

# Reactive Extraction of 2-methylenesuccinic acid using Tri-N-Butyl Phosphate In Natural Non-Toxic Diluent

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**Abstract:**-- Reactive extraction is one of the most promising technique emerging as a substitute to recover carboxylic acids from the fermentation broths compared to conventional methods. However the toxicity of the extractants and diluents is the major limitation to use this technique for the recovery of carboxylic acids from bioreactors. Selection of an extractant and diluent for reactive extraction should be on the basis of minimal toxicity and maximum extractive efficiency. Present paper deals with reactive extraction of 2-methylenesuccinic acid using tri-n-butyl phosphate in natural non-toxic sesame oil. Results were presented in terms of effect of dose of extractant, distribution coefficients, loading ratio and degree of extraction. Both physical and chemical extraction methods were studied and the better performances of extractant-diluent combination over the diluent alone were observed.

**Index Terms**— Itaconic acid, reactive extraction, tri-n-butyl phosphate, sesame oil.

## I. INTRODUCTION

Methylenesuccinic (2- Methylenesuccinic ) acid is one of the most important substances within the group of carboxylic acids. It is derived by conjugation of one of its two acids groups with its methylene. Therefore, it is a functionalized analog of acrylic acid. It can take part in addition polymerization by giving polymers with a lot of free carboxyl groups. Methylenesuccinic acid was synthesized with thermal decomposition of citric acid. It is a white crystalline powder. Methylenesuccinic acid is a naturally occurring compound, non-toxic, and readily biodegradable. It is also called as itaconic as was devised as an anagram of aconitic. Historically, Methylenesuccinic acid was obtained by the distillation of citric acid. Since the 1960s, it is produced industrially by the fermentation of carbohydrates such as glucose using *Aspergillus terreus*. As such, it is a fully sustainable industrial building block. It is primarily used as a co-monomer in the production of acrylonitrile-butadiene-styrene and acrylate latexes with applications in the paper and architectural coating industry.

Due to the rise in petroleum costs, the large-volume production of carboxylic acids by fermentation has been the focus of attention [1-2]. But a major drawback in the use of fermentation to produce these acids is the difficulty in recovery from dilute solutions, in which they are produced. In the fermentation based process, the downstream purification cost i.e. the costs associated with product recovery, concentration, acidification, and purification accounts for 60–70% of the production cost

[3]. Hence there is a need for the economical recovery process of acid from the fermentation broth. Number of methods are available such as adsorption, precipitation, distillation, membranes, ion exchange, dialysis, reactive extraction etc. to recover carboxylic acids from fermentation broths or aqueous streams. However, there are certain disadvantages to some of the methods. Calcium hydroxide precipitation has few shortcomings like consumption of large quantities of reagents (H<sub>2</sub>SO<sub>4</sub> and lime), huge amount of waste generation per ton of acid produced, disposal problem of waste and very poor sustainability. Dialysis has good potential but has drawbacks of frequent cleaning requirement, membrane fouling and requirement of larger dialysis unit as compared to 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 huge waste generation. Distillation method is a well-established technology, but its drawbacks are formation of high-boiling internal esters, dimers and consume more power [4-9]. Reactive extraction uses the reactions between extractants and the materials extracted. Extractants mainly hydrocarbon, phosphorous, and aliphatic amines in the organic phase reacts with the material in the aqueous phase and the reaction complexes thus formed are then solubilized in the organic phase. Increased reactor productivity, use of a high-concentration substrate as the process feed to reduce process wastes and production costs, and ease in reactor pH control without requiring base addition are some of the advantages of reactive extraction process [4].

Since most of extractants are viscous, diluents are dissolved alongwith them to improve their physical properties. Diluent increases the extraction power of extractant by providing the solvation of the extractant – acid complexes formed. Further prevention of third phase formation due to the association of carboxylic acid and extractant can be achieved.

Strongly solvating extractants like Phosphorous-bonded Oxygen Donor Extractants contain a phosphoryl group that is a stronger Lewis base than carbon-bonded oxygen donor extractants which makes it suitable for the extraction of weak acids. The high polarity of the phosphoryl group in tributyl phosphate (TBP) enables it to act as a strong Lewis base and as a result it can form acid base complex when contacted with acid [10-11].

The distribution of Methylsuccinic acid between water and tri-n-butyl phosphate (TBP) dissolved in sesame oil, and a comparison with the extraction capacity of pure diluent alone were studied at isothermal conditions. An effort was made to prove the suitability of sesame oil as a diluent for the extraction of the acid on the basis of comparison of distribution coefficient.

## II. MATERIAL AND METHODS

### 2.1 Materials

TBP (mass fraction of 99 %) (CDH Laboratory Reagent, India), a phosphorus-bonded oxygen donor, is a light colorless liquid with the molar mass of 266.32 g•mol<sup>-1</sup> and density of 0.975 g•cm<sup>-3</sup> is used as an extractant. Methylsuccinic acid was obtained from S.D. Fine Chem Ltd, India. Sesame oil (Agro Tech Foods Ltd, India) was used as diluent. Distilled water obtained from distilled water unit (Remi India Ltd.) was used to prepare the solutions of various concentrations of picolinic acid and nicotinic acid. NaOH (S.D. Fine Chem Ltd, India) used for titration is of laboratory grade. oxalic acid (mass fraction of 99.8 %) was used for the standardization of the NaOH. Phenolphthalein solution (pH range 8.2 to 10.0) was used as an indicator. The initial tri-n-butyl phosphate (TBP) concentrations of (0.732, 1.464 and 2.197) mol•L<sup>-1</sup> and the initial aqueous acid concentration range of (0.01 to 0.25) mol•L<sup>-1</sup> were used. Low concentration was used because picolinic and nicotinic acid concentration in the fermentation broth is not greater than 0.25 mol•L<sup>-1</sup> [1].

### 2.2 Experiments

The extraction experiments were performed using a temperature-controlled reciprocal shaker (Remi Equipment Pvt. Ltd., India) at constant temperature (298 K ± 1 K) and atmospheric pressure. Equal volumes (15 cm<sup>3</sup>) of aqueous (Methylsuccinic acid) and organic phases

were taken in a 100 mL conical flask and were shaken for 12 h. For attaining equilibrium this could be considered as an appropriate time [24]. The mixed phase was then allowed to settle for at least 2 h for the effective phase separation. Aqueous phase pH was measured by a digital pH meter (Model R/594, Superfit, India). It was assumed that there was no change in phase volumes after extraction. Aqueous phase acid concentration was determined by titration with NaOH which was freshly prepared for each titration. Weighing balance of Shimadzu make (Model AW220 with accuracy up to 0.1 mg) was used to weigh the solid NaOH for preparation of NaOH solution. The concentration of acid in organic phase was determined by material balance. To check the consistency of results in both acids, a few experiments were repeated and the results were found within limit of (± 1%).

## III. RESULTS AND DISCUSSION

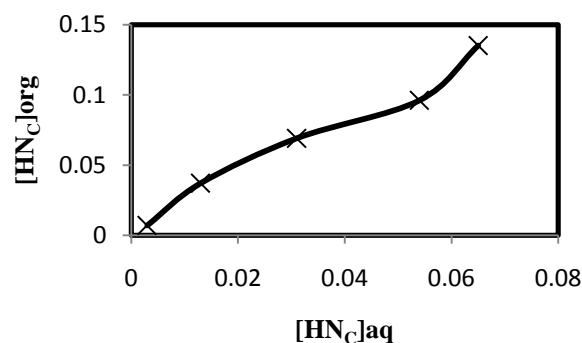
### 3.1 Physical Extraction

Physical extraction was carried out by using Sesame oil by partial dissociation of acid in aqueous phase and dimerization in the diluent phase. The equation for distribution coefficient is given as: it can written in other form as,

$$[\text{HNc}]_{\text{org}} = P [\text{HNc}]_{\text{aq}} + 2P_2D [\text{HNc}]_{\text{aq}}^2$$

where, P = Partition coefficient and D = Dimerization constant

The values of partition coefficient, dimerization constant were obtained from figure 1 and distribution coefficient and degree of extraction were reported in Table 1.



**Fig. 1: Physical equilibria for extraction of Methylsuccinic acid using sesame oil at 298 K.**

Table 1. Partition and Dimerization Coefficients, Distribution Coefficient and Degree of Extraction for Methylsuccinic Acid Extracted from Water into edible oil at 301 K

([HNC]aq initial = 0.01 to 0.20 mol L<sup>-1</sup>)

Diluent	Partition Coefficient(P)	Dimerization Coefficient(D)	Range of K <sub>D</sub>	Average K <sub>D</sub>	Range of %E	Average %E
Sesame oil	0.628	0.489	1.5-3.15	2.8	60-81.12	70.56

### 3.2 Chemical Extraction

Studies on chemical extraction of Methylsuccinic acid using tri-n-butyl phosphate an organophosphorous compound was carried out using the TBP concentration range of 10 & 40 %. Very low solubility in aqueous phase (mass fraction is 0.039 %) and low water coextraction (mass fraction is 4.67 %) are the factors for the selection of tri-n-butyl phosphate. Because of the presence of both electron donor and electron acceptor groups in =PO<sub>4</sub>-grouping, it undergoes specific interactions like self association and molecular complex formation with diluents or other solutes [12]. For the chemical extraction process, distribution coefficient and degree of extraction (E%) was defined as[13]:

$$K_D^{overall} = \frac{[HNp]_{org}}{[HNp]_{aq} + [Np^-]_{aq}}$$

and 
$$E\% = \frac{100 \times K_D^{overall}}{1 + K_D^{overall}}$$

It is observed from figure 2 that the distribution coefficient increases with the increase in the TBP concentration from 10 & 40 % at a fixed concentration of picolinic acid. This shows that TBP is a good extractant for picolinic acid. At higher concentrations of extractant, the viscosity of system increases so high that the non-polar diluent soybean oil may not be able to solvate the complex at higher nicotinic acid concentrations.

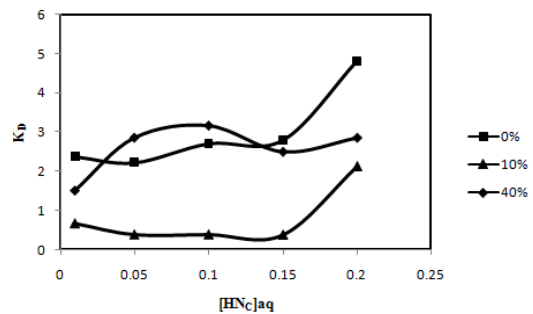


Fig. 2: Chemical extraction of Methylsuccinic acid by sesame oil with TBP. Variation of distribution coefficient (KD) with initial aqueous phase acid concentration.

Loading ratio (z) is expressed as the extent to which the organic phase (TBP + diluent) can be loaded with carboxylic acid. Figure 3 shows the effect of TBP on loading of the extractant (z). From figure 3, it is observed that, loading decreases with increasing TBP concentration for all concentrations of acid in both the acids. The values of loading are relatively low (<0.5) because the non-polar diluents by itself are relatively poor solvating medium for the polar complexes.

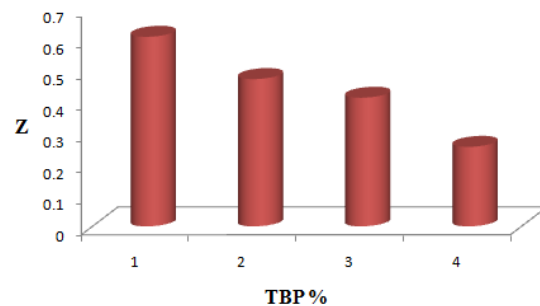


Fig. 3: Plot of loading factor vs TBP concentration for different acids

### IV. CONCLUSION

The extraction of Methylsuccinic acid using TBP in sesame oil was studied. Both physical and chemical extractions were studied and the better performances of extractant-diluent combination over the diluent alone were observed. Different parameters like distribution coefficient increases with increase in concentration, loading ratio decreases with TBP concentration. Since the loading ratio was less than 0.5 in most of the cases, no overloading was obtained and only (1:1) acid - TBP complex was formed.

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