter (Thermo Electro Corporation). The organic phase concentration was calculated by material balance.

## 3. Results and discussion

### 3.1. Physical extraction

For physical extraction, the distribution coefficient, represents the ratio between concentration of extracted species in the volume of corresponding solvent and the total concentration of acid in aqueous phase and can be written in the form of Eq. (1) as,

$$K_{D(\text{diluent})} = \frac{[HA]_{\text{org}}}{[HA]_{\text{aq}} + [A^-]_{\text{aq}}} \quad (1)$$

Fig. 1 shows the extraction of propionic acid ( $0.05$ – $0.4 \text{ kmol}/\text{m}^3$ ) by *n*-heptane, petroleum ether, 1-decanol, and 1-octanol. The distribution coefficients were found to be very low for *n*-heptane and petroleum ether. The removal of acid by physical extraction is primarily by the solvation of the acid molecules by donor

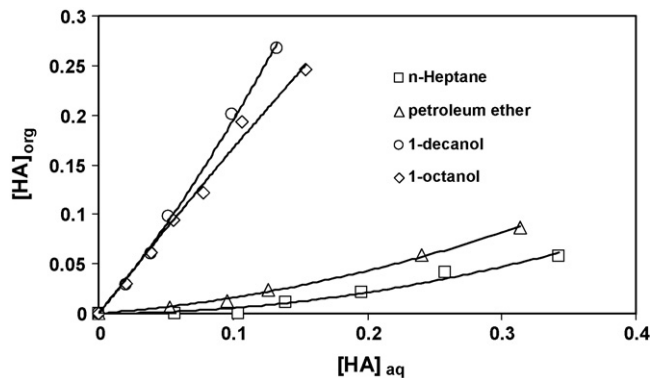


Fig. 1. Physical equilibria for the extraction of propionic acid in various diluents. (□) *n*-Heptane; (△) petroleum ether; (○) 1-decanol; and (◇) 1-octanol.

**Table 1**

Partition and dimerization coefficients for the extraction of propionic acid from water into organic solvents at 305 K  $[HA]_{org} = A[HA]_{aq} + B[HA]_{aq}^2$ .

Diluent	Partition coefficient (A)	Dimerization coefficient (B)
<i>n</i> -Heptane	0.0052	0.5058
Petroleum ether	0.1044	0.5547
1-Octanol	1.7345	–
1-Decanol	1.6255	3.2153

bonds and equilibrium solubility is the criteria of determining the maximum loading of the solvent. Heavier alcohols (1-octanol and 1-decanol) show higher distribution coefficients than inert diluents (*n*-heptane) and ether (petroleum ether). The experimental data of physical extraction for propionic acid–diluents systems used is given in Table 1.

### 3.2. Chemical extraction

The low distribution coefficient for pure diluents, suggested the use of an extractant to improve the extraction. Aliquat 336, a quaternary amine was used for the study in volume percentage range of 10–30% in different diluents. Higher concentration of Aliquat 336 was not taken, as, Aliquat 336 was highly viscous and would lead to the problem of third phase formation during extraction. Quaternary ammonium chloride (Aliquat 336) extracts both the dissociated and undissociated forms of acids [10]. For the extraction of propionic acid by Aliquat 336 with chemical interaction, the distribution coefficient of propionate ions can be written as Eq. (2):

$$K_{D(A^-)} = \frac{[R_4N^+Cl^- : A^-]_{org}}{[HA]_{aq} + [A^-]_{aq}} \quad (2)$$

and of the undissociated molecules as (Eq. (3)):

$$K_{D(HA)} = \frac{[R_4N^+Cl^- : HA]_{org}}{[HA]_{aq} + [A^-]_{aq}} \quad (3)$$

The overall distribution coefficient can be represented by Eq. (4):

$$K_D = K_{D(A^-)} + K_{D(HA)} \quad (4)$$

Propionic acid dissociates in aqueous solution and dimerizes in a non-polar solvent. Since, the experiments were performed at pH smaller than the *pK*<sub>a</sub> of acid (4.67), it can be presumed that acid dissociation is negligible. Therefore, only acid–extractant complex and undissociated acid are presumed to exist in the organic and aqueous solutions, respectively.

The extraction involves a chemical reaction between quaternary amine and acid. Tables 2–5 show the chemical equilibria for the extraction of propionic acid using Aliquat 336 (0.22–0.66 kmol/m<sup>3</sup> (10–30%)) in various diluents such as, *n*-heptane, petroleum ether 1-decanol, and 1-octanol. With all these diluents (except at higher acid concentrations and higher concentrations of Aliquat 336 in *n*-heptane and petroleum ether), problem of phase separation or dense three phase formation were not encountered. Phase separations in the exceptional cases were carried out by centrifugation. Extraction involving Aliquat 336 with *n*-heptane and petroleum ether clearly shows the enhanced extraction as compared to physical extraction. However, for the extraction involving Aliquat 336 in 1-decanol and 1-octanol, the *K*<sub>D</sub> was not significantly affected by the Aliquat 336 addition, since these diluents themselves are good extracting solvents (Tables 4–5).

#### 3.2.1. Effect of acid concentration on distribution coefficient

The chemical extraction by Aliquat 336 in *n*-heptane, petroleum ether, 1-decanol, and 1-octanol for various acid concentrations (0.05–0.4 kmol/m<sup>3</sup>) are shown in Tables 2–5. The distribution coefficients obtained were found to be much higher than the pure diluents, thus signifying the advantage of chemical extraction over physical extraction. It was found that for extraction involving Aliquat 336 in different diluents (*n*-heptane, petroleum ether, 1-decanol, and 1-octanol) and unit *V*<sub>org</sub> to *V*<sub>aq</sub> ratio, *K*<sub>D</sub> is, either slightly effected by the acid concentration or is higher at lower acid concentration (0.05 kmol/m<sup>3</sup>). At higher initial propionic acid concentrations, the amount of Aliquat 336 may be the limiting factor for the amine–acid reaction. The results were completely opposite to that obtained for the lactic acid recovery using a tertiary amine [17]. Kahya et al. [17] has studied the extraction of lactic acid with Alamine 336, and reported a large *K*<sub>D</sub> decrease from 10.5 to 0.5 and 13 to 4 upon increasing initial lactic acid concentration from 10 to

**Table 2**

Chemical extraction of propionic acid using Aliquat 336 in heptane at 305 K.

<i>B</i> <sub>0</sub> (kmol/m <sup>3</sup> )	[HA] <sub>0</sub> (kmol/m <sup>3</sup> )	[HA] <sub>aq</sub> (kmol/m <sup>3</sup> )	[HA] <sub>org</sub> (kmol/m <sup>3</sup> )	<i>K</i> <sub>D</sub>	<i>E</i> %	pH <sub>aq</sub>	<i>z</i>
0.22	0.05	0.031	0.019	0.61	38.00	3.26	0.613
	0.1	0.063	0.037	0.59	37.00	3.08	0.587
	0.15	0.091	0.059	0.65	39.33	2.99	0.648
	0.2	0.133	0.067	0.50	33.50	2.90	0.504
	0.3	0.162	0.138	0.85	45.93	2.85	0.850
	0.4	0.241	0.159	0.66	39.75	2.76	0.660
0.31	0.05	0.028	0.022	0.77	43.60	3.29	0.773
	0.1	0.042	0.058	1.38	58.00	3.18	1.381
	0.15	0.079	0.071	0.89	47.08	3.02	0.890
	0.2	0.116	0.084	0.73	42.18	2.93	0.730
	0.3	0.176	0.124	0.70	41.20	2.84	0.701
	0.4	0.225	0.175	0.77	43.65	2.78	0.775
0.44	0.05	0.027	0.023	0.85	46.00	3.30	0.852
	0.1	0.049	0.051	1.04	51.00	3.14	1.041
	0.15	0.083	0.067	0.80	44.47	3.01	0.801
	0.2	0.116	0.084	0.73	42.18	2.93	0.730
	0.3	0.172	0.128	0.74	42.51	2.84	0.739
	0.4	0.240	0.160	0.67	39.98	2.77	0.666
0.66	0.05	0.032	0.018	0.58	36.80	3.26	0.582
	0.1	0.057	0.043	0.76	43.20	3.11	0.761
	0.15	0.089	0.061	0.68	40.55	3.00	0.682
	0.2	0.120	0.080	0.67	40.22	2.93	0.673
	0.3	0.148	0.152	1.03	50.67	2.88	1.027
	0.4	0.259	0.141	0.55	35.32	2.75	0.546

**Table 3**  
Chemical extraction of propionic acid using Aliquat 336 in petroleum ether at 305 K.

$B_o$ (kmol/m <sup>3</sup> )	[HA] <sub>o</sub> (kmol/m <sup>3</sup> )	[HA] <sub>aq</sub> (kmol/m <sup>3</sup> )	[HA] <sub>org</sub> (kmol/m <sup>3</sup> )	$K_D$	E%	pH <sub>aq</sub>	$z$
0.22	0.05	0.030	0.020	0.69	40.80	3.27	0.093
	0.1	0.061	0.039	0.65	39.24	3.09	0.178
	0.15	0.080	0.070	0.87	46.43	3.02	0.317
	0.2	0.095	0.105	1.10	52.47	2.98	0.477
	0.3	0.149	0.151	1.01	50.18	2.87	0.684
	0.4	0.185	0.215	1.16	53.70	2.82	0.976
0.31	0.05	0.028	0.022	0.80	44.40	3.29	0.072
	0.1	0.051	0.049	0.96	49.04	3.13	0.158
	0.15	0.080	0.070	0.87	46.43	3.02	0.225
	0.2	0.096	0.104	1.08	51.98	2.98	0.335
	0.3	0.213	0.087	0.41	29.11	2.79	0.282
	0.4	0.214	0.186	0.87	46.59	2.79	0.601
0.44	0.05	0.033	0.017	0.50	33.36	3.24	0.038
	0.15	0.087	0.063	0.72	41.85	3.00	0.143
	0.2	0.108	0.092	0.86	46.10	2.95	0.210
	0.3	0.143	0.157	1.10	52.31	2.88	0.357
	0.4	0.179	0.221	1.23	55.17	2.83	0.502
0.66	0.05	0.042	0.008	0.19	15.72	3.18	0.012
	0.1	0.058	0.042	0.73	42.18	3.10	0.064
	0.15	0.084	0.066	0.78	43.81	3.01	0.100
	0.2	0.146	0.054	0.37	26.99	2.88	0.082
	0.3	0.122	0.178	1.47	59.49	2.92	0.270
	0.4	0.185	0.215	1.16	53.70	2.82	0.325

100 g/L with 15 and 50% Alamine 336 in oleyl alcohol, respectively. Thus, it can be concluded that against tertiary amine, quaternary amine could successfully extract acid at all acid concentrations prevailing in the fermentation broth.

### 3.2.2. Effect of diluent and extractant concentration on distribution coefficient

Diluent is added to improve the physical properties of extractant and the solvation efficiency of acid–extractant complex. The distribution coefficient also depends on the type of diluent and the resulting concentration of extractant in the solvent phase [5]. In general, a polar solvent should improve the extracting power of the non-polar amine by providing solvation of acid–amine complexes. For an inactive diluent, the  $K_D$  would be

expected to be proportional to the concentration of the extractant.

In extraction of propionic acid using pure Aliquat 336, the  $K_D$  value of 6.98 was obtained [10]. Aliquat 336 is highly viscous, therefore, diluents are used with it to reduce its viscosity and to improve its physical properties. As can be seen from Tables 2–5, increasing Aliquat 336 volume fraction from 0 to 30% in the inert diluents (heptane and petroleum ether), average  $K_D$  value of acid were found to increase from 0.13 and 0.15 in the case of only heptane and petroleum ether to 0.76 and 0.85 using 10–30% Aliquat 336 in these diluents, respectively. On the other hand in both the alcohols (1-octanol and 1-decanol), no effect of Aliquat 336 addition was observed.  $K_D$  values were found to be nearly constant in the case of only 1-octanol ( $K_{D(\text{diluent})}$  (average)=1.62) and 1-decanol

**Table 4**  
Chemical extraction of propionic acid using Aliquat 336 in 1-octanol at 305 K.

$B_o$ (kmol/m <sup>3</sup> )	[HA] <sub>o</sub> (kmol/m <sup>3</sup> )	[HA] <sub>aq</sub> (kmol/m <sup>3</sup> )	[HA] <sub>org</sub> (kmol/m <sup>3</sup> )	$K_D$	E%	pH <sub>aq</sub>	$z$
0.22	0.05	0.019	0.031	1.65	62.23	3.40	0.141
	0.1	0.037	0.063	1.73	63.34	3.22	0.288
	0.15	0.058	0.092	1.60	61.49	3.10	0.419
	0.2	0.079	0.121	1.52	60.28	3.02	0.548
	0.3	0.107	0.193	1.81	64.45	2.95	0.879
	0.4	0.166	0.234	1.42	58.62	2.85	1.066
0.31	0.05	0.019	0.031	1.65	62.23	3.40	0.100
	0.1	0.039	0.061	1.57	61.12	3.20	0.197
	0.15	0.060	0.090	1.50	60.00	3.09	0.290
	0.2	0.084	0.116	1.38	58.06	3.01	0.375
	0.3	0.113	0.187	1.65	62.23	2.94	0.602
	0.4	0.169	0.231	1.37	57.78	2.85	0.746
0.44	0.05	0.019	0.031	1.65	62.23	3.40	0.071
	0.1	0.041	0.059	1.47	59.45	3.19	0.135
	0.15	0.050	0.100	2.00	66.67	3.14	0.227
	0.2	0.081	0.119	1.47	59.45	3.02	0.270
	0.3	0.119	0.181	1.51	60.19	2.93	0.410
	0.4	0.173	0.227	1.31	56.67	2.84	0.515
0.66	0.05	0.018	0.032	1.81	64.45	3.41	0.049
	0.1	0.039	0.061	1.57	61.12	3.20	0.093
	0.15	0.061	0.089	1.45	59.26	3.09	0.135
	0.2	0.086	0.114	1.32	56.95	3.00	0.173
	0.3	0.120	0.180	1.50	60.00	2.92	0.273
	0.4	0.181	0.219	1.21	54.73	2.83	0.332

**Table 5**

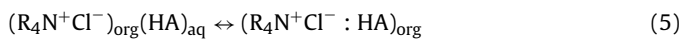
Chemical extraction of propionic acid using Aliquat 336 in 1-decanol at 305 K.

$B_0$ (kmol/m <sup>3</sup> )	$[HA]_0$ (kmol/m <sup>3</sup> )	$[HA]_{aq}$ (kmol/m <sup>3</sup> )	$[HA]_{org}$ (kmol/m <sup>3</sup> )	$K_D$	E%	pH <sub>aq</sub>	z
0.22	0.05	0.018	0.032	1.76	63.74	3.41	0.145
	0.1	0.039	0.061	1.58	61.29	3.20	0.279
	0.15	0.060	0.090	1.51	60.15	3.09	0.410
	0.2	0.081	0.119	1.46	59.33	3.02	0.539
	0.3	0.127	0.173	1.35	57.53	2.91	0.785
	0.4	0.163	0.237	1.46	59.33	2.85	1.079
0.31	0.05	0.019	0.031	1.69	62.76	3.40	0.101
	0.1	0.040	0.060	1.49	59.82	3.19	0.193
	0.15	0.063	0.087	1.39	58.19	3.08	0.282
	0.4	0.171	0.229	1.35	57.37	2.84	0.740
0.44	0.05	0.017	0.033	2.00	66.68	3.43	0.076
	0.1	0.040	0.060	1.52	60.31	3.20	0.137
	0.2	0.082	0.118	1.43	58.84	3.01	0.267
	0.3	0.131	0.169	1.28	56.23	2.90	0.383
	0.4	0.168	0.232	1.39	58.11	2.85	0.528
0.66	0.05	0.017	0.033	2.00	66.68	3.43	0.051
	0.1	0.038	0.062	1.62	61.78	3.21	0.094
	0.2	0.084	0.116	1.37	57.86	3.01	0.175
	0.3	0.131	0.169	1.28	56.23	2.90	0.256
	0.4	0.172	0.229	1.33	57.13	2.84	0.346

( $K_{D(diluent)}$  (average) = 1.53) and 10–30% Aliquat 336 in the respective diluents ( $K_D$  (average) for Aliquat 336 in 1-octanol = 1.54 and  $K_D$  (average) for Aliquat 336 in 1-decanol = 1.51). However, overall it can be seen that  $K_D$  values for Aliquat 336 in 1-octanol and 1-decanol are much higher than in *n*-heptane and petroleum ether, suggesting the formers to be better diluents. Other advantage of 1-decanol and 1-octanol is the clear phase separation obtained in two, which was not found in some cases for extractions involving Aliquat 336 in *n*-heptane and petroleum ether, respectively.

### 3.2.3. Extraction mechanism and equilibrium complexation constant

The quaternary ammonium chloride extracts both dissociated and undissociated forms of acid. Kyuchoukov et al. [9] experimented with the lactic acid extraction with quaternary ammonium chloride (Aliquat 336) and found that at low pH value and low acid concentration (5 g/l), the part of whole molecule removed by the extractant is bigger than the part of the extracted anions, but with the rise of pH, the ratio turns. Thus the concentration of undissociated acid is the function of the pH of the aqueous phase. Since the present study is at pH of 2.65–3.13, it can be assumed that only undissociated acid is being involved in the extraction. The extraction of the undissociated molecules of propionic acid by chemical interaction thus can be represented as Eq. (5),



with the extraction constant

$$K_{E(HA)} = \frac{[R_4N^+Cl^- : HA]_{org}}{[HA][R_4N^+Cl^-]_{org}} = \frac{[R_4N^+Cl^- : HA]_{org}(K_a + [H^+])}{[H^+]\{[HA] + [A^-]\}[R_4N^+Cl^-]_{org}}$$

$$= \frac{K_{D(HA)}}{[R_4N^+Cl^-]_{org}(1 - \alpha)} \quad (6)$$

$K_a$  in Eq. (6) is the dissociation constant of the acid and  $\alpha = K_a/(K_a + [H^+])$  represents the part of dissociated form of acid. Rearranging Eq. (6) we get Eqs. (7) and (8) as,

$$K_{D(HA)} = \frac{[R_4N^+Cl^- : HA]_{org}}{\{[HA] + [A^-]\}} = K_{E(HA)}(1 - \alpha)[R_4N^+Cl^-]_{org} \quad (7)$$

or

$$\frac{K_{D(HA)}}{(1 - \alpha)} = \frac{[R_4N^+Cl^- : HA]_{org}}{(1 - \alpha)C_{HA}} = K_{E(HA)}[R_4N^+Cl^-]_{org} \quad (8)$$

The distribution coefficient and equilibrium extraction coefficient of undissociated molecules can be determined under condition that  $\alpha = 0$ , i.e. mineral acid must be added, but in this way, the extraction system changes and  $K_{D(HA)}$  will not be the same as in the absence of mineral acid.

Taking log of Eq. (8), we get Eq. (9):

$$\log K_D = \log K_{E(HA)} + \log [R_4N^+Cl^-]_{org} \quad (9)$$

The plot of  $\log K_D$  against  $\log [R_4N^+Cl^-]_{org}$  would provide a straight line with the intercept of  $\log K_{E(HA)}$ . From above equation it can be seen that the distribution coefficient of the propionic acid depends on the free extractant concentration in the organic phase. The equilibrium concentration of free extractant can be represented as Eq. (10):

$$[R_4N^+Cl^-]_{org} = [R_4N^+Cl^-]_{org}^0 - [R_4N^+HA]_{org} \quad (10)$$

Fig. 2 shows the plot of Eq. (9) for the propionic acid extraction using Aliquat 336 in *n*-heptane. As shown in Fig. 2, the slope is far less than unity; this implies the extraction mechanism is different from the assumed form. Similar results were obtained with the other systems (Aliquat 336 + petroleum ether, Aliquat 336 + 1-decanol and Aliquat 336 + 1-octanol).

Keeping in view that the exact chemistry involved in the uptake of extra acid is unknown, the distribution coefficient can be inter-

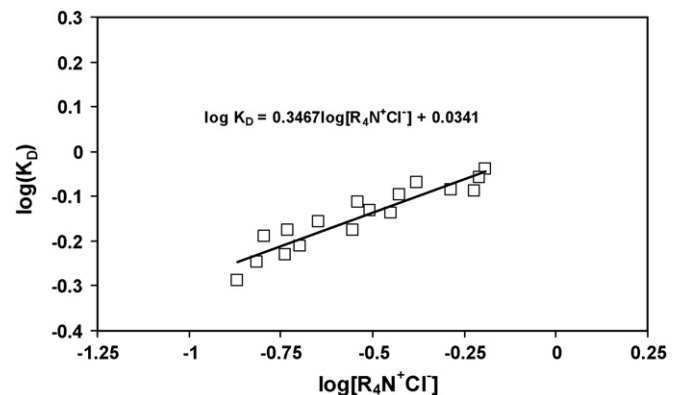


Fig. 2. Distribution coefficient of propionic acid in Aliquat 336 in *n*-heptane as a function of free amine concentration in organic phase. (□) *n*-Heptane.

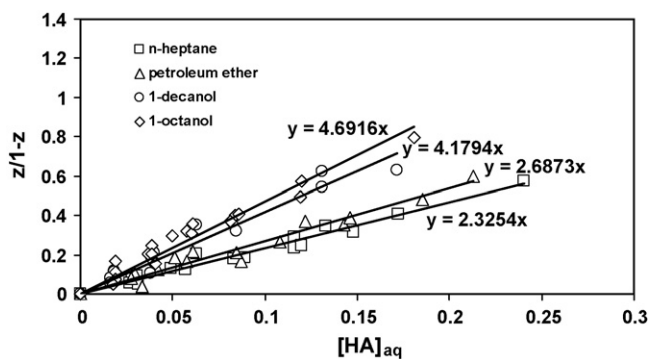
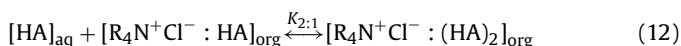
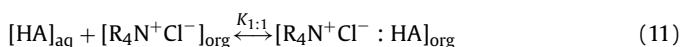
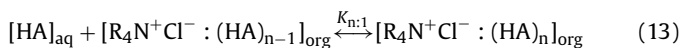


Fig. 3. Plot of  $z/(1-z)$  vs.  $[HA]_{aq}$  for the estimation of (1:1) propionic acid-amine equilibrium complexation constant in various diluents. (□) *n*-Heptane; (Δ) petroleum ether; (○) 1-decanol; and (◇) 1-octanol.

preted by the following set of Eqs. (11)–(13),



⋮  
⋮



The equilibrium complexation constant for the reaction represented by above equations is (Eq. (14)):

$$K_{E(n:1)} = \frac{[R_4N^+Cl^- : (HA)_n]_{org}}{[R_4N^+Cl^-]_{org} [HA]_{aq}^n} \quad (14)$$

The extent to which the organic phase (amine + diluent) can be loaded with carboxylic acid is expressed as the loading ratio,  $z$ :

$$z = \frac{[HA]_{org}}{[R_4N^+Cl^-]_{i,org}} \quad (15)$$

The value of  $z$  in Eq. (15) depends on the extractability of the acid (strength of the acid–base interaction) and its aqueous concentration. The stoichiometry of the overall extraction reaction depends on the loading ratio in the organic phase,  $z$ . Since in extraction of propionic acid using Aliquat 336 in various diluents, organic phase is not highly concentrated, i.e. loading ratios is less than 0.5, the (1:1) complex is formed and the following Eq. (16) holds

$$\frac{z}{1-z} = K_{E1} [HA]_{aq} \quad (16)$$

Fig. 3 shows the plot of  $z/(1-z)$  vs.  $[HA]_{aq}$  for the extraction of propionic acid using Aliquat 336 in *n*-heptane, petroleum ether, 1-decanol, and 1-octanol. A straight line passing through the origin was obtained. The values of  $K_{E1}$  increase in the following trend Aliquat 336 + *n*-heptane < Aliquat 336 + petroleum ether < Aliquat 336 + 1-decanol < Aliquat 336 + 1-octanol and are given in Table 6.

Table 6

Equilibrium distribution coefficient for the extraction of Aliquat 336 (0.22–0.66 kmol/m<sup>3</sup>) in various diluents.

Diluent	$K_{E1}$ (m <sup>3</sup> /kmol)
<i>n</i> -Heptane	2.33
Petroleum ether	2.69
1-Decanol	4.18
1-Octanol	4.69

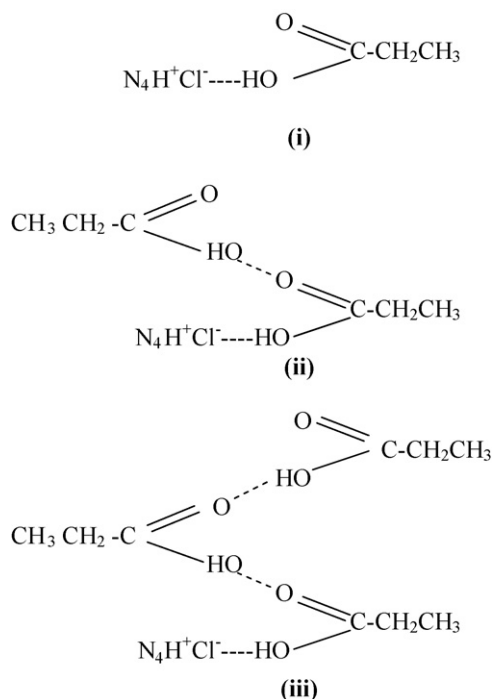


Fig. 4.  $n:1$  propionic acid–Aliquat 336 complex structures: (i) 1:1; (ii) 2:1; and (iii) (3:1).

Thus highest value of  $K_{E1}$  was obtained for Aliquat 336 in 1-octanol. The extent of solvation of the acid-amine complex was found to decrease in the order 1-octanol (alcohol) > 1-decanol (alcohol) > petroleum ether (ether) > *n*-heptane (aliphatic hydrocarbon). The results were in agreement with the work of Kertes and King [18].

The large difference among  $K_{E1}$  values for the same acid in different diluents indicates that solvation by the diluent is a critical factor in the extraction of acid. Inert diluents—alkanes, give very low distribution of the acid into the solvent phase. Alkanes being non-polar, provide for very little solvation of polar complexes. Alcohols on the other hand have greater abilities to solvate the acid-amine complex. In case of extraction using alcohols as diluents, the specific hydrogen bonding between the proton of the diluent and the acid-amine complex is the reason of the extra solvation and thus high equilibrium constants.

For low acid concentrations of the acid (1:1) propionic acid–Aliquat 336 complex is common, and its structure is shown in Fig. 4(i). The formation of (2:1) and (3:1) complexes depends on the propionic acid concentration in the aqueous phase, and the ratio of (1:1) to (2:1) complex formation is diluent dependent [18]. At higher concentrations of propionic acid, the (2:2) and (3:1) complexes are formed [19]. This overloading phenomenon results from second propionic acid molecule hydrogen bonding to the propionic acid that is already involved in (1:1) complex (Fig. 4(ii)). At still higher loading (3:1) complexes are formed in which a third propionic acid is hydrogen bonded to the second propionic acid of the (2:1) complex as shown in Fig. 4(iii). In most of the cases only (1:1) complex was observed.

### 3.2.4. Effect of physical properties of diluents on extraction

Different approaches have been used to quantify the effect of diluents on the (1:1) complexation. Both partition and self-association constants are strongly dependent on the nature of the diluents; i.e. the thermodynamic activity of the species taking part in the organic phase equilibria is changed when one diluent is replaced by other. The effect of diluent on partition and self-association constants was explained by specific interactions

only between the Aliquat 336 and the diluents. King et al. [19] has suggested the use of Hilderband solubility parameter as the measure of solvation of the complex by the diluent. The sequence alkane < ethers < alcohols corresponds to increasing acid distribution and increasing solubility parameters. The same sequence for the distribution coefficient was found by Aliquat 336 in the corresponding diluents (*n*-heptane, petroleum ether, 1-decanol, and 1-octanol).

In some of the work, a relationship was found between the distribution coefficient and other physio-chemical diluent parameters such as dielectric constant, dipole moment, refractive index, boiling points, etc. [21]. In the present case it was tried to correlate the extraction using these different diluents properties, however except for dielectric constant, no trend was observed. The value of equilibrium complexation constant was found to increase with increase in the dielectric constant of the diluents. The increasing value of dielectric constant is according: *n*-heptane (1.9) < 1-decanol (8.1) < 1-octanol (10.3), which is the same trend as equilibrium complexation constants. The reason of this may be that the high value of dielectric constant makes the distance inside the material look bigger, thus allowing better solvation of the acid–Aliquat 336 complex in the case of 1-octanol than other.

The extraction constant has been correlated with solvation energy: 'inert' the solvent, the smaller is the extraction constant; which frequently occurs in solvent extraction practice. The effect of the diluents is determined by the ratio of contributions of solvation of extractant and the extracted complex to the free energy of extraction. Solvation, in turn, depends on different kinds of intermolecular forces which cannot be determined merely from the above-mentioned physical parameters. However in some cases solvation energy is represented in terms of empirical parameters of solvent polarity. The parameters most frequently used are *Z* parameter (proposed by Kosower) which account for the influence of the solvent on the position of the charge transfer band in the spectrum of alkylpyridine iodide, and the  $E_T$  parameter which is based on the absorption spectrum of pyridinium-*N*-phenol-betaine. The greater the  $E_T$  and *Z* values, the greater the solvating power of solvent. An  $E_T$  value of 1-octanol (48.3) is greater than for other diluents (1-decanol, 48; *n*-heptane, 31.1). The higher value of distribution coefficient of alcohols over the other two diluents can thus also be interpreted because of the higher  $E_T$  values of 1-octanol.

### 3.2.5. Water co-extraction

Water co-extraction is the term used to describe the water that enters the organic phase with solute. This may effect process economics, as this entered water would have to be removed during the regeneration phases, and would lead to extra expenditure on power and cost. King and Tamada [2] had stated that the water co-extraction decreases in the same trend as the solubility of the diluents in water.

The mutual solubility between an aqueous solution and a given solvent at a fixed temperature is affected by the nature of acid and its concentration. With weak acids like propionic acid, mutual solubilities cause substantial volume change which can be related to the co-extraction of water along with the acid. Volume change depends on the type of diluent and the type and concentration of extractant as well as temperature.

Fig. 5 shows the plot of  $V_{org}/V_{aq}$  ratio for the extraction of propionic acid using Aliquat 336 in 1-octanol. It can be clearly seen that for the extraction involving 10 and 15% Aliquat 336 in various diluents, the ratio of organic phase volume to aqueous phase volume increases with the increase in acid concentration. For 20 and 30% Aliquat 336 concentrations, with rise in acid concentrations, the value of the phases first increases and then decreases. The explanation of the phenomenon can be explained on the basis of the diluent and equilibrium characteristics. Since diluent is mainly responsible

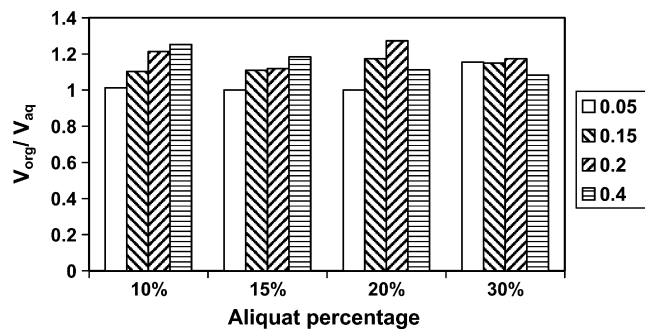


Fig. 5. Effect of water co-extraction in the extraction of propionic acid (0.05–0.4 kmol/m<sup>3</sup>) using Aliquat 336 in 1-octanol. (□) 0.05; (▨) 0.15; (▩) 0.2; (▬) 0.4.

for water co-extraction, at higher diluent concentration, the water co-extraction is higher. Further, as water is extracted along with the complexes, at high diluent concentrations, more water will be extracted if more acid is present. It leads to more acid–Aliquat 336 complexes and better solvation provided to them by the diluent, which is in excess. On the contrary at low diluent concentrations, the extraction would increase only to the point when diluent concentration become the limiting factor as this limit the solvation of the complexes from interface to the organic phase. King and Tamada [2] found in the extraction of lactic acid, that the amount of co-extracted water and lactic acid extracted are increase with an increase in the number of moles of tertiary amine (TOA), however the type and concentration of active diluent is more important factor than the number of moles of extractant for the extraction of lactic acid. Similar results can be seen here in the extraction of propionic acid by quaternary amine (Aliquat 336). Fig. 5 clearly shows that at higher concentration of propionic acid (0.4 kmol/m<sup>3</sup>), the increase in Aliquat 336 concentration or the decrease in diluent concentration, decreases the water co-extraction. However in general, the selectivity of acid over water in the extraction by amine extractant is high relative to the results with conventional solvent and in all cases the water co-extraction is not above 10–12%, which has little effect upon process viability.

### 3.2.6. Back extraction/regeneration

Back extraction of acid is another important point in context to the choice of extractant. The overall degree of concentration relative to the feed that can be achieved by reactive extraction is limited by the extent to which the distribution equilibrium for the carboxylic acid can be exchanged between forward extraction and back extraction. There are numerous methods found in literature for back extraction, like: back extraction with water at higher temperature (temperature swing) [20], back extraction with caustic [22], diluent swing [2], distillation [22], and using volatile amine [22]. In order to avoid consumption of chemicals and creation of a salt byproduct, the method of using volatile amine for back extraction in a counter-current back-extractor, thereby enabling thermal decomposition of the acid–base complex in the aqueous counter current back extract can be proposed to be the regeneration method. With a counter current back-extractor, the existing acid-depleted organic phase would have last contacted an entering aqueous base containing little of no acid, and there would therefore be substantial partitioning of the base into that existing organic stream. This would however require a subsequent base-removal step. The decomposition of the base–acid complex formed, will form propionic acid as product and the free volatile base as a vapour that can be reabsorbed in water and recycled for reuse in the back extraction. In order to achieve high degree of back-extraction into the volatile base, it is proposed to keep the base/acid ratio in the back-extractor close to or higher than stoichiometric ratio.

#### 4. Conclusions

The extraction of propionic acid using quaternary amine; Aliquat 336 was studied in the presence of petroleum ether, *n*-heptane 1-decanol, and 1-octanol as diluents. Aliquat 336 extracts both the dissociated and undissociated form of acid. However, the presence of the two forms of acid is dependent on the pH of the system. At low pH only undissociated form of acid was found, which is the case of present study. Though Aliquat 336 alone can provide a high distribution coefficient, yet being highly viscous, it was used in different diluents. The diluents lower the viscosity of Aliquat 336, thus allowing its easier handling. The four different diluents used belong to the category of alcohol (1-decanol and 1-octanol), liquid hydrocarbon mixture (petroleum ether) and aliphatic hydrocarbons (*n*-heptane). The work was to find the effectiveness of the respective diluents in the extraction of propionic acid using Aliquat 336. The physical extraction and chemical extraction was determined and the result shows the better performance of extractant–diluent combination over the diluent alone. However, it is the Aliquat 336 which is contributing mainly to the improvement in the case of *n*-heptane and petroleum ether, the diluents just provides the improvement in the dissolution of the complexes. Aliquat 336 in 1-decanol and 1-octanol shows no improved performance. With increasing the Aliquat concentration in 1-octanol and 1-decanol there was no significant improvement in the distribution coefficient of the acid. Yet in comparison to the other two diluents (petroleum ether and *n*-heptane), 1-decanol and 1-octanol (alcohols) provides the higher equilibrium complexation constants. Since the loading ratio was less than 0.5 in all cases, no overloading was obtained and (1:1) acid: amine complex can be assumed to be formed. The extraction constant was also tried to be correlated to the physical constants of diluents and success have been there using dielectric constant and  $E_T$  parameter. In the end water co-extraction was studied and was found to be not more than 10–12%.

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