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Reactive Extraction of Levulinic Acid Using TPA in Toluene Solution: LSER Modeling, Kinetic and Equilibrium Studies

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Abstract: Levulinic acid, a carboxylic acid containing ketone structure, is a clear to brownish semi-solid melting at 37°C; soluble in alcohol, ether, and chloroform, levulinic acid can be used as an acidulant in foods and beverages. Organic solutions of amines are being used increasingly to separate organic acids from aqueous mixture solutions by reactive extraction. The design of an amine extraction process requires kinetic data for the acid–amine + solvent system used. Kinetic studies for the extraction of levulinic acid from aqueous solution with tripropylamine (TPA) diluted in toluene were carried out using a stirred cell for kinetic studies. Equilibria for levulinic acid extraction by TPA in toluene as a diluent have been determined. All measurements were carried out at 298.15 K. The equilibrium data were also interpreted by a proposed mechanism of complexation by which (1:1) and (2:1) acid-amine complexes are formed. Kinetics of extraction of levulinic acid by TPA in toluene has also been determined. The results of the liquid-liquid equilibrium measurements were correlated by a linear solvation energy relationship (LSER).

Keywords: Levulinic acid, LSER, reactive extraction, TPA, toluene, kinetics

INTRODUCTION

Levulinic acid, or 4-oxopentanoic acid, is a white crystalline keto acid prepared from levulose, inulin, starch, etc., by boiling them with dilute

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hydrochloric or sulfuric acids. It is soluble in water, ethanol, and diethyl ether, but essentially insoluble in aliphatic hydrocarbons. Levulinic acid is used in the manufacture of nylons, synthetic rubbers, plastics, and pharmaceuticals. It is a precursor in the industrial production of other chemical commodities such as methyltetrahydrofuran, valerolactone, and ethyl levulinate. As well, levulinic acid is used in cigarettes to increase nicotine delivery in smoke and binding of nicotine to neural receptors (1).

The recovery of carboxylic acids from diluent aqueous solutions, such as a fermentation broth or a wastewater stream that has acid concentrations lower than 10% (w/w), has recently received increasing attention. The fermentation process, due to various impurities of fermentation broth, needs an economic separation method to compete with the synthetic process. Reactive extraction is particularly attractive due to the possibility of high selectivity for desired compounds (2–4).

Reactive extraction uses reaction between the extractant and the material being extracted. The extractant in the organic phase reacts with a material in aqueous phase and reaction complex is solubilized into the organic phase. It has been reported that long chain tertiary amines are suitable for the recovery of carboxylic acid from aqueous solution. Due to physical properties of aliphatic amines they must always be used in the form of solutions in organic diluents. These organic diluents affect the basicity of amines, thereby the extraction behavior of amine significantly varied. Recently, the influence of the chain length of tertiary amine on extractability has been investigated in polar diluent and nonpolar diluent, respectively. In polar diluent such as 1-butanol, 1-hexanol, and 1-octanol, the extractability of tertiary amines increases with the chain length of the amines. However, the extractability of tertiary amines decreases with the chain length of amines in nonpolar diluent such as *n*-heptane (5, 6).

Organic bases such as amine extractants can provide much higher equilibrium distribution coefficients (K_D) for extraction of carboxylic acids than solvents. Solvent extraction with tertiary amines has been widely used to recover fractionate metals such as uranium, iron, cobalt, etc. from aqueous solutions. Most of these extractions are essentially ion-exchange extractions, because the amine group is protonated in sufficiently acidic solutions and forms an ion pair with a metal that is present in anionic form. Tertiary amine extractants are effective, with K_D strongly dependent upon the nature of the diluent used and the concentration of amine in that diluent. Tertiary amines are found to be effective in extracting levulinic acid and alcohols are among the best diluents, with the additional advantage that a levulinic acid ester can be produced after the extraction process is completed (7–9).

In Uslu's previous studies, Uslu studied the extraction of tartaric acid and propionic acid with tertiary amine (Alamine 336) and quaterniary amine (Aliquat 336), respectively. As a result of these studies, Uslu demonstrated that Alamine 336 give a much higher distribution coefficient then Aliquat 336 (10, 11). The advantage of this higher distribution coefficent is more acid in aqueous solution can extracte with tertiary amine. So less using tertiary amine than quaterniary amine is more usefull.

THEORETICAL

The extraction of levulinic acid (HA) with TPA (NR_3) can be described by the reaction.

$$pHA + qNR_3 \longrightarrow (HA)_p(NR_3)_q \qquad (1)$$

Where, HA is the acid in the aqueous phase. Reaction 1 can be characterized by the overall equilibrium constant, K.

$$K = (a_{HA \cdot NR3})/(a_{HA}) \cdot (a_{NR3}) \qquad (2)$$

In Eq. (2), a_{HA} is the molal activity coefficient of acid, $a_{NR3}$is the molal activity coefficient of amine, $a_{HA.NR3j}$ is the molal activity coefficient of complex.

Replacing the activities by the products of molalities, ($mol \cdot kg^{-1}$) and molal activity coefficients, γ, Eq. (2) takes the Eq. (3).

$$K = (m_{HA.NR3} \cdot \gamma_{HA.NR3})/(m_{HA} \cdot \gamma_{HA}) \cdot (m_{NR3} \cdot \gamma_{NR3}) \qquad (3)$$

In Eq. (3), m_{HA}, is the molality of acid, m_{NR3} is the molality of amine, γ_{HA} is the molal activity coefficient of acid, γ_{NR3} is the molal activity coefficient of amine, $\gamma_{HA\ NR3}$ is the molal activity coefficient of complex.

The loading of the extractant, *Z* is defined as the total concentration of acid in the organic phase, divided by the total concentration of amine in organic phase (7, 8). The expression for the loading, *Z*, can be written in the form (12).

$$Z = C_{a,org}/C_{e,org} \qquad (4)$$

In Eq. (4), $C_{a,org}$, is the total concentration of acid in the organic phase, $mol \cdot L^{-1}$. $C_{e,org}$, is the total concentration of amine in the organic phase, $mol \cdot L^{-1}$. Distribution coefficients, D for levulinic acid extracted from water into the organic phase were determined as,

$$D = C_{a,org}/C_a \qquad (5)$$

where, C_a is the concentration of acid in the aqueous phase after extraction, $mol \cdot L^{-1}$. The efficiency of extraction, E is expressed as

$$E = (1 - (C_a/C_{ao})) \cdot 100 \qquad (6)$$

where, C_{ao} is the initial concentration of acid in the aqueous phase, $mol \cdot L^{-1}$. An E value of 100% means that all of the acid in the aqueous phase has been removed and is present in the organic phase (13–15).

Though the exact nature of the chemistry involved in the uptake of extra acid is known, and, in spite of the obvious non-ideality of the organic phase, the distribution data can be interpreted by a set of equilibria involving the formation of complexes with *n* acid molecules and one amine molecule (16).

$$\mathrm{HL_w} + \mathrm{B_o} \overset{K_{11}}{\longleftrightarrow} \mathrm{BHL_o} \tag{7}$$

$$\mathrm{HL_w} + \mathrm{BHL_o} \overset{K_{21}}{\longleftrightarrow} \mathrm{B(HL)_{2,o}} \tag{8}$$

$$\mathrm{HL_w} + \mathrm{B(HL)}_{n-1,\mathrm{o}} \overset{K_{n1}}{\longleftrightarrow} \mathrm{B(HL)}_{n,\mathrm{o}} \tag{9}$$

The equilibrium complexation constant for the reaction represented by above equations is:

$$\mathrm{K_{En}} = \frac{[\mathrm{B(HL)}_n]_\mathrm{o}}{[\mathrm{B}]_\mathrm{o}[\mathrm{HL}]_\mathrm{w}^n} \tag{10}$$

In Eq. (7), (8), (9), (10), HL_w, levulinic acid concentration in aqueous phase, B_o, alamine concantration after exraction in the organic phase, BHL_o, (1:1) levulinic acid complex concentration in organic phase, K_{En}, (n:1) levulinic acid alamine equilibrium complexation constant.

LSER Model Theory

According to Kamlet (22) the Linear Solvation Energy Relationship (LSER) that measures the property, XYZ, in terms of solvent properties is

$$\mathrm{XYZ} = \mathrm{XYZ}^0 + \mathrm{P}(\delta_\mathrm{h})^2/100 + \mathrm{s}(\pi{*} + \mathrm{d}\delta) + \mathrm{b}\beta + \mathrm{a}\alpha \tag{11}$$

In Eq. (11), Where δ_h is the Hildebrand's solubility parameter, π^* and δ are the solvatochromic parameters that measure solute + solvent, dipole + dipole and dipole + induced dipole interactions, respectively. The solvatochromic parameter α scale of solvent HBA (hydrogen-bond donor) acidities describes the ability of the solvent to donate a proton in a solvent to solute hdyrogen bond. The β 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 include the properties of solute. Rather than p, s, d, a are regression coefficients. The values of solvatochromic parameters π^*, δ, α, β have been found several hundreds of compounds. Equation 11, can be adopted to describe the effect of diluents on the values of partitioning coefficients K_D in the form

$$\ln \mathrm{K_D} = \ln \mathrm{K_D^0} + \mathrm{P}^2(\delta_\mathrm{h})^2/100 + \mathrm{s}(\pi^* + \mathrm{d}\delta) + \mathrm{b}\beta + \mathrm{a}\alpha \tag{12}$$

In Eq. (12), where the parameters π^*, δ, α and β refer to the diluent, and K_D represents the partitioning coefficients for an ideal inert diluent. The second term of Eq. (12) which contains the solubility parameter δ_h does not affect the values of the objective function significantly. Thus Eq. (12) reduces to

$$\ln K_D = \ln K_D^0 + s(\pi^* + d\delta) + b\beta + a\alpha \tag{13}$$

MATERIALS AND METHODS

Kinetic Studies

Levulinic acid was dissolved in water to prepare the solutions with initial concentrations of acid 8% (1.17 $mol \cdot L^{-1}$). Comparatively low concentration range was used because in the practical case of acid recovery from fermentation broths, the acid concentrations are not expected to be high equal volumes of an aqueous levulinic acid solution and an organic solution of TPA were stirred for 2 h, which preliminary tests demonstrated to be a sufficient time for equilibration. The stirring has been carried out in glass flasks immersed in a water bath at 298.15°K. A stirred cell of 0.07 m in diameter and 0.1 m in height, with a flat bottom was used for the kinetic studies. Aqueous solution of levulinic acid of known (half of volume of the stirred cell) concentration was first placed in the vessel. The position of the four-blade paddle (0.058 m in diameter and 0.01 mm in width) double stirrer was adjusted to 1 cm below and above the interface. A fixed volume of the organic extractant mixture was then added, and stirred. Using acid–base titration with 0.1 N NaOH (relative uncertainty = 1%) and phenolphthalein as an indicator, and the acid concentration in the aqueous phase was determined periodically. Concentration of levulinic acid in the organic phase was determined by mass balance. Acid analysis was checked against the material balance, and the uncertainty in the results was 2%.

Equilibrium Studies

Initial concentration of levulinic acid (1.17 $mol \cdot L^{-1}$) and different concentration of organic phases (Toluene containing different concentrations of TPA) of known concentrations were equilibrated in a temperature-controlled shaker bath for 3 h. After equilibration, both phases were separated and the aqueous phase was analysed. The reactive component was TPA to determine the concentration of levulinic acid, the aqueous phase was titrated with 0.1 N NaOH and phenolphthalein as an indicator. The acid concentrations in the organic phase were calculated by mass balance (16, 17).

RESULTS AND DISCUSSION

Extraction Equilibria and Kinetics

Experiments were carried out to describe the physical and chemical equilibria for carboxylic acid. There is only a very slight effect, if any, of temperature in the range of 20–90°C on the distribution ratio of carboxylic acid into alcohols, ketones, diethyl carbinol and ethers (18, 19). The physical equilibrium distribution coefficients were measured at 25°C in Toluene. The results are shown in Fig. 1. The distribution coefficients were measured at 25°C for TPA concentrations of 0.244, 0.468, 0.853, 1.271, 1.536, 1.807, and 2.111 $\text{mol} \cdot \text{L}^{-1}$ in toluene diluent. The distribution coefficients are shown in Fig. 1 and Table 1.

The extraction efficiencies are represented in Fig. 2. It was observed that the extraction efficiency increased with an increase in TPA concentration. have reported that the degree of extraction increased up to a concentration of 2.111 $\text{mol} \cdot \text{L}^{-1}$ of the TPA and then remained constant.

In Fig. 3, the plot of log K_D versus log$[B]_o$ should yield a straight line with a slope of unity. So the slope is far less than unity (0.8), which implies that the organic phase extracts more acid than would be expected on the basis of 1:1 complex.

The value of z depends on the extractability of the acid and its aqueous concentration, and is independent of the amine content in an inert diluent.

$$z = \frac{[HL]_0}{[B]_{i,0}} \tag{14}$$

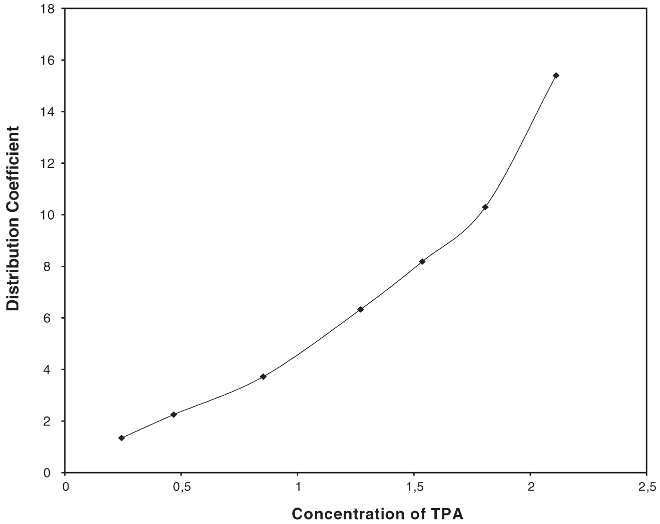

Figure 1. Distribution coefficient of levulinic acid with various ratios of TPA in toluene.

Table 1. The results of extraction of Levulinic acid with TPA in a toluene solution for equilibrium studies

Diluent	C_{eorg}/ (mol · L^{-1})	C_a/ (mol · L^{-1})	C_{aorg}/ (mol · L^{-1})	K_D	Z	E
Toluene	0,244	0,294	0,395	1,343	1,619	57,329
	0,468	0,212	0,477	2,250	1,019	69,231
	0,853	0,146	0,543	3,719	0,636	78,80
	1,271	0,094	0,595	6,329	0,468	86,357
	1,536	0,075	0,614	8,186	0,399	89,114
	1,807	0,061	0,628	10,295	0,347	91,146
	2,111	0,042	0,647	15,404	0,306	93,904

The stoichiometry of the overall extraction reaction depends on the loading ratio in the organic phase, z. If the organic phase is not highly concentrated, i.e. at very low loading ratios ($z < 0.5$), the (1:1) complex is formed and a plot of $z/(1-z)$ versus $[HL]_w$ is a straight line whose slope gives the complexation constant K_{E1}.

$$\frac{z}{1-z} = K_{E1}[HL]_w \tag{15}$$

A straight line of the plot of Eq. (14) is shown in Fig. 4 with a slope of 1.1046. Hence, the equilibrium complexation constant for the (1:1) acide:amine complex at 25°C for the extraction of levulinic acid with TPA

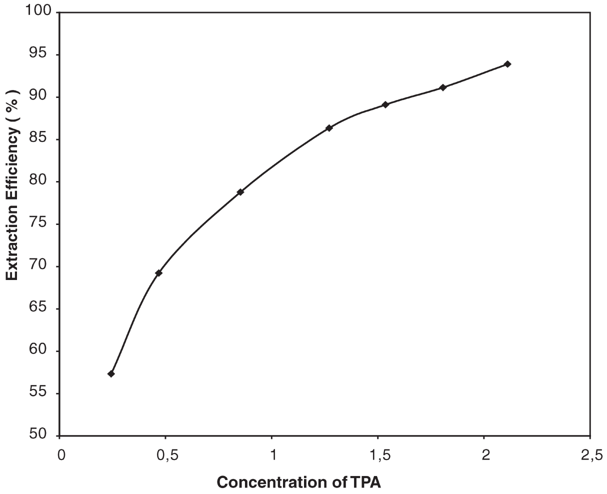

Figure 2. Extraction efficiency of levulinic acid with various ratios of TPA in toluene.

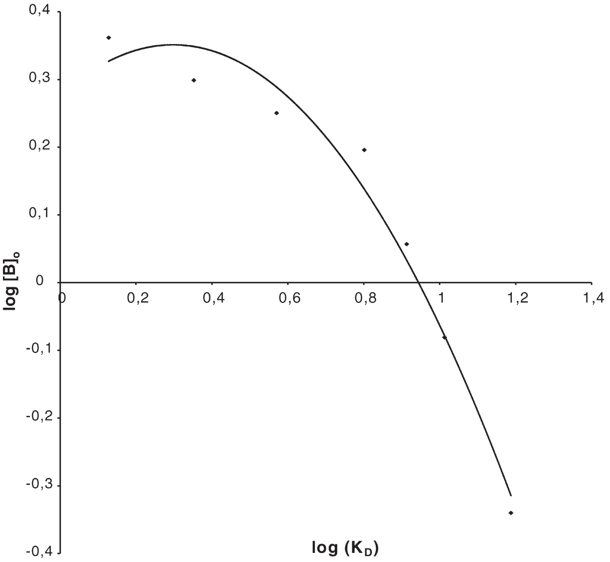

Figure 3. Distribution coefficient of levulinic acid in TPA dissolved in toluene as a function of free amine concentration in organic phase.

dissolved in toluene, for low concentrations of levulinic acid in the organic phase is: $K_{E1} = 1.1046\ \mathrm{m}^3 \cdot \mathrm{kmol}^{-1}$

For higher loading ratios, the (2:1) acide:amine complex is formed, and a plot of $z/(2 - z)$ versus $[\mathrm{HL_W}]^2$ should yield a straight line, whose slope gives the complexation constant for the (2:1) complex. K_{E2} is found from Eq. (16).

$$\frac{z}{2 - z} = K_{E2}[HL]_w^2 \tag{16}$$

A straight line of the plot of Eq. (16) is shown in Fig. 5 with a slope of 13.484. Hence, the equilibrium complexation constant for the (2:1) complex at 25°C for the extraction of levulinic acid with TPA dissolved in toluene is: $K_{E2} = 13.484\ (\mathrm{m}^3 \cdot \mathrm{kmol}^{-1})^2$

The value of physical mass transfer coefficient k_L is required for confirming the regime of extraction. This was obtained by conducting physical extraction (diluent only) of levulinic acid from water. For a batch process a differential mass balance yields the following equation,

$$V_{aq}\frac{dC_{org}}{dt} = k_L A_C (C_{org}^* - C_{org}) \tag{17}$$

Integration of this equation yields,

$$k_L = \frac{V_{aq}}{A_c t}\int_0^{C_{org}} \frac{dC_{org}}{(C_{org}^* - C_{org})} \tag{18}$$

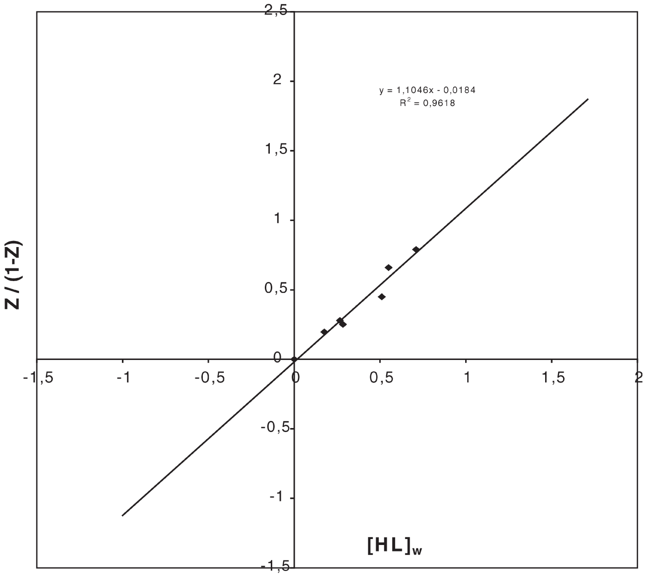

Figure 4. Estimation of equilibrium complexation constant K_{E1} of levulinic acid.

Where, Ac is the cross sectional area of stirred cell (m^2) and V_{aq} is the volume of aqueous phase (m^2). The value of k_L evaluated using Eq. (18) for different speeds of agitation is plotted in Fig. 6. The regression relation between the mass transfer coefficient and the speed of agitation obtained by a statistical analysis data is given below.

$$k_L = 1.312 \times 10^{-3} \cdot N^{3.9} \tag{19}$$

The reaction between levulinic acid and TPA is reversible, particularly under conditions of high loading in the organic phase. To avoid problems due to this reversibility, only initial rates were considered for evaluation of the kinetics.

The effect of agitation in the extraction of levulinic acid by TPA is discerning the mechanism proposed was used (20, 21). The speed of agitation was varied from $0.44\,\text{rev} \cdot s^{-1}$ to $1.8\,\text{rev} \cdot s^{-1}$. In this range the liquid–liquid interface was flat and the interfacial area for extraction was equal to the geometric area.

LSER Model Results

As shown by Kamlet (22), gives the values of solvatochromic parameters for several hundred compounds. Knowing the values of K_D, s, d, b, and a parameters for the given extraction system (TPA + aqueous levulinic acid in

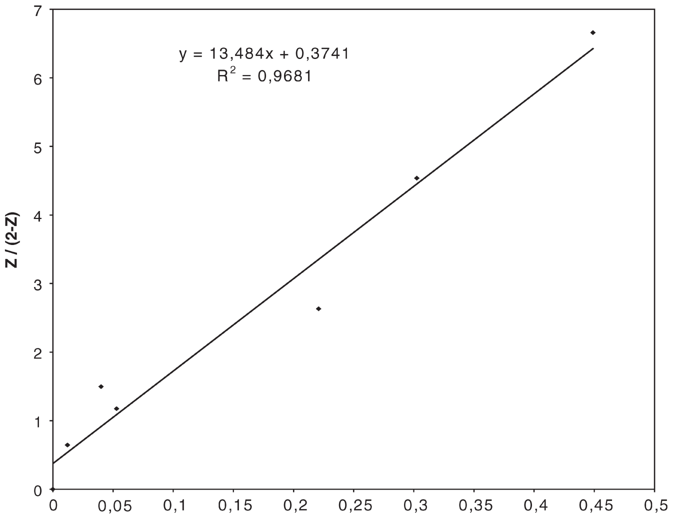

Figure 5. Estimation of equilibrium complexation constant K_{E2} of levulinic acid.

this case) Eq. (13) enables to estimate partitioning coefficients for a wide range of diluents, for which comparatively narrow confidence interval has been found.

The values of solvatochromic parameters of toluene were taken from Table 2 (23). The remaining parameters were fitted to the experimental

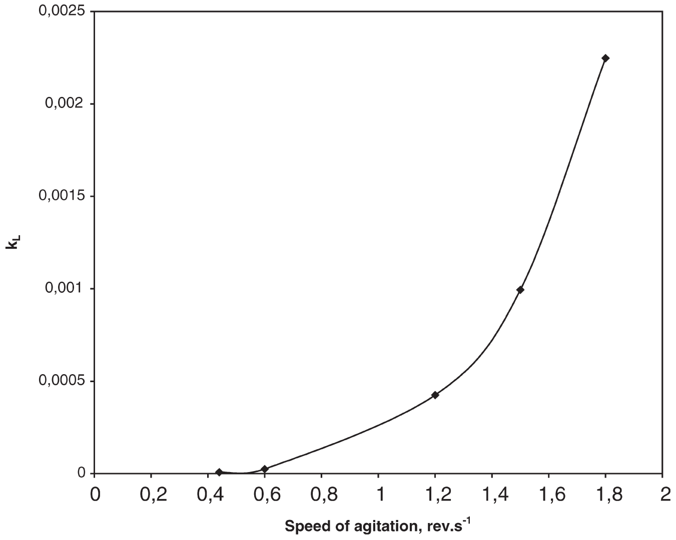

Figure 6. Effect of various of speed agitation on mass transfer coefficient.

Table 2. Solvatohromic parameters, hydrogen-bond donor acidities, π^* and δ, hydrogen-bond acceptor basicities, α, β, for diluents mixtures

	π^*	β	α	δ
Toluene	0.54	0.11	0	1

results. Experimental results compared to model predictions in Table 3 and Fig. 7. It can be seen that the final correlation gives a good description of the distribution of levulinic acid over a wide concentration range.

For the optimal estimation of the model parameters, regression technique assisted computer program (ANALYSE) was used to minimize deviation between the model prediction and experimental data. All predicted partition coefficients agree well with each other, and also the agreements between predcitions and measurements is acceptable considering experimental uncertainty. The estimated values of parameters of the model are presented in Table 4. The experimental data shows a good correlation to the calculated values It is been concluded that by using this model, distribution coefficents of levulinic acid between water and amine + toluene system can be described.

The system constants in Tables 2–4 reveal that the partition coefficients are strongly correlated to a solute's partition coefficient, which means that the organic solute/amin partitioning equilibrium of a solute is strongly affected by the cavity effect and dispersive solute/amine interactions. The solute hydrogen acidity and basicity, a and b, also show a significant correlation with the partition coefficient. This confirms that an organic solvent serves as both a hydrogen donor and an acceptor. The relative size of the standardized system constants (beta), which are the regression coefficients derived from standardized dependent and variables, relays information on the relative importance of different types of solute/solvent interactions. Suggesting that

Table 3. Molar concentration of amine in the organic phase, C_{eorg}, experimental results, K_D, model results, K_D', for comparison of experimental results and model predictions

Diluent	C_{eorg}mol · L^{-1}	K_D	K_D'
Toluene	0,244	1,343	1.474
	0,468	2,250	2.284
	0,853	3,719	3.291
	1,271	6,329	6.647
	1,536	8,186	8.440
	1,807	10,295	11.030
	2,111	15,404	15.674

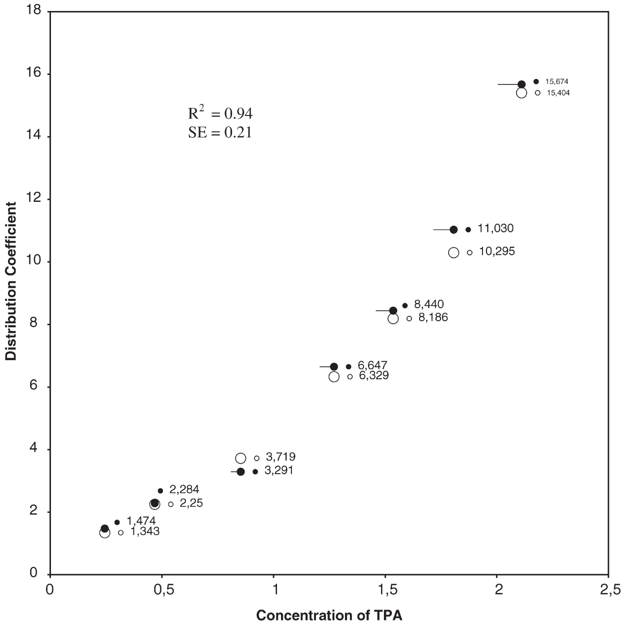

Figure 7. Comparison of variation of partitioning coefficients K_D with concentration of TPA C_{eorg} (B_o) and LSER model predictions K_D' : ○, experimental, ●, model.

the strength of the interaction decreases from dispersive interactions, hydrogen bonding, solute/solvent σ/π electron pair interaction to solute/solvent dipolarity/polarizability interaction.

The values of distributions coefficients can be correlated with the solvatochromic parameters of the Toluene. π^*, δ, α, β, according to the Eq. (19).

The resulting fitting curves are included in Fig. 7. The resulting LSER regression is:

$$\ln K_D = 3.748 + 95.104(\pi^* - 1.748\delta) + 0\alpha - 107.418\beta \qquad (20)$$

This equation was used to predict ln K_D for the organic solutes.

Table 4. The values of LSER model parameters (s, d, b, a), coefficient of linear regression, *R^2*, standart error, *SE*

Models	$\ln K_D^O$	S	d	a	b	R^2	SE
LSER model parameters	3.748	95.104	−1.748	0	−107.418	0.94	0.21

CONCLUSION

The aim of this study is to determine the extractability of levulinic acid by TPA dissolved in toluene. Some physical and chemical equilibria for levulinic acid extraction by TPA in toluene as a diluent have been determined. The loading of the extractant *Z*, is defined as the total concentration of acid in the organic phase, divided by the total concentration of amine in organic phase. Calculations based on the stoichiometry of the reactive extraction and the equilibria involved indicated that more levulinic acid is transferred to the organic phase than would be expected from a 1:1 stoichiometry of the reaction. In Lser model the predicted partition coefficients agree well with each other, and also the agreements between predcitions and measurements is acceptable considering experimental uncertainty.

The extraction equilibrium was interpreted as a result of a consecutive formation of two acid–amine species with stoichiometries of 1:1 and 2:1. Equilibrium complexation constants K_{11} and K_{21} have been determinated. The mass-transfer coefficients k_L were obtained by the diffusion.

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