

Reactive extraction of propionic acid using Aliquat 336 in MIBK: Linear solvation energy relationship (LSER) modeling and kinetics study

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This study presents linear solvation energy relationship (LSER) modeling of reactive extraction of propionic acid using Aliquat 336 in MIBK as diluent. Reaction was slow in Aliquat 336 + MIBK with rate constant at $0.0079 \text{ (m}^3/\text{kmol)}^{0.55} \text{ s}^{-1}$. Order of reaction with respect to acid and Aliquat 336 was 1 and 0.9 respectively. Modeling of reactive extraction equilibria using LSER was carried out and predicted a close resemblance of experimental data.

Keywords: Aliquat 336, Kinetics, LSER model, MIBK, Propionic acid, Reactive extraction

Introduction

Reactive extraction (RE) of propionic acids from dilute aqueous solutions [fermentation broth and wastewater (acid content, < 10% w/w)] involves use of an extractant-diluent system to extract acid¹⁻⁸. Organo phosphorous compounds (tri-n-butyl phosphate, tri-n-octylphosphine oxide etc.) and high molecular weight aliphatic amines (tri-n-octylamine, Aliquat 336, Alamine 336) were primarily used in RE studies for propionic acid. Conventional solvents (ketones, ethers, aliphatic hydrocarbons etc.) were found inefficient in extraction of propionic acids from dilute solutions, due to low acid activity resulting in low distribution coefficients^{3,4,9-12}. Aliphatic amines (long chain tertiary amines and quaternary amines) have been found to be more effective extractants¹³. Propionic acid is an important carboxylic acid used in food (in grain preservation, as mould preventatives in silage and hays, and as antifungal agent in bread and other foods), pharmaceutical (antiarthritic drugs) and chemical industries (manufacture of cellulose plastics, plastic dispersions, herbicides, perfumes and flavors, plasticizers etc.). Fermentation is a clean alternative for propionic acid production but suffers from low yield and

productivity of acid and expensive downstream separation of acid. Equilibrium of propionic acid using Aliquat 336 in different diluents has been studied^{3,4,14,15} but no study on reaction kinetics is found.

This study presents extraction kinetics of propionic acid using Aliquat 336 in MIBK and linear solvation energy relationship (LSER) model for equilibrium study of RE of propionic acid.

Experimental

Materials

Aliquat 336 (Methyltricaprylammonium chloride from Himedia, India; molar mass, 404.17; density 0.888 g cm^{-3}) was used as extractant (volume fraction, 10-30% in diluent). Propionic acid ($\text{CH}_3\text{CH}_2\text{COOH}$, 99% purity, molar mass 74.08, density 0.992 g cm^{-3}) was obtained from Himedia, India Ltd. MIBK (Ranbaxy Ltd, India) was of technical grade. Double distilled water was used to prepare acid solutions of various concentrations. NaOH (Ranbaxy, India), used for titration, was of analytical grade. For standardization of NaOH, oxalic acid (99.8%) was obtained from S. d. fine-Chem Ltd, India. Phenolphthalein solution (pH 8.2-10.0) was used as an indicator for titration and was obtained from Ranbaxy Ltd, India. Initial aqueous acid concentrations range ($[\text{HA}]^0$, $0.05\text{-}0.4 \text{ kmol m}^{-3}$) were used since in wastewater and in fermentation broth⁸, its concentration is expected to be less than 0.5 kmol m^{-3} .

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Table 1—Experimental and model values of different parameters for reactive extraction of propionic acid using Aliquat 336 in MIBK at 305 K

[HA] _o kmol m ⁻³	S _o kmol m ⁻³	Experimental			LSER model		
		[HA] _{org} kmol m ⁻³	K _D	z	[HA] _{org} kmol m ⁻³	K _D	z
0.05	0.22	0.0320	1.777778	0.145455	0.03186	1.770010	0.144819
0.1		0.0702	2.355705	0.319091	0.0702	2.355001	0.319091
0.2		0.1499	2.992016	0.681364	0.1499	2.991902	0.681364
0.4		0.3077	3.333694	1.398636	0.3077	3.333022	1.398636
0.05	0.44	0.0335	2.030303	0.076136	0.033495	2.030009	0.076125
0.1		0.0725	2.636364	0.164773	0.0725	2.636002	0.164773
0.2		0.1525	3.210526	0.346591	0.1525	3.25832	0.346591
0.4		0.313	3.597701	0.711364	0.313	3.597688	0.711364
0.05	0.66	0.03463	2.25309	0.05247	0.038353	2.495327	0.058111
0.1		0.0738	2.816794	0.111818	0.0738	2.820013	0.111818
0.2		0.155	3.444444	0.234848	0.155	3.449993	0.234848
0.4		0.3138	3.640371	0.475455	0.3138	3.639869	0.475455

Methods

Kinetics experiments were carried out in 6.516 cm i.d. glass stirred cell. Effective interfacial area was 33.33 cm². Vessel was equipped with stainless steel dual four flat blade stirrer (diam, 4.8 cm). Stirred cell¹⁶⁻¹⁸ was kept in a constant temperature water bath to maintain temperature at 305 K ± 1K. Known volumes of organic and aqueous phase (100 ml each) were taken and RE was carried out for a definite period. Samples of aqueous phase (1 ml each) were taken out at 1, 3, 5, 10, 20 and 30 min. Kinetic experiments were performed until equilibrium, which was established within 30 min. To ensure concentration corresponds to time when samples were taken, separation of phases was carried out quickly and successively. Aqueous phase acid concentration was determined by titration with 0.02 N NaOH solution. 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 top of burette. Acid content in organic phase was determined by mass balance. Few experiments were carried out in duplicate and consistency was found within ± 2%. Method of discerning mechanism¹⁹ was used to determine reaction regime based on physicochemical and hydrodynamics conditions.

Results and Discussion

At experimental condition [pH (4.67), smaller than pK_a of acid], it can be fairly assumed that only acid-extractant complex and undissociated acid exists in

organic and aqueous solutions respectively. Distribution coefficient (K_D) of acid is given as

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

where [HA] is acid concentration, superscript “total” represents total concentration and subscripts “aq” and “org” represent aqueous and organic phase. Extraction of propionic acid (HA) by chemical interaction using Aliquat 336 (S) can be represented as



where [S:HA] represents Aliquat 336-acid complexes.

Chemical equilibria of extraction of propionic acid (Table 1) using Aliquat 336 in MIBK presents overall distribution coefficient, acid concentration in organic phase and overall loading ratio (z, ratio of total extracted acid in organic phase to initial extractant concentration). LSER model²⁰ was modified^{21,22} to describe effect of diluents on K_D as

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

where δ_h is Hildebrand's solubility parameter and π^* , d , and δ are solvatochromic parameters that measure solute

+ solvent, dipole + dipole, and dipole + induced dipole interactions, respectively. K_D^0 represents extraction constant for an "ideal inert" diluent. Solvatochromic parameter α scale of solvent HBA (hydrogen-bond donor) acidities describes ability of solvent to donate a proton in a solvent to solute hydrogen bond. The β scale of HBA basicities provides a measure of solvent's ability to accept a proton (donate an electron pair) in a solute to solvent hydrogen bond, respectively. Coefficients p , s , d , a and b include properties of solute, rather than p , s , d and a are regression coefficients. Values of solvatochromic parameters π^* , δ , α , β have been found several hundreds of compounds. Since solubility parameter δ_h does not affect values of objective function significantly^{21,22}, Eq. (3) reduces to

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

Hydrogen bond donor acidity (π^* , δ) and hydrogen bond acceptor basicities (α , β) for MIBK were obtained as reported²⁰. Comparing model predicted results with experimental data (Table 1), a good description of distribution of propionic acid was observed using LSER model with coefficient of linear regression (0.99). Thus, LSER model successfully predict equilibrium behavior of propionic acid extraction using Aliquat 336 in MIBK. Model parameter equation for Aliquat 336 (0.66 kmol m⁻³) and acid concentration (0.05-0.4 kmol m⁻³) was presented as

$$\ln K_D = -0.473 + 6.696 (\pi + 0.424 \delta) + 38.463 \alpha - 38.818 \beta \quad \dots (5)$$

RE of propionic acid using Aliquat 336 involves principle of mass transfer accompanied by reaction. Reaction regime could be found from experimental results. In liquid-liquid systems, it would be desirable to use a stirred cell or a small mechanically agitated contractor¹⁹. Since solubility of extractant (reactive component in organic phase) is negligible in aqueous phase, whereas acid (reactive component in aqueous phase) has significant solubility in organic phase (in diluent), resistance to mass transfer is confined to organic phase. Overall extraction rate is determined by interfacial chemical kinetics and molecular diffusion of components towards and away from interface. Two resistances to transfer are by diffusion and chemical complexation, which are function of mode of contact and transport properties of components. Equilibrium complexation

reaction is reversible. However, to avoid problems due to reversibility, only initial rate were considered for evaluation of kinetics. Plot of concentration versus time were drawn to obtain initial rate for various concentrations of acid and TBP respectively. Initial rate was obtained by regression analysis. This was divided by total interfacial area ($A=33.33 \text{ cm}^2$) and multiplied by volume of aqueous phase (V) to obtain specific rate of reaction (R_A , kmol m⁻²s⁻¹) as

$$R_A = \frac{V}{A} \left. \frac{d[\text{HA}]}{dt} \right|_{t=0} \quad \dots (6)$$

Doraiswamy & Sharma¹⁹ classified mass transfer with reaction into four regimes: i) very slow reaction; ii) slow reaction; iii) fast reaction; and iv) instantaneous reactions. For each regime, rate equation and method of discerning reaction regime were given. For slow reaction, rate of reactive extraction is

$$R_A = k_{mn} ([\text{HA}^*]^m [\text{S}_o]^n) \quad \dots (7)$$

where k_{mn} is reaction rate constant [$\text{s}^{-1}(\text{kmol m}^{-3})^{1-(m+n)}$], $[\text{S}_o]$ is concentration of Aliquat 336 in bulk of solution (kmol m^{-3}), $[\text{HA}^*]$ is equilibrium concentration of acid in organic phase (kmol m^{-3}), m is reaction order with respect to acid, n is reaction order with respect to Aliquat 336.

Concentration versus time plot (Fig. 1) determined effect of acid concentration and effect of Aliquat concentration on rate of reaction, R_A . Regression analysis of experimental data yielded rate of reaction to be First Order with respect to acid concentration (Fig. 2) and 0.9th order with respect to A-336 concentration (Fig. 3). Effect of speed of stirring (50-80 rev min⁻¹) and phase volume ratio was studied (Fig. 4) on R_A for acid concentration (0.2 kmol m⁻³) and Aliquat 336 concentration (0.66 kmol m⁻³) in MIBK. R_A was found to be independent of speed of stirring, whereas, it increases with increase of volume phase ratio. Thus, according to conditions of Doraiswamy & Sharma¹⁹, it can be concluded that reaction falls in Regime 1 or a kinetic-controlled slow reaction occurring in bulk organic phase. Specific rate of absorption R_A for $m=1$ and $n=0.9$ can thus be given as

$$R_A = k_1 ([\text{HA}^*][\text{S}_o]^{0.9}) \quad \dots (8)$$

Rate constant (k_1) was obtained from Eq. (8) as 0.0079 (m^3/kmol)^{0.55} s⁻¹.

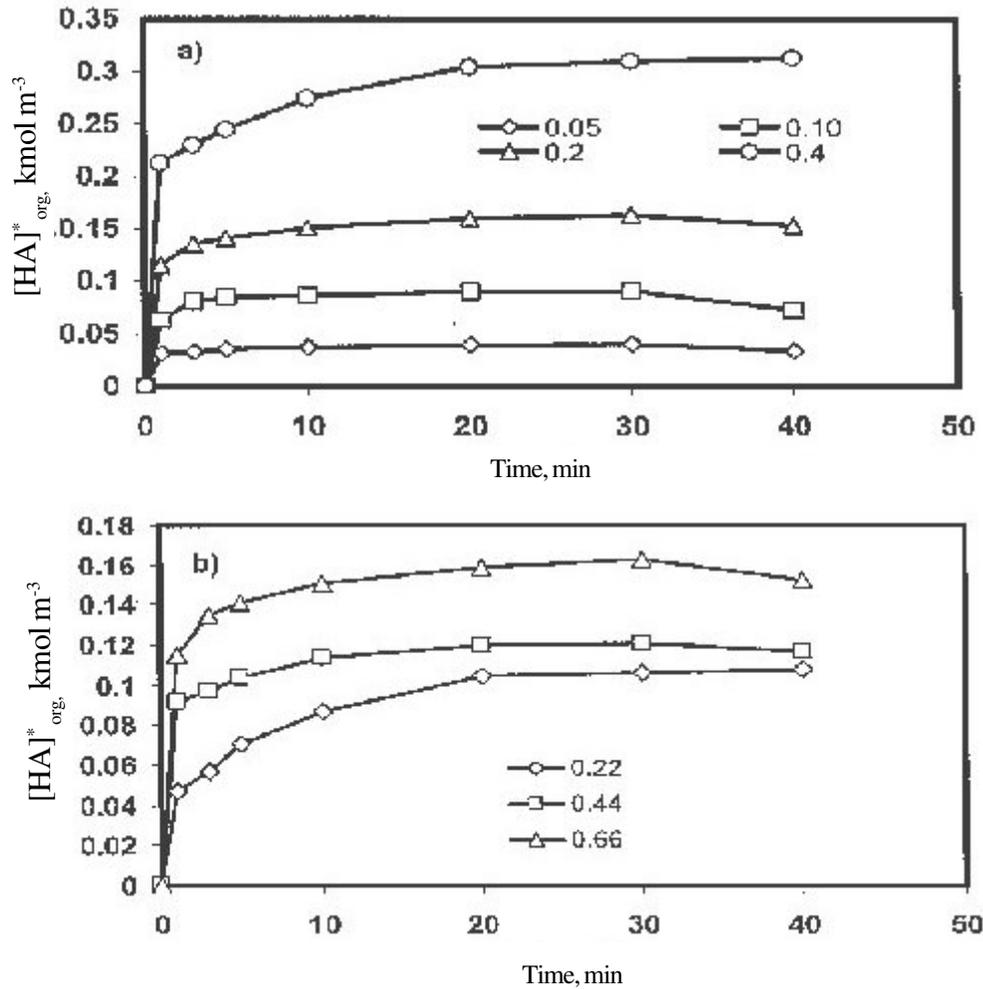


Fig 1—Concentration vs time plot to determine values of R_A at different concentration of: a) Acid (0.05-0.4 kmol m⁻³) and 0.66 kmol m⁻³ Aliquat 336 in MIBK; b) Aliquat 336 (0.22-0.66 kmol m⁻³) in MIBK and 0.2 kmol m⁻³ propionic acid

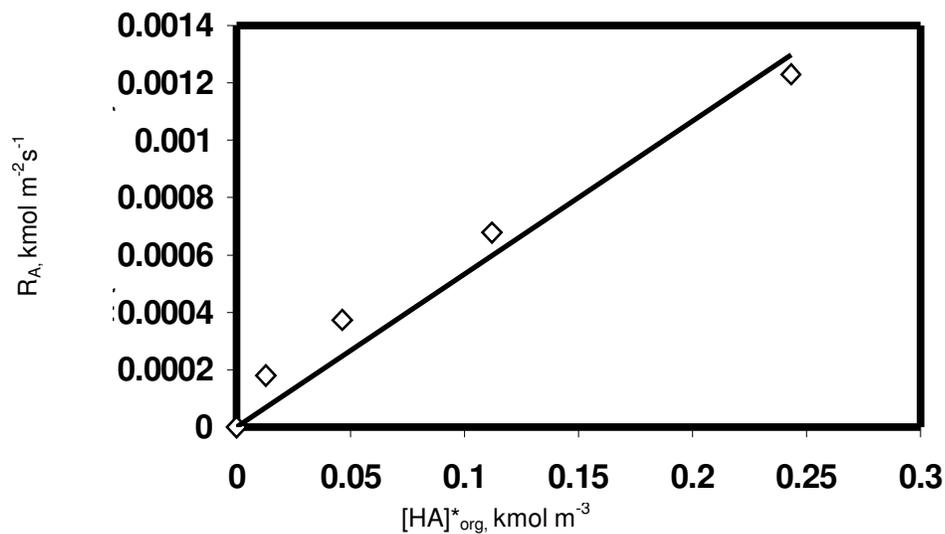


Fig. 2—Effect of propionic acid concentration in organic phase on specific rate of extraction for reactive extraction of propionic acid with Aliquat 336 in MIBK [TBP concentration = 30% (0.66 kmol m⁻³); speed of agitation = 80 rpm]

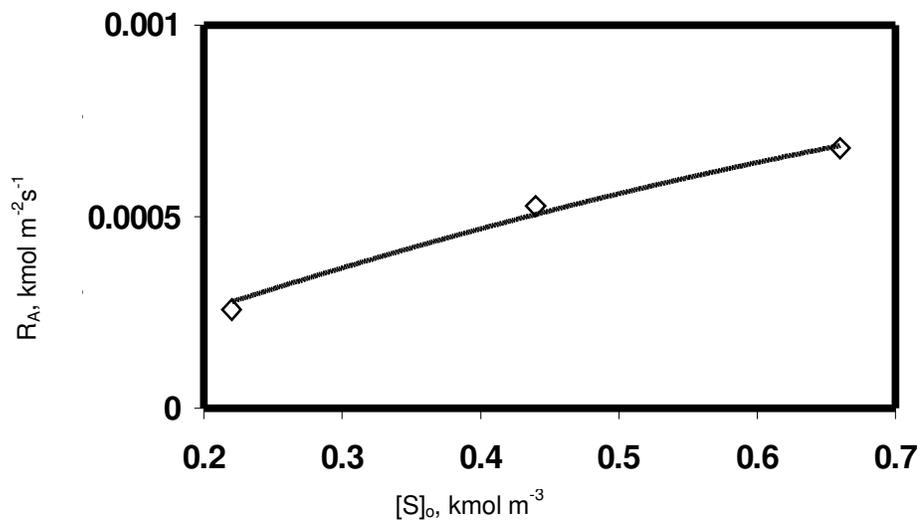


Fig. 3—Effect of TBP concentration on specific rate of extraction for reactive extraction of propionic acid with Aliquat 336 in MIBK (Propionic acid conc. = 0.2 kmol m^{-3} ; speed of agitation = 80 rpm)

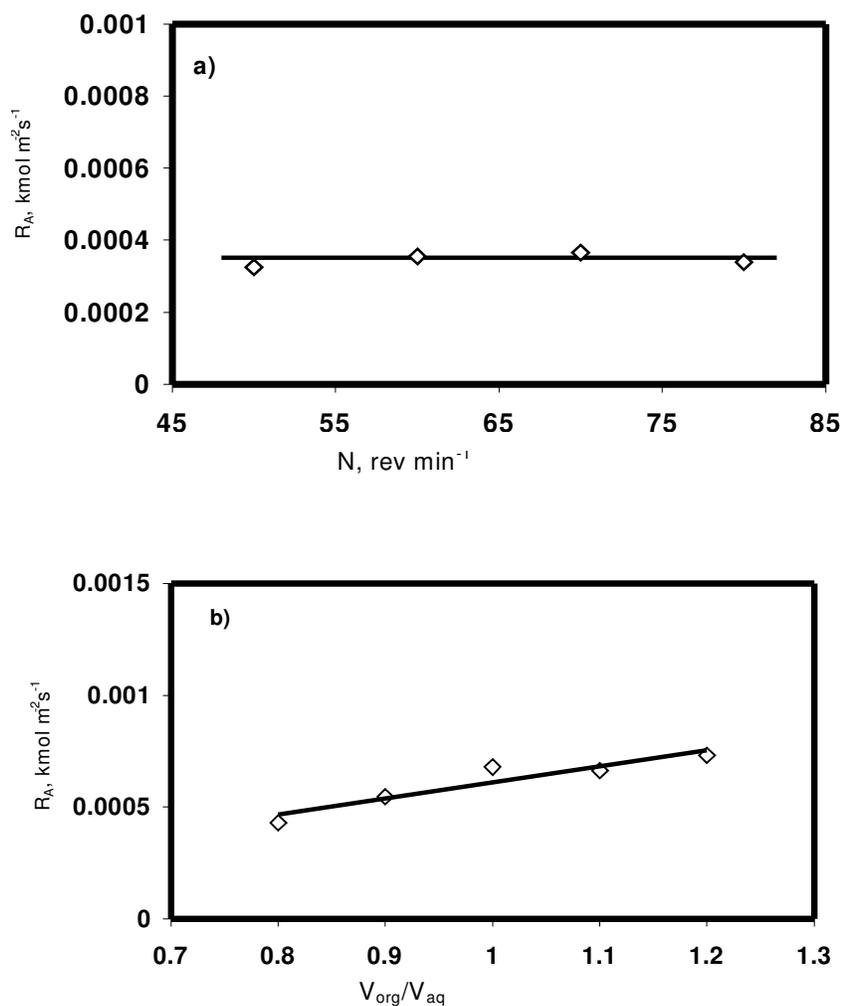


Fig. 4—Effect on rate of reaction for extraction of propionic acid ($0.2 \text{ kmol mAu}^{-3}$) using Aliquat 336 (0.66 kmol m^{-3}) in MIBK at 305 K of: a) speed of agitation; b) phase ratio

Conclusions

For Aliquat 336 in MIBK, a good description of distribution of propionic acid using LSER model with coefficient of linear regression (0.99) was obtained. Thus, LSER model successfully predict equilibrium behavior of propionic acid extraction using Aliquat 336 in respective diluents. Kinetics of RE of propionic acid using Aliquat 336 in MIBK was found to be 1st order in acid concentration and 0.9th power in Aliquat 336 concentration. Though, speed of stirring has no effect on rate, whereas increasing volume phase ratio was found to increase RE rate. Thus, reaction was slow and rate constant (k_1) was $0.0079 \text{ (m}^3 \text{ /kmol)}^{0.55} \text{ s}^{-1}$.

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