Stoichiometric and Spectroscopic Study of Reactive Extraction of Phenylacetic Acid with Tri-*n*-Butyl Phosphate

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Phenylacetic acid is widely used in the pharmaceutical industry for production of antibiotics. The recovery of phenylacetic acid from dilute aqueous waste with tri-*n*-butyl phosphate in methyl isobutyl ketone and petroleum ether has been attempted, and the results are presented in terms of distribution coefficient, extraction efficiency, apparent equilibrium constant, and loading ratio. The mechanism of reactive extraction was analyzed and the stoichiometric ratio of phenylacetic acid to tri-*n*-butyl phosphate in methyl isobutyl ketone and petroleum ether was found to be 1:0.5 and 1:1.2. Mass action law was used to represent the reactive extraction equilibrium for phenylacetic acid−tri-*n*-butyl phosphate−diluents which satisfied much in the present study. FTIR spectroscopy was studied for confirmation of the formation of a complex between acid and extractant. Further relative basicity approach has been extended to represent the experimental results. The model is best suited to experimental results.

Key words:

reactive extraction, phenylacetic acid, tri-*n*-butyl phosphate, methyl isobutyl ketone, petroleum ether, relative basicity model

Introduction

Phenylacetic acid, also known as benzeneacetic acid (IUPAC Name: 2-phenylacetic acid), is an organic compound containing a phenyl ring and an acidic functional group. It has a white scale-like crystal appearance, and a honey-like odour at low concentration. Phenylacetic acid is used as a precursor in the production of penicillin G (as shown in Fig. 1),[1,2] *β*-lactam, and amphetamine. Due to multifunctional biological and medicinal activities of phenylacetic acid, it is necessary to recover it from the effluent streams.

Phenylacetic acid can also be produced by strains of *Bacteroides asaccharolyticus* and *Bacteroides melaninogenicus* subspecies isolated from human and animal sources.[3] Fermentation technology for the production of carboxylic acids in the form of aqueous solutions has been known in the last few decades. There are various severe inhibiting effects on the rate of conversion and recovery methods from fermentation broths. Several separation techniques such as adsorption[4–7], distillation[8], electro-dialysis[9,10], ion-exchange[11], liquid surfactant membrane extraction[12,13], liquid-liquid extraction[14], precipitation[15], reverse osmosis[16,17] and ultrafiltration[18,19] have been reported in the literature, but all these methods have inherent drawbacks. Calcium hydroxide precipitation has a few shortcomings such as consumption of large quantities of reagents (H_2SO_4 and lime), a large amount of waste generation per ton of acid produced, waste disposal problems of waste, and very poor sustainability. Dialysis has good potential but its drawbacks involve frequent cleaning requirement, membrane fouling, and a requirement of a larger dialysis unit as compared to a fermenter. Higher power consumption is the main problem with electrodialysis, although it allows simultaneous separation and concentration of the acid. Ion-exchange requires a large amount of chemicals, and generates a large amount of waste. The distillation method is a well-established technology, but its drawbacks involve formation of high-boiling internal esters, dimers, and greater power consumption.[20–25] Reactive extraction with the proper selection of diluents and extractants can provide high selectivity and extraction but suffers from toxicity problems of solvents toward microbial strains. Selection of an extractant and diluent for reactive extraction should be on the basis of minimal toxicity and maximum capacity.

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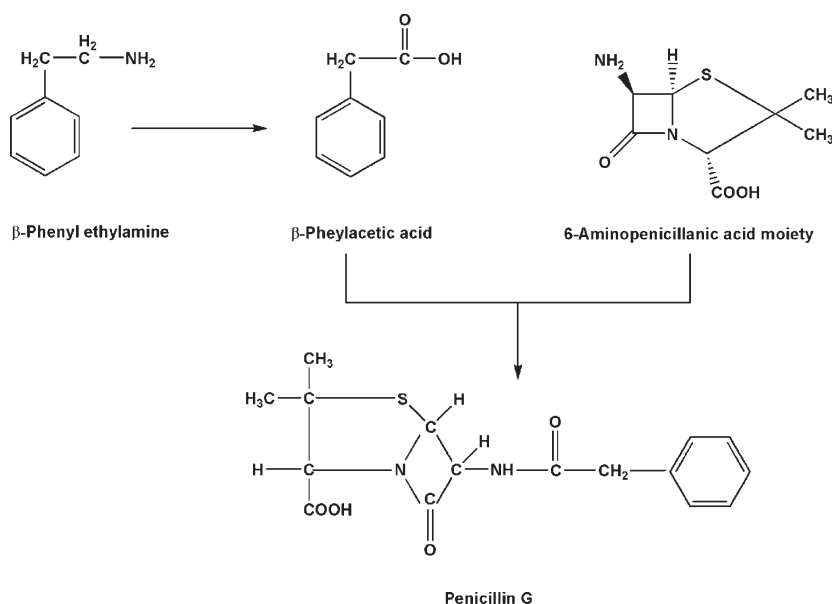klwasewar@che.vnit.ac.in; Tel.: +91-712-2801561,
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F i g . 1 – *β-Phenyl ethylamine, β-phenylacetic acid, which is subsequently attached to the 6-amino group of penicillanic acid to give benzyl penicillin (penicillin G)[1]*

Among the various available alternative processes for simultaneous removal of the product, liquid-liquid extraction is often the most suitable. Consequently, reactive extraction method has been proposed to be an effective primary separation step for the recovery of carboxylic acids from dilute fermentation broths and aqueous streams.[26–28]

Extraction of carboxylic acid from dilute aqueous solution by solvent extraction has in the last few decades been drawing much attention in the scientific community. Organic solvents used for extraction can be classified into three major categories: (a) Conventional oxygen-containing and organic solvents such as alcohols, glycol, ethers, esters, ethyl acetate, ketones etc.[29] (b) Phosphorous-bonded oxygen containing extractants like tri-*n*-butyl phosphate (TBP)[30], trialkylphosphine oxide (TOPO) etc.[31]; (c) Higher molecular weight aliphatic amines such as tri-*n*-octyl amine, alamine 336, aliquat 336 etc.[29,30,32]. For extraction of carboxylic acids, the first types of solvents provide low distribution coefficient because of high affinity of acid molecule towards water molecules, whereas the second and the third types of solvents give higher distribution coefficients in organic phase.

Scare literature is available on spectroscopic studies between acid-extractant complex[20,33–35] and reactive extraction of phenylacetic acid.[36–38]

In the present work, the data on stoichiometric and spectroscopic analysis of reactive extraction of phenylacetic acid with tri-*n*-butyl phosphate at interface of aqueous and organic phase the data are presented in terms of extraction efficiency, distribution coefficient, loading factor, and overall equilibrium constant. Tri-*n*-butyl phosphate was used as extractant while methyl isobutyl ketone and petroleum ether as diluents.

Materials and method

Materials

Tri-*n*-butyl phosphate, methyl isobutyl ketone, petroleum ether (mixture of volatile aliphatic hydrocarbon and primarily pentane and isohexane), phosphoric acid, and acetonitrile were procured from Merck, Germany, whereas phenylacetic acid with 98.5 % purity was supplied by Acros Organics, Belgium. All the chemicals were used as supplied. Physicochemical properties of the extractant and diluents are listed in Table 1.

Method

Extraction experiments were conducted in 100 mL Erlenmeyer flasks at room temperature 298 ± 0.5 K. The initial concentration of phenylacetic acid was 0.099 mol L^{-1}. The reactive extraction was carried out with tri-*n*-butyl phosphate in methyl isobutyl ketone, and petroleum ether. Tri-*n*-butyl phosphate concentration in organic solution was varied in the range of 10–60 v/v % (0.366–2.199 mol L^{-1}). The volumetric ratio of the aqueous and organic phase was kept as 1:1 (15 mL of each phase). Initial pH of aqueous phenylacetic acid was measured using pH meter (Lab India, Mumbai) and observed as 2.767. The equilibrium pH was found to be different from the initial pH because of the removal of acid from aqueous phase to organic phase.

Table 1 – *Physical properties of the diluents and extractant*

Diluent & extractant	IUPAC name	Assay (%)	Chemical formula	Molecular weight (g mol⁻¹)	Viscosity (Pa s)	Density (g mL⁻¹)	Dipole moment (Debye)
Methyl isobutyl ketone	4-Methyl-2-pentanone	98	$(CH_3)_2CHCH_2COCH_3$	100.16	0.000585 at 293 K	0.779	4.2
Petroleum ether	–	90	Mixture of hydrocarbons (C_5 to C_{13})	80–100	–	0.645–0.670	–
Tri-*n*-butyl phosphate	–	97	$CH_3(CH_2)_3O)_3PO$	266.31	0.0038 at 298 K	0.975	–

The flasks containing the mixture of aqueous and organic solution was shaken for 12 hours in a temperature-controlled water bath shaker RSB-12 (REMI Laboratory Instruments, Mumbai, India) and the solution was allowed to settle for 2–3 hours at room temperature (298 ± 0.5 K) and atmospheric pressure (101324.99 Pa). The upper layer (organic phase) was used for FTIR study, and the bottom layer (aqueous phase) was taken for pH measurement and acid concentration analysis. The organic phase volume increased by approximately 5 %, with a corresponding decrease in the aqueous-phase volume, which could be due to the water transfer (water co-extraction) into the organic phase to solvate the complex[39] and the results are presented in Table 5.

Liquid chromatographic analysis

Phenylacetic acid concentrations were determined using High Performance Liquid Chromatography technique (Agilent 1200, California USA). Analysis was performed with Eclipse XDB-C18 (4.6 mm ID × 250 mm, 5 μm) column. Acetonitrile (25 %) and 20 mmol L⁻¹ of aqueous solution of phosphoric acid (75 %) was used as a mobile phase and the flow rate was set at 1 mL min⁻¹. The detector (DAD) wavelength was set at λ = 215 nm. The column was operated at 308 K with the injection volume of 5 μL. Before injecting, the samples were filtered through a syringe filter with pore size 0.2 μm PVD filter media supplied by WHATMAN, U.S.A. Retention time of pure phenylacetic acid and extracted samples was found to be about 6.3 minutes (see Fig. 2). Each analysis was done in triplicate under identical conditions, and the concentration was reported as the average value. The maximum experimental error was observed as below ± 5 %.

Results and discussion

Stoichiometry of complex formation of phenylacetic acid and tri-*n*-butyl phosphate

Using mass action law[40], the extraction equilibrium for phenylacetic acid can be written as a reaction of one molecule of phenylacetic acid and γ
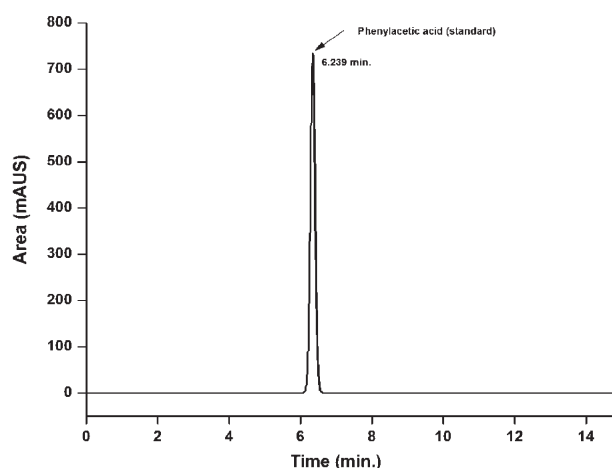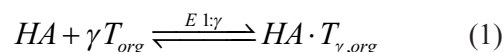

F i g . 2 – *HPLC chromatogram of phenylacetic acid standard*

molecule of tri-*n*-butyl phosphate participating in the formation of the complex. The mechanism of reactive extraction of phenylacetic acid in terms of apparent equilibrium constant, E can be written as:

$$HA + \gamma T_{org} \xrightleftharpoons[]{E \; 1:\gamma} HA \cdot T_{\gamma,org} \tag{1}$$

where, HA and T is denoted by phenylacetic acid and tri-*n*-butyl phosphate molecules respectively and '*org*' is represented as a species in organic phase.

$$E = \frac{\left[HA \cdot T_\gamma \right]_{org}}{\left[HA \right]_{aq} \left[T \right]_{org}^{\gamma}} \tag{2}$$

The distribution coefficient, D of phenylacetic acid with solvents (tri-*n*-butyl phosphate + diluents) can be expressed as:

$$D = \frac{\left[HA \cdot T_\gamma \right]_{org}}{\sum \left[HA \right]_{aq}} \tag{3}$$

where, $\left[HA \cdot T \right]_{org}$ is the complex (phenylacetic acid-tri-*n*-butyl phosphate) concentration in the organic phase and $\sum \left[HA \right]_{aq}$ is the total phenylacetic acid concentration in the aqueous phase, i.e. the summation of associated and dissociated form of phenylacetic acid in the aqueous phase.

$$\sum [HA]_{aq} = [HA]_{aq} + [A^-] \qquad (4)$$

Dissociation of carboxylic acid in aqueous phase at equilibrium is expressed as:

$$HA_{aq} \xrightleftharpoons[]{K_a} H^+ + A^- \qquad (5)$$
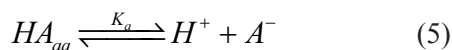
The dissociation constant, K_a can be given by (Dippy et al., 1959)

$$K_a = \frac{[H^+][A^-]}{[HA]_{aq}}, \qquad pKa = 4.31^{41} \qquad (6)$$

By simplifying Eqs. (4) and (6), the concentration of undissociated and unextracted phenylacetic acid molecules in aqueous phase can be written as:

$$[HA]_{aq} = \frac{\sum [HA]_{aq}}{\left(1 + \dfrac{K_a}{[H^+]}\right)} \qquad (7)$$

By rearranging the Eqs. (3), (5) and (7), the following expression for the overall distribution coefficient is obtained as:

$$D = \frac{E[T]^{\gamma}_{org}}{\left(1 + \dfrac{K_a}{[H^+]}\right)} \qquad (8)$$

Eq. (8) can be expressed in the Logarithmic form which represents a straight line

$$\ln D + \ln \left(1 + \frac{K_a}{[H^+]}\right) = \ln E + \gamma \ln [T]_{org} \qquad (9)$$

The initial concentration of tri-n-butyl phosphate, 0.366 mol L^{-1} was higher than initial concentration of phenylacetic acid; therefore $[T]_{org}$ was assumed to be sufficient concentration of tri-n-butyl phosphate in the solvent phase.[42] The slope of the
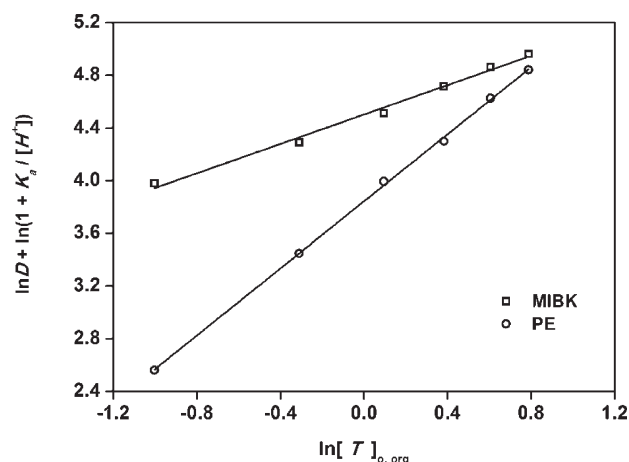

F i g . 3 – Determination of the number of moles of TBP per moles of phenylacetic acid in phenylacetic acid-tri-n-butyl phosphate complex as per equation (9)

straight line of Eq. (9) was used to determine the numbers of tri-n-butyl phosphate molecule participating in the interfacial reaction with the acid molecule and the extraction equilibrium constant, E is evaluated by intercept of the line.

Influence of the various concentrations of tri-n-butyl phosphate on the extraction efficiency in methyl isobutyl ketone and petroleum ether was studied to investigate the stoichiometric coefficient of tri-n-butyl phosphate molecule reacted with phenylacetic acid, and also the influence of diluent polarity on the structure of the complex at interface. The slopes of the straight lines with coefficient of determination, $R^2 > 0.99$ (Fig. 3) and other calculated parameters are mentioned in Tables 2–3. The results indicate the modification of the complex between extractant and acid at interface as a function of the polarity of the organic phase. In less polar solvents (petroleum ether) tri-n-butyl phosphate has low solubility, dispersibility, and low interaction with phenylacetic acid, hence only 1:1 acid-extractant complex can be formed. In polar solvent, (MIBK) tri-n-butyl phosphate has high solubility, dispersibility and interactions with phenylacetic acid, so, 2:1 complex between phenylacetic acid – tri-n-butyl phosphate can be formed.

T a b l e 2 – Number of extractant molecules and overall equilibrium constant

Diluent	No. of extractant molecules[a]	Expression for apparent equilibrium constant	Apparent equilibrium constant value	Coefficient of determination	Standard deviation
	γ		E	R^2	RMSE
Methyl isobutyl ketone	0.5	$E = \dfrac{[HA \cdot T_{0.5}]_{org}}{[HA]_{aq}[T]^{0.5}_{org}}$	90.197 L mol^{-1}	0.991	0.03741
Petroleum ether	1.2	$E = \dfrac{[HA \cdot T_{1.2}]_{org}}{[HA]_{aq}[T]^{1.2}_{org}}$	46.665 L^2 mol^{-2}	0.999	0.0225

[a]Tri-n-butyl phosphate molecules participating in the complex with phenylacetic acid molecule

Table 3 – *Equilibrium data of reactive extraction of phenylacetic acid (0.099) mol L⁻¹*

Diluents	$[HA]_o$	$[T]_{o, org}$	Area under the curve	$[HA]_{aq}$	$[HA]_{aq}$	$[HA]_{org}$	pH*	D	φ	η
	ppm	mol L⁻¹	mAU S	ppm	mol L⁻¹	mol L⁻¹				%
Methyl isobutyl ketone	13480	0.366	1793.17	262.31	0.001927	0.097082	3.10	50.39	0.265	98.05
	13480	0.733	1369.41	200.32	0.001471	0.097537	3.32	66.29	0.133	98.51
	13480	1.099	1108.17	162.11	0.001191	0.097818	3.35	82.15	0.089	98.80
	13480	1.466	906.96	132.67	0.000974	0.098034	3.36	100.60	0.067	99.02
	13480	1.832	794.31	116.20	0.000853	0.098155	3.41	115.01	0.054	99.14
	13480	2.199	726.32	106.25	0.000780	0.098228	3.44	125.87	0.045	99.21
Petroleum ether	13480	0.366	6941.86	1015.49	0.007459	0.091550	3.06	12.27	0.250	92.47
	13480	0.733	3035.46	444.04	0.003261	0.095747	3.16	29.36	0.131	96.71
	13480	1.099	1821.89	266.51	0.001958	0.097051	3.28	49.58	0.088	98.02
	13480	1.466	1354.18	198.10	0.001455	0.097553	3.30	67.05	0.067	98.53
	13480	1.832	1000.03	146.29	0.001074	0.097934	3.39	91.15	0.053	98.91
	13480	2.199	808.56	118.28	0.000869	0.098140	3.40	112.97	0.045	99.12

Thus, it can be observed that, the extraction efficiency in methyl isobutyl ketone is increased significantly with increasing tri-*n*-butyl phosphate concentration up to 2.199 mol L⁻¹ which corresponds to 1:0.5 molar ratio of phenylacetic acid and tri-*n*-butyl phosphate while, in petroleum ether it increased considerably with molar ratio of 1:1.2 of phenylacetic acid and tri-*n*-butyl phosphate. Using the mass action law, the value of γ can be explained by stoichiometric analysis of complex formation of phenylacetic acid and tri-*n*-butyl phosphate was 1:1 and 2:1. The first acid molecule interacts directly with the phosphate molecule to form an ion pair, and the OH of the carboxyl group of the second acid molecule forms a hydrogen bond with the conjugate CO of the carboxylate of the first acid molecule to form 2:1 complex, and it is not dependent on the ionisation strength of acid (pK_a).[43]

Influence of extractant concentration on equilibrium pH and extraction efficiency

Equilibrium pH in the reactive extraction of phenylacetic acid depends on concentration of tri-*n*-butyl phosphate, and was found to increase up to 3.40–3.44 due to transfer of acid molecule into organic phase. From Figs. 4(a)-(b), it was observed that the increase of tri-*n*-butyl phosphate concentration favours extraction efficiency, which subsequently leads to increase in equilibrium pH. At higher concentration of tri-*n*-butyl phosphate 2.199 mol L⁻¹, equilibrium pH was found as 3.44 and 3.40 in methyl isobutyl ketone and petroleum ether, respectively. In strong acidic domain (pH < 4), con-
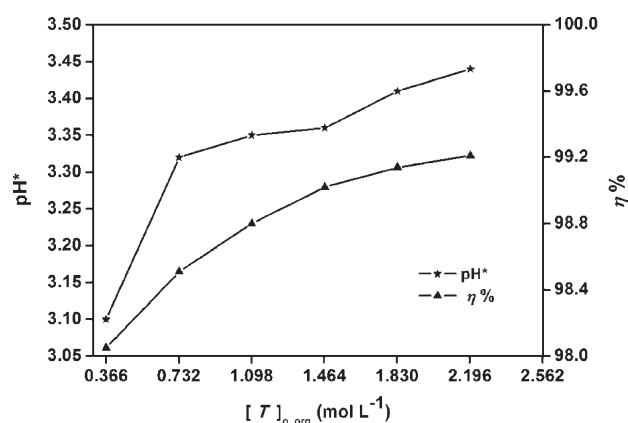

Fig. 4(a) – *Influence of tri-n-butyl concentration on equilibrium pH* and extraction efficiency for methyl isobutyl ketone*
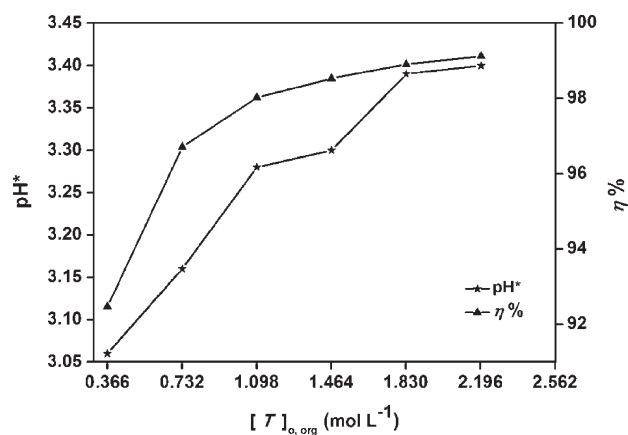

Fig. 4(b) – *Influence of tri-n-butyl concentration on equilibrium pH* and extraction efficiency for petroleum ether*

centration of H$^+$ ions is very low because the carboxyl group is not dissociated, which allows transfer of undissociated acid molecules into the organic phase.

The above results, as shown in Table 3, confirm that, at variable concentration of tri-*n*-butyl phosphate, methyl isobutyl ketone gives higher extraction efficiency to the extent of 98.79 % (average), whereas petroleum ether provides 97.29 % (average). This can be attributed to the strong hydrogen bonding between acid molecules and methyl isobutyl ketone, whereas, petroleum ether, being a mixture of long chain aliphatic hydrocarbons (non-polar diluent) and less interaction in water, gives lower extraction efficiency.

Effect of extractant concentration on distribution coefficient and loading ratio

Fig. 5(a)-(b) reveals that the average distribution coefficients for phenylacetic acid with tri-*n*-butyl phosphate in methyl isobutyl ketone was (D_{avg} = 90.5) higher than in petroleum ether (D_{avg} = 60.40).

The loading ratio, i.e. total phenylacetic acid molecules loaded on the extractant molecules can be expressed as:

$$\varphi = \frac{[HA]_{org}^{Total}}{[T]_{o,\,org}} \qquad (10)$$

where $[HA]_{org}^{Total}$ and $[T]_{o,org}$ are the concentration of phenylacetic acid in all the forms (free acid molecule, dimer or complex) extracted in organic phase and initial concentration of tri-*n*-butyl phosphate in organic phase, respectively.

Carboxylic acids are dissociated in water and extracted into extracted phase through their physical solubility and reactivity with extractant molecule and form 1:1, 2:1, 3:1 and 1:2 acid-extractant complexes, where 2:1 and 3:1 complexes result from the formation of dimer and trimer respectively.[44] Formation of hydrogen bond between acid and extractant molecule and the hydroxyl and aldehyde group of carboxylic acid favours 1:2 complexes. Most of the complexes exist in 1:1 form when the carboxylic acid concentration is low ($\varphi < 1$).[45]

Overloading ($\varphi > 1$) occurs at relatively high equilibrium aqueous solute concentration. This phenomenon may be attributed to three reasons: co-extraction of water into the organic phase, acid dimerization in the organic phase, and the physical extraction of acid by the complex in organic phase. All three reasons are hydrogen bonding mechanism that depends only on the hydrophobicity of solute and not the extractant. The loading factor gradually decreases with increasing in tri-*n*-butyl phosphate
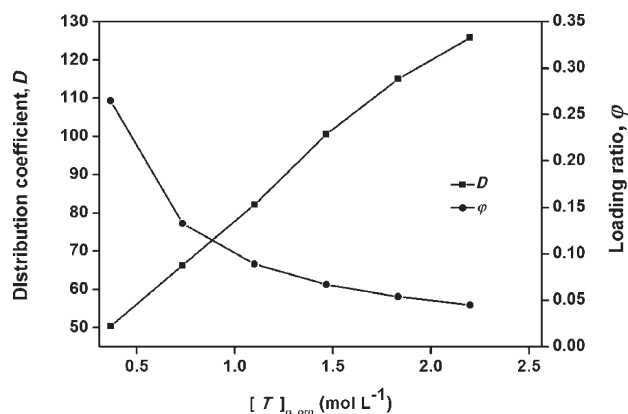

F i g . 5 (a) – *Effect of tri-n-butyl concentration on distribution coefficient and loading ratio for methyl isobutyl ketone*
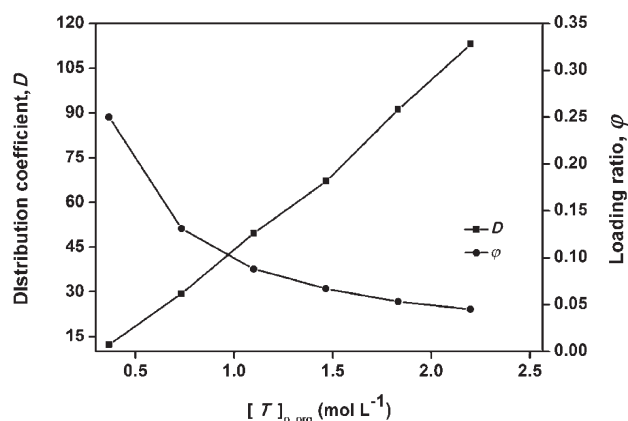

F i g . 5 (b) – *Effect of tri-n-butyl concentration on distribution coefficient and loading ratio for petroleum ether*

concentration in both diluents, as shown in Figs. 5(a)-(b). In the active diluents (e.g. 1-octanol, methyl isobutyl ketone, petroleum ether, and chloroform) with high extractant concentration, the loading ratio decreases with increase in extractant concentrations at $\varphi < 1$ as the solvation occurs in the less favourable solvating medium.

Relative basicity model

Relative basicity model in terms of apparent equilibrium constant and relative basicity of extractant has been reported.[46] The three major factors have been reported which interrupt the extraction equilibrium behaviour of carboxylic acids such as: acid hydrophobicity (log$P$), the dissociation equilibrium constant of the acid (pK_a), and the relative basicity of the extractant mixture to HCL (pK_b) except the nature of the solute. If the basicity of the extractant mixture is relative to the solute, this relative basicity of the extractant can represent the nature of the solute, diluent, and extractant, as well as special association like solvating power. A model equation is expressed as:[47]

$$\log E_{1:\gamma} = \left[\delta_1 \left(pK_b - pK_a\right) + \log\left(\delta_2 P\right)\right] \quad (11)$$

were, δ_1 and δ_2 are the constants.

Extraction equilibrium behaviour of carboxylic acids with the extractant-diluent system was predicted by model Eq. (11) and the constant values are shown in Table 4. Parity plot (see Fig. 7) represents the conformity of model results with the experimental results. The average values of $E_{1:\gamma}$ obtained for 10 – 60 % by volume of tri-*n*-butyl phosphate are shown in Table 4. To maintain the suitability of fit, the root mean square error deviation (RMSD) value was calculated using the difference between experimental ($E_{1:\gamma, Exp.}$) and the predication of the relative basicity model ($E_{1:\gamma, RBM}$) by using the following equation:

$$RMSD = \sqrt{\frac{1}{N} \sum_{i=1}^{n} \left(E_{1:\gamma, Exp} - E_{1:\gamma, RBM}\right)^2} \quad (12)$$

where N is the number of experimental data value. The Root mean square error deviation of the relative basicity model was determined to be ±4.4 %, which shows that all the predicated apparent equilibrium constants agree well with the experimental values, which is acceptable, considering the experimental uncertainty.

Spectroscopy analysis

The qualitative infrared spectra of organic phases (methyl isobutyl ketone, petroleum ether, and tri-*n*-butyl phosphate) were recorded on FTIR (Shimadzu – IR Affinity model Japan), in the range of $4000 - 400$ cm^{-1} with 4 cm^{-1} resolution using 0.02 cm NaCl window. The spectra of pure phenylacetic acid were also taken with diffusive reflective spectrum (DRS) accessory.

Description of pure phenylacetic acid spectrum

The band $3500 - 2500$ cm^{-1} represents the hydrogen bonding of carboxylic group (–COOH), 1699 cm^{-1} assigned to the characteristic stretching vibration of ketone group (C=O), presence of aromatic ring due to stretching vibration of C=C in $1600 - 1498$ cm^{-1} region and about 1240 cm^{-1} represents the stretching vibration of C–O.

Description of presence of phenylacetic acid in solvents

Figs. 6(a-b) confirm that stretching vibration of ketone group (C=O) in phenylacetic acid at 1699 cm^{-1} was overlapping with methyl isobutyl ketone peaks in $1714 - 1680$ cm^{-1} region and the aromatic

Table 4 – *Comparison of experimental and model results*

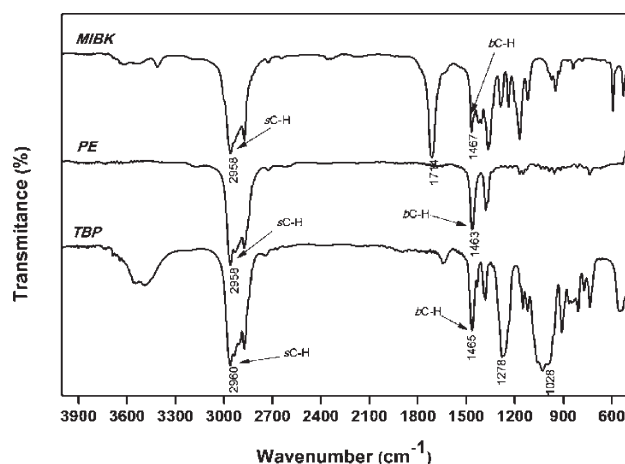| Diluents	pK_b	δ_1	Log($\delta_2 P$)	$E_{1:\gamma \, (Exp.)}$	$E_{1:\gamma \, (RBM)}$
Methyl isobutyl ketone	6.20	−0.733	3.668	187.04	191.70
	6.64	−0.733	3.668	104.32	91.84
	6.70	−0.733	3.668	82.02	81.88
	6.71	−0.733	3.668	73.54	80.79
	6.83	−0.733	3.668	66.32	66.42
	6.88	−0.733	3.668	59.92	60.84
Petroleum ether	6.11	0.114	1.437	44.64	43.92
	6.32	0.114	1.437	46.07	46.31
	6.57	0.114	1.437	49.46	49.45
	6.60	0.114	1.437	49.00	49.90
	6.78	0.114	1.437	52.55	52.31
	6.79	0.114	1.437	53.77	52.50

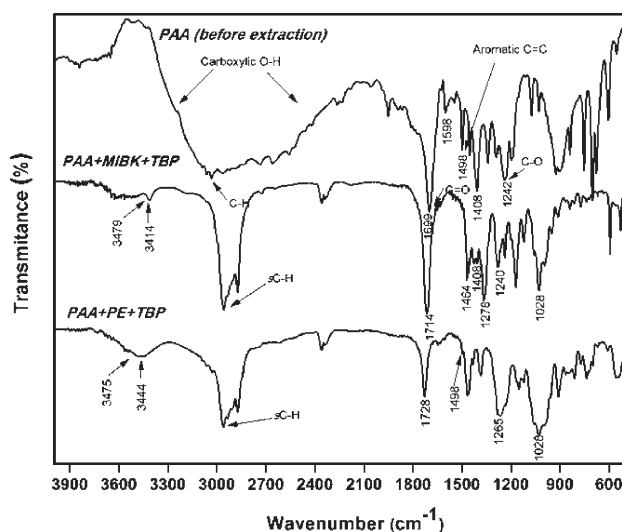Fig. 6(a) – *FTIR spectra of methyl isobutyl ketone, petroleum ether, and extractant*

Fig. 6(b) – *FTIR spectra of pure phenylacetic acid and extracted organic phases (methyl isobutyl ketone and petroleum ether with tri-n-butyl phosphate)*

T a b l e 5 – *Water co-extraction results for phenylacetic acid without TBP (physical extraction) system at 298 K for various concentrations of TBP at fixed concentration of phenylacetic acid*

Diluent	$[HA]_o$	Post extraction			
		Methyl isobutyl ketone		Petroleum ether	
		HA_{aq}	HA_{org}	HA_{aq}	HA_{org}
(mol L^{-1})	(mol L^{-1})	(mL)	(mL)	(mL)	(mL)
0.366	0.099	14.85	15.15	14.78	15.22
0.733	0.099	14.82	15.18	14.77	15.23
1.099	0.099	14.80	15.2	14.75	15.25
1.466	0.099	14.79	15.21	14.75	15.25
1.832	0.099	14.79	15.21	14.74	15.26
2.199	0.099	14.76	15.24	14.73	15.27
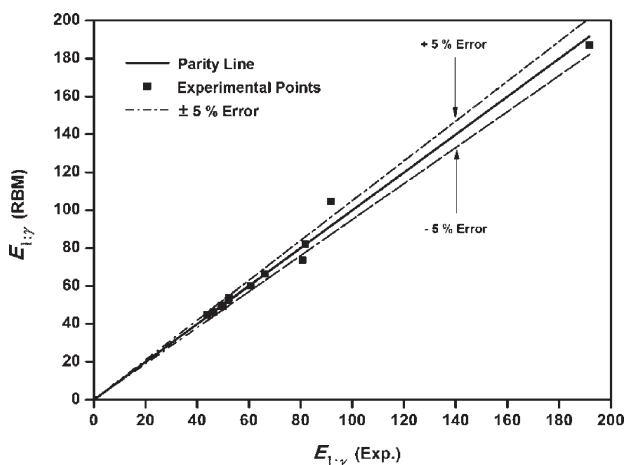
F i g . 7 – *Parity plot for relative basicity model predicted $E_{1:\gamma}$ for reactive extraction of phenylacetic acid with tri-n-butyl phosphate in methyl isobutyl ketone and petroleum ether*

ring peak of phenylacetic acid at 1498 cm^{-1} merged with the band of bending vibration of C–H at 1467 cm^{-1}. Thus, parent peaks of phenylacetic acid are not clearly visible in methyl isobutyl ketone, whereas distinct peaks about 1240 cm^{-1} are evidence of the existence of phenylacetic acid with tri-*n*-butyl phosphate in methyl isobutyl ketone. On the other hand, strong peaks of 1728 cm^{-1} and 1256 cm^{-1} assigned to the stretching vibrations of C=O and C–O, respectively, indicate clearly the presence of phenylacetic acid with tri-*n*-butyl phosphate in petroleum ether.

Evidence of the presence of tri-*n*-butyl phosphate in diluents

Characteristic parent peak of tri-*n*-butyl phosphate i.e. 3545 and 3491 cm^{-1} appears in the spectra with partial shift as 3479, 3414 cm^{-1} and 3475, 3444 cm^{-1} in methyl isobutyl ketone and petroleum ether, respectively. 1028 cm^{-1} appeared, which may be attributed to symmetric stretching vibrations of phosphate (P–O) with both diluents in finger print region.

Ion-pair complexation of phenylacetic acid and tri-*n*-butyl phosphate (1:1)

The 3500 – 2500 cm^{-1} band represents the hydrogen bonding of carboxylic group (COOH) and its disappearance after extraction into the organic phase (TBP+MIBK and TBP+PE), indicates that phenylacetic acid and tri-*n*-butyl phosphate form the ion-pair complex. In other words, the reactive extraction reaction is a proton transfer from acid to extractant.

Conclusion

The reactive extraction of phenylacetic acid with tri-*n*-butyl phosphate in methyl isobutyl ketone and petroleum ether was investigated. The distribution coefficient, loading ratio, and extraction efficiency were obtained for the existing system. Average extraction efficiency, η_{avg} = 98.79 % and 97.29 % were found for TBP+MIBK and TBP+PE with average distribution coefficient, D_{avg} = 90.05 and 60.40, respectively. The higher values of distribution coefficient are attributed to ion pair formation between phenylacetic acid and tri-*n*-butyl phosphate. Stoichiometric analysis of reactive extraction mechanism confirms 1:1 and 2:1 complex formation between phenylacetic acid and tri-*n*-butyl phosphate molecule. Ion pair complex was confirmed by IR spectroscopy. To represent the experimental data, relative basicity model was used and found within ± 5 %.

N o m e n c l a t u r e

D – Distribution coefficient
E – Overall equilibrium complexation constant, L mol^{-1}
HA – Undissociated acid in aqueous phase
$[HA]$ – Concentration of phenylacetic acid, mol L^{-1}
pK_a – Dissociation constant
pK_b – Relative basicity of tri-*n*-butyl phosphate

N – Total number of experimental data

T – Free tri-*n*-butyl phosphate molecules in organic phase

$[T]_{org}$ – Tri-*n*-butyl phosphate concentration in organic phase, mol L^{-1}

Abbreviations

DRS   – Diffusive reflectance spectrum

MIBK   – Methyl isobutyl ketone

PE   – Petroleum ether

RBM   – Relative basicity model

RMSD   – Root mean square error deviation

RSME   – Root square mean error

TBP   – Tri-*n*-butyl phosphate

Greek words

γ – Stoichiometric coefficient of extractant

η – Extraction efficiency

φ – Loading ratio

δ_1 and δ_2 – Constants for relative basicity model

Superscripts and Subscripts

aq   – Aqueous solution

org   – Organic solution

o   – Initial concentration

avg   – Average

*   – Equilibrium state

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