



LIQUID-LIQUID EXTRACTION EQUILIBRIUM FOR PYRUVIC ACID RECOVERY: EXPERIMENTAL DATA AND MODELING

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ABSTRACT – Physical extraction studies of pyruvic acid from dilute aqueous solutions (0.025 kmol·m⁻³ to 0.200 kmol·m⁻³) using several pure solvents (tri-*n*-butylphosphate (TBP), 1-decanol, 1-octanol, toluene, Methyl-isobutylketone (MIBK), and *n*-heptane) and their binary mixtures are reported in this work. All the batch extraction experiments were carried out at isothermal conditions (T=303±1K) and the results are reported in terms of distribution coefficient (K_D). The results obtained by the equilibrium studies of the different extraction system were correlated with solvatochromic parameters of the solvents. A linear solvation energy relationship (LSER) model was applied to interpret the extraction equilibrium which specifically considers physical interactions. The values of the LSER model parameters for the extraction system were optimized by regression technique and the model equations have been proposed. Experimental and model values were in good agreement (RMSD < 0.1). Reported outcomes are useful in the selection of a suitable extraction system and understanding the extraction mechanism for the separation of pyruvic acid from dilute aqueous solutions.

Keywords: Solvent Extraction, Separation, Pyruvic acid, LSER modeling, Equilibrium

INTRODUCTION

Due to ever increasing demand for pyruvic acid in food and agrochemical industries, its production through bio-route is gaining attention as low cost, eco-friendly alternative technology (Li et al., 2001). However, a few technical problems exist at the purification and separation

stage that could be resolved by using liquid –liquid extraction (Marti et al., 2011). Extraction is a highly energy efficient, cheap and sustainable technique that could provide high yield and selectivity over conventional methods of separation of carboxylic acids from fermentation broth. In this process, various organic solvents are chosen as an extraction media. The solvents are categorized as active

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and inactive solvents based on the nature of interaction with organic acids during the extraction process. Inactive solvents comprise aliphatic hydrocarbons, while active solvents include the hydrocarbons with active functional groups. With no doubt, active diluents are more effective than inactive diluents and provide better extraction media by virtue of specific chemical interactions.

Physical extraction of carboxylic acids refers to the use of conventional organic solvents as extraction media. In the course of extraction, the organic phase (solvent phase) is allowed intimate contact with the aqueous phase (solute phase) containing the acid. The physical interaction between the solute (acid) and the solvent occurs that facilitates the carboxylic acid to be extracted from the aqueous phase to the organic phase.

Several equilibrium studies on physical extraction of different carboxylic acids such as propionic acid (Wasewar et al., 2010), nicotinic acid (Senol, 2000) lactic acid (Uslu et al., 2008), citric acid (Uslu, 2008), butyric acid (Kumar et al., 2010), pyridine carboxylic acids (Datta and Kumar, 2012) etc., can be found in the literature. However, reported extraction studies on pyruvic acid are limited (Ma et al., 2005; Senol, 2006; Marti et al., 2011; Pal and Keshav, 2014; Pal and Keshav, 2015, Pal et al., 2015). Marti et al. (2011) have reported an equilibrium study of physical extraction of pyruvic acid with alcohols as solvents and found a higher distribution coefficient ($K_D=0.30$) with 1-octanol over oleyl alcohol. Further, Senol (2006) examined the effect of various solvents, e.g. proton donating and accepting, inert and polar type, on the distribution of pyruvic acid between water and tertiary aliphatic amines and found that the cyclic alcohol was the best solvent ($K_D=0.932$) for the physical extraction of pyruvic acid. Generally, solvents are mixed in different proportion to meet the desired property of the extraction system. Various researchers have studied the synergistic effect of mixed solvents (Bizek et al., 1993; Kyuchoukov et al., 2004; Marinova et al., 2005) on the distribution coefficient.

Modeling of the extraction process has generated much interest in recovery of carboxylic acids. Linear solvation energy relationships (LSER) are widely applied in extraction system modeling. Kamlet et al. (1983) have given the correlation (known as LSER model) based on solvatochromic parameters of the solvents that can predict physicochemical parameters of the solvents. Several successful applications of LSER modeling for the extraction of lactic acid (Uslu et al., 2008), citric acid (Uslu, 2008), butyric acid (Kumar et al., 2010), pyridine carboxylic acids (Datta and Kumar, 2012), glycolic acid (Datta and Kumar, 2011), and so forth can be found in the literature. However, there are very few papers available in the literature where LSER modeling for physical extraction of pyruvic acid has been reported (Senol and Baslioglu, 2012).

In the present study, a LSER model was applied to develop appropriate equations for the extraction of pyruvic acid in view of its separation from dilute aqueous solutions. The aim of this study was to develop LSER-based best fit model equations that can be applied for pure solvents as well as for mixed solvents in different combinations and compositions.

MATERIALS AND METHODS

Materials

Aqueous solutions of pyruvic acid (SRL Pvt. Ltd., Mumbai, India) were prepared by mixing 98% pyruvic acid in ultrapure deionized water (Millipore Elix). The organic phase (solvents) was used as received (tri-n-butylphosphate (TBP), 1-decanol, 1-octanol, toluene, Methyl-isobutylketone (MIBK), n-heptane) from the different suppliers.

Experimental Method

Isothermal batch extraction experiments were carried out at $T=303\pm 1K$, in Erlenmeyer flasks (100 mL capacity) with glass-stopper. The aqueous and organic phases were taken in 1:1 volume ratio. Vigorous mixing was performed in a constant temperature water bath shaker (REMI instruments (P) Ltd., India). Shaking was carried out at least for 4 hours to ensure intimate contact of phases. The solutions were centrifuged for a sufficient period of time and then allowed to settle for 3 hours to ascertain the clear phase separation.

Analysis Method

The aqueous phase was separated with a funnel and then analyzed by potentiometric titration using standardized sodium hydroxide solutions (0.005 N), with phenolphthalein as an indicator. For weighing solid, a Soritorious - CP 2245 model balance with an accuracy of 1×10^{-5} g was used.

The data analysis tool of Microsoft Excel was used to perform regression analysis to develop LSER equations. Deviation between observed and predicted values was assessed in terms of root mean square deviation (RMSD). RMSD values were calculated using experimental and model values of distribution coefficients (K_D) as:

$$RMSD = \sqrt{\frac{1}{n} (K_D^{\text{exp}} - K_D^{\text{mod}})^2} \quad (1)$$

where K_D^{exp} and K_D^{mod} are the experimental and model values of distribution coefficient and n is the sample size.

RESULTS AND DISCUSSION

Physical Extraction Equilibrium

Extraction by the organic solvents, S, is based on the solvation of organic acid, HA, in bulk solvent phase by virtue of mass transfer through the interface. The process of extraction involves the dissociation of pyruvic acid, HA, in the aqueous phase, as presented by Eq (2), and successive formation and solvation of acid-solvates, $(HA_m \cdot S_n)_{org}$, in the organic phase as shown in Eq (3).



The over bar indicates the organic phase. The equilibrium between the acid and solvent is characterized by the distribution coefficient (K_D) that is defined as the ratio of concentration of acid in organic and aqueous phases.

$$K_D = \frac{[HA]_{org}}{[HA]_{aq}} \quad (4)$$

The equilibrium distributions of pyruvic acid between organic and aqueous phase were interpreted for various solvents (Fig. 1). The distribution coefficient (K_D) was found to be higher for the active solvents in the order of TBP > decanol > MIBK > toluene > n-heptane. This trend reflects the higher extraction strength of active solvents over the inactive ones. TBP possesses the phosphate group which is able to form a strong hydrogen bond with the target solute (pyruvic acid) in the aqueous phase, thus providing higher extraction efficiency ($K_{D,avg} = 1.612$). Alcohols also proved to be a better extraction media; however, their extraction strength decreases with the increase in carbon chain length (Marti et al., 2011). The $K_{D,avg}$ value for octanol is 0.296, while for decanol it is slightly lower ($K_{D,avg} = 0.280$). Besides, the short chain alcohols are soluble in water. Thus, alcohols such as octanol, decanol etc. are often preferred as solvents for the extraction. In the case of MIBK probably the keto ($>C=O$) group forms a strong hydrogen bond ($H-O-H$) with the carboxylic group ($-COOH$) of pyruvic acid, and thus provides fairly good $K_{D,avg} = 0.245$. The aliphatic and aromatic hydrocarbons (without functional groups) such as toluene ($K_{D,avg} = 0.055$) and heptane ($K_{D,avg} = 0.017$) used in this study provided low extraction efficiency. They extract the acid through solvation mechanism and ionic interaction involving weak van der Waals' forces.

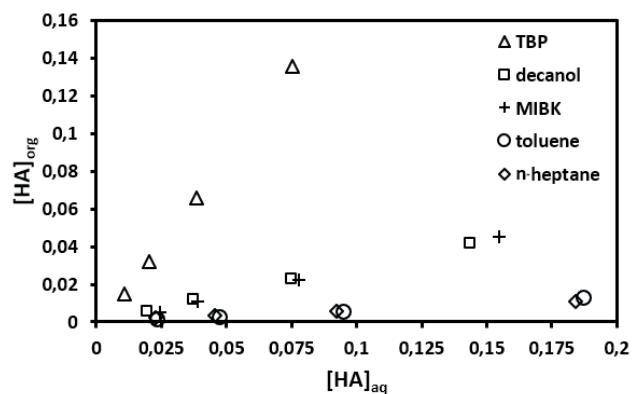


Figure 1. Physical equilibrium isotherm for extraction of pyruvic acid (0.025 to 0.200 kmol·m⁻³) using different solvents at T=303±1K.

Linear Solvation Energy Relationship (LSER) Modeling

Kamlet et al. (1983) suggested that the solvation properties of different solvents can be predicted on the basis of different solvatochromic parameters. In general, the extraction capability of solvents can be characterized and equilibrium distribution can be predicted by a linear relation as given by Eq (5).

$$XYZ = XYZ^0 + s(\pi^* + d\delta) + a\alpha + b\beta + h\delta_H + e\zeta \quad (5)$$

where, XYZ represents the specific solvent property. The π^* and δ scale of solvent polarizability (dipole) and induced-dipole respectively, measures the capability of the solvent to stabilize a charge with its dielectric effect. The α scale of solvent hydrogen-bond donor (HBD) acidities measures the capability of the solvent to donate a proton in a solvent-solute hydrogen bond. The β scale of hydrogen-bond acceptor (HBA) basicities measures the solvent's capability to accept a proton, i.e., donate an electron-pair, in a solute-solvent hydrogen bond. The δ_H term is the Hildebrand solubility parameter, a measure of the solute/solvent interactions and the ζ parameter is a measure of coordinate covalency, equal to -0.20 for P=O bases and 0.0 for CO, S=O, and N=O bases. The model equation can be fitted to the natural logarithm of the distribution coefficient (K_D). Eq (5) is simplified to Eq (6) by eliminating δ_H and ζ terms as they do not affect the value of the objective function ($\ln K_D$) significantly.

$$\ln K_D = \ln K_D^0 + s(\pi^* + d\delta) + a\alpha + b\beta \quad (6)$$

where K_D is the distribution coefficient of pyruvic acid between the aqueous and organic phases. The values of the regression coefficients s , d , a , and b are utilized for comparing solvent properties. Hence, by a well judged choice of solvents, Eq. (6) can be reduced to a more

manageable form as to be fitted for the distribution coefficient of pyruvic acid between organic and aqueous phases.

Solvatochromic parameter values have been determined by measuring intensities of maximal absorption in NMR, ESR, IR, and UV/vis spectra. The solvatochromic parameters of the solvents used in this work are taken from the literature (Kamlet et al., 1983) and given in Table 1.

Once the optimized values of the coefficients of π^* , α , β , and δ are known, the LSER modeling (using Eq (6)) of equilibrium data enables one to estimate the distribution coefficient for any diluent.

Model equations for different solvents

The distribution data obtained for the physical extraction of pyruvic acid using various solvents were utilized for the LSER modeling. Using the values of solvatochromic parameters, Eq (6) is subsequently solved by regression analysis.

The values of the coefficients were determined and the final proposed model equations for different initial acid concentrations (0.025 to 0.200 kmol·m⁻³) are presented in Table 2.

Table 1. Solvatochromic parameters of various solvents used in this work

Solvent	π^*	δ	α	β	Source
TBP	0.650	0	0.000	0.000	Kamlet et al. (1983)
decanol	0.400	0	0.330	0.450	Datta and Kumar (2012)
octanol	0.400	0	0.330	0.450	Bizek et al. (1992)
toluene	0.540	1	0.000	0.110	Bizek et al. (1992)
MIBK	0.630	1	0.000	0.480	Bizek et al. (1992)
n-heptane	0.000	0	0.000	0.000	Kamlet et al. (1983)

Table 2. Model equations for various solvents at different initial acid concentrations (0.025 to 0.200 kmol·m⁻³)

$\downarrow [\text{HA}]_{\text{aq}}^0$ (kmol·m ⁻³)	Model equations for extraction of pyruvic acid	R ²	SE
0.200	$\ln K_D = -3.33 + 6.03(\pi^* - 0.37\delta) + 4.05\alpha - 3.55\beta$	0.99	0.236
0.100	$\ln K_D = -3.56 + 6.30(\pi^* - 0.38\delta) + 4.34\alpha - 3.47\beta$	0.99	0.086
0.050	$\ln K_D = -3.63 + 6.27(\pi^* - 0.36\delta) + 4.72\alpha - 3.97\beta$	0.99	0.068
0.025	$\ln K_D = -3.69 + 6.16(\pi^* - 0.35\delta) + 4.83\alpha - 3.76\beta$	0.99	0.067

The model equations were utilized to evaluate the value of distribution coefficients (K_D^{mod}). The predicted values derived from the developed LSER model equation were found to be very close to the experimental values (observed values) as RMSD values are low (0.01) (Table 3), which confirms the validity of the model. The larger value of s (average value=6.19) compared to d (average value=0.37), signifies that the solute-solvent interactions are more dominant than dipole-dipole interactions. Strong correlation of solute hydrogen acidity and basicity with the distribution coefficient is evident from significant values of a and b . Furthermore, larger absolute values of a (average value=4.49) compared to b (average value=3.69) reveals that the solvents serve more as a proton donor than proton-acceptor.

Table 3. RMSD values for distribution coefficients of various solvents for the extraction of pyruvic acid at different initial acid concentrations

Solvents	$K_{D,\text{avg}}^*$	RMSD
TBP	1.611	0.00
decanol	0.279	0.02
octanol	0.295	0.03
toluene	0.055	0.00
MIBK	0.245	0.00
n-heptane	0.017	0.00

* Initial acid concentration range: 0.025-0.200 kmol·m⁻³

Model equations for binary solvents

The solvents properties can be tuned according to the need of the extraction system by mixing two solvent of different categories (Morales et al., 2003). Various types of solvent combinations were chosen for this study and the results were analysed based on distribution coefficients. The solvatochromic parameters for the mixture of solvents can be determined using the correlation as proposed by Bizek et al. (1992). Accordingly, solvatochromic parameters (SP) for binary mixture can be computed as:

$$SP_{12} = X_1 \cdot SP_1 + X_2 \cdot SP_2 \quad (7)$$

where X_1 and X_2 are the mole fraction of solvents. Eq (7) can be extended for more solvents. Initially the solvents (TBP, decanol, octanol, toluene, MIBK, and n-heptane) are mixed in all possible combinations in a fixed ratio (1:1) and equilibrium data were generated (Table 4). Further, using the LSER modeling approach the model equations were developed for binary solvent mixtures and presented in Table 4.

The model equations generated for the combination of mixed solvents (Table 4) reflect lesser hydrogen bond donor acidity of the solvents ($a < b$). At the $0.025 \text{ kmol} \cdot \text{m}^{-3}$ aqueous concentration of pyruvic acid, the absolute value of the coefficient of α (i.e. $\alpha=0.30$) is almost twenty times

smaller than the coefficient of β (i.e. $b=5.90$). Also, the values for solute-solvent interactions and dipole-dipole interactions are negligible ($s=d=0$). Therefore, no direct correlation was found with these interactions when various combinations of solvents were used. By applying the above model equations, the distribution coefficients were calculated and compared with the experimental results (Table 5). In most of the cases, a good resemblance is found between observed and predicted values as *RMSD* values are on order of 10^{-1} , (Table 6).

Model equations for different compositions of solvents

Effect of the composition was also examined in the case of mixed solvents. The equilibrium isotherms for binary solvents (TBP + decanol) are shown in Fig. 2. The equilibrium shifts towards a higher K_D value with increasing TBP fraction in the mixture, demonstrating that TBP is a comparatively better solvent than decanol.

Initially, with 10% TBP concentration in decanol, the distribution coefficient is low and decreases with the initial acid concentration. Further increase in the TBP concentration (up to 30%) leads to a gradual increase in distribution coefficients. However, a sudden increment in K_D value is evident at 50% concentration of TBP, which reflects the better hydrogen (H—O—H) bonding of solvents with acid molecules.

Table 4. Model equations for various binary solvents (TBP+decanol, TBP+octanol, TBP+toluene, TBP+MIBK, decanol+octanol, decanol+toluene, decanol+MIBK, octanol+toluene, octanol+MIBK, toluene +MIBK) at different initial acid concentrations

$\downarrow [\text{HA}]_{\text{aq}}^0 \text{ (kmol} \cdot \text{m}^{-3})$	Model equations for extraction of pyruvic acid	R^2	<i>SE</i>
0.200	$\ln K_D = 1.48 - 0.33 \alpha - 5.79 \beta$	0.98	0.146
0.100	$\ln K_D = 1.41 - 0.25 \alpha - 5.69 \beta$	0.98	0.122
0.050	$\ln K_D = 1.41 - 0.10 \alpha - 6.34 \beta$	0.986	0.122
0.025	$\ln K_D = 1.17 + 0.30 \alpha - 5.90 \beta$	0.984	0.121

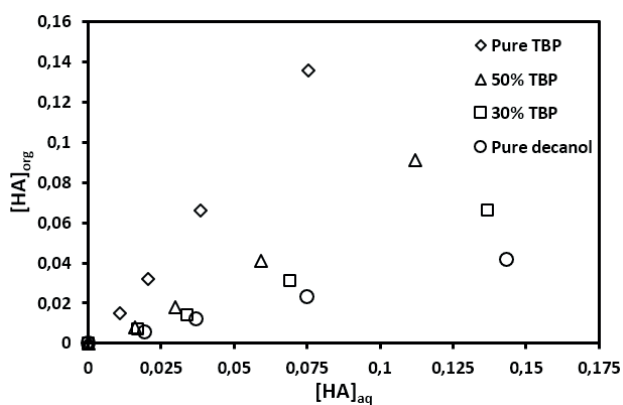
Table 5. *RMSD* values for various binary solvents combinations for extraction of pyruvic acid at different initial acid concentrations

Binary Solvent Combination	$K_{D,\text{avg}}^*$	<i>RMSD</i>
TBP+decanol	0.950	0.083
TBP+octanol	0.956	0.077
TBP+toluene	0.836	2.035
TBP+MIBK	0.934	0.031
decanol+octanol	0.290	0.021
decanol+toluene	0.168	0.580
decanol+MIBK	0.264	0.020
octanol+toluene	0.177	0.571
octanol+MIBK	0.272	0.026
toluene+MIBK	0.153	0.542

* Initial acid concentration range $0.025\text{-}0.200 \text{ kmol} \cdot \text{m}^{-3}$

Table 6. Model equations for binary solvent (TBP+decanol) mixtures for various proportions(0:10, 1:9, 2:8, 3:7, 5:5, 10:0)at different initial acid concentrations (0.025-0.200 kmol·m⁻³).

↓ [HA] _{aq} ⁰ (kmol·m ⁻³)	Model Equations	R ²	SE
0.200	$\ln K_D = 0.655 - 4.72\beta$	0.96	0.16
0.100	$\ln K_D = 0.505 - 4.26\beta$	0.93	0.21
0.050	$\ln K_D = 0.427 - 4.22\beta$	0.97	0.12
0.025	$\ln K_D = 0.281 - 4.15\beta$	0.95	0.16

**Figure 2.** Equilibrium distribution of pyruvic acid in the organic phase (TBP+decanol).

The model equations obtained by applying the LSER model for a binary solvent (TBP+decanol) mixture are presented in Table 6. A significant value of β scale hydrogen bond acceptor basicity coefficient, i.e. b , reflects that the solvents serve purely as a proton acceptor. The phosphate group of TBP possesses lone pair electrons on the phosphorus atom that contribute to hydrogen bonding with organic acid molecules by donating the electron pair. Thus, TBP shows electron pair donor (or proton acceptor)

basicity. On the other hand, decanol purely behaves as a proton donor (Lewis acid). As the value of the coefficient of α , (i.e. a) equals zero, the model resembles accurately at higher concentration of TBP as well. Also, the absence of the solute-solvent, dipole-dipole, and dipole-induced dipole interaction terms ($s=0$, $d=0$) can be understood because the distribution coefficients are not much dependent on these interactions.

The root mean square deviation (RMSD) for the model equations generated are found in the range of (0.00—0.03), for the different individual solvents (0.02—0.58) for different binary solvent's mixtures and (0.02-0.08) for different compositions of binary solvents (Table 3, Table 5, and Table 7, respectively). Hence, LSER model can be successfully applied for predicting the solvation mechanisms for the extraction of pyruvic acid from dilute aqueous solutions.

CONCLUSION

The LSER model can be successfully applied for predicting the solvation mechanisms for the extraction equilibria of pyruvic acid. A good fit of the LSER model at lower concentration of pyruvic acid assures the applicability of the model in infinitely dilute systems. Also,

Table 7. RMSD values for different solvents composition for pyruvic acid extraction.

Solvent Composition	$K_{D,avg}^*$	RMSD
Pure decanol	0.300	0.057
10% TBP	0.234	0.042
20% TBP	0.303	0.041
30% TBP	0.435	0.021
50% TBP	0.657	0.080
Pure TBP	1.612	0.074

* Initial acid concentration range 0.025-0.200 kmol·m⁻³

LSER modeling for binary solvents resembles the data more closely than pure solvents. The lower values (0.1) of root mean square deviation (*RMSD*) indicate the good fit to the experimental data. Reported findings are useful in the selection of a suitable extraction system and design of extractor for the separation of pyruvic acid from dilute aqueous solutions.

NOMENCLATURE

Symbol	Description	Units
α	Scale of proton donor capacity	–
β	Scale of proton acceptor capacity	–
δ	Scale of dipole + induced dipole interactions	–
δ_H	Hildebrand solubility parameter	–
d	Scale of dipole + dipole interactions	–
E%	Percentage extraction efficiency	–
[HA]	Concentration of organic acid	kmol·m ⁻³
S	Solvent	
K_D	Distribution coefficient	–
RMSD	Root mean square deviation	–
SP	Solvatochromic parameters	–
ξ	Coordinate covalence	–
Subscript		
aq	= Aqueous phase	
org	= Organic Phase	
avg	= Average value	
Superscript		
exp	= Experimental value	
mod	= Model value	

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