Liquid-Liquid Extraction of Itaconic Acid from the Aqueous Phase Using Natural and Chemical Solvents

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Abstract

Itaconic acid, also known as methylene succinic acid, is a colorless, crystalline substance that is found in nature. Due to its two functional carboxylic acid forms and - unsaturated bond, it can be used in a variety of sectors (plastics, super-absorbents, biopolymers, anti-scaling agents, etc.). Itaconic acid can be produced via thermally decarboxylating citric acid, catalysing the condensation of succinic acid derivatives with formaldehyde, decarboxylating aconitic acid, and fermentation utilizing Aspergillus terreus and other microbes. It is quite expensive and harmful to extract itaconic acid from the fermentation broth. In the present study, Iso-butanol, iso-octanol, groundnut, soybean, mustard, and rice bran oil were incorporated as solvents for separating itaconic acid from their solutions in distilled water. Liquid-liquid extraction experiments were conducted over the range of 0.08-0.533 mol.L-1 of itaconic acid. The results thus obtained were defined as the separation efficiency (E) and distribution coefficient (K_D). Separation was observed at maximum efficiencies of 69.33%, 47.8%, 12.93%, 17.9%, 15.625% & 14.18% with iso-butanol, iso-octanol groundnut, soybean, mustard, and rice bran oil respectively. Since the solvents used in this study were natural and chemical, it can be helpful to make the process more eco-friendly and the efficiency of the process can be further increased with the help of reactive extractants.

Keywords: *Itaconic acid, Solvents, Distribution coefficient, Organic phase, Aqueous phase, Separation efficiency*

1. Introduction

Since many years ago, petrochemical feedstock has been the main source of organic compounds. But given the impending shortage of fossil fuels, this will be a significant problem in the years to come. An alternative source of chemicals that is mostly renewable, i.e., agricultural waste, feedstock, and waste matter from food processing, is being considered as a better, more sustainable approach towards industrial chemical synthesis [1-3].

Itaconic acid (IA), also known as methylene succinic acid, is a colorless, crystalline substance that naturally exists. Its molar weight is 130.1 g/mol. Due to its two functional carboxylic acid forms and unsaturated link, it can be used to create a variety of polymers [4-6]. It is frequently utilised as an alternative to acrylic acid [7]. A few itaconic acid-derived polymers are styrene butadiene itaconic acid, polytechnic acid, and methyl methacrylate [8]. These chemicals are used as raw materials for various

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products, such as SBR latex, synthetic latex, and cooling dispersants. Plastics, super-absorbents, and anti-scaling agents are a few other widely used applications. The ecologically friendly synthesis of biopolymers is one of the most significant applications for this monomer [9]. In the industrial manufacturing of resins, polymers, antimicrobials, biocides, buffering agents, emollients, skin conditioners, and softeners, it has a wide range of applications. Industrial uses of itaconic acid include adhesives and sealant chemicals, non-pesticidal agricultural chemicals, paint additives, and coating additives that are not described by other categories, along with plasticizers. [10,11]

The market demand for itaconic acid comes primarily from pharmaceuticals, agriculture, and the light industry. As mentioned earlier, it is used for the manufacture of SBR latex for use in the construction industry for bonding cement layers, mortar, and concrete and to improve chemical resistance and bond. Since it is used in construction, paints, and coatings, the itaconic acid market is expected to rise significantly as far as the growth of the construction industry is concerned. It is also a highly suitable solvent for cosmetics, and hence, the increasing demand for cosmetics is also one of the factors for growth. Despite all these applications, the cost of itaconic acid is higher than its counterparts, and this is one of the market restraints. The availability of substrates required for the fermentation process is one of the major challenges in the production process, as there is increasing demand for sugars and molasses from the food and drink industry and biofuels.

The itaconic acid market size in China is expected to exceed 21 million U.S. dollars in valuation by the year 2025, according to a report. Asia-Pacific is the leading producer and consumer, supplying more than 54% of the global demand for itaconic acid. Itaconic acid was thought to have a market value of nearly $4 million in Germany by 2020. [12] The market for itaconic acid has been stable for the last decades, with production estimated at around 40,000 tons/year and an installed capacity of 70 to 80,000 tons/year [13]. Many companies are producing IA, most in China, and some in the US working mainly with speciality derivatives of IA.

Thermal decarboxylation of citric acid was the first method for itaconic acid synthesis performed in 1837 [14]. It can also be synthesized by the catalysed condensation of the derivatives of succinic acid using formaldehyde. Alternatively, the decarboxylation of aconitic acid also produces itaconic acid. Fermentation using bacteria such as Aspergillus terreus is considered better than other methods of synthesis [15].

For the manufacture of a variety of carboxylic acids, including propionic acid, lactic acid, acetic acid, and citric acid, fermentation provides a significant alternative to the petrochemical route. The difficulty in recovering from diluted solutions, where they are created, is a barrier to using fermentation to produce these acids. The fundamental issue with fermentation technology is that it causes the pH of the system to decrease as acid is produced. The bacteria that are responsible for growth are eliminated by lowering the pH. As a result, a high concentration of acid is produced [16]. Sugars and molasses are used as the substrates for fermentation using producer microorganisms for itaconic acid, namely Ustilago, Pseudozyma, and importantly, Aspergillus; A. terreus being the primary commercial producer.

The fermentation broth contains itaconic acid in considerable amounts and thus it needs to be extracted to make the production process feasible. Itaconic acid can be separated using some techniques, including crystallisation, extraction, precipitation, electrodialysis, diafiltration, and adsorption. Since these methods are costly compared to the liquid-liquid extraction for the separation of itaconic acid from the fermented broth, there is a need for a low-cost and safe method for separating the itaconic acid from downstream. Liquid-liquid extraction or solvent extraction is a simple, low-cost, and environment-friendly method for the recovery of carboxylic acids. Liquid-liquid extraction method can be used as recovery steps when coupled to fermentation and help in potentially increasing the overall extraction yield. Some authors studied liquid-liquid extraction with natural solvents for the recovery of carboxylic acid like succinic acid, lactic acid, glutaric acid, levulinic acid, etc. from the aqueous phase [17-22]. A few authors also studied on separation of itaconic acid using liquid-liquid extraction methods without

any extractants from the fermentation broth and aqueous phase (Table 1). In Wasewar et al.'s (2011) study they obtained higher extraction efficiency at 45.33 and 20.66 with ethyl acetate and sunflower oil, while in the present study, extraction efficiency was obtained at 69.48 and 17.90 with iso-butanol and soybean oil respectively.

Table 1. Separation of itaconic acid using a liquid-liquid extraction process.

Solvents	Distribution coefficient (K_D)	Extraction efficiency (E%)	References
Sunflower oil	0.26	20.66	[23]
Ethyl Acetate	0.82	45.33	
Kerosene	0.06	5.71	[24]
Toluene	0.209	17.33	
Hexane	0.234	19	
Rice bran oil	0.17	14.18	
Soybean oil	0.22	17.90	
Groundnut oil	0.15	12.93	Present
Mustard oil	0.18	15.48	study
Iso-butanol	2.28	69.48	
Iso-octanol	0.91	47.62	

The present study used a liquid-liquid extraction method with various natural and chemical solvents like rice bran oil, soybean oil, groundnut oil, mustard oil, iso-butanol, and iso-octanol for the separation of itaconic acid from an aqueous phase. The experimental results were defined in the form of important parameters: distribution coefficient and extraction efficiency. The natural solvents were used in this study for decreasing toxicity and building an environment-friendly path during the separation of itaconic acid.

2. Materials and method

2.1 Materials

The chemical details like name, properties, and supplier are listed in Table 2. Without any pretreatment, all listed chemicals were utilised in the experimental study.

Table 2. The following chemicals were used in the experimental study

Chemicals	Purity (%)	MW ($g.mol^{-1}$)	S_{water} (g/L)	Viscosity (Pa s)	P (kg/m^3)	Supplier
Itaconic acid	99	130.099	83.33	_	1.632	Himedia Pvt. Ltd.

Rice bran oil	-	368.34	Immiscible	5.93×10^{-2}	916	Patanjali Ayurveda Ltd
Soybean oil	-	138.12	Immiscible	3.86×10^{-2}	919	Patanjali Ayurveda Ltd
Groundnut oil	-	611.7	Immiscible	4.56×10^{-2}	912	Patanjali Ayurveda Ltd
Iso-butanol	99	74.122	Immiscible	3.95×10^{-2}	802	Merck Specialties Pvt. Ltd
Iso-octanol	99	130.23	Immiscible	10.6×10^{-2}	832	Lobachemie Pvt. Ltd
Mustard oil	-	99.154	Immiscible	6.34×10^{-4}	925	Dabur, India

MW = molecular weight, S_{water} = solubility in water, ρ = density

2.2 Experimental method

Aqueous solutions of itaconic acids were prepared by mixing measured quantities of the acid (amorphous) in distilled water. There were a total of five such solutions with concentrations ranging from (0.08–0.533 mol.L^{-1}). The concentrations were checked by titrating it against NaOH solution of concentration 0.1 N and using a phenolphthalein indicator. Conical flasks were filled with equal volumes of IA (the aqueous phase) and the specific solvent (the organic phase) and then placed in an orbital incubator (Model: S-24BL, REMI India) for physical extraction after the actual concentrations were measured. Samples were fully mixed for 4 hours at a constant temperature of 298.15 K with the incubator set to 200 rpm. Following the occurrence of equilibrium, the samples were extracted, divided into individual centrifuge tubes, and centrifuged at 4000 rpm for 5 minutes. The aqueous and organic phases were successfully separated by this process. Then, the aqueous phase was separated from the tubes with the help of a syringe and put into separate conical flasks. After titrating the aqueous phases with 0.1 N NaOH and a phenolphthalein indicator, the estimated IA concentration in the aqueous phase following solvent extraction was performed. The experiments were performed as follows:

$$[IA]_{in} + [S]_{org} \leftrightarrow [IA]_{org}.[S]_{org} \quad (1)$$

Where $[IA]_{in}$ is the initial concentration of itaconic acid; $[S]_{org}$ are solvents in the organic phase; and $[IA]_{org}$ is itaconic acid in the organic phase.

The organic phase concentrations were determined by mass balancing using the aqueous phase concentrations.

$$[IA]_{in} - [IA]_{org} = [IA]_{aq} \quad (2)$$

Each experiment has been run three times to ensure accuracy.

3. Theory

Liquid-liquid extraction is frequently applied to sample cleansing and enrichment of a particular compound. A solute or analyte can disperse itself in a certain ratio between two immiscible solvents, often water (aqueous phase) and an organic solvent, according to the theory underlying liquid-liquid extraction (LLE) (organic phase). LLE is frequently applied to sample cleansing and enrichment, which improves the signal. The distribution ratio is the ratio of an analyte's concentration in the organic phase to that in the aqueous phase measured at equilibrium. During the extraction of the desired compound,

the distribution ratio of the analyte is larger and that of the matrix is smaller. The recovery of the organic compound is directly proportional to the enrichment factor. Enrichment must proceed in the opposite direction after matrix removal via extraction to be effective. Following extraction, the enrichment factor is improved by selectively backwashing matrix components from the organic phase into the aqueous phase [23]. The efficiency (%E) and distribution coefficient (K_D) parameters are used to define the liquid-liquid separation of Itaconic acid.

The distribution coefficient is the ratio of the number of molecules of itaconic acid present in the organic phase and the number of molecules of itaconic acid remaining in the aqueous phase.

At equilibrium conditions, the distribution coefficient can be calculated using the following equation:

$$Distribtion\ coefficient\ (K_D) = \frac{[IA]_{org}}{[IA]_{aq}} \quad (3)$$

Where $[IA]_{aq}$ and $[IA]_{org}$ are, the itaconic acid concentrations in the aqueous and organic phases. In terms of the distribution coefficient, the extraction efficiency is defined as follows:

$$Extraction\ efficiency\ (E\%) = \frac{K_D}{1 + K_D} \times 100 \quad (4)$$

4. Results and discussion

Using natural and chemical solvents such as iso-butanol, iso-octanol, groundnut, soybean, mustard, and rice bran oil, itaconic acid separation from the aqueous phase was examined. The equilibrium data were used to compute the separation parameters. At various IA concentrations, the distribution coefficients (K_D) and separation efficiencies (%E) were calculated using equations (3) and (4). The distribution coefficients for iso-butanol, iso-octanol, groundnut, soybean, mustard, and rice bran oil were observed as 1.99–2.26; 0.7–0.91; 0.098–0.148; 0.024–0.218; 0.185-0.16; and 0.03-0.165, respectively (Table 3). The IA with the iso-butanol concentration of 0.1875 mol.L^{-1} had the highest distribution coefficient, 2.26, due to the higher relative solubility. The strength of the intermolecular interactions between the solvent molecules and the solute improves the solute's solubility in the solvent. It has a higher acid solubility and is more capable of generating hydrogen bonds [25-26]. The separation efficiencies using iso-butanol, iso-octanol, groundnut, soybean, mustard, and rice bran oil were discovered to be 66.64-69.33%, 41-47.4%, 8.92-12.93%, 2.37-17.90%, 13.83-15.6%, and 2.97-14.18%, respectively. With 0.18 mol.L^{-1} of itaconic acid, iso-butanol had a greater separation efficiency of 69.33%. Natural solvents like rice bran oil, soybean oil, mustard oil, and groundnut oil are immiscible in water due to higher viscosity. The higher viscosity and density create a resistance middle of the aqueous and organic phase so that itaconic acid is less soluble in natural solvents compared to chemical solvents. These elements prohibit the molecules of the aqueous and organic phases from interacting, which results in the creation of a barrier between them [20]. Since there is little to no chance of mixing between the two phases, these solvents have poor separation efficiency and a low distribution coefficient value. The higher efficiencies using groundnut, soybean, mustard, and rice bran oil were 12.93%, 17.90%, 13.78%, and 14.18%, respectively. However, the efficiencies of iso-butanol and iso-octanol were significantly higher, at 68% and 44.16%, respectively. The overall results show that iso-butanol and iso-octanol have higher extraction efficiency compared to the other solvents because they are both polar and have dipole moments (2.96 D and 1.8 D).

Table 3. Extraction equilibrium data of itaconic acid with natural and chemical solvents

Solvents	$[IA]_{in}$ ($mol.L^{-1}$)	$[IA]_{aq}$ ($mol.L^{-1}$)	$[IA]_{org}$ ($mol.L^{-1}$)	K_D	%E
Groundnut oil	0.084	0.077	0.008	0.10	8.93
	0.170	0.153	0.017	0.11	9.95
	0.270	0.240	0.030	0.13	11.11
	0.398	0.347	0.051	0.15	12.87
	0.534	0.465	0.069	0.15	12.93
Rice bran oil	0.084	0.082	0.003	0.03	2.98
	0.170	0.165	0.006	0.04	3.46
	0.270	0.257	0.013	0.05	4.70
	0.398	0.353	0.045	0.13	11.24
	0.534	0.458	0.076	0.17	14.18
Soyabean oil	0.084	0.082	0.002	0.02	2.38
	0.170	0.158	0.013	0.08	7.57
	0.270	0.246	0.024	0.10	8.89
	0.398	0.362	0.036	0.10	8.98
	0.534	0.438	0.096	0.22	17.90
Mustard oil	0.084	0.071	0.013	0.18	15.48
	0.170	0.145	0.025	0.18	14.91
	0.270	0.231	0.039	0.17	14.44
	0.398	0.343	0.055	0.16	13.75
	0.534	0.460	0.074	0.16	13.78
Iso-butanol	0.084	0.027	0.057	2.15	68.21
	0.170	0.052	0.118	2.28	69.48
	0.270	0.083	0.187	2.25	69.26
	0.398	0.131	0.267	2.04	67.06
	0.534	0.178	0.356	2.00	66.64
Iso-octanol	0.084	0.044	0.040	0.91	47.62
	0.170	0.094	0.076	0.81	44.84
	0.270	0.152	0.118	0.78	43.70
	0.398	0.226	0.172	0.76	43.17
	0.534	0.314	0.220	0.70	41.14

* $[IA]_{in}$ = initial concentration of itaconic acid; $[IA]_{aq}$ = levulinic acid in aqueous phase; $[IA]_{org}$ = levulinic acid in organic phase.

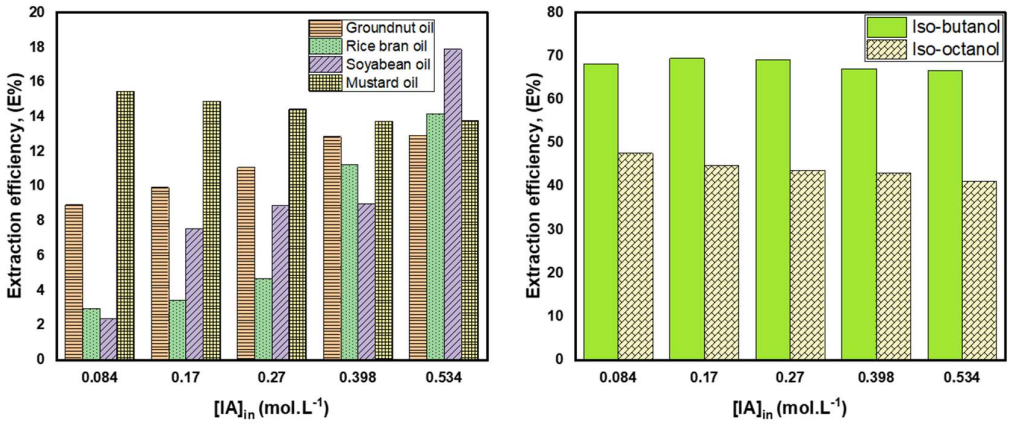

Figure 1. Extraction efficiency effect using various natural and chemical solvents at 0.008-0.534 mol.L^{-1} of itaconic acid.

Natural solvents provided lower extraction efficiency compared to chemical solvents, due to the fatty acid chain structure and non-polarity. The natural solvents have zero dipole moment; therefore, they did not have free electrons for complexation with acid in the organic phase. They are incapable of acting as a hydrogen donor for more than iso-butanol and iso-octanol. Therefore, they provided a lower extraction efficiency and distribution coefficient.

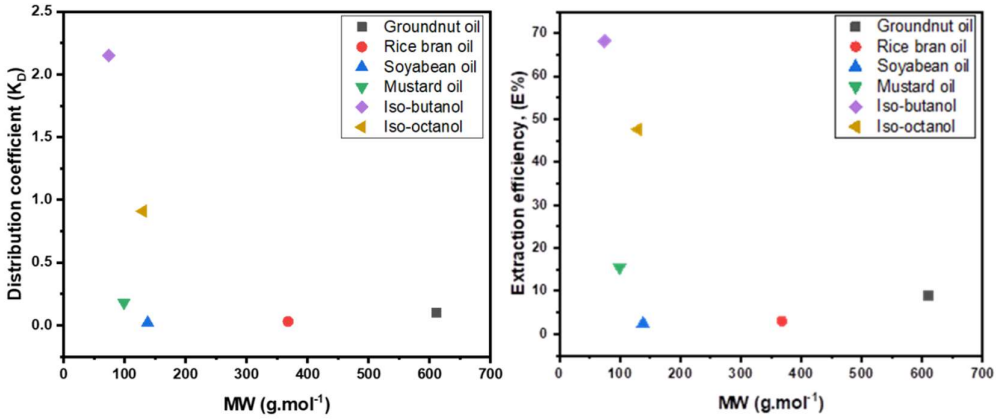

Figure 2. Distribution coefficient and extraction efficiency effect by the molecular weight of solvents.

Figure 2 shows that lower molecular weight solvents (iso-butanol and iso-octanol) provided higher distribution coefficients and extraction efficiency due to the short-chain structure solvents. While natural solvents (rice bran oil, soybean oil, groundnut oil, and mustered oil) have long chain tightly packed molecules, thus requiring more energy to overcome the hydrogen bonds between the alcohol molecules. Therefore, they show less distribution coefficient and extraction efficiency during the separation of itaconic acid.

To improve the separation efficiency of IA, natural solvents can be used with extractants like tributyl phosphate, trioctylamine, aliquat 336, etc. Natural solvents can help to decrease toxicity and cost during the separation of itaconic acid.

5. Conclusion

The average separation efficiency observed in descending order were iso-butanol (68%), iso-octanol (44.16%), groundnut oil (11.15%), soybean oil (9.102%), mustard oil (14.48%), and rice bran oil (7.315%). From the results, it can be concluded that iso-butanol and iso-octanol gave higher average separation efficiency than all the other solvents. In comparison to other diluents, iso-butanol was shown to have higher distribution coefficient values. Itaconic acid is challenging to separate because of its low relative volatility and a strong attraction to water. Due to itaconic acid's low activity toward these diluents and its higher solubility in water than in organic solvents, the low distribution coefficient (<1) is the result. Back-recovery is very costly because these solvents are generally soluble in water. Thus, the traditional extraction methods are not profitable [10]. To enhance the extraction process using non-toxic solvents i.e. mustard oil and groundnut oil, reactive extractants such as tributyl phosphate, trioctylamine, Aliquat 336, etc. can be used with both solvents. The reactive extraction method, which has worked well to recover carboxylic acids, offers better prospects by utilising amines and organophosphorus chemicals. Also, multiple reactors can be used in series to enhance efficiency.

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