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Recovery of Glutaric acid by Reactive Extraction using Tri-n-Octylamine in Different Biodiesels

SHOURABH SINGH RAGHUWANSHI[1*], ASHWANI KUMAR RATHORE[1] and SUNDER LAL PAL[2]

[1]Chemical Engineering Department, MANIT Bhopal, India.
[2]Chemical Engineering Department, MANIT Bhopal, India.
*Corresponding author E-mail: shourabh.raghuwanshi@gmail.com

ABSTRACT

This paper is aimed to recover glutaric acid from aqueous solution by using Tri-n-octyl amine in different biodiesels through an experimental investigation by reactive extraction. Here glutaric is extracted by reversible complexion reaction with tri-n-octylamine extractant present in three types of biodiesel-sunflower, sesame and rice bran. The distribution coefficients (K_D) for experimental investigation system comes out to be (9.38-25.37) for sunflower biodiesel, (9.61-30.88) for sesame biodiesel and (10.62-29.92) rice bran diesel. The determined loading ratios (Ø) were in the range (0.27-4.05) for sunflower biodiesel, (0.27-4.02) for sesame biodiesel and (0.27-4.05) rice bran biodiesel, indicating overloading of the extractant. A very high average extraction efficiency (%E) is in the range of (90.36-96.20) for sunflower biodiesel, (90.57-96.86) for sesame biodiesel and (91.40-96.30) rice bran biodiesel) were obtained in the present investigation.

Keywords: Glutaric acid, Reactive extraction, Batch Process, Diluent, Extractant.

INTRODUCTION

Glutaric acid is a five-carbon chained naturally occurring white crystalline dicarboxylic acid with pKa1=4.31 and pKa2=5.41. It is also a part of blood and urine. It is used in the production of polyester, polyols, polyamides, ester plasticizers, and corrosion inhibitors as well as for the synthesis of pharmaceuticals, surfactants, and metal finishing compounds. Industrially it is produced through the ring-opening of butyrolactone followed by hydrolysis, and biologically through microorganisms via lysine degradation[1-2]. The produced glutaric acid needs to be recovered from fermentation broth without killing the microbes. Precipitation is one of the most preferred method for its extraction but has a problem of generated salt disposal. Reactive extraction has shown a lot of promise in separating carboxylic acid from the fermentation broth or wastewater streams[3-4]. Reactive extraction makes use of toxic extractants and diluents to get high extraction efficiency so it cannot be used for *in-situ* extraction, so there is a need and scope to develop a nontoxic system for recovery of glutaric acid. One of the way for reducing the toxicity of solvent(extractant+diluent) is to use nontoxic diluent to avoid direct contact

of extractant and microorganisms. is prevented. Recently a lot of work is available in the literature involving vegetable oils as diluents for the recovery of carboxylic acids using high molecular weight amines or organophosphorus compounds(extractants) but no work is done on the separation of glutaric acid using natural oils[5-13]. The current study focuses on glutaric acid recovery usingtri-n-octylamine extractant in biodiesels (diluent) to explore the extraction feasibility.

MATERIALS AND METHODS

Chemicals and Reagents

Glutaric acid (GA) (Assay > 0.99%) and Tri-n-octylamine (TOA) (Assay > 0.95%) were supplied by Sisco Research Laboratories Pvt. Ltd., Mumbai, Maharashtra, Biodiesels (sunflower oil, sesame oil and rice bran oil) were supplied by a local vendor at Bhopal. Phenolphthalein indicator (pH 8.2–10.0) was supplied by Merck & Co life science Pvt. Ltd., Mumbai, India. The sodium hydroxide used in the experiments was of reagent grade, and 0.1 N solution was prepared by dissolving an appropriate amount in de-ionized water. All the chemicals were used without further purification. De-ionized (DI) water was used for all the experiments and standardization of sodium oxide was done by 0.1N oxalic acid.

METHOD

The extraction experiments were performed by pouringequal volumes of aqueous and organic phases in a conical flask and then shaking at a temperature of 298K in microprocessor controlled shaking incubator. The mixture was shaken for 12 h and then centrifuged at 6000 rpm for 20 minutes to separate the two different phases. Organic phase being lighter is at the top of the aqueous phase. Aqueous phase acid concentration was determined by titration with 1 N NaOH solution after standardization. The acid content in the organic phase was determined by a mass balance.

Theory of Reactive extraction

The dissociation of weak carboxylic acidslike glutaric acid is generallyneglected as it is very small for weak acid. The reactive extraction of the glutaric acid by TOA extractant can be represented as given in equation (1)[14].

$$m[GH]_{aq} + p[TOA]_{org} \underset{<\ K_s\ >}{} [(GH) m.(TOA)_p]_{org} \quad (1)$$

By the law of mass action, an interaction between the extractant and the extracted species to Extraction equilibrium constant (K_s) can be written as:

$$K_s = [(GH)_m.(TOA)_p]_{org}./H]^m{}_{aq}.OA]^p{}_{org}. \quad (2)$$

Where $[GH]_{aq}$ represents glutaric acid (concentration) in the aqueous phase and $[TOA]_{org}.$, $[(GH)m.(TOA)_p]_{org}$ or $[GH]_{org}$ represents concentration of extractants and acid complex in the organic phase and K_s depends upon properties of acids and the solvation(dissolving capacity) of the diluent used.

The extractionefficiency (%E) is defined by following experimentally measured distribution coefficient (K_D) as:

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

Prediction of Models of complexes based on Ø values

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

$$\varnothing = \frac{[GH]org}{[TOA]} \quad (4)$$

The loading ratio (Ø) can be used to predict the nature of various types of complexes between acid and extractant that can be formed. The possible forms of complexes are (1:1, 2:1 and 3:1) and all depends on the values of Ø. At low values of Ø< 0.5, (1:1) complex is formed. For higher values of Ø> 0.5, the formation of (1:2 and 1:3) complexes is a possibility.

RESULTS AND DISCUSSION

The recovery of glutaric acid from the aqueous solution so far has been studied by using three extractants [Tri-n-octyl amine(TOA), Tri butyl phosphate (TBP) and Tridodecylamine (TDDA)] in various diluents. The TOA was chosen for the present studies due to high reactivity and easy availability at low cost. The biodiesels were used in the study as they are nontoxic and has better flow properties as compared to vegetable oils. Tri-n-octylamine was added to the biodiesel oils to resolve the toxicity

issues which is preventing *in-situ* extraction of it from a fermentation broth.

Experiments were performed to extract Glutaric acid by varyinginitial acid concentration and concentration of TOA in biodiesels. The results obtained are given in Tables 1-3, and the chemical equilibrium of extraction of glutaric acid using TOA(Tri-n-Octylamine) in biodiesels of sunflower oil, sesame oil and rice bran oilrespectively are shown in Fig. 1 – 3. It can be seen that the addition of 10%-30% TOA in sunflower oil biodiesels has a favorable effect on the degree of extraction (E%). The average degree of extraction reaches 91.68%(10% TOA)-95.50% (30% TOA) in sunflower oil biodiesel,

91.19%-10% TOA)-96.35% (30% TOA) in sesame oil biodiesel and 92.00%-10% TOA)-96.30% (30% TOA) in rice bran oil biodiesel. This increase in E% clearly suggests that extractant is highly efficient and diluent is also compatible for extraction (as it is readily solvating the complex formed in the reaction).

The average distribution coefficient also changes from 11.12 (10% TOA)-21.88 (30% TOA) in sunflower oil biodiesel, 10.4 (10% TOA)- 26.83 (30% TOA) in sesame oil biodiesel and 11.48(10% TOA)- 26.14 (30% TOA) in rice bran oil biodiesel. The average distribution coefficient increases with TOA is in the following order sesame oil biodiesel > rice bran oil biodiesel >sunflower oil biodiesel.

Table 1: Extraction equilibrium of glutaric acid and TOA in sunflower oil at 298 K

TOA(v/v%)	$[GH]_{INI}$.mol/litre	$[GH]_{aq}$.	$[GH]_{org}$	$KD=[GH.]_{org}./[GH]_{aq}$.	Ave. K_D	$E\%=K_D/1+K_D*100$	Ave. E%	Ø
10	0.2	0.01926	0.18073	9.38	11.12	90.36	91.68	0.7926
10	0.4	0.03371	0.36629	10.86		91.56		1.6065
10	0.6	0.04816	0.55184	11.45		91.96		2.4203
10	0.8	0.06381	0.73618	11.53		92.01		3.2288
10	1	0.07464	0.92535	12.39		92.53		4.0585
20	0.2	0.01384	0.18616	13.45	15.00	93.07	93.72	0.4064
20	0.4	0.02528	0.37472	14.82		93.67		0.8181
20	0.6	0.03708	0.56292	15.18		93.81		1.2290
20	0.8	0.04816	0.75184	15.61		93.97		1.6415
20	1	0.05899	0.94100	15.95		94.10		2.0545
30	0.2	0.01161	0.18839	16.22	21.88	94.19	95.50	0.2746
30	0.4	0.01962	0.38038	19.38		95.09		0.5544
30	0.6	0.02383	0.57617	24.17		96.02		0.8398
30	0.8	0.03166	0.76834	24.26		96.04		1.1200
30	1	0.03792	0.96204	25.37		96.20		1.4023

Table 2: Extraction equilibrium of glutaric acid and TOA in Sesame oil at 298 K

| TOA(v/v%)	$[GH]_{INI}$.mol/liter	$[GH]^{aq}$.	$[GH]_{org}$	$K_D=[GH]_{org}./[GH]_{aq}$.	Ave. K_D	$E\%=K_D/1+K_D*100$	Ave. E%	Ø
10	0.2	0.01884	0.18116	9.61	10.40	90.57	91.19	0.7945
10	0.4	0.03708	0.36292	9.78		90.72		1.5917
10	0.6	0.05315	0.54685	10.28		91.13		2.3984
10	0.8	0.06622	0.73378	11.08		91.72		3.2183
10	1	0.08145	0.91855	11.27		91.85		4.0287
20	0.2	0.01384	0.18616	13.45	17.93	93.07	94.56	0.4064
20	0.4	0.02383	0.37617	15.78		94.04		0.8213
20	0.6	0.03226	0.56774	17.59		94.62		1.2396
20	0.8	0.03612	0.76388	21.14		95.48		1.6678
20	1	0.04406	0.95593	21.69		95.59		2.0871
30	0.2	0.00842	0.19157	22.75	26.83	95.78	96.35	0.2792
30	0.4	0.01565	0.38434	24.55		96.08		0.5602
30	0.6	0.02185	0.57815	26.45		96.35		0.8427
30	0.8	0.02618	0.77382	29.55		96.72		1.1280
30	1	0.03136	0.96864	30.88		96.86		1.4120

Table 3: Extraction equilibrium results for glutaric acid and TOA in Bice bran oil at 298 K

| TOA(v/v%)	$[GH]_{INI}$.mol/liter	$[GH]_{aq.}$	$[GH]_{org}$	$K_D=[GH.]_{org.}/[GH]_{aq.}$	Ave. K_D	E%=$K_D/1+K_D$*100	Ave. E%	Ø
10	0.2	0.01721	0.18278	10.62	11.48	91.40	92.00	0.8016
10	0.4	0.03311	0.36689	11.08		91.72		1.6091
10	0.6	0.04816	0.55184	11.45		92.03		2.4203
10	0.8	0.06146	0.73853	12.01		92.36		3.2391
10	1	0.07525	0.92475	12.28		92.53		4.0559
20	0.2	0.01193	0.18806	15.76	18.16	94.03	94.73	0.4106
20	0.4	0.02252	0.37747	16.76		94.38		0.8241
20	0.6	0.03369	0.56630	16.80		94.43		1.2364
20	0.8	0.03704	0.76295	20.59		95.40		1.6658
20	1	0.04562	0.95437	20.92		95.43		2.0837
30	0.2	0.00823	0.19176	23.30	26.14	95.88	96.30	0.2795
30	0.4	0.01587	0.38412	24.20		96.04		0.5599
30	0.6	0.02210	0.57789	26.14		96.34		0.8424
30	0.8	0.02822	0.77177	27.34		96.50		1.1250
30	1	0.03234	0.96766	29.92		96.77		1.4105

Effect of Extractant on initial acid concentration for Reactive Extraction of glutaric acid

Table 1-3 gives the values of extraction efficiency (%E) for the reactive extraction by TOA in biodiesel oils for acid concentrations (0.2,0.4,0.6,0.8 and 1 mols/liter). It is found that the extraction efficiency increases with the increase in TOA concentration for all biodiesel oils at all initial acid concentrations but the increase in efficiency is not large as compared with the increase in the percentage of the extractant. One of the reasons may be due to poor solvation of complex in the diluent.
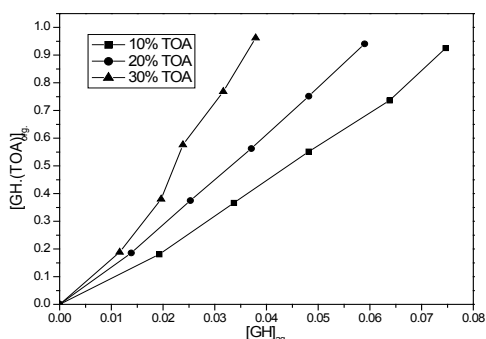
Fig. 1. Chemical equilibrium data of glutaric acid and TOA in sunflower oil
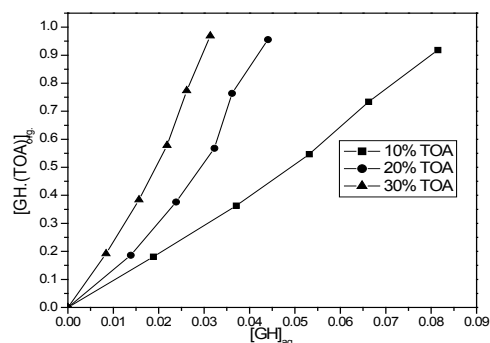
Fig. 2. Chemical equilibrium data of Glutaric acid and TOA in Sesame oil
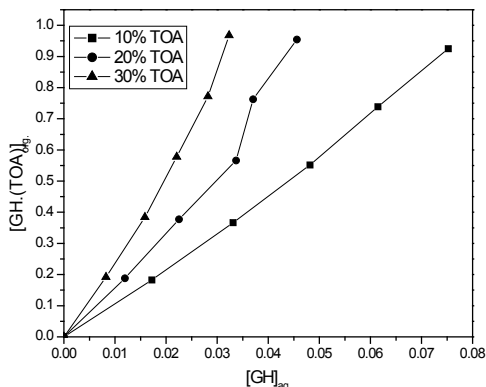
Fig. 3. Chemical equilibrium data of glutaric acid and TOA in Bice bran oil

Extraction mechanism based on loading values (Ø)

The loading values were found to decrease with the increase in TOA percentage indicating limiting amount of extractant available in the batch extraction system resulted in the overloading of acid molecules. Table 1- 3 and Fig. 4-6 shows the effect of loading of the extractant (Z) with the increase in TOA concentration. It is also worth noting that loading values decrease with the increase in TOA concentration for all initial acid concentrations in biodiesel oils. There is a decrease in the values of loading factor decreases due to increase in extractant concentration as now more acid is available for a reaction with acid molecules and but poor solvating resulting in the marginal increase in extraction efficiency.
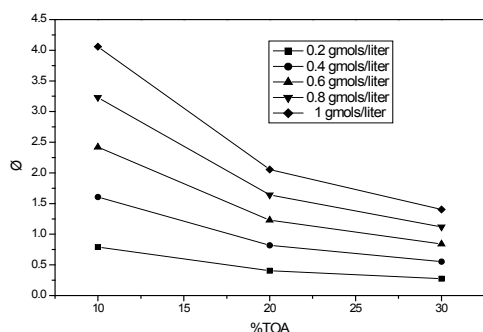
Fig. 4. Loading ratios (Ø) for the reactive extraction of glutaric acid using sunflower oil biodiesel

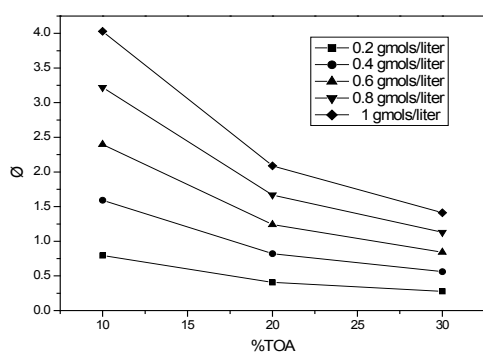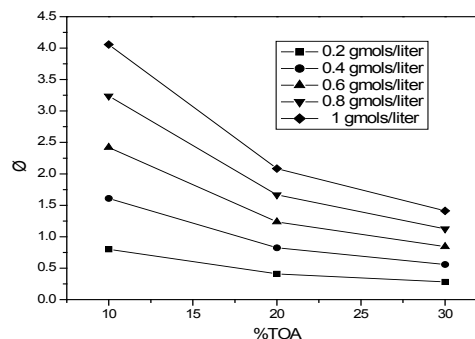**Fig. 6. Loading ratios (Ø) for the reactive extraction of glutaric acid using rice bran oil biodiesel**

Fig. 5. Loading ratios(Ø) for the reactive extraction of glutaric acid using sesame oil biodiesel

sunflower, rice bran and sesame was investigated. The distribution coefficients(K_D), loading factors (Ø), and extraction efficiencies (%E) were obtained for this batch extraction system. The extraction efficiencies obtained by the system of TOA in biodiesels for the extraction of glutaric acid are highest as per values available in the literature. The loading values were higher than 0.5 indicating the formation of higher complexes.

CONCLUSION

The reactive extraction of glutaric acid by using TOA dissolved in biodiesels made from oils of

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Conflict of Interest

The authors declared no competing financial interest.

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