ISSN: 0975-8585

Research Journal of Pharmaceutical, Biological and Chemical Sciences

Recovery Of Itaconic Acid From An Aqueous Solution By Using Chemically Modified Vegetable Oil As Diluent.

Shourabh Singh Raghuwanshi[1], A K Rathore[1], Alok deep[2], and Sunderlal Pal[3]*.

[1]Research Scholar, Department of Chemical Engineering, MANIT Bhopal.
[2]Research Scholar, Department of Chemical Engineering, HBTU Kanpur.
[3]Assistant Professor, Department of Chemical Engineering, MANIT Bhopal.

ABSTRACT

The present work was carried out to study the extraction of itaconic acid with tri-n-butyl phosphate and Tri-n-Octyl amine as extractants dissolved in the laboratory-modified nontoxic diluent. Laboratory-made nontoxic diluent failed to extract any itaconic acid from aqueous solution. The performance of Tri –n-Octyl Amine is much better than Tri Butyl Phosphate. The addition of decanol (modifier) to Tri-n-Octyl Amine increases the recovery of itaconic acid from aqueous solution. The loading factors (Z) of itaconic acid in extractants were also determined and based on the values of Z, it can be concluded that there is a formation of 1:1 complexes between Extractants and Itaconic acid.

Keywords: Tri Butyl Phosphate, Itaconic acid, Laboratory modified diluent, Reactive extraction, Tri-n Octyl Amine

Corresponding author

ISSN: 0975-8585

INTRODUCTION

Itaconic acid (IA) is an unsaturated carboxylic acid (functional analogue of acrylic acid) has two functional carboxyl groups and one carbon-carbon double bond. Due to the presence of these functional groups the itaconic acid can undergo a variety and highly diversified kind of reactions [1]. A lot advancement has taken place in the production of itaconic acid by fermentation in order to create an industry for sustainable development of society by replacing petrochemical-based products with renewable and environmentally friendly chemicals [2]. The methods presently used for separation of products from fermentation broth are inefficient or highly costly; making them uncompetitive with petroleum feedstock. The development of economically viable downstream process is a need of the hour for successful commercialization of fermentation technology [3]. Crystallization and precipitation are mostly used throughout the world for recovery of itaconic acid. However, other recovery methods, such as reactive extraction, electrodialysis, and adsorption are getting upgraded every now and then. These methods will soon become completive with crystallization and precipitation methods making fermentation viable alternative to petroleum-based products. Reactive extraction has the potential to replace crystallization or precipitation only when it is integrated with fermentation broth or in situ extraction. The present work is aimed to analyze the studies for recovery of IA from the fermented broth by using chemically modifying natural edible oil as diluent (in order to reduce the toxicity of extractants.

Simple extraction utilizes organic solvents, such as long chain alcohols, esters and alkanes etc for recovery of itaconic acid but turned out to be ineffective for the recovery of organic acids due to the low distribution coefficient of the itaconic acid and their higher solubility in water than in organic solvents [4]-[6]. The distribution coefficient can be altered by using reactive extractants such as Tri Butyl Phosphate (TBP), Tri-n-Octyl Amine (TOA), Tri Octyl Phosphine Oxide(TOPO) and Aliquat etc. These extractants are capable of reacting with itaconic acid. These extractants form an acid-extractant complex which has a strong affinity for the organic phase. The acid may be recovered from this complex very easily through temperature swing or back extraction with NaOH. The released extractant can be recycled for reuse in another extraction process. Reactive extraction is one of the most promising methods which can compete with the existing methods for recovery of itaconic acid for which on a combination of extractants and diluents. Only those extractants which are thermally stable and have low water solubility should be selected so that they can be recycled again and again. Organophosphorus compounds (TBP, TOPO etc) and aliphatic amines (TOA, THA etc) have been reported as effective extractants for the separation of itaconic acid from aqueous phase [7]-[9]. Matsumoto et al. demonstrated that TOA is more effective extractant than TBP for extraction of itaconic acid when hexane was used as diluent. The literature shows that only Wasewar et al. has studied extraction of itaconic acid using sunflower as the nontoxic diluent and overall very little work is done on the extraction of itaconic acid. Recently researchers [10]-[17] have focused their attention towards using vegetable oils as the diluent in order to decrease toxicity. The results can be useful in designing a new integrated system for extraction of itaconic acid for in-situ recovery from fermentation broth without harming microorganisms.

EXPERIMENTAL SECTION

Materials Procured

All the experiments were carried out with chemicals as supplied by the vendors without any kind of treatment and solutions were prepared using de-ionized water. Itaconic acid was supplied by Thomas Baker. Extractants Tri-n-butyl phosphate (TBP) and Tri Octyl Amine were supplied by SRL Pvt. Limited through a local vendor. The nontoxic natural diluent was prepared from vegetable oil by applying a chemical process in the lab. A solution of phenolphthalein was used as an indicator. A freshly prepared NaOH was used to determine aqueous phase acid concentration each time and was standardized with 0.1 N Oxalic acid before use. The acid content of organic phase is determined by mass balance.

Experimental setup used and Procedure

Initially, a stock solution of concentration 0.5 kmols/m^3 of itaconic was prepared using de-ionized water and then diluted to desired concentrations were prepared by diluting the stock solution. The extractants TBP and TOA were dissolved in the natural non-toxic diluent. The solutions of 10%-40% by volume of extractants were prepared. An equal volume of aqueous and organic solutions was taken in 250 ml conical

flasks. These flasks were shaken in the Orbital shaking incubator at 25^{O}C and at 150 rpm for 16 hours. Next, the phases were separated with the help of Centrifuge (Make: REMI) by operating it at 10,000 rpm for 10 minutes. Only a few runs were duplicated to check the reproducibility of the data and were observed to be ±2% of accuracy.

Theory:

Reactive extraction:

Weak carboxylic acid dissociates in aqueous solution to some extent but when the pH of the aqueous solution is smaller than p*K*a of the acid, the effect of the acid dissociation is neglected. The following equation can be used to describe the extraction of the carboxylic acid by extractants in the laboratory made non-toxic diluent [19].

$$[HA]_{aq} + p[E]_{org} \underset{<}{\overset{K_E}{\rightleftharpoons}}{}_{>} [HA.(E)_p]_{org} \quad (1)$$

From the law of mass action, the general equation of interaction between the extractant and the extracted species to Extraction equilibrium constant (K_E) can be written as:

$$K_E = [(HA).(E)_p]_{org} / [HA]_{aq} [E]^p_{org} \quad (2)$$

K_E strongly depends on properties of acids and the solvation capacity of the diluent used. At pH below pKa, an undissociated form of acid is only extracted so the extraction process can be analyzed by means of the distribution coefficient (K_D).

The Overall degree of extraction (E %) in terms of distribution coefficient is calculated as given below:

$$\% E = K_D \times 100 / (1 + K_D) \quad (3)$$

Loading Ratios:

Loading ratio (Z) represents the extent of loading of the organic phase (extractant + diluent) with carboxylic acid and is given below as:

$$Z = \frac{[HA]_{org}}{[E]} \quad (4)$$

The values of the loading ratio model predict the nature of complexes. The various types of complexes (1:1, 2:1 and 3:1) between acid and extractant can be formed. For low values of Z< 0.5, a complex of (1:1) is formed but at higher values of Z> 0.5,(1:2 and 1:3) complexes are formed.

RESULTS AND DISCUSSIONS

Physical Extraction:

When the experiments with pure laboratory made diluent (chemically modified vegetable oil) and were performed. The modified oil could not extract any amount of itaconic acid from the aqueous phase. This is due to very weak interactions between itaconic acid and oil. The addition of extractants to the modified oil is necessary to recover itaconic acid.

ISSN: 0975-8585

Reactive Extraction:

Effect of TBP Extractant Concentration on the recovery of itaconic acid:

The recovery of itaconic acid from aqueous solution in the modified nontoxic diluent solely depends on the ability of extractant to form a complex as diluent failed to capture any itaconic acid from aqueous solution (physical extraction). Although the performance of TBP in extracting is not great as reported in the literature for hexane, the TBP is still used as an extractant in order to check the performance in the new modified nontoxic diluent. The average extraction efficiency increases from 7.06% to 74.69% with the increase in TBP extractant from 10% to 70%. Researchers have suggested limiting the percentage of TBP up to 30% due to viscosity issues. The average extraction with 30%TBP is only 52.47%.

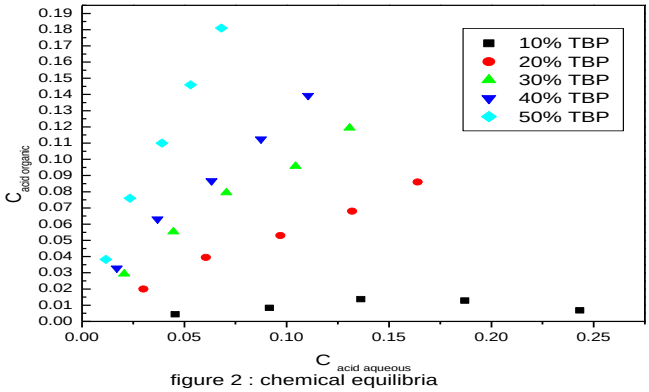

figure 2 : chemical equilibria

Recovery of itaconic acid with and without a modifier (Octanol) in TOA:

The TOA is most preferred extractant among researchers for extraction of itaconic acid as there is a huge difference in the percentage recovery over TBP. The chemical equilibria obtained also verify this trend in the new modified nontoxic diluent for the same percentage of TBP. The average extraction efficiency increases from 61.95 % to 86.27% with the increase in TOA extractant from 10% to 30%. It is also reported in the literature that higher alcohols such as octanol, decanol etc, when added to TOA, enhances the recovery of acids and a mixture of decanol and dodecane is often regarded as biocompatible. When a 30%(by volume) of decanol was added to a solution of 30% TOA in a modified nontoxic diluent, the extraction efficiency increased to 94.474%.

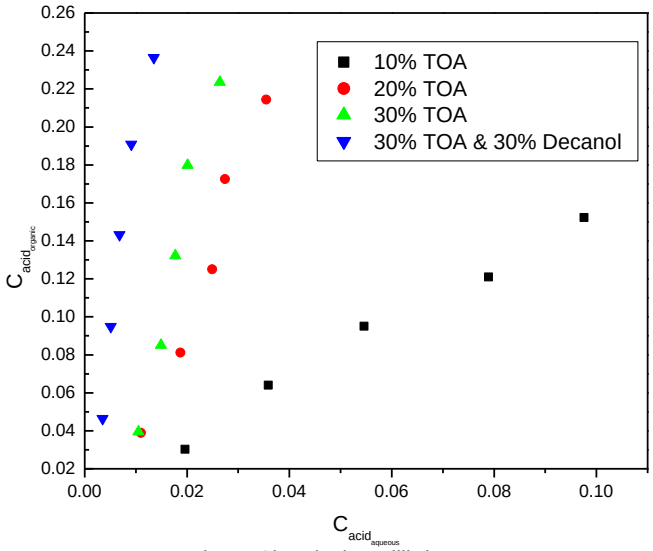

Figure:Chemical Equilibria

Loading Ratio (Z): The values of loading factor Z for 10-50% of TBP is lower than 0.1 indicating a formation of 1:1 complex of acid and TBP. The values of loading factor are smaller than 0.5 (except for 30% TOA and initial acid concentration 0.23 kmol/ m^3, where Z=0.525) for all acid concentration indicating a formation of 1:1 complex of acid and TOA. The loading values for TOA are much higher than TBP, so we can conclude that the TOA is more effective in extracting itaconic acid from aqueous solution.

CONCLUSIONS

In this study, chemically modified nontoxic diluent with TBP and TOA was evaluated for use in recovering itaconic acid by reactive extraction in order to replace organic solvents (diluents).For the concentration of the reactants in the diluent; TOA outperforms TBP as extractant as reported in the literature. The recovery of itaconic acid reached 94.7% when 30% decanol is added to 30% TOA-laboratory made diluent. The addition of decanol influences the polarity of organic phase resulting in better solvation complex of acid and amine. As the values of loading ratios are less than 0.5, 1:1 acid-amine complexes formation is proposed.

Symbols used:

[E] = concentration of extractant inorganic phase (kmol/m^3)
[HA] = acid concentration, (kmol/m^3)
(K_E)=Extraction equilibrium constant
E% =degree of extraction
K_D = distribution coefficient of acid in the organic phase
Z= loading ratio

SUBSCRIPTS

aq	=	aqueous phase
org	=	organic phase

REFERENCES

[1] Kuenz A, Gallenmüller Y, Willke T, Vorlop KD. *Microbial production of itaconic acid: developing a stable platform for high product concentrations. Appl. Microbiol. Biotechnol,*2012*, 96* 1209–1216

[2] Willke T, Vorlop KD. Biotechnological production of itaconic acid, Appl. Microbiol Biotechnol, 2001,56(3-4),289-95.

[3] Garzon L, Straathof CS, A. J., , Recovery of Carboxylic Acids Produced by Fermentation, Biotechnology Advances, 2014,32 (5), pp. 873-904.

[4] Wasewar KL, Shende D, Keshav A. Reactive extraction of itaconic acid using quaternary amine Aliquat 336 in ethyl acetate, toluene, hexane, and kerosene, Industrial & Engineering Chemistry Research, 2011,50, pp.1003-1011.

[5] Wasewar KL, Shende D, Keshav A. Reactive extraction of itaconic acid using tri-n-butyl phosphate and Aliquat 336 in sunflower oil as a non-toxic diluent, Journal of Chemical Technology and Biotechnology, 2011, 86, pp. 319-323.

[6] Kaur G, Elst K. Development of reactive extraction systems for itaconic acid: a step towards in situ product recovery for itaconic acid fermentation, RSC Advances, ,2014, 4, pp. 45029-45039.

[7] Hano T, Matsumoto M, Ohtake T, Sasaki K, Hori F, Kawano Y. Extraction equilibria of organic acids with tri-n-octylphosphineoxide, Journal of Chemical Engineering of Japan, 1990, 6, pp. 734-738.

[8] Bressler E , Braun S. Separation mechanisms of citric and itaconic acids by water-immiscible amines, Journal of Chemical Technology and Biotechnology, 1999,74,pp. 891-896.

[9] Matsumoto M, Otono T, Kondo K. Synergistic extraction of organic acids with tri-n-octylamine and tri-n-butylphosphate , Separation and Purification Technology, 2001,24 , pp. 337-342.

[10] Harington T, Hossain Md M. Extraction of lactic acid into sunflower oil and its recovery into an aqueous solution, Desalination , 2008, 218 , pp. 287-296.

[11] Uslu H, Gemici A, Gok A , Kirbaslar I. Reactive extraction of (E)-butenedioic acid (fumaric acid) by nontoxic diluents, J Chem Eng Data, 2014 ,59, pp. 3767-3772.

[12] Keshav A, Wasewar KL, Chand S. Reactive Extraction of Propionic Acid using Tri-n-Octylamine, Tri-n-butyl Phosphate and Aliquat 336 in Sunflower Oil as Diluent", Journal of Chemical Technology and Biotechnology, 2009, 84 (4), pp. 484-489.

[13] Keshav A, Norge P, Wasewar KL. Reactive Extraction of Citric Acid Using Tri-n-octylamine in Nontoxic Natural Diluents: Part 1—Equilibrium Studies from Aqueous Solutions", Applied Biochemistry and Biotechnology, 2012, 167 (2), pp. 197–213.
[14] Waghmare MD, Wasewar KL, Sonawane SS, Shende D Z. Natural Nontoxic Solvents for Recovery of Picolinic Acid by Reactive Extraction, Industrial and Engineering Chemistry Research, 2011, 50 (23), pp. 13526–13537.
[15] Waghmare MD, Wasewar K L, Sonawane SS, Shende DZ. Reactive Extraction of Picolinic and Nicotinic Acid by Natural Non-toxic Solvent, Separation and Purification Technology, 2013 , 120, pp. 296-303.
[16] Mustafa EM. Recovery of formic acid by reactive extraction using an environmentally friendly solvent, SUJEST, 2017,5(1), 2017
[17] Kar A, Bagde A, Athankar KK, Wasewar KL, Shende DZ. Reactive Extraction of Acrylic Acid with Tri-n-Butyl Phosphate in Natural Oils, Journal of Chemical Technology and Biotechnology, 2017, 92 (11), pp. 2825-2834.
[18] Pal SL , Shende DZ , Shahida A , Rathore AK. Reactive Extraction of Itaconic Acid using Tri –n-Butyl Phosphate in 1-Butanol, 1-Octanol and 1-Dodecanol ,IJIRSET , 2016,5(2).
[19] Kertes AS, King CJ. Extraction chemistry of fermentation product carboxylic acids, Biotechnol. Bioeng, 1986,28, pp. 269–282.