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Kinetics Studies and Equilibrium Modeling of Recovery of Propionic Acid

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ABSTRACT

Kinetics of reactive extraction and solvation modeling (LSER) of propionic acid extraction using TOA in MIBK was studied. Model and experimental values shows a close resemblance particularly at low concentrations of acid. Stirred cell was employed for the kinetics studies. Reaction was found to be fast with zero order with respect to TOA concentration and first order with respect to acid concentration. A rate constant was evaluated to be 0.764×10^4 1/s.

Keywords: Propionic acid, reactive extraction, modeling, kinetics, TOA.

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INTRODUCTION

Carboxylic acids could be successfully produced by bio route provided an efficient method of recovery could be designed. Propionic acid, a monocarboxylic acid having wide use for animal feed preservation, in human foods, in synthesis of herbicides, cellulose acetate–propionate plastics, in pharmaceuticals industries, as perfumes and as solvent, has a lot of scope to be produced by fermentation [1]. The challenge of recovery lies on the major issues such as the presence of acid in dilute form, lower extractions by conventional recovery techniques and costlier and unclean conventional method of separation. In this view, reactive extraction has been proved to be efficient and clean method of recovery that provides ease in reactor pH control without requiring base addition, and allows use of a high-concentration substrate as a process feed to reduce process wastes and production costs.

Tertiary amines have been selective and effective extractants for removal of propionic acid [2]. Tri-n-octylamine in this regard has been found to be a good extractant. This has led the author of present work to study the reactive extraction of propionic acid from dilute aqueous solutions using tri-n-octyl amine in different diluents [3,4]. While selecting diluents, it was found that higher extractions of propionic acid by TOA were found in dipolar aprotic and protic solvents. Difference in equilibrium extraction values for TOA in different diluents could be better explained if kinetics could be studied. Jet apparatus, stirred cell, mechanically agitated contactor and stirred contactor are some of the setups successfully employed to carry out kinetic studies of fluid-fluid systems. However in liquid-liquid systems it would be desirable to use a stirred cell or a small mechanically agitated contactor. Further it would be important if some mathematical model accounting the solvation characteristic of the solvent be proposed that could help to predict the efficiency of the extraction system.

Some work on reactive extraction of carboxylic acids using stirred cell could be found in literature. The relevant studies are given. Reschke and Schugerl [5] developed kinetic model and identified the model parameters for extraction of penicillin using Amberlite LA-2 (secondary amine) in a stirred cell extractor using two film model. Wasewar et al. [6] studied the kinetics of extraction of lactic acid by Alamine 336 (tertiary amine) in MIBK and Alamine 336 in decanol [7] using stirred cell. In both cases the kinetics was found to be fast reaction occurring in diffusion film. The reaction was found to be of zero order in Alamine and first order in lactic acid. Similar results were obtained by Gaidhani et al. [8] in extraction of phenyl acetic acid using Alamine 336 in kerosene in a stirred cell.

In present paper, linear solvation energy relationship (LSER) modeling and kinetics of extraction of propionic acid using TOA in methyl isobutyl ketone (MIBK) was presented. Model and experimental values were compared. Diffusivities, physical mass transfer coefficients, order of reaction, rate constants and effect of hydrodynamics were studied. The results of Keshav et al. [4] were used to predict a solvation model for the equilibrium data.



MATERIAL AND METHOD

TOA ($C_{24}H_{51}N$) (ACROS, India), a tertiary amine, is a light colorless liquid with the molecular weight of 353.66 and density of 0.809 g/cm^3 . Propionic acid (CH_3CH_2COOH ; 99 % purity; molar mass 74.08; density 0.992) was obtained from Himedia, India Ltd. MIBK (Ranbaxy Ltd., India) was of technical grade and 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 supplied by Ranbaxy, India. For the standardization of the NaOH, oxalic acid (99.8 %) was obtained from s. d. Fine-Chem Ltd, India. Phenolphthalein solution (pH range 8.2-10) was used as indicator for titration and was obtained from Ranbaxy, India. The initial aqueous acid concentrations range ($[HA]^0$) of $0.05\text{-}0.4 \text{ kmol/m}^3$ were used as in waste water streams and in fermentation broth, its concentration is expected to be less than 0.5 kmol/m^3 .

Experiments were carried out in 6.516 cm i.d. glass stirred cell with an effective interfacial area of 33.33 cm^2 . The design of the stirred cell was similar to that used by Wasewar et al. [6,7]. The vessel was equipped with a stainless steel dual four flat blade stirrer (dia. = 4.8 cm). Known volumes of organic solvent and aqueous phase were taken and reactive extraction was carried out for a definite period. Samples of aqueous phase were taken out at different time intervals for analysis till it reaches its equilibrium. It was found that the equilibrium is established within 30 minutes. Aqueous phase acid concentration was determined by titration with sodium hydroxide solution (0.02 N). In order to eliminate the problem of alkali reacting with carbon dioxide in air, it was prepared fresh each time and a soda lime absorbent was used at top of burette. The acid content in the organic phase was determined by mass balance. Few experiments were repeated to check the consistency in the results. The variation was found within $\pm 2 \%$.

RESULTS AND DISCUSSION

Reactive extraction involves the extraction of solute using chemical reaction and the reaction is either kinetics or mass transfer limited. Overall extraction rate is determined by interfacial chemical kinetics and molecular diffusion of components towards and away from interface. Doraiswamy and Sharma [9] suggested using stirred cell contactor for lab scale studies for finding kinetics of liquid-liquid extractions. The reaction phase for reactive extraction of propionic acid using TOA has been the organic phase owing to very low solubility of TOA in aqueous phase. Transport phenomenon could be explained both in view of reaction and diffusion step. The association of propionic acid with TOA has been found to be 1:1 with low loading [3]. Thus there is only (1:1) stoichiometric complexation of acid and TOA. The equilibrium complexation reaction is reversible in nature. However, to avoid problems due to reversibility only initial rate were considered for evaluation of the kinetics. Initial rate was obtained by regression analysis and is divided by the total interfacial area (33.33 cm^2) and multiplied by volume of aqueous phase to obtain the specific rate of reaction (R_A ; $\text{kmol/m}^2\text{s}$)

Doraiswamy and Sharma [9] describe in method of discerning mechanism to obtain the regime in which the reaction falls based on hydrodynamics of the system. Effect of organic

phase acid concentration and initial TOA concentration on the rate of reaction is presented in Fig. 1 and 2, respectively. Effect of acid concentration was studied by varying it from 0.05 kmol/m³ to 0.4 kmol/m³. A regression analysis of the experimental data yield a straight line through origin with unit slope, indicating the reaction to be first order in propionic acid concentration (Fig. 1). To determine order with respect to TOA concentration, TOA was varied from 0.229 kmol/m³ to 0.915 kmol/m³ in MIBK for fixed acid concentration of 0.2 kmol/m³. No effect of TOA concentration on the rate of extraction was observed hence the reaction is zero order in TOA. Thus the reaction is overall pseudo first order for studied range of concentrations of acid and TOA.

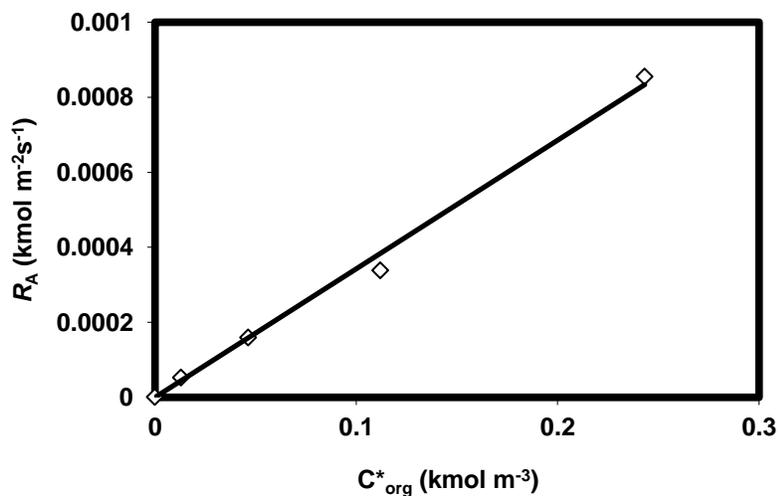


Figure 1: Effect of propionic acid concentration in the organic phase on the specific rate of extraction for the reactive extraction of propionic acid TOA and MIBK. TOA concentration = 40% (0.915 kmol/m³); speed of agitation = 80 rpm.

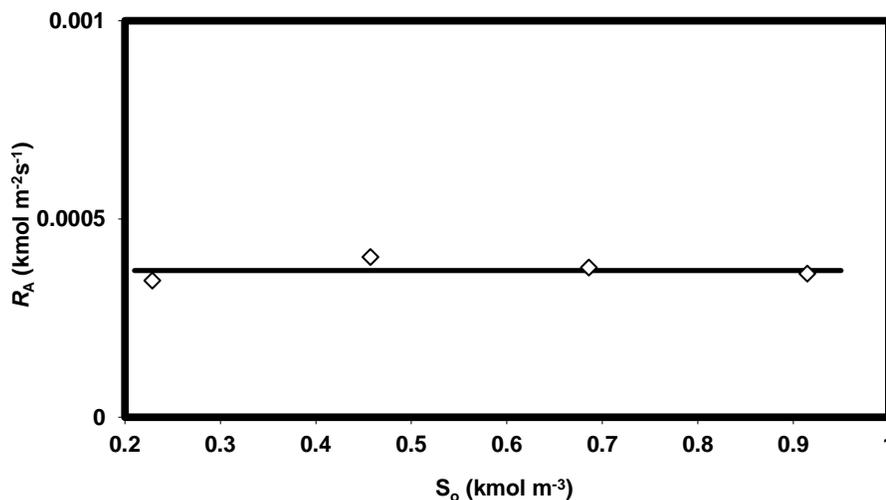


Figure 2: Effect of TOA concentration on the specific rate of extraction for the reactive extraction of propionic acid with TOA and MIBK. Propionic acid concentration = 0.2 kmol/m³; speed of agitation = 80 rpm.

Hydrodynamic parameters such as speed of stirring and volume phase ratio were studied to find the reaction regime. Stirring speed was varied from 50-80 rpm and in this range R_A was found to be independent of speed of stirring (Fig. 3). The other conditions of

experiments were: acid concentration of 0.2 kmol/m^3 and TOA concentration of 0.915 kmol/m^3 in MIBK. Varying the volume phase ratio (volume of organic phase to volume of aqueous phase), at constant speed of stirring for 40 % TOA in MIBK and 0.2 kmol/m^3 propionic acid solution, were again found to have no effect on the R_A values. Thus it could be found that reactive extraction of propionic acid using TOA in MIBK is independent of hydrodynamics of the system. According the method of discerning mechanism this type of condition ascertains that the reaction is fast occurring in the diffusion film i.e regime 3. Rate could be defined as:

$$R_A = C^* \sqrt{\frac{2}{m+1} D_{HA} k_{mn} C^{*m-1} S_o^n} \quad (1)$$

The condition under which the reaction of acid occurs entirely in the film is given as:

$$1 \ll \frac{\sqrt{\frac{2}{m+1} D_{HA} k_{mn} C^{*m-1} S_o^n}}{k_L} \quad (2)$$

where the term on right hand side represents the ratio of the amount of acid reacting in the film to that reacting in the bulk. The specific rate of reaction R_A for $m=1$ and $n=0$ can thus be given as:

$$R_A = C^* \sqrt{D_A k_1} \quad (3)$$

The value of D_A was estimated using Wilke- Chang equation [10] as $1.512 \times 10^{-9} \text{ m}^2/\text{s}$ and the rate constant (k_1) obtained from (3) was $0.764 \times 10^4 \text{ s}^{-1}$.

Physical mass transfer coefficient k_L were evaluated from the following equation [11]:

$$\frac{dC_{org}}{dt} = k_L \left[\frac{A}{V} \right] (C^*_{org} - C_{org}) \quad (4)$$

At 80 rpm, k_L was obtained as $3.5 \times 10^{-6} \text{ m/s}$. For the range of stirring speed (70-80 rpm), $\frac{\sqrt{D_A k_1}}{k_L}$ vary from 324-971, which is greater than 1. Hence the mentioned results reflect the reaction regime to be pseudo fast order reaction occurring in diffusion film. It implies that acid reacts with TOA within a very short distance of the surface and there is none in the bulk liquid.

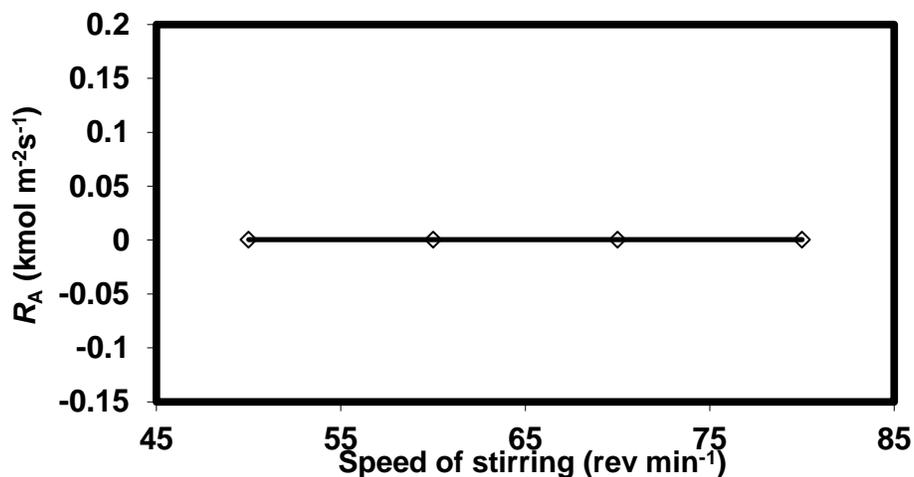


Figure 3: Effect of speed of agitation on rate of reaction for extraction of propionic acid (0.2 kmol/m³) using TOA (0.915 kmol/m³) and MIBK at 305 K.

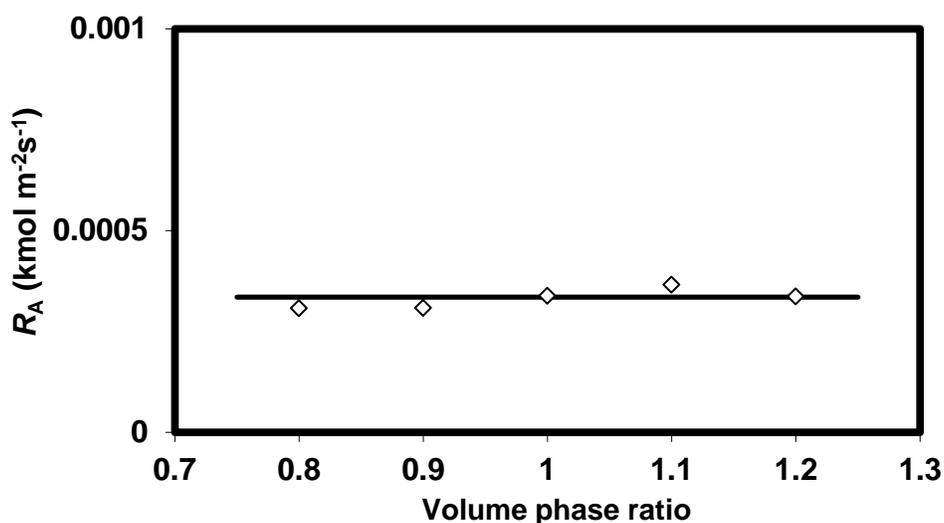


Figure 4: Effect of phase ratio on rate of reaction for extraction of propionic acid (0.2 kmol/m³) using TOA (0.915 kmol/m³) and MIBK at 305 K

Kamlet et al. [12] and Bizek et al. [13] and Uslu [12] presented the linear solvation energy relationship (LSER) model to account for the effect of diluents on the values of distribution coefficients D in the form

$$\ln D = \ln D^0 + s(\pi^* + d\delta) + b\beta + a\alpha \quad (5)$$

where π^* , d , and δ are the solvatochromic parameters. D^0 represents the extraction constant for an "ideal inert" diluent. α and β represents the hydrogen-bond donor and hydrogen-bond acceptor parameters respectively and p, s, d, a are regression coefficients. The parameter values are defined in literature [12] as $\pi^* = 0.51$, $\delta = 1$, $\alpha = 0$, $\beta = 0.11$. Model predicted results were compared with experimental data (Table 1).

Table 1: Experimental and model extraction equilibrium results for TOA/ MIBK/ propionic acid system at 305 K.

| C_o kmol m ⁻³ | $D^{\text{experimental}}$ | D^{model} | $D^{\text{experimental}}$ | D^{model} | $K_S^{\text{experimental}}$ m ³ kmol ⁻¹ | K_S^{model} m ³ kmol ⁻¹ |
|-------------------------------|---------------------------|--------------------|---------------------------|--------------------|--|---|
| | 30 % TOA | | 40 % TOA | | | |
| 0.05 | 2.125 | 2.157 | 1.857 | 2.047 | 4.317 | 4.171 |
| 0.1 | 3.321 | 3.126 | 3.000 | 3.013 | | |
| 0.2 | 4.263 | 3.965 | 5.666 | 3.907 | | |
| 0.4 | 5.666 | 4.894 | 5.896 | 5.053 | | |

There was found a close resemblance of experimental and model data points. The model predicts values of distribution coefficients lower than that obtained experimentally. However in general the model resembles the experimental data closely at lowest concentration of acid employed (0.05 kmol/m³). The maximum deviation in model and experimental values were found at highest concentration of acid chosen (0.4 kmol/m³). Thus LSER model can be successfully employed to determine model data for low concentrations of acid in the present case. However there was found resemblance in the trend of both model and experimental. Equilibrium complexation constant (K_S) were also reported in Table 1 (model equations obtained by replacing D in (2) by K_E). Analogous for D , model K_S values shows only slight deviation for TOA + MIBK (3.38 %).

CONCLUSION

Kinetics of extraction of propionic acid using TOA in MIBK using Stirred cell was presented and the reaction was found to be first order in acid concentration and zero order in TOA concentration. Rate of reaction of propionic acid extraction was independent of hydrodynamics conditions with rate constants were evaluated to be $0.764 \times 10^4 \text{ s}^{-1}$. Equilibrium modeling using LSER model was performed to obtain the model values of extraction of propionic acid using TOA in MIBK. A good fit of experimental data by the model values were obtained for the system. At lowest concentration of acid (0.05 kmol/m³) model and experimental values closely resembles.

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