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Equilibrium analysis and LSER modelling for extraction of Trans-aconitic acid using Tri-butyl Phosphate by using Xylene and Benzene

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ABSTRACT

Reactive extraction of Trans-aconitic acid from its aqueous solution has been carried out by Tri-butylphosphate as extractant and benzene, xylene as diluents. The study has been performed at room temperature and distribution coefficient (KD), extraction efficiency (E %) and equilibrium complexation constant (K11) has been found out. The maximum value of KD = 9.098454, E%=90.09749 was found out for 0.689219 mol/L trans-aconitic acid, 1.40733mol/L (40%) Tri- butylphosphate and benzene. The paper has presented linear solvation energy Relationship (LSER) model for trans-aconitic acid using tri-butyl phosphate in benzene, xylene.The LSER model with regression coefficient of 0.9845 is obtained. The model value is close to the experimental data.

Keywords: Trans-aconitic acid, Tri-butylphosphate, LSER, benzene, xylene

I. INTRODUCTION

Aconitic acid is naturally occurring acid present in plants like sugar cane, beet root. It can also be prepared from sugar cane juice and molasses. It is also an intermediate acid in TCA cycle. It can be produced by fermentation of aspergillus niger. (GB Patent No. 0146378A2, 1985)It is unsaturated tri-carboxylic acid and polybasic acid. It can be used as plasticizer for synthetic rubber, wetting agent and resin manufacturing units. It can be found in two isomers, Cis and Trans. The Cis-aconitic acid can be prepared by hydrolysis of the cis-anhydride under careful controlled condition rather Trans-aconitic acid is prepared by the sulfuric acid dehydration of citric acid. Trans- aconitic acid is more stable acid rather Cis-aconitic acid is a strong acid. It has been found during research that in equilibrated solution contains approximately 85% Trans- aconitic acid. By fermentation aconitic acid can be recovered as aconitate from Cuban and Louisiana blackstrap molasses require large amount of chemicals. Aconitic acid can be used as basic reactant for many components like Itaconic acid, Citraconic acid, Tricarballylic acid, many polymers such as copolymers of alkyl aconitates and vinyl chloride. It can also be used as plasticizers in the preparation of stabilized vinylidene chloride composition (M.Cantor, 1951).

Reactive extraction of Trans-aconitic acid has been studied by tri-n-butylphosphate and found suitable (Vilas C.Renge, 2012).After this research there is no work found in the current topic. The behavior of aconitic acid is similar to Maleic acid and Fumeric acid (M.Cantor, 1951).Reactive extraction of Citric acid and maleic acid has been carried out by using phosphorous extractant and amine extractant with different solvents by (Erdem Hasret, 2017).In their investigation, TOPO and DOA has been used as extractant with nine different solvents for the extraction of Citric acid and maleic acid and found that phosphorous or amine extractant enhance the recovery of carboxylic acid from their aqueous solution. Fumeric acid has been produced by fermentation of Rhizopus oryzae and extracted by organic liquid membrane. (Yadvaindra Sood, 2014).Extraction of citric acid, pyruvic acid, Caproic acid, Acrylic acid, Vulneric acid, mallic acid has been studied by researchers using Tri-n-butyl phosphate as an extractant (Amit Keshav, 2009).The present work is focused on reactive extraction of Trans-aconitic acid from its aqueous solution by using tri-butyl phosphate as extractant and benzene and xylene as a diluent. The basic factors required for extraction has been studied and linear solvation energy relationship (LSER) model has been applied for the interpretation of data.

II. MATERIALS

Aconitic acid, ($C_6H_6O_6$), Molecular weight 174 g/mol is an unsaturated tribasic aliphatic acid existing in two geometric forms, the trans- isomer, TAA, and the cis- isomer . Trans Aconitic acid, also known as TAA, is a white to yellowish crystalline solid, with melting point 195 °C. Its IUPAC name is trans-propene-1, 2, 3,-tri carboxylic acid and the molecular formula is $C_6 H_6 O_6$. Its Hydrogen bond donor count is 3 whereas its Hydrogen bond acceptor count is 6. It is soluble in water and alcohol. Its solubility in water increases from 18.6 g/100 mL at 13

°C to 110.7 g/100 mL at 90°C (Patarau, 1989). TAA used here was 98% + pure, supplied by Sigma Aldrich.

Tri-n-butyl phosphate, also called as TBP, is a phosphorus bonded oxygen donor. It is a light liquid with pale yellowish colour. It has molar mass of 266.32 g · mol-1 and density of 0.976 g·cm-3. The molecular formula of TBP is $C_{12} H_{27} O_4 P$. It is an odourless liquid. The freezing point of TBP is -79°C. The Boiling point of TBP ranges from 180°C-183°C. The Hydrogen bond donor count for TBP is 0, whereas Hydrogen bond acceptor count for it is 4. It is slightly soluble in water with solubility 280 mg/L at 25°C (Saegar VW et al.) It is a viscous liquid with coefficient of viscosity 3.39 cP at 25°C (Riddick J.A. et al). The TBP used was of extraction grade

(Volume fraction of 99%) and it was supplied by Loba Chemie Pvt. Ltd. India.

The solvents used during extraction were benzene, xylene and one natural solvent as Rice bran oil. Benzene is an aromatic compound with molecular formula $C_6 H_6$. Its molecular weight is 78.11g/mol. Its Hydrogen bond dono & acceptor count is 0. It is a colourless liquid with characteristic aromatic odour. Its boiling point is 80.08 °C. Its viscosity & density is 0.562 cP and 0.8680 g/cm3 respectively at 30 °C. The benzene was also supplied by Loba Chemie Pvt. Ltd. India.

Xylene is also an aromatic compound. It exists in three isomers o-xylene, m-xylene &p-xylene. As they are structural isomers, the physical properties are almost similar. Xylene has a molecular formula $C_8 H_{10}$; with molecular weight 106.168 g/mol. It is a colourless watery liquid with sweet smell. It is less dense than water. The Hydrogen bond donor & acceptor count for Xylene is 0. Its boiling point is 138.3°C. Xylene was also supplied by Loba Chemie Pvt. Ltd. India.

III. EXTRACTION EQUILIBRIUM

Physical Extraction:

The physical extraction has been carried with equal volumes of Trans-aconitic acid and Tri-butyl phosphate for 8 hrs. in a shaker without diluents. After 1 hr. of settling in separating funnel the aqueous phase has been titrated with freshly prepared 0.1 N NaOH .The concentration of organic phase has been calculated by mass balance. According to (C.J.King, 1986), physical extraction has been carried out in three steps (1) Ionization of acid in aqueous phase $KHAA$ (2)partition of un-dissociated acid in organic phase (P) (3)dimerization of acid in organic phase (D)

Ionization of acid in aqueous phase

$$HA_A \leftrightarrow H^+ + A_A^- \qquad (1)$$

(1) Partition of un-dissociated acid between aqueous (aq) phase and organic(org) phase

$$[HA_A]_{aq} \leftrightarrow [HA_A]_{org} \qquad (2)$$

(3) Dimerization of acid in organic phase

$$2[HA_A]_{org} \leftrightarrow [HA_A]_{2org} \qquad (3)$$

The overall distribution coefficient for physical extraction will be given by

$$K_D{}^{diluent} = \frac{P+2P^2D[HA_A]_{aq}}{1+{}^{K_{HA_A}}/_{[H^+]_{aq}}} \qquad (4)$$

In a simpler form it can be written as

$$[HA_A]_{org} = P[HA_A]_{aq} + 2P^2D[HA_A]_{aq}^2 \qquad (5)$$

The degree of extraction %E of Trans-aconitic acid is given by

$$E\% = K_D^{diluent} * 100/(1 + K_D^{diluent}) \qquad (6)$$

The values of partition coefficient and dimerization coefficient and degree of extraction has been mentioned in Table No. 3.1.The degree of extraction is obtained from equation (6) is very low for physical extraction. The regression equation for the physical extraction using benzene and xylene are obtained in the form

$$[HA_A]_{org} = P[HA_A]_{aq} + D[HA_{A\,aq}]^2 \qquad (7)$$

The partition coefficient and dimerization coefficient for xylene and benzene are represented in Table No.3.1 found out from equation no.7.The values of partition coefficient is less and dimerization coefficient is low .Though the value of Regression coefficient $R2$ is nearly equal one. Though the average values of distribution coefficient KD and extraction coefficient %E is higher for benzene rather than xylene. The Tri-butyl Phosphate has found to be effective extractant (Mangesh D.Waghmare, 2011)

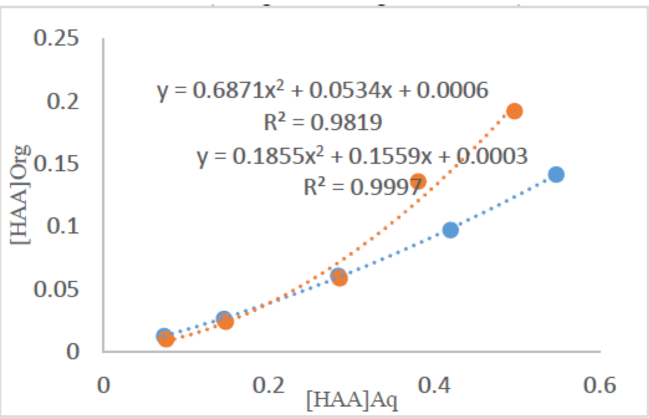

Fig. 1 Physical extraction of Trans-aconitic acid by

Benzene and Xylene

B. Chemical Extraction:

For chemical extraction, the initial concentration of Trans-aconitic acid concentration is in range of 0.086152 mol /m3 to 0.689219 mol /m3. Benzene and xylene are used as a solvent in combination with tri-butyl phosphate is 0.703665 mol /m3 and 1.40733 mol /m3 (20 % and 40%) as a diluent as it has low water co-extraction and low solubility in organic solvent. TBP has a phosphoryl group which is a stronger lewis base than the carbonyl group (Mangesh D.Waghmare, 2011). The basic aim of chemical extraction is to increase the extraction efficiency of solvent. When diluent is added with the solvent in appropriate proportion it increases its extraction efficiency thereby increasing the distribution coefficient .The diluent lowers the viscosity of the solvent and decreases surface tension at the interface. (Mangesh D.Waghmare, 2011).The ratio of concentration of solvent to concentration of diluent is called as loading ratio, represented by Z.

Table 1. Partition coefficient & dimerization coefficient of Trans-Aconitic acid by using benzene & xylene

Solvent	Partition coefficient (P)	Dimerization coefficient (D)	Regression Coefficient R^2	Average K_D	Average %E
Xylene	0.6871	0.0534	0.9819	0.212119	17.44516
Benzene	0.1855	0.1559	0.9997	0.249614	19.44124

$$Z = \frac{[HA_A]_{org}}{S_{Org}^{Initial}} \qquad (8)$$

Where, $[HA_A]_{org}$ is the concentration of undissociated Trans-aconitic acid and $S_{Org}^{Initial}$ is initial concentration of tri-butyl phosphate in organic phase. S_{Org} can be expressed as

$$[S]_{Org} = [S]_{Org}^{Initial} + p[HA]_{Org} \qquad (9)$$

Where, p is solvation number

Since the Trans aconitic acid and tri butyl phosphate was used in all experimental runs were in (1:1) proportion, thus the plot of $\frac{Z}{1-Z}$ vs$[HAA]_{aq}$ gives the value pf equilibrium complexation constantK_{11}.

$$\frac{Z}{1-Z} = K_{11}[HAA]_{aq} \qquad (10)$$

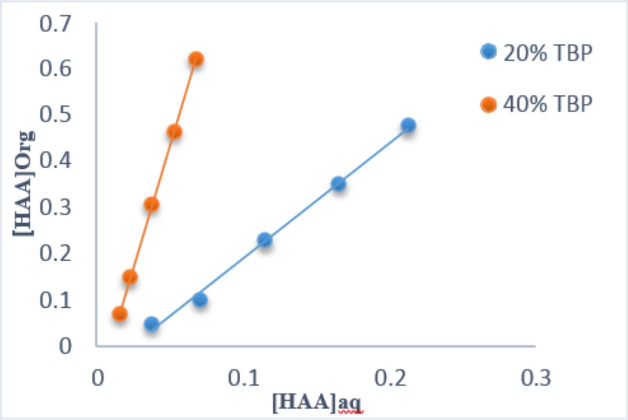

Fig. 2. Chemical extraction of Trans -aconitic acid by using 20% and 40% TBP with benzene as a diluents

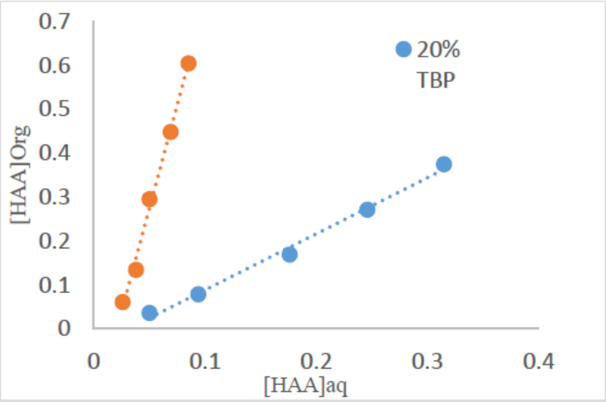

Fig. 3. Chemical extraction of Trans aconitic acid by using 20% and 40% TBP with Xylene as a diluents

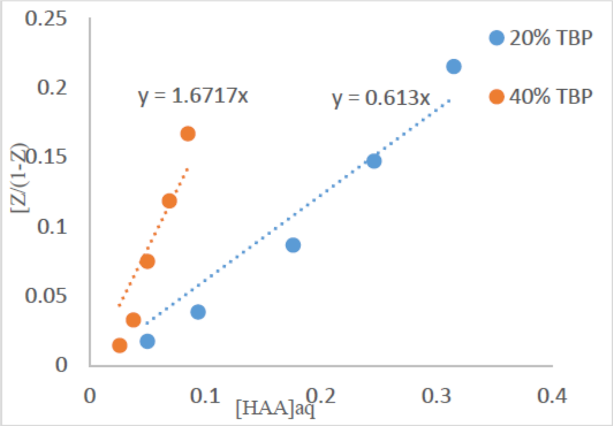

Fig. 3.2.3 Equilibrium complexation Constant of Trans-aconitic acid by using 20% and 40% TBP with Xylene as a diluents

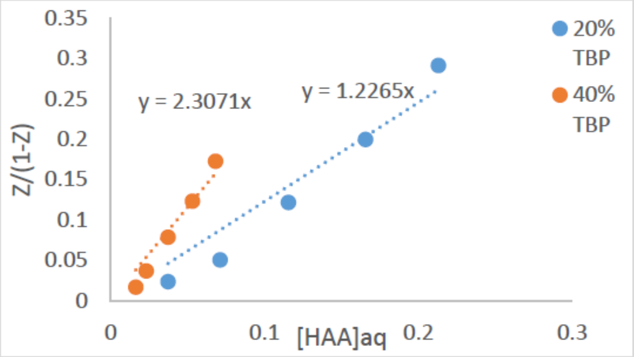

Fig.4. Equilibrium Complexation Constant of Trans Aconitic acid by using 20% and 40% TBP with Benzene as a diluents

IV. LINEAR SOLVATION ENERGY RELATIONSHIP (LSER)

According to (Mortimer J Kamlet.Jous-Luis, 1983); the linear solvation energy relationship (LSER) that measures property XYZ, in terms of solvent properties, is

$$xyz = xyz^0 + P\frac{{\delta_h}^2}{100} + s(\pi^* - d\delta) \qquad (11)$$

Where, δ is the Hildebrand's solubility parameter, $\pi *$, d, and δ are the solvatochromic parameters that measure the solute + solvent, dipole + dipole, and dipole + induced dipole interactions, respectively. The solvatochromic parameter α scale of solvent HBD (hydrogen-bond donor) acidities describes the ability of the solvent to donate a proton in a solvent-to-solute hydrogen 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. The coefficients p, s, d, a, and b include the solute properties; p, s, d, and a are regression coefficients. The values of the solvatochromic parameters $\pi *$, δ , α and β have been found for several hundreds of compounds. Equation 11 can be adopted to describe the effect of diluents on the values of partitioning coefficients KD, in the form

$$lnK_D = lnK_D{}^0 + P\frac{{\delta_h}^2}{100} + s(\pi^* - d\delta) + a\alpha + b\beta \qquad (12)$$

Where the parameters (Mortimer J Kamlet.Jous-Luis, 1983)refer to the diluent, and K_D represents the partitioning coefficients for an ideal inert diluent. The second term of equation 4, which contains the solubility parameter, does not affect the values of the objective function significantly. Thus, equation 12 reduces to equation 13

$$lnK_D = lnK_D{}^0 + s(\pi^* - d\delta) + a\alpha + b\beta \qquad (13)$$

(Vladislav Bizak, 1993) calculated the solvatochromic parameters of the solvent mixtures according to equation 14

$$SP_{12} = X_1SP_1 + (1 - X_1)SP_2 \qquad (14)$$

Where X_1 is the mole fraction of the first solvent and $X_2 = (1 - X_1)$ is the mole fraction of the second solvent. SP_1 is the solvatochromic parameters of the first solvent and SP_2 is the solvatochromic parameters of the second solvent in solvent mixtures.

The resulting LSER regression equation by using curve fitting technique is

$$lnK_D = 6.221307864 + 0.437210413(\pi * -18.5115\delta) + 0\alpha + 2.61475369\beta \qquad (15)$$

The above equation 15 has been obtained by using equation (13) which is obtained by neglecting the solubility term (S.H.Hilal, 2004) and shown in Table 4.3. The solvatochromic parameters are available for wide variety of solvents (Mortimer J Kamlet.Jous-Luis, 1983). The values of solvatochromic parameters has been obtained from (Mortimer J Kamlet.Jous-Luis, 1983) and mentioned in Table 4.1.The experimental value of distribution coefficient K_D has been plotted against model value which are mentioned in Table 4.2 The graph between experimental value of distribution coefficient K_D has been plotted against model value shown in Figure 4.1which shows a regression coefficient (R^2) as 0.9845 which is near to 1.

Solvent	π*	δ	B	A
Xylene	0.43	1	-	0.00
Benzene	0.59	1	0.10	0.00

Table 2. Solvatochromic Parameter Hydrogen-Bond Donor Acidities (π*and δ) and Hydrogen-Bond Acceptor Basicity's (β and α) for Diluent Mixture:

LSER model parameter	$lnK_D{}^0$	Model Parameters				Coefficient of linear regression R^2
		s	d	a	B	
	6.221307864	0.437210413	-18.5115	0	2.61475369	0.9845

Table 3. Values of the LSER model parameters(s,d,b,a) & the Coefficient of Linear Regression(R2)

Solvent	Concentration of TBP (V/V) %	Experimental Distribution Coefficient K_D	Model Predicted Distribution Coefficient K_D
Xylene	0	0.249613766	0.18561085
	20	0.960673214	1.1323879
	40	5.068013662	5.19955687
Benzene	0	0.212118859	0.25854799
	20	1.810751661	1.47620088
	40	7.325536837	6.34350101

Table 4.Comparison of experimentally determined & model predicted Distribution Coefficients

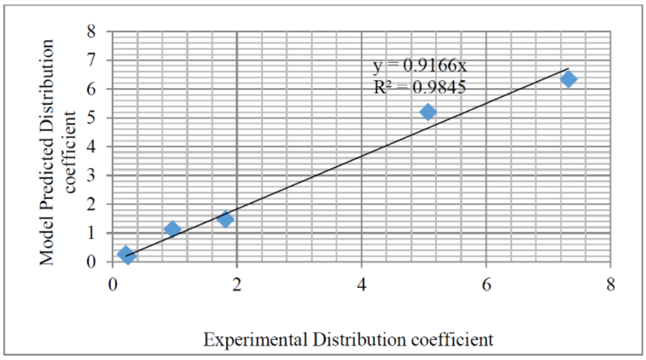

Fig. 5. Comparative graphical representation of experimental distribution coefficient Vs. model predicted distribution coefficient

V. CONCLUSION

The reactive extraction of Trans-aconitic acid is carried out from its aqueous solution by using TBP as extractant and benzene and xylene as a diluents. Physical extraction is seen to be less efficient as compared chemical extraction. The distribution coefficient, extraction efficiency and loading ratio and equilibrium complexation constant has been found out. The highest KD= %E = and K11= has been found out for Trans aconitic acid and xylene and TBP system. The LSER model with regression coefficient of 0.9845 is obtained. Thus, LSER model predicts the equilibrium behavior of Trans-aconitic acid using TBP in benzene and xylene. References:

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