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RESEARCH ARTICLE

Synergistic organic liquid formulation for succinic acid extraction from simulated aqueous solution

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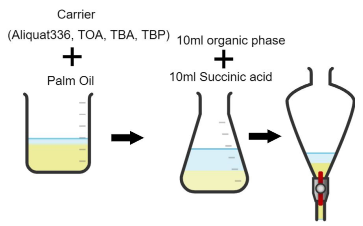
Graphical abstract



Abstract

Bio-succinic acid (SA) is a new compound that will replace petroleum based succinic acid. The application of bio-based succinic acid is still restricted due to its excessive downstream processing cost. Liquid-liquid extraction (LLE) is one of the promising methods for the successful extraction of SA. Single extractant in the LLE formulation commonly had drawbacks of long extraction time and tiny loading capacity. The aim of this study is to create synergistic formulation to enhance the SA extraction performance. The diluent is fixed as palm oil as the characteristic shows that it is safer, renewable, and non-toxic to environment. Four different types of extractants including Aliquat 336, Trioctylamine (TOA), Tributylamine (TBA) and Tributyl-phosphate (TBP) was tested to find the best combination of synergist extractants. The result shows that almost 100 % of SA was extracted using synergistic mixture of TOA and Aliquat 336 at 0.2M with synergistic coefficient (SC) of 640. In conclusion, synergistic mixture has high potential to extract SA.

Keywords: liquid-liquid extraction, organic liquid formulation, succinic acid, synergist

INTRODUCTION

Succinic acid (SA) also known as butanedioic acid, is a dicarboxylic acid that can be applied in the cosmetics, pharmaceutical, biodegradable polymer, food additives, detergents, toners and cement additives. The process for producing SA is carried out commercially via the chemical route derived from petrol, such as benzene or butane but this process however is high costs and has environmental drawbacks (Nghiem *et al*., 2017).

Higher production costs of fuels result in a higher opportunity for bio-succinic acid market. Bio-succinic acid has a net fossil energy consumption of 30-40 % lower than production based on petroleum (Londono, 2010). The demand for bio-based SA is expected to substantially increase due to growing environmental concerns. A few companies and enterprises have started the development of industrial bio-succinic production such as food ingredients, personal care products, resins, and coatings (Ahn *et al*., 2016; Pratiwi *et al*., 2015). Some of SA producers are *Actinobacillus succinogenes*, *Anaerobiospirillum succiniciproducens*, *Mannheimia succiniciproducens* and recombinant *Escherichia coli* (Ventorino *et al*., 2017). The existence of contaminants such as unconsumed carbon, lactic acid, acetic and formic by-product, as well as protein have minimizes SA yield and cause complicated purification process (Huh *et al*., 2006).

Several operations have been developed to purify SA such as solvent extraction, crystallization, precipitation and membrane filtration. In crystallization, the extracted product can be obtained without difficult and complex unit operation but had disadvantage of low product yield (Li *et al*., 2010). Precipitation is a simple operation in which calcium hydroxide, $Ca(OH)_2$, is added to precipitate succinate. High SA yields can be derived from this process, but process costs are high because it involves the consumption of reagents that cannot be recycled (Sosa-Fernández & Velizarov, 2018).

One of the promising method that could effectively extract succinic acid is liquid-liquid extraction (LLE). LLE is an economical, simple, efficient and environmentally friendly process (Shah *et al*., 2016; Sprakel *et al*., 2019). Other than that, LLE is seen as an efficient primary step for purifying carboxylic acids from aqueous solutions (Cascaval & Galaction, 2004). The concept of LLE is basically relies on the distribution of a solute between two immiscible liquid phases. For instance, a solute that initially dissolved in aqueous phase eventually distribute in organic phase that is in contact with each other. Another component called extractant is usually introduced in the system to facilitate the distribution process. The application of a single extractant during the solute extraction has suffered from such limitations as poor loading capacity of solute molecules into the organic phase. Therefore, a combination of various extractants is applied to the LLE systems for obtaining enhanced extraction efficiency (%) owing to the synergistic effect of extractant (Padhan & Sarangi, 2017). Synergism is defined as cooperation between two carrier molecules to improve the extraction effectiveness and collaboration of two extractants/carriers that further facilitates the transportation of solute from the aqueous to organic phase (Kumar & Thakur, 2019; Sulaiman & Othman, 2017). Recently, the applications of a synergistic mixture of extractants during the various extraction studies have been observed.

On the other hand, diluent is one of the important component in the LLE process. Generally, diluent has several properties such as low surface tension for good dispersion, miscible with carrier, high solute capacity, low viscosity and also non-corrosive and non-toxic. Petroleum based diluent achieved high extraction performance but the properties of the diluent are toxic, flammable, non-renewable and volatile in nature. Thus, the use of more environmentally product such as vegetable oil, sunflower oil and corn oil are applied in liquid-liquid extraction process as alternative that lead to the green and environmentally process (Rahman *et al*., 2019; Sulaiman & Othman, 2017).

To date, there has been no study reported on the extraction of succinic acid using synergistic extractant and green diluent. In this present investigation, LLE was attempted for separating SA from the aqueous solution by means of environmentally benign green solvents and a synergistic mixture of extractants. The purpose of this study is to create synergistic formulation to enhance the SA extraction performance. The individual and synergistic effects of various extractants TOA (basic), TBA (basic), TBP (neutral) and Aliquat 336 (basic) on SA extraction performance were investigated. In the organic phase, palm cooking oil was used as a green-based diluent. The effect of base and synergist extractant composition mixture in terms of synergistic coefficient was also investigated

EXPERIMENTAL

Reagents

The cooking palm oil (BURUH) by Lam Soon Edible Oils Sdn. Bhd. as diluent was bought from one of Mart located in Johor. The extractants studied including Trioctylamine (98 %, TOA), Aliquat 336 (95 %), Tributylamine (99 %, TBA) were purchased from Merck while Tributyl phosphate (95 %, TBP) were purchased from Sigma-Aldrich. Succinic acid (SA) (99 %, SA) were procured from Sigma Aldrich. All chemicals were of analytical grade and used without further purification. The strucure of extractants used are shown in Fig. 1.

Liquid-Liquid Extraction Process

Liquid-liquid extraction (LLE) process was carried out to study the feasibility of synergistic extractants on SA extraction process (Rahman *et al*., 2019). 10 mL of simulated succinic acid solution were mixed with 10 mL of organic solution (extractant in palm oil) in a 25 mL conical flask. The solution was then mixed using a mechanical shaker and was shaken at 300 rpm for 18 hr. After the extraction process, the mixture was then poured into a separating funnel and left for 15–30 mins to assure complete phase separation. The treated succinic acid in aqueous phase was separated from the organic phase through the gravity settling. Consequently, the succinic acid concentration in the aqueous phase was analysed using a HPLC.

The extractants with the highest extraction performance efficiency was determined. Afterwards, the synergist extractant formulation were determine by mixing different extractants. 10 mL of single extractant were tested with different extractant at a concentration of 0.1M. Then, both the phase separation and succinic acid concentration analysis were performed using the above mentioned methods. Then, the experiment was conducted by varying the concentrations of extractant and synergist extractant (0.01–0.1M) where at one time, one concentration was changed while maintaining concentration of the other extractant.

Determination and Calculation

For this study, the percentage of extraction performance were determined using Equation (1) while distribution ratio (D) and synergistic coefficient (SC) was calculated using Equation (2) and (3):

$$\text{Extraction (\%)} = \frac{C_i - C_f}{C_i} x\ 100 \quad (1)$$

$$\text{Distribution ratio, } D = \frac{C_{org}}{C_{aq}} \quad (2)$$

$$\text{Synergistic Coefficient, } SC = \frac{D_{mix}}{D_{extractant} + D_{synergist}} \quad (3)$$

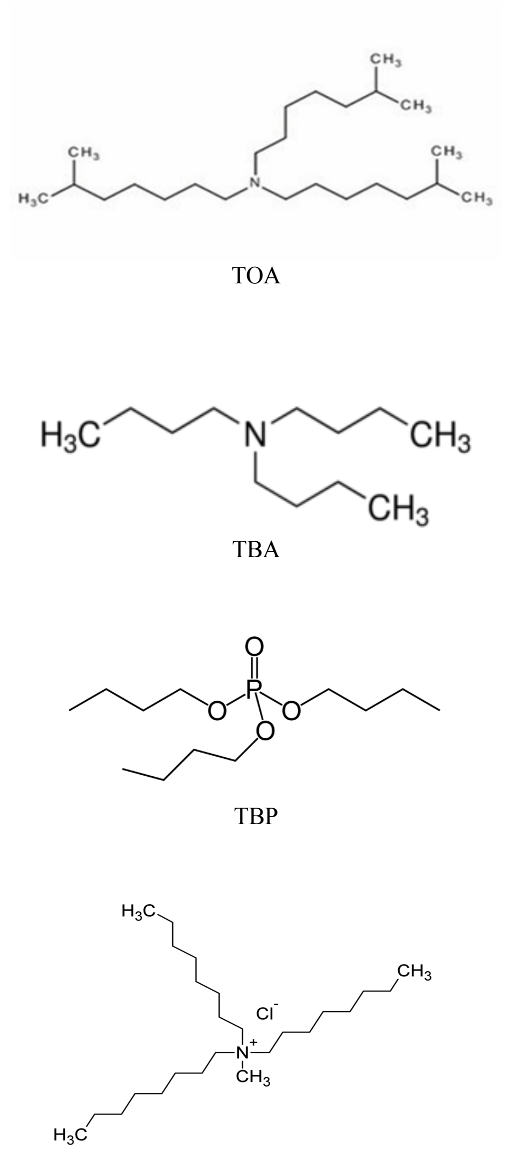


Fig. 1. Chemical structure of extractants

Based on the above equations, C_i is the initial succinic acid concentration in the external phase, C_f is the final acid concentration in the external phase, C_{org} is the concentration of succinic acid in the organic phase, $D_{extractant}$ and $D_{synergist}$ are the distribution ratios of extractant and synergist extractants respectively. D_{mix} represents the distribution ratio with the mixture of extractant and synergist extractant.

RESULTS AND DISCUSSION

Selection of base extractant

LLE was conducted for extraction of SA using single extractant such as TBA, TOA, TBP and Aliquat 336. TOA, TBA, and Aliquat 336 contain amine structure and are classified as basic extractants. Meanwhile, TBP is solvating extractant that contains oxygen bonded to phosphorus. These extractants were proven to benefit the extraction of organic acids in previous study (Kumar and Thakur, 2019; Inyang and Lokhat, 2020).

The extraction performance on different concentrations (0.1M and 0.2M) are shown in Fig. 2 and 3. The highest extraction for both extractant concentration were provide by Aliquat 336, TBA and TOA. This is expected that the combination of the extractant will promote synergist of extraction.

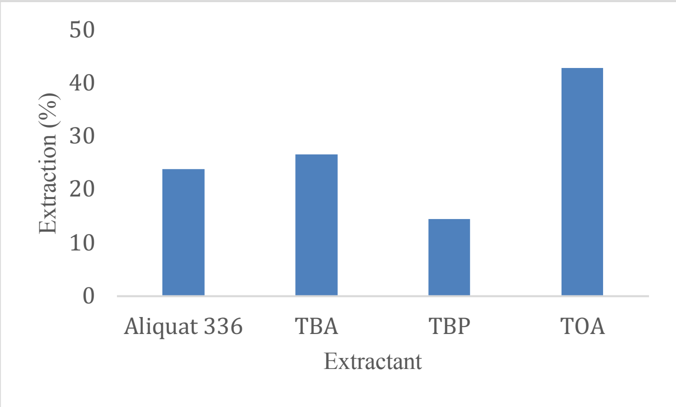


Fig. 2. Effect of different extractants on SA extraction performances (Experimental conditions: Extraction concentration: 0.1M, Time= 18h. aqueous volume = 10ml, volume organic = 10ml, agitation speed = 300rpm)

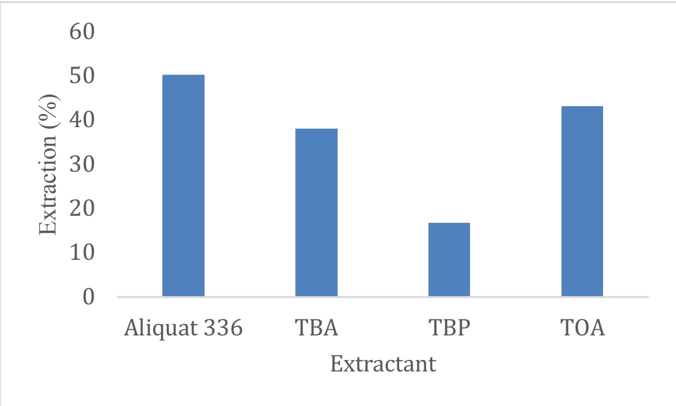


Fig. 3. Effect of different extractants on SA extraction performances (Experimental conditions: Extractant concentration: 0.2M, Time= 18h. aqueous volume = 10ml, volume organic = 10ml, agitation speed = 300rpm

On the other hand, according to Le Châtelier's principle, increasing of the extractant concentration will increase the reaction rate by increasing the rate of collisions. Based on the results obtained, the extraction percentage for all extractants increased due to increasing extractant concentration. This condition provided the potential gradient for both the feed and the organic phases that stimulated SA and extractan complexationt (Rahman *et al*., 2018).

Among the amines, only tertiary amines (TOA, TBA) and quaternary amine (Aliquat 336) was attempted on succinic acid extraction. This is due to primary and secondary amines such as 1-hexylamine,1-heptyla-mine, 1-octylamine and methylene was reported to react irreversibly with carboxylic acids. Amine reacts with the molecules of succinic acid between the aqueous and organic phases, resulting in the formation of complex amine acids which is then are solubilized into the organic phase (Magdum *et al*., 2017). It was found that TOA provides higher performance than TBA which has the same functional tertiary amine groups. Based on Fig. 1, TOA has long-chain aliphatic tertiary amine with each alkyl group has seven to nine carbon atoms that has been studied as an efficient and widely employed extractants for carboxylic acids. Other than that, when dissolved in various modifiers (solvent), they are great extractant reagents for the carboxylic acids (Inyang & Lokhat, 2020). In addition, TOA is not soluble in water and is able to form oil soluble salts of anionic species at low pH. TOA as a basic nitrogen atom can normally react with inorganic and organic acids to form amine salts that go through ion exchange reactions with many other anions. This can be supported by Kumbasar (2008) who studied separation of chromium (VI) from acidic solution using TOA as extractant. Ion exchange is a chemical reaction in which free mobile ions are substituted in solution for various ions of a similar charge (Kumar & Jain, 2013).

On the other hand, Aliquat 336 generally a quaternary amine which has strong extraction capacity, high enrichment ratio, and wide-ranging pH range (Liu *et al*., 2020). The extraction performance obtained in this study is owing to anionic exchange reaction between succinic acid and Aliquat 336. However, the complexation between Aliquat 336 and SA is low because of the nature of Aliquat 336 is highly viscous and corrosive as discussed by Datta *et al*. (2015). Consequently, this will also lead to further reduction in the rate of transportation of solute molecules.

Meanwhile, TBP has the lowest extraction performance. This can be explained by the fact that TBP as solvating reagent undergoes different molecular complex formation with other diluents and solutes. Other than that, TBP is also a great extractant which carry =P–(O)–OH grouping. The grouping has intermolecular hydrogen bonding and undergoes liquid anion exchanger. Anion exchange carry anion and anionic complex which may not be suitable for extraction of SA (Gaikwad, 2004). It is also found that TBP has low water co-extraction and low solubility which may cause the result of low SA extraction. This finding is consistent with that of Keshav *et al*. (2008).

Extraction using mixed extractant

Extraction of succinic acid using synergism system was conducted. The extractants involved are TOA (basic), Aliquat 336 (basic), TBA (basic) and TBP (neutral). Fig. 4 illustrates the various of synergistic extractants towards extraction of SA and the best combination of synergistic system is by following order Aliquat 336-TOA (100 %) > Aliquat 336-TBA (99 %) > Aliquat 336-TBP (74 %) > TOA-TBA (39 %) > TOA-TBP (37 %) > TBP-TBA (36 %).

The result indicates that Aliquat 336-TOA and Aliquat 336-TBA provide highest extraction performance which is almost 100 % and 99 % respectively. This is due to SA has been extracted by two extractant simultaneously. Note that succinic acid can exist in the aqueous phase in dissociated and undissociated form, which depending on the pH solution. The molecules of SA will dissociate at pH higher than pKa value, which reported to be 4.2 and 5.6 (Pratiwi *et al*., 2015). TOA and TBA are tertiary amine which have capability of extracting SA in the undissociated form.

Other than that, Aliquat 336 possess permanently positive and negative charge and are able react with dissociated SA. This finding can be supported by Jusoh *et al*. (2020) which study Aliquat 336 as synergist extractant in extraction of pholyphenols. In addition, the synergist effect can also be explained by the effect of Aliquat 336 which act as extractant and also phase transfer catalyst (PTC).

The increasing of extraction performance was also observed when TBP is being mixed with other extractants compared to single TBP. This shows that there is synergism takes place. However, the synergistic effect of TBP is still low compared to other extractant combinations. The low synergism may be because of formation of hydrated species of TBP and the fact that hydrogen bond among the amine is stronger than TBP. This finding reflect the idea of Atanassova *et al*. (2016) who stated the destruction of synergism using TBP.

In order to determine the best synergistic system, the effect of Aliquat 336-TOA and Aliquat 336-TBA concentration on extraction performance was studied. It can be seen the extraction performance increases with extractant concentration. The result can be related to the increased capacity of the extractant to extract SA. This finding can be supported by Le Chatelier's principle where the forward shifting of reaction occur when the concentration increases. Consequently, the number of extractant molecules will also increase which promote complexation with SA at feed-organic interface. A similar trend of extraction was also found by Rahman *et al.* (2019) who studied synergistic extractant mixture for dye extraction. In addition, the synergistic coefficient (SC) was also calculated as demonstrated in Table 1. Generally, SC more than 1 indicates synergistic extraction, SC lower than 1 implies that there is antagonistic extraction, while SC equal to 1 represents no synergistic effect (Jusoh *et al*., 2020). The result shows that the best combination is Aliquat 336-TOA (0.2M) provide highest SC of 640.

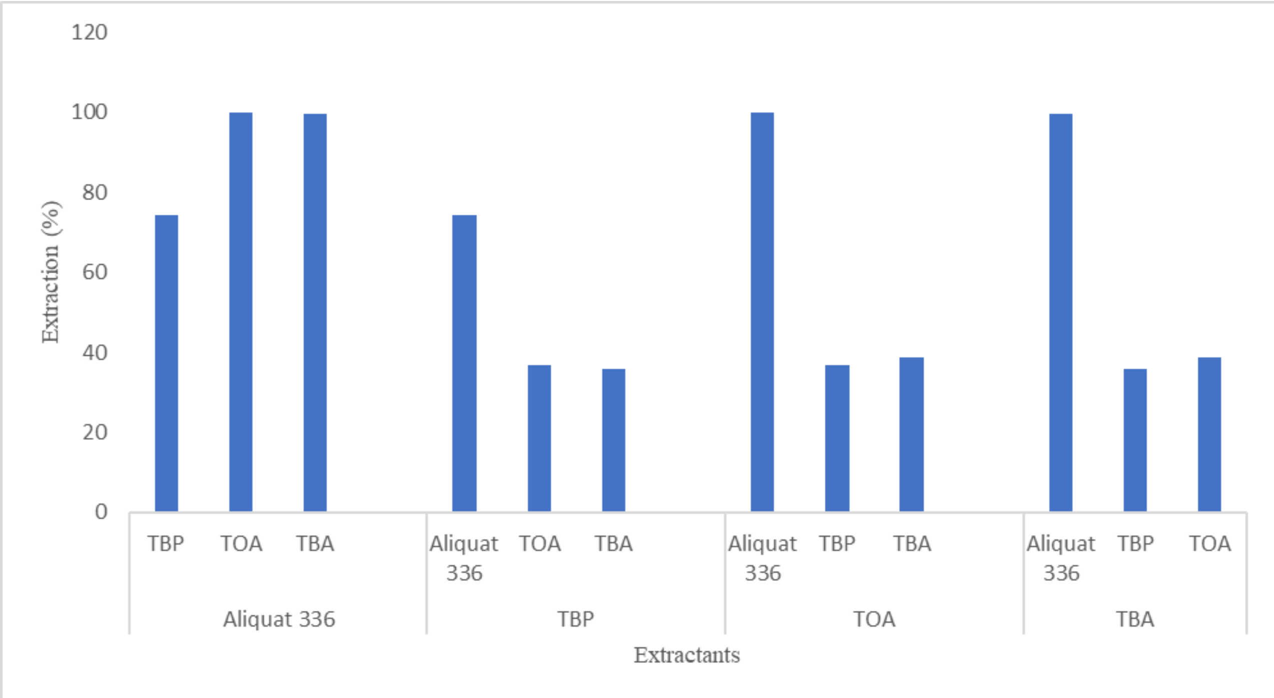


Fig. 4. Effect of types of synergists extractants on SA extraction performances (Experimental conditions: Extractant concentration: 0.2M, Time= 18h. aqueous volume = 10ml, volume organic = 10ml, agitation speed = 300rpm)

Table. 1. Synergistic coefficient of different combinations of extractants (Experimental conditions: Time= 18h. aqueous volume = 10ml, volume organic = 10ml, agitation speed = 300rpm)

	Concentration (M)	Extraction performance (%)	Synergistic Coefficient, SC
Aliquat 336 + TOA	0.02	35	0.5
	0.1	66	1.8
	0.2	100	640
Aliquat 336 + TBA	0.02	13	0.2
	0.1	70	3.6
	0.2	100	351

CONCLUSION

The synergist system for extraction of SA was successfully studied. The highest extraction performance for single extractant was TOA (43 %) at 0.1M and Aliquat 336 (50 %) at 0.2M. The extraction performance increased as the concentration increased. The excellent combination for synergist extractants are Aliquat 336-TOA with extraction performance of 100 % followed by Aliquat 336-TBA with 99 % extraction performance. At concentration of 0.1M, Aliquat 336-TOA contribute the highest SC which is 640. In conclusion, synergistic mixture has high potential to extract SA.

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