

## Reactive Extraction of Propionic Acid Using Aliquat-336 in 2-Octanol: Linear Solvation Energy Relationship (LSER) Modeling and Kinetics Study

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Reactive extraction is an important recovery method for extraction of propionic acid from dilute streams, providing numerous advantages like high selectivity and recovery. Equilibrium and kinetic study of reactive extraction is essential to choose a proper extractant-diluent for acid recovery and ascertain the kinetic parameters essential for design of the process. In this paper, the linear solvation energy relationship (LSER) modeling of reactive extraction of propionic acid using Aliquat 336 in 2-octanol as diluent was presented to obtain the model parameters. Also, the kinetics of extraction in stirred cell was presented to explain the progress of reactive extraction of propionic acid using Aliquat 336 in the diluent. The reaction was found to be fast pseudo first order. To design the reactor to carry out reactive extraction, the kinetic parameters evaluated are essential. Modeling using LSER model predict a close resemblance of experimental data.

*Key words:*

Propionic acid, reactive extraction, Aliquat 336, LSER model, kinetics, stirred cell

### Introduction

Propionic acid uses in food (in grain preservation; as mould preventatives in silage and hays; and as antifungal agents in bread and other foods), pharmaceutical (anti-arthritis drugs) and chemical industries (manufacture of cellulose plastics, plastic dispersions, herbicides, perfumes and flavors, plasticizers etc.) have made it a commodity chemical. Production is primarily by petrochemical routes which includes oxidation of propane, propanaldehyde and propanol and from carbonylation of ethylene.<sup>1</sup> The rapid increase of petrochemical prices in the last few decades have lead to the search for an alternative method of production. Fermentation is a clean alternative for propionic acid production but suffers from disadvantages of low yield and productivity of acid and expensive downstream separation of acid. A solution to the above problem lies in search of technology that can separate acid as soon as it is produced so that pH fall – the reason of low production, can be prevented.

Many separation processes are available, like stripping, adsorption, electrodialysis, liquid-liquid

extraction, pertraction, pervaporation, and membrane solvent extraction. All these processes have their own advantages and disadvantages. However, there are numerous advantages of reactive extraction, as it links chemical sources and sinks to enhance reaction rates, conversions and selectivities. Since most of chemical processes are equilibrium driven, removal of product as soon as it is produced would lead to enhanced reaction rates; increased feed conversions reduce reaction severity and provide operation under milder conditions. Further, in reaction and separation operations, the duo would lead to high local driving forces for separation, leading to reduction in equipment size, elimination of recyclable streams and reductions in utility costs. Reactive separators also lead to safer equipment since it reduces the working inventory of reactive chemicals in the equipment. The lower the hazardous chemical usage, the lower the chance of its leakage, spill and environmental release. Coupling reaction and separation also leads to suppression of byproduct reactions which are likely to exhibit runaway behavior; the reactive separator design will increase the inherent safety in the unit against severe process upsets. The combination also provides low cost equipment through the consolidation of

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multiple pieces of process equipment into a single piece and/or through the elimination of process recycle streams. Reactive extraction being a clean process, since the extractant for the recovery of the acid can be completely recovered and reused, along with simple and cheap operation have greatly rendered it an efficient recovery process. The reactive substance forms the reversible complex with acid, which promotes the transfer of polar acid from the aqueous phase to the nonpolar organic phase. Results show that process intensification is a vital tool to realize an improved process. Further, the reactive extraction process does not affect the thermal stability of bioproducts, and energy demand is substantially low.

Extractive recovery (reactive extraction) of propionic acid from dilute aqueous solution, such as fermentation broth and wastewater, has been receiving increasing attention.<sup>2–8</sup> The acid fraction in these sources is less than  $w = 10\%$ .<sup>9</sup> Reactive extraction involves the 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) Organo-phosphorous compounds; (iii) High molecular mass aliphatic amines.<sup>9</sup> Conventional solvents like ketones, ethers, aliphatic hydrocarbons etc. were found to be inefficient in the extraction of carboxylic acids from dilute solutions. The reason for this may be the low activity of acids in aqueous phase resulting in low distribution coefficients.

Aliphatic amines: primary, secondary, tertiary and quaternary; have been found more effective and less expensive than other categories of extractants. Primary amines are excessively water soluble, secondary amines show the problem of gel formation, which interferes with the phase separation, tertiary amines having chain length less than six carbon atoms show low extraction.<sup>10</sup> Consequently, long-chain tertiary amines and quaternary amines have received the most attention. A lot of work on reactive extraction of carboxylic acids using Aliquat 336 as extractant could be found in literature.

Kyuchoukov *et al.*<sup>11</sup> 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.*<sup>12</sup> 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 a 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. Keshav *et al.*<sup>4,5</sup> presented reactive ex-

traction of propionic acid from aqueous solution using tri-*n*-butylphosphate (TBP), tri-*n*-octylamine (TOA) and Aliquat 336 as extractants in 1-octanol<sup>4</sup> and sunflower oil,<sup>5</sup> respectively. A comparison among the different categories of extractants was made. It was found that the performance of the extractant is the function of the type of diluent chosen. In the study involving 1-octanol as diluent, Aliquat 336 was found to be better than TBP but not TOA, whereas in sunflower oil it was better than the other two.

Distribution of citric acid between water and trialkylamine C<sub>7</sub>-C<sub>9</sub>, dissolved in 7 various diluents (*p*-xylene, toluene, benzene, MIBK, 1-octanol, methylene chloride, chloroform) was studied by Bizek *et al.*<sup>13</sup> The estimated values of overall extraction constants were correlated with solvatochromic parameters of the diluents according to the linear solvation energy relationship (LSER). Using this correlation, the extractability of citric acid can be predicted for a wide range of diluents or their mixtures. Liquid-liquid equilibrium measurements for the extraction of propionic acid by Alamine 336 in toluene were correlated by a linear solvation energy relationship (LSER) model, which takes into account physical interactions.<sup>14</sup> From the regression coefficients, information on the solvent-solute interaction is obtained and solvation models are proposed. Equilibrium and kinetic studies for the extraction of succinic acid from aqueous solution with tridodecylamine diluted in MIBK are reported by Inci.<sup>15</sup> The equilibrium data were also interpreted by a proposed mechanism of three reactions of complexation by which ( $r = 1 : 1$ ) and ( $r = 2 : 1$ ) acid-amine complexes are formed. Kinetics of extraction as well as linear solvation energy relationship (LSER) model were discussed.

Wasewar *et al.*<sup>16–18</sup> studied the kinetics of extraction of lactic acid by Alamine 336 (tertiary amine) in MIBK and Alamine 336 in decanol using stirred cell. In both cases the kinetics was found to be a fast reaction occurring in diffusion film. The reaction was of zero order in Alamine and first order in lactic acid. Similar results were obtained by Gaidhani *et al.*<sup>19</sup> in extraction of phenyl acetic acid using Alamine 336 in kerosene in a stirred cell. Nikhade *et al.*<sup>20</sup> studied the kinetics of citric acid extraction by Alamine 336 in MIBK as diluent, in a stirred cell and found the reaction to be a slow second order reaction. Reschke and Schugerl<sup>21</sup> developed the kinetic model and identified the model parameters for extraction of penicillin using Amberlite LA-2 (secondary amine) in a stirred cell extractor using the two film model. They explained the kinetic behavior at two pH, 5 and 6. At lower pH, extractant concentration has no significant influence on extraction; however at higher pH, the ef-

fect is significant. At pH 5, the rate of extraction was controlled by transport of penicillin, however at pH 6, there was a shift in the distribution equilibrium and reduction in the penicillin concentration at the interface.

Although many equilibrium studies using Aliquat 336 can be found in literature, to date no work on kinetics of reactive extraction of propionic acid could be found. Determination of kinetics is important to ascertain the progress of reaction and the type of reaction. Therefore, in this paper the kinetics of extraction of propionic acid using Aliquat 336 in 2-octanol was studied. Also, the linear solvation energy relationship (LSER) modeling was presented for equilibrium study of reactive extraction of propionic acid.

## Materials and methods

### Materials

Aliquat 336 (Methyltricaprylammonium chloride) (Himedia, India), a quaternary amine, with molar mass of  $404.17 \text{ g mol}^{-1}$  and density of  $888 \text{ kg m}^{-3}$  was used as extractant. Propionic acid ( $\text{CH}_3\text{CH}_2\text{COOH}$ ; 99 % purity; molar mass  $74.08 \text{ g mol}^{-1}$ ; density  $992 \text{ kg m}^{-3}$ ) was obtained from Himedia, India Ltd. Diluent: 2-octanol (Himedia, India Ltd.) was of technical grade and was used as supplied. Double-distilled water was used to prepare the solutions of various concentrations of acid. NaOH used for the titration was of analytical grade and supplied by Ranbaxy, India. For the standardization of NaOH, oxalic acid (99.8 %) was obtained from S. D. Fine-Chem Ltd., India. Phenolphthalein solution (pH range 8.2–10.0) was used as indicator for titration and obtained from Ranbaxy, India. The initial aqueous acid concentration range ( $[\text{HA}]^0$ ) of  $c = 0.05\text{--}0.4 \text{ kmol m}^{-3}$  were used since in waste stream and in fermentation broth, its concentration is expected to be less than  $c = 0.5 \text{ kmol m}^{-3}$ .<sup>22</sup>

### Methods

Kinetics experiments were carried out in 6.516 cm i.d. glass stirred cell. The effective interfacial area was  $A = 33.33 \text{ cm}^2$ . The design of the stirred cell was similar to that used by Wasewar *et al.*<sup>16–18</sup> and Gaidhani *et al.*<sup>19</sup> The vessel was equipped with stainless steel dual four flat blade stirrer ( $d = 4.8 \text{ cm}$ ) (Fig. 1). The stirred cell was kept in a water bath where the temperature could be kept constant within about  $T = \pm 1 \text{ K}$  at 305 K. A known volume of organic and aqueous phase was taken and reactive extraction was carried out for a definite period. Samples of aqueous phase were

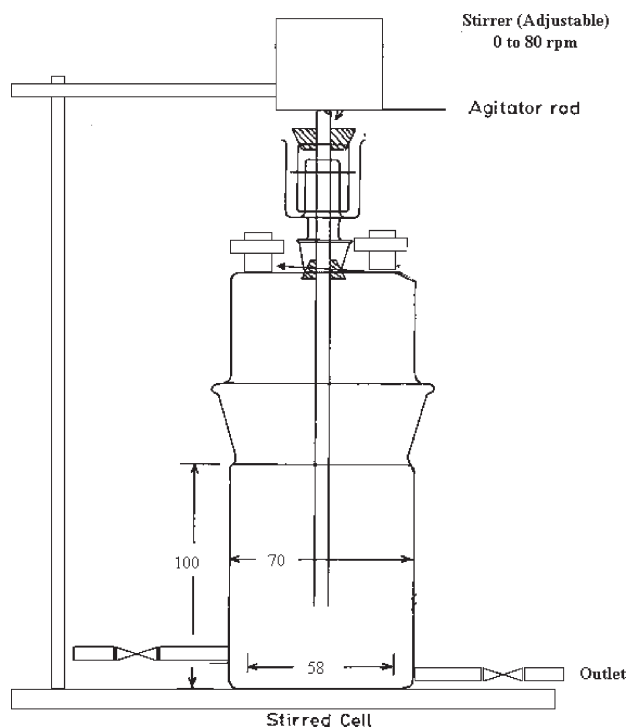


Fig. 1 – Stirred cell used for kinetic study of reactive extraction of propionic acid

taken out at  $t = 1, 3, 5, 10, 20$  and 30 min. The kinetic experiments were performed until equilibrium was achieved, and it was found that equilibrium was established within  $t = 30 \text{ min}$ . To ensure that concentration corresponds to the time when the samples were taken, the separation of the phases was carried out quickly. Aqueous phase acid concentration was determined by titration with sodium hydroxide solution ( $c = 0.02 \text{ kmol m}^{-3}$ ). In order to remove problems of alkali reaction with carbon dioxide in environments, it was always prepared fresh and a soda lime absorbent was used at the top of the burette. The acid content in the organic phase was determined by mass balance.

## Results and discussion

### Equilibrium modeling using LSER

Aliquat 336, a quaternary amine was used for the study in volume fractions of 10–30 % in 2-octanol. Higher concentration of Aliquat 336 was not taken, since Aliquat 336 is highly viscous and this would lead to the problem of third phase formation during extraction. Using Aliquat 336 in 2-octanol,  $K_D$  values were slightly higher than using diluent alone. However, there is only a marginal effect of increasing Aliquat 336 volume % in the diluent. A similar observation was made by Yang *et al.*<sup>23</sup> However, it can be stated that Aliquat has the advantage that it can give effective extractions

even at higher pH values (5–7). Since optimal pH of fermentation broths is 6–7, Aliquat can be an effective extractant in that case. Propionic acid dissociates in aqueous solution and dimerizes in a non-polar solvent. The experiments in the present study were performed at pH range of 2.8–3.2, which is smaller than the  $pK_a$  of acid (4.67). It can be presumed that only an undissociated form of acid could exist. Therefore, only undissociated acid – extractant complex<sup>11</sup> is presumed to exist in the organic and undissociated acid in aqueous solutions respectively. The distribution coefficient of acid is given as:

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

where  $[HA]_{org}^{total}$  is the total acid extracted into the organic phase. The extraction of propionic acid by chemical interaction can be represented as:

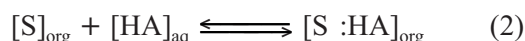


Table 1 shows the chemical equilibria of extraction of propionic acid using Aliquat 336 in 2-octanol.<sup>24</sup> Distribution coefficients and acid concentration in the organic phase were presented. The experimental data were fitted to LSER model.

Table 1 – Experimental and model values of different parameters for reactive extraction of propionic acid using Aliquat 336 in 2-octanol at 305 K

Experimental				LSER model	
$[HA]^0$ kmol m <sup>-3</sup>	$[S]^0$ kmol m <sup>-3</sup>	$[HA]_{org}$ kmol m <sup>-3</sup>	$K_D$	$[HA]_{org}$ kmol m <sup>-3</sup>	$K_D$
0.05	0.22	0.0335	2.032	0.0335	2.031
0.15		0.1049	2.323	0.1048	2.323
0.2		0.1401	2.339	0.1401	2.339
0.4		0.2845	2.465	0.2846	2.465
0.05	0.44	0.0335	2.032	0.0335	2.032
0.15		0.1135	3.114	0.1135	3.115
0.2		0.1401	2.339	0.1401	2.373
0.4		0.2810	2.364	0.2811	2.364
0.05	0.66	0.0344	2.200	0.0344	2.200
0.15		0.1023	2.142	0.1023	2.142
0.2		0.1401	2.339	0.1401	2.339
0.4		0.2862	2.518	0.2862	2.518

The linear solvation energy relationship (LSER) model by Kamlet<sup>25</sup> was modified by Bizek *et al.*<sup>13</sup> and Uslu<sup>14</sup> to describe the effect of diluents on the values of distribution coefficients  $K_D$  in the form

$$\ln K_D = \ln K_D^0 + p(\delta_h)^2/100 + s(\pi^* + d\delta) + b\beta + a\alpha \quad (3)$$

where  $\delta_h$  is the Hildebrand's solubility parameter and  $\pi^*$ ,  $d$ , and  $\delta$  are the solvatochromic parameters that measure the solute + solvent, dipole + dipole, and dipole + induced dipole interactions, respectively.  $K_D^0$  represents the extraction constant for an "ideal inert" diluent. The solvatochromic parameter  $\alpha$  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  $\beta$  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  $b$  included the properties of solute and were estimated by the regression analysis of the experimental data. The values of solvatochromic parameters  $\pi^*$ ,  $\delta$ ,  $\alpha$ ,  $\beta$  have been found for several hundreds of compounds. The second term of eq. (3) which contains the solubility parameter  $\delta_h$  does not affect the values of the objective function significantly. Thus eq. (3) reduces to

$$\ln K_D = \ln K_D^0 + s(\pi^* + d\delta) + b\beta + a\alpha \quad (4)$$

The solvatochromic parameters: hydrogen bond donor acidity ( $\pi^*$ ,  $d$ ) and hydrogen bond acceptor basicities ( $\alpha$ ,  $\beta$ ) for different diluents were obtained from literature.<sup>13,25</sup> Model predicted results were compared with experimental data (Table 1). It can be seen that there is a good description of the distribution of propionic acid using LSER model with coefficient of linear regression value of 0.99. Thus, the LSER model successfully predicts the equilibrium behavior of propionic acid extraction using Aliquat 336 in 2-octanol. Model parameters equation for different concentrations of Aliquat 336 ( $c_A = 0.22 - 0.66$  kmol m<sup>-3</sup>) for acid concentration of  $c_P = 0.05 - 0.4$  kmol m<sup>-3</sup> were presented as: For  $[S]_0 = 0.22$  kmol m<sup>-3</sup>

$$\ln K_D = -0.53108 + 5.969 (\pi^* + 0.369 \delta) + 31.348 \alpha - 31.534 \beta \quad (5)$$

For  $[S]_0 = 0.44$  kmol m<sup>-3</sup>

$$\ln K_D = -0.207 + 6.495 (\pi^* + 0.512 \delta) + 44.696 \alpha - 44.971 \beta \quad (6)$$

For  $[S]_0 = 0.66$  kmol m<sup>-3</sup>

$$\ln K_D = -0.473 + 6.696 (\pi^* + 0.424 \delta) + 38.463 \alpha - 38.818 \beta \quad (7)$$



### Kinetics of extraction of propionic acid using Aliquat 336 in 2-octanol

Reactive extraction of propionic acid using Aliquat 336 involves the principle of mass transfer accompanied by reaction. The reaction regime could be found from the experimental results. In liquid-liquid systems it would be desirable to use a stirred cell or a small mechanically agitated contactor. Since the solubility of extractant (reactive component in the organic phase) is negligible in the aqueous phase, whereas acid (reactive component in aqueous phase) has significant solubility in the organic phase (in the diluent), resistance to mass transfer is confined to the organic phase. The overall extraction rate is determined by interfacial chemical kinetics and molecular diffusion of components towards and away from interface. The two resistances to transfer are by diffusion and chemical complexation, which are a function of mode of contact and transport properties of the components. The extraction equation is as given in eq. (2). Extraction rates were calculated from the slope of the tangent of concentration vs. time by the following equation based on the initial rate technique:

$$J_A = \frac{V_{\text{org}}}{A} \left. \frac{d[\text{HA}]}{dt} \right|_{t=0} \quad (8)$$

Doraiswamy and Sharma<sup>26</sup> classified mass transfer with reaction into four regimes: i) very slow reaction; ii) slow reaction; iii) fast reaction; and iv) instantaneous reaction. The classification was based on the physico-chemical and hydrodynamic parameters.

For fast reaction

$$J_A = [\text{HA}]^* \sqrt{\frac{2}{m+1} D_A k_{mn} [\text{HA}^*]^{m-1} [S_0]^n} \quad (9)$$

The validation of regime to be a fast reaction lies in:

$$3 < \frac{\sqrt{\frac{2}{m+1} D_A k_{mn} [\text{HA}^*]^{m-1} [S_0]^n}}{k_L} \quad (10)$$

The dependence of the rate of reaction per unit volume of the liquid in the contactor on the concentration of reactants for a particular regime is described by Doraiswamy and Sharma.<sup>26</sup> Acid reacts with the Aliquat 336 to form an acid-Aliquat 336 complex which is extracted into the organic phase. The equilibrium complexation reaction is reversible in nature. However, to avoid problems due to reversibility, only the initial rates were considered for evaluation of the kinetics. The concentration vs time plot was drawn to obtain the initial rate for various concentrations of acid and Aliquat 336 re-

spectively. The initial rate was obtained by regression analysis. This was divided by the total interfacial area ( $A = 33.33 \text{ cm}^2$ ) and multiplied by the volume of aqueous phase to obtain the molar flux rate ( $J_A/\text{kmol m}^{-2} \text{ s}^{-1}$ ).

Figs. 2 and 3 represent the plot of  $J_A$  against the organic phase acid concentration and initial Aliquat 336 concentration respectively. In Fig. 2, aqueous phase propionic acid concentration was varied from  $c_0 = 0.05 \text{ kmol m}^{-3}$  to  $0.4 \text{ kmol m}^{-3}$ . A regression analysis of the experimental data yielded a straight line. Thus, the reaction was found to be first order in propionic acid concentration. To determine order with respect to Aliquat 336 concentration, Aliquat 336 was varied from 10 to 30 % ( $c_A = 0.22 \text{ kmol m}^{-3}$  to  $0.66 \text{ kmol m}^{-3}$ ) in 2-octanol for fixed acid concentration of  $c_p = 0.2 \text{ kmol m}^{-3}$ . As it may be seen from Fig. 3, there is no effect of Aliquat 336 concentration on the rate of extraction, thus indicating that the reaction is zero order in Aliquat 336. This confirms that the reaction of acid with Aliquat 336 is a pseudo first order reaction. To confirm the regime in which the reactive extraction of propionic acid using Aliquat 336 in 2-octanol decreases, the following checks were performed. Doraiswamy and Sharma<sup>26</sup> have given an exhaus-

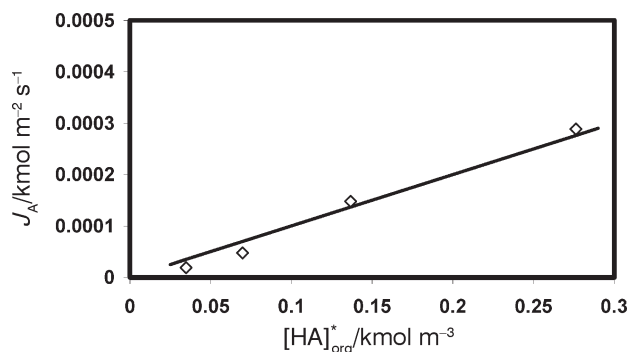


Fig. 2 – Effect of propionic acid concentration in the organic phase on the molar flux rate for the reactive extraction of propionic acid with Aliquat 336 in 2-octanol (Aliquat 336 concentration  $c_A = 0.66 \text{ kmol m}^{-3}$ , stirring speed 80 rpm)

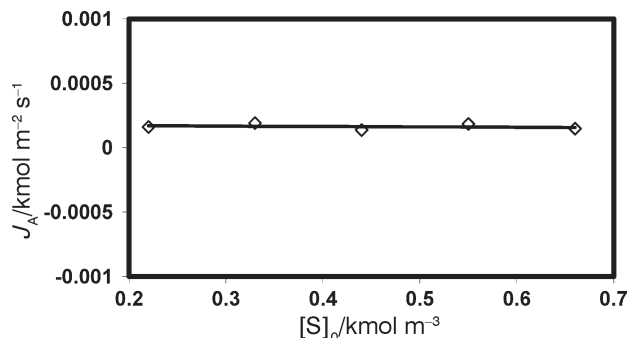


Fig. 3 – Effect of Aliquat 336 concentration on the molar flux rate for the reactive extraction of propionic acid with Aliquat 336 in 2-octanol (Propionic acid concentration  $c_p = 0.2 \text{ kmol m}^{-3}$ ; stirring speed 80 rpm)

tive discussion on the theory of extraction accompanied by a chemical reaction to predict the reaction regime. Following his ideas, the effect of hydrodynamics of the system was studied to find the reaction regime. Fig. 4 shows the effect stirring speed (50–80 rpm) on  $J_A$  for acid concentration of  $0.2 \text{ kmol m}^{-3}$  and Aliquat 336 concentration of  $0.66 \text{ kmol m}^{-3}$  in 2-octanol.  $J_A$  was found to be independent of the stirring speed. The effect of the phase volume ratio on  $J_A$  was also presented (Fig. 5).  $J_A$  was plotted for various phase volume ratios ( $V_{\text{org}}/V_{\text{aq}}$ ; volume of organic phase to volume of aqueous phase) at constant stirring speed for 40 % Aliquat 336 in 2-octanol and  $c_p = 0.2 \text{ kmol m}^{-3}$  propionic acid solutions. Again  $J_A$  was found to be independent of the volume phase ratio. Thus, the reactive extraction of propionic acid using Aliquat 336 in 2-octanol is independent of the system's hydrodynamics and thus is a fast chemical reaction occurring in the diffusion film, i.e. regime 3. The specific rate of absorption  $J_A$  for  $m = 1$  and  $n = 0$  may thus be given as

$$J_A = [\text{HA}]^* \sqrt{D_A k_1} \quad (11)$$

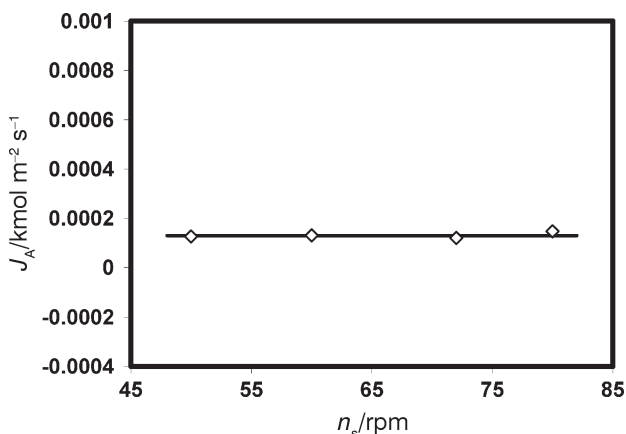


Fig. 4 – Effect of stirring speed on the molar flux rate of propionic acid extraction ( $c_p = 0.2 \text{ kmol m}^{-3}$ ) using Aliquat 336 ( $c_A = 0.66 \text{ kmol m}^{-3}$ ) in 2-octanol at 305 K

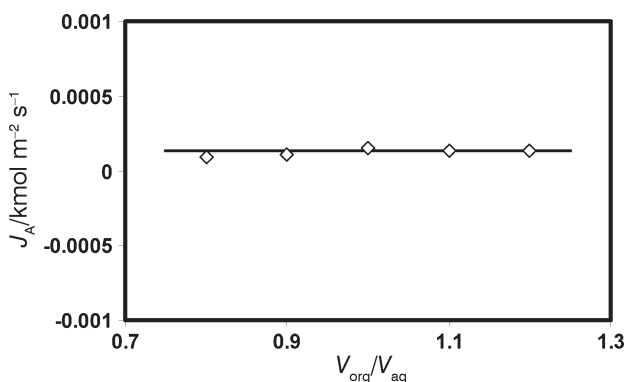


Fig. 5 – Effect of phase ratio on the molar flux rate of propionic acid extraction ( $c_p = 0.2 \text{ kmol m}^{-3}$ ) using Aliquat 336 ( $c_A = 0.66 \text{ kmol m}^{-3}$ ) in 2-octanol at 305 K

The value of  $D_A$  was estimated using Wilke-Chang equation<sup>27</sup> as  $1.724 \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1}$ . The rate constant ( $k_1$ ) was obtained from eq. (11) as  $0.58 \cdot 10^3 \text{ s}^{-1}$ .

Approximate value of physical mass transfer coefficient  $k_L$  is needed to check the conditions for reaction to be fast chemical reaction occurring in the diffusion film (eq. 10). The values of  $k_L$  for 2-octanol – propionic acid system was obtained by measuring concentration of organic phase as a function of time. The experimental data were correlated using the expression:<sup>28</sup>

$$\frac{d[\text{HA}]_{\text{org}}}{dt} = k_L \left[ \frac{A}{V} \right] ([\text{HA}]_{\text{org}}^* - [\text{HA}]_{\text{org}}) \quad (12)$$

where,  $[\text{HA}]_{\text{org}}^*$  is the equilibrium concentration of acid in diluent only. Integration of the above equation yields

$$\ln \left( 1 - \frac{[\text{HA}]_{\text{org}}}{[\text{HA}]_{\text{org}}^*} \right) = -k_L \left( \frac{A}{V} \right) t + \ln \left( 1 - \frac{[\text{HA}]_{0,\text{org}}}{[\text{HA}]_{\text{org}}^*} \right) \quad (13)$$

Thus the plot of  $\ln \left( 1 - \frac{[\text{HA}]_{\text{org}}}{[\text{HA}]_{\text{org}}^*} \right)$  against time  $t$  enables determination of  $k_L$ . At 80 rpm,  $k_L$  was obtained as  $2.05 \cdot 10^{-5} \text{ m s}^{-1}$ . For the range of stirring speed (70–80 rpm),  $\frac{\sqrt{D_A k_1}}{k_L}$  vary from 47–53, which is greater than 3. Hence the mentioned results reflect the reaction regime to be pseudo 1<sup>st</sup> order reaction occurring in diffusion film.

## Conclusion

Modeling and kinetics of reactive extraction of propionic acid was presented and the following may be concluded:

a) It may be seen that for Aliquat 336 in 2-octanol, a good description of the distribution of propionic using LSER model with coefficient of linear regression value of 0.99 was obtained. Thus, the LSER model successfully predicts the equilibrium behavior of propionic acid extraction using Aliquat 336 in respective diluents. Model parameters were evaluated.

b) Kinetics of reactive extraction of Aliquat 336 in 2-octanol was found to be first order in acid concentration and independent of Aliquat 336 concentration respectively. Hydrodynamic conditions have no effect on kinetics of reactive extraction and this confirms that the reaction is a fast reaction occurring in diffusion film. The rate constant ( $k_1$ ) was obtained as  $0.58 \cdot 10^3 \text{ s}^{-1}$ .

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## NOMENCLATURE

- $A$  – interfacial area,  $m^2$   
 $c$  – molar concentration,  $kmol\ m^{-3}$   
 $K_D^{overall}$  – overall distribution coefficient of acid  
 $K_S$  – extraction equilibrium constant,  $m^3\ kmol^{-1}$   
 $[HA]$  – concentration of acid,  $kmol\ m^{-3}$   
 $[S]$  – concentration of Aliquat 336,  $kmol\ m^{-3}$   
 $[HA.S]$  – concentration of acid-extractant complex,  $kmol\ m^{-3}$   
 $J_A$  – molar flux rate,  $kmol\ m^{-2}\ s^{-1}$   
 $D_A$  – diffusivity of acid in the solution,  $m^2\ s^{-1}$   
 $k_{mn}$  – reaction rate constant,  $s^{-1}(kmol\ m^{-3})^{1-(m+n)}$   
 $k_1$  – first order or pseudo first order reaction rate constant,  $s^{-1}$   
 $[S_0]$  – concentration of the Aliquat 336 in the bulk of solution,  $kmol\ m^{-3}$   
 $[HA]^*$  – equilibrium concentration of acid in the organic phase,  $kmol\ m^{-3}$   
 $m$  – order of reaction with respect to acid  
 $n$  – order of reaction with respect to Aliquat 336  
 $n_s$  – stirring speed, rpm  
 $r$  – mole ratio  
 $t$  – time, s  
 $k_L$  – physical mass transfer coefficient,  $m\ s^{-1}$   
 $w$  – mass fraction, %

## Subscripts

- aq – aqueous phase  
 org – organic phase

## Superscripts

- 0 – initial

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