

Chemical Equilibria for Reactive Extraction of Trans-Aconitic Acid Using Tri-*n*-Butyl Phosphate in Benzene and Toluene

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ABSTRACT: Reactive extraction is an alternative to conventional methods. It is advantageous since the extraction process, if properly applied, does not affect the stability of the bioproducts and the energy demand is substantially low like liquid-liquid extraction, two liquid phases; one being the aqueous phase containing aconitic acid and the other being the organic phase into which aconitic acid is extracted, are contacted in reactive extraction. But in the case of reactive extraction, the organic phase contains an extractant (or reactant) which yields higher distribution coefficients for aconitic acid than the traditional organic solvents. Compared to physical liquid-liquid extraction, the selectivity of separation is remarkably enhanced in reactive extraction because the reactant present in the organic phase promotes the transfer of aconitic acid to the organic phase.^[1,2] The values of distribution coefficient using 20% TBP (KD=1.5) & 40% TBP (KD = 2.5) for Toluene and for Benzene using 20% TBP (KD=1.2) & 40% TBP (KD=2.1).

KEYWORDS: Trans-acconitic Acid, Tri-*n*-Butyl Phosphate, Benzene, Toluene, Reactive Extraction.

I. INTRODUCTION

Aconitic acid is a tricarboxylic unsaturated acid and is of special interest in the production of resins, plastics, plasticizers, flavors, etc. Liquid-liquid extraction (LLE), solid-liquid extraction and ion exchange were evaluated for the recovery of Trans aconitic acid from cane leaf matter stillage. It is an intermediate in the tricarboxylic acid cycle produced by the dehydration of citric acid.^[3,4] Reactive extraction employs an extractant to remove the acid. Extractants are usually classified as: (i) anion exchange extractants (e.g., aliphatic primary, secondary, and tertiary amines), which form ion pairs (salts) in acidic medium; (ii) cation exchange extractants (e.g., phosphine and phosphoric acid), which exchange the proton against the cation; (iii) solvating extractants (e.g., phosphoric and phosphinic acid, esters, and phosphin oxides), which are Lewis bases and form nonstoichiometric compounds with neutral solutes; and (iv) chelate-forming extractants (e.g., aliphatic and aromatic hydroxyines), which exchange the cation and form coordinate binding. Extractants are generally viscous liquids or solids, so they are dissolved in diluents, which improve their physical properties like surface tension and viscosity. Diluents provide the solution of the extractants and also general and specific solvation to the extractant-acid complexes formed. Polar diluents are more favorable than low polarity, low dielectric constant, aliphatic, or aromatic hydrocarbons. The dipole-dipole interaction plays an important role for the solvation of the whole extractant-acid complex and has been found to play an important role in the neutralization reaction between acid and extractant, which is promoted by increasing the polarity of the diluent. Reactive extraction with specified extractant giving a higher distribution coefficient has been proposed as a promising technique for the recovery of carboxylic and hydroxycarboxylic acids.^[5] This method is advantageous for alcohol and organic fermentations. The advantages include increased reactor productivity, ease in reactor pH control without requiring base addition, and use of a high-concentration substrate as the process feed to reduce process wastes and production costs. This method may also allow the process to produce and recover the fermentation product in one continuous step and reduce the downstream processing load and the recovery costs. For the separation of carboxylic acids from dilute aqueous solution Long-chain aliphatic amines are effective extractants.^[6]

Generally, the amine extractants are dissolved in a diluent, an organic solvent that dilutes the extractant. It controls the viscosity and density of the solvent phase. For the reactive extraction of organic acids, the pH of the aqueous phase is an important parameter. ^[7] There has been a resurgence of interest in large-scale production of fermentation chemicals due to the sharp increase in petroleum cost over the last 3 decades. So the potential role of a new energy efficient fermentation technology is receiving growing attention. Thus, for fermentation products to penetrate the organic chemicals industry, substantial improvements in the existing recovery technology are needed. In the food, pharmaceutical and chemical industries, organic acids are widely used. Fermentation technology for the production of organic acids in particular has been known for more than a century and acids have been produced in aqueous solutions. ^[8] The conventional method for the recovery of Aconitic acid from fermentation broth is the calcium hydroxide precipitation method. This method of recovery is expensive and unfriendly to the environment as it consumes lime and sulphuric acid and also produces a large quantity of calcium sulphate sludge as solid waste. Thus there is a need to look at other methods of producing Aconitic acid. By bioprocessing of natural products such as by fermentation a number of carboxylic acids are obtained. Pharmaceutical and food industries challenge the recovery of these valuable products, which are their major users. A number of methods are available such as precipitation, adsorption, membranes, dialysis, distillation, ion exchange, or reactive extraction to recover carboxylic acids from fermentation broths. ^[9] Conventionally, precipitation by calcium hydroxide was employed to extract carboxylic acids, but the method is expensive as it employs a large amount of chemicals and is environmentally unfriendly as it produces a large amount of waste sludge. Alternative methods have always been discussed to recover the acid. For the recovery of carboxylic acids reactive extraction is an important recovery technique, which has received increasing attention over the past decade. ^[9] Reactive liquid-liquid extraction has the advantage that Aconitic acid can be removed easily from aqueous stream. Further, the aconitic acid can be re-extracted and the extractant recycled to the process. When selecting an extractant, along with other considerations such as price, availability, ease of regeneration, very high distribution coefficients, and low toxicity, one must ensure that the extractant is environment friendly. In other words, the extractant should have as low solubility in water as possible, so that it does not add substantially to COD of the aqueous raffinate. ^[10] Diluents is usually added along with the extractant to enhance its physical properties by providing general solvation and affect the extraction power of the extractant by providing specific interaction. The diluent may consists of one or more components, inert or active. Various active polar and proton or electron donating diluents (halogenated aliphatic/aromatic hydrocarbons, ketones, nitrobenzenes, higher alcohols), enhance the extraction. On the otherhand, inert diluents (long chain paraffins, benzene etc.), limit the solvent capacity. The three important variables which can influence the equilibrium extraction characteristics of the system are the nature of the acid extracted, the concentration of the extractant, and the type of diluent. Wasewar and his group have extensively worked on reactive extraction of various carboxylic acids. ^[11] The distribution coefficient KD was measured for the extraction of caproic acid from aqueous waste stream and also the effect of presence of salts such as sodium sulphate and sodium chloride was studied. ^[12] In the present work, reactive extraction of aconitic acid was studied using TBP, an organophosphorous compound. A comparison of the type of diluents on extraction was investigated. Physical extraction using these diluents and chemical extraction using TBP with a volume fraction of (20 to 40) % in respective diluents were performed and compared. Extraction mechanism, distribution coefficient, and equilibrium complexation constants were determined. The difference in degree of extraction is discussed. A lot of work has been done on the reactive extraction of different carboxylic acids using tertiary and quaternary amine but very little work on aconitic acid extraction can be found. In view of this, attempts were made to study the extraction of aconitic acid using TBP in Benzene and Toluene. The distribution of aconitic acid between water and TBP dissolved in various diluents, and a comparison with the extraction capacity of pure diluent alone were studied at isothermal conditions. The data on the distribution coefficient, equilibrium complexation constant were presented.

II. EXPERIMENTAL

For the practical work of equilibrium study, experimental set-up consists of magnetic stirrer, conical flasks, separating funnels and burette for titration.

A. CHEMICALS

Trans-Aconitic acid (volume fraction of 98+ %) (Lancaster Synthesis, England) and the diluents: Benzene (Loba Chemie Pvt.Ltd.India), Toluene (Loba Chemie Pvt.Ltd.India) are of Analytical grade and were used as supplied by suppliers. These diluents are in Aromatic Group to see the effect on extraction of Trans-Aconitic Acid Tri-*n*-butyl phosphate (volume fraction of 99 %)(Loba Chemie Pvt.Ltd. India), a phosphorus-bonded oxygen donor, is a light colorless liquid with the



molar mass of 266.32 g · mol⁻¹ and density of 0.92 g·cm⁻³. The solutions of various concentrations of Trans-aconitic acid. NaOH used for titration is of analytical grade & prepared in distilled water and was supplied by Loba Chemie Pvt.Ltd. India. For the standardization of the NaOH, oxalic acid (99.5%) was obtained from Loba Chemie Pvt.Ltd. India. Phenolphthalein solution (pH range 8.0 to 10.0) was used as an indicator for titration and was obtained from Loba Chemie Pvt.Ltd.India. The initial TBP concentrations in the range of (0.732 to 1.4647) mol·L⁻¹ and the initial aqueous acid concentration range of (0.01 to 0.2) mol· L⁻¹ were used (where superscript “o” signifies the initial).

B.REACTIVE EXTRACTION

Experiments were carried out in 200 ml shake flasks with a working volume of 30 ml in the magnetic stirrer with capacity of 1 flask. Equal volumes (15 ml) of the aqueous phase and the organic phase in 200 ml of flask were shaken for 6-8 hrs. at room temperature. Aqueous Trans-aconitic acid solution of the required concentration was prepared by diluting the Trans-aconitic acid (99%v/v) with distilled water. Our preliminary studies had shown that 6-8 hrs. of mixing time is sufficient to reach equilibrium and the settling time for the solution was 2-3 hrs. The initial pH of the Trans aconitic acid solution was taken as such by initial concentration of solutions. After attaining equilibrium, the phases were brought into contact for separation

C.ANALYTICAL METHOD

Phases were separated after settling and the volume of each phase was determined. The standardization of NaOH with the 0.1 N Oxalic Acid has been carried out and the 0.1 N NaOH was freshly prepared before every Titration for taking the accurate burette reading. The initial TBP concentrations in the range of (0.732 to 1.4647) mol · L⁻¹ and the initial aqueous acid concentration range of (0.01 to 0.2) mol ·L⁻¹ were used. The Trans-aconitic acid concentration in equilibrium aqueous phases was determined by potentiometric titration using 0.1 N NaOH solution. The acid concentration in the organic phase was obtained by the mass balance. The extraction ability was represented by the distribution coefficient. The calculated distribution coefficient, *KD*, is calculated with following relation as given by Eq.1

$$KD = C_{org}/C_{aq} \quad \text{---(1)}$$

Where, *C_{org}* is the concentration of Trans-aconitic acid in organic phase and *C_{aq}* is the concentration of Trans-aconitic acid in aqueous phase after reaching equilibrium.

Degree of extraction (*E%*) is defined as the ratio of Trans-Aconitic acid concentration in organic phase to the sum of acid concentration in organic and aqueous phase and is defined in term of

KD as

$$E \% = (KD * 100) / (1 + KD) \quad \text{---(2)}$$

III. RESULTS AND DISCUSSION

The physical and chemical equilibria for Trans-aconitic acid using Tri-butyl Phosphate in Benzene and Toluene were carried out by experiments.

A.PHYSICAL EQUILIBRIA

Experiments were carried to know the effect of initial acid concentration on distribution coefficient for a particular solvent. The results are shown in Fig.1 shows the equilibrium curves with Benzene and Toluene are much steeper from Fig.1. So Toluene show better recovery of Trans-Aconitic Acid in organic phase than Benzene. At higher initial Trans Aconitic acid concentration, the amount of solvent may be the limiting factor for the strength of solvation of the complex..The physical equilibrium was studied for Trans-aconitic acid using solvents like aromatics Benzene and Tolene were used to find the distribution coefficient of Trans-aconitic acid

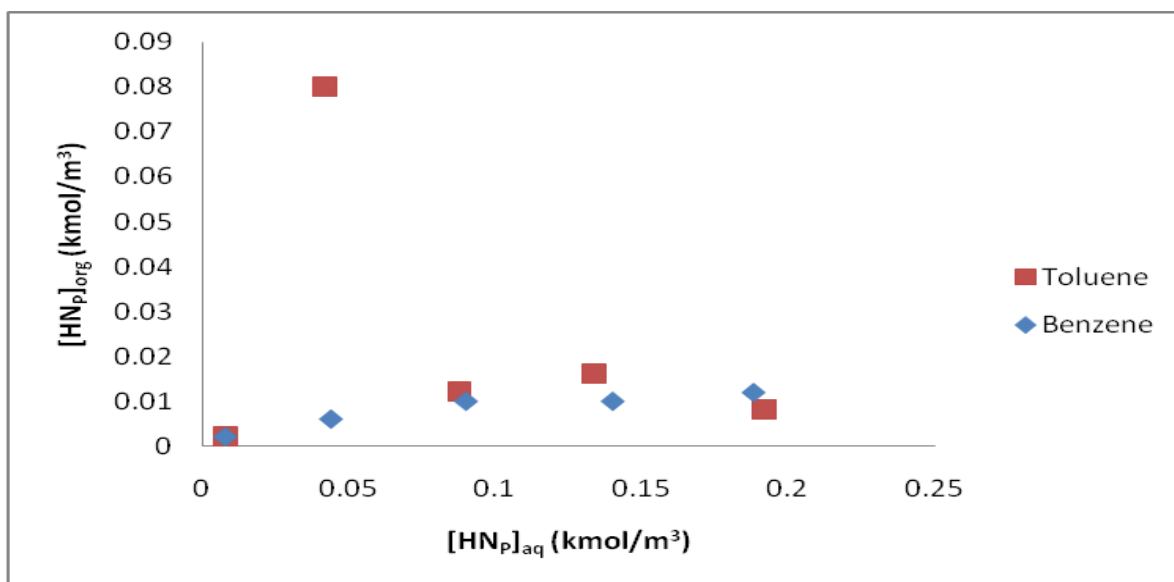


Fig.1 Physical equilibria for extraction of Trans-Aconitic acid using Benzene & Toluene at 301K

B. CHEMICAL EQUILIBRIA

Experimental studies show that TBP is dissolved in diluents, Benzene & Toluene that dilute the extractant. TBP controls the viscosity and density of the solvent phase. Tri-Butyl Phosphate, an effective organophosphorous compound, are effective extractants for separation of carboxylic acids from dilute aqueous solutions of Trans-aconitic acid. Chemical equilibria results for extraction of Trans Aconitic acid are shown in Fig.3 & Fig.4. The Trans Aconitic acid extraction with TBP, the variation of KD with initial acid concentration is given in Fig.3 with 20% TBP in Toluene, 20% TBP in Benzene, and a unit C_{org} to C_{aq} ratio. KD decreased from 1.5 to 1.2 and increases from 2.5 to 2.1 for 40% TBP in Benzene and 40% TBP in Toluene upon increasing initial Trans aconitic acid concentration from 0.732 to 1.464 gmol/L. At higher initial acid concentrations, the amount of TBP may be the limiting factor for the TBP: acid reaction. Fig.3 & Fig.4 show chemical equilibria for extraction of Trans-Aconitic acid using various percentages of TBP in Benzene and Toluene. The interactions between the complex and solvent can, somewhat arbitrarily, be divided into "general solvation" and "specific interaction" of the diluent with the complex. Fig.3 & 4 show the Distribution coefficient vs Initial Concentration of Trans Aconitic Acid using various percentages of TBP in Benzene and Toluene. Our experimental study shows that acid is recovered from aqueous solution to organic solvent. Solvent can be regenerated to give pure acid. The differences among distribution coefficient and equilibrium values for the same acid in different diluents indicate that solvation of the complex by the diluent is a critical factor in the extraction of acid. So an extractive separation and recovery process normally involves two steps: extraction and solvent regeneration. By stripping with a small volume of alkaline solution, extractant can be easily regenerated. There are various methods for back extraction such as temperature swing, diluent swing, and gas anti-solvent methods using NaOH, HCl, ammonia, and trimethyl amine. Wasewar et al. (2004) have given an exhaustive discussion on these processes for the back extraction of carboxylic acids. [9]

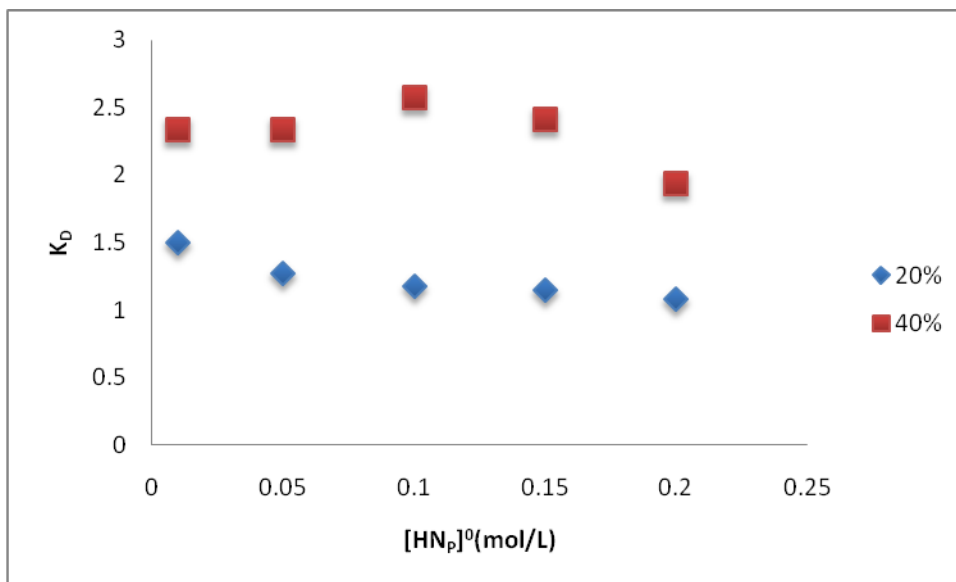


Fig.3 Plot of Distribution coefficient Vs Initial Concentration of Trans –Aconitic Acid using various percentages of TBP in Toluene.

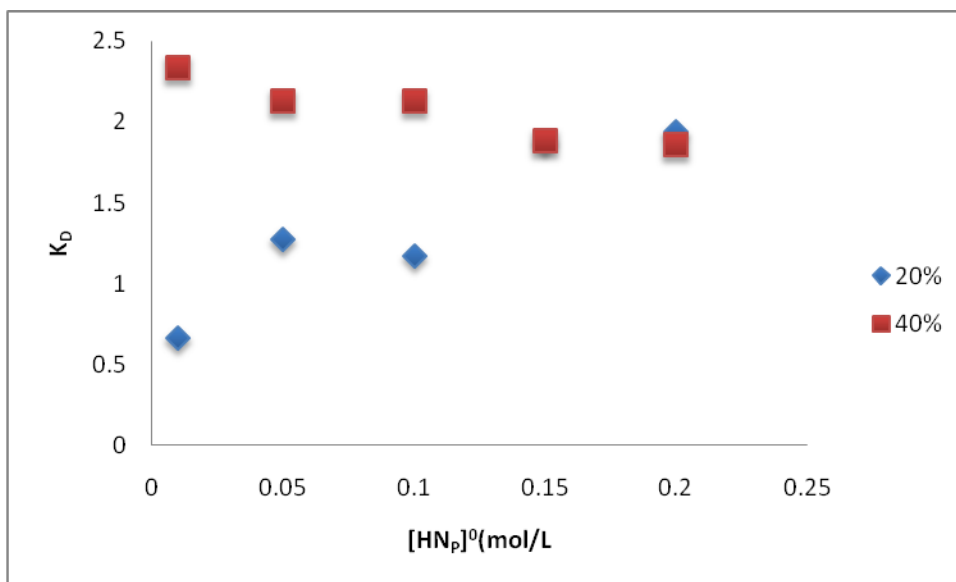


Fig.4 Plot of Distribution coefficient Vs Initial Concentration of Trans –Aconitic Acid using various percentages of TBP in Benzene.

IV. CONCLUSIONS

By the experimental study of Physical and chemical equilibria for Trans Aconitic acid extraction by dissolved in Benzene & Toluene have been determined. Distribution coefficient for extraction of Trans- aconitic acid using Tri-Butyl Phosphate in Toluene was higher than Benzene. It has been found that the combination of TBP and solvent gave a higher distribution coefficient as compared to pure solvent by using the initial TBP concentrations in the range of (0.732 to 1.4647) mol · L⁻¹ and the initial aqueous acid concentration range of (0.01 to 0.2) mol·L⁻¹.

V. NOMENCLATURE

[HN_p] = Trans Aconitic acid concentration, (mol/l)

[H⁺] = H⁺ ion concentration in aqueous phase (mol/l)

[N_p⁻] = concentration of dissociated Trans Aconitic acid in aqueous phase (mol/l)

K_D = distribution coefficient of acid in organic phase

E% = degree of extraction

SUBSCRIPTS :

aq = aqueous phase

org = organic phase

o = initial

SUPERScript :

diluent = for diluent only

max = maximum

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