A Comparative study of TOA in diluents for Reactive Extraction of Succinic Acid

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Abstract

Succinic acid recovery from the aqueous phase is an intrinsic downstreaming process because of its numerous applications in the pharmaceutical and food industries. Distillation, sorption, adsorption, membrane, dialysis, and electrodialysis these are the conventional methods used for acid separation. Apart from these methods, a novel technique developed called reactive extraction that delivers good selectivity and yield. Separation of succinic acid from its aqueous phase was investigated in a recent work using a tertiary amine, such as tri-n-octyl amine (TOA), with different diluents. The study based on the acid concentration ranged from 0.14 to 0.5 mol/kg, while the TOA concentration ranged from 0.11 to 0.57mol/kg to study the parameters like the distribution coefficient, loading ratio, equilibrium complexation constant, and degree of extraction. The physical extraction of succinic acid by using these three diluents was done. As compare to physical extraction, reactive extraction gives better separation efficiency. The comparison of results by using different diluents in TOA was studied. The best result was obtained at the initial concentration of acid 0.26 mol/kg and initial concentration of TOA 0.57 mol/kg in the benzyl alcohol that gives 99.44 % extraction efficiency. The order of extraction power for the diluents was found to be benzyl alcohol > 2-octanol > 1-decanol.

Keywords:succinic acid; reactive extraction; distribution coefficient; degree of extraction

1. Introduction

Succinic acid (SA) is a significant dicarboxylic acid, generally known as butanedioic acid or amber acid [1]. SA market is going to increase due to its usage in food and chemical industry mainly as an acidity regulator. The 7% growth rate of SA in the period 2019 to 2025 is estimated [2]. Rather than other synthetic methods of production of SA, fermentation process taking attention due to environmental concern [3]. In fermentation process, A. succinogenes, M. succiniciproducens and A. succiniciproducens microorganisms used for efficient SA production [4] [5]. The SA produced from fermentation broth is in aqueous form and need to recover the acid. The separation and purification of the desired product are difficult because sometimes the concentration of acid in water produced is less than 10% by weight and the affinities between water and acid are very strong [6]. As a result, the downstream process for acid purification consumes nearly 60% of the total production cost [4]. There are numerous techniques developed

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for downstream process like precipitation, adsorption, distillation, membrane-based separation and solvent extraction [7][8]. Among the various methods available for the down streaming process, reactive extraction is efficient and effective method of separation. It is a more attractive novel technique wherein the reaction accomplished between extractant and acid in an aqueous phase [9]. Kertes and King divided extractants used for reactive extraction into three parts (i) Carbon-bonded oxygen-donor extractants (ii) Phosphorus-bonded oxygen donor extractants and (iii) Aliphatic amine extractants [10].

Many authors use amine extractants for the carboxylic acid recovery because amine provides the high yield and selectivity to extract selective acid [11-14]. Primary amines have large solubility in water as well as secondary amines produces amide after extraction, hence tertiary and quaternary amines mostly preferred. But regeneration of quaternary amine is not easy, thus tertiary amines widely used for recovery of acid from its aqueous phase [15]. Although the tertiary amines have advantages like good extractability and high distribution coefficient, they have some disadvantages like high viscosity and its high corrosiveness property. To recover these disadvantages, amines always used with diluents. Researchers [16] investigates the extraction equilibrium of succinic acid from aqueous solutions with tertiary amines. In their work, they used various tertiary amines like TPA, TBA, TpeA, and TOA along with active and inactive diluents like 1-octanol and n-heptane. The extraction power gets increases when 1-octanol used as diluent as compare to n-heptane. Thus, active diluents like alcohol, ketones, and chlorinated hydrocarbon were successfully used to extract succinic acid. Depending on the polarity of organic phase the reaction mechanisms between solute and extractant get varied that ultimately effect on extraction efficiency [17].

The present study based on the succinic acid recovery from its aqueous solution using reactive extraction. Tri-n-octyl amine (TOA), a tertiary amine used as extractant along with three different active diluents like Benzyl alcohol, 2-octanol, and 1-decanol. The effect of diluent on the extraction efficiency, distribution coefficient, loading factor, and equilibrium complexation were investigated using these three diluents.

2. Experimental section

2.1 Chemicals

TOA ($C_{24}H_{51}N$), a tertiary amine, is a colorless liquid with a minimum assay of 98% (molecular weight of 353.67 g/mol and a density of 0.809 g/cm^3). Succinic acid (99.5%) (Himedia Laboratories Pvt. Ltd. India) is a dicarboxylic acid. The diluents such as Benzyl alcohol (Spectrochem Pvt. Ltd. Mumbai, India), 1-Decanol (Himedia Laboratories Pvt. Ltd., India), and 2-Octanol (Tokyo Chemicals Industry Co. Ltd, Japan) are of the analytical grade and were used without further purification. To prepare the different concentrations of succinic acid distilled water was used. NaOH used for the titration was supplied by Merck Specialities Pvt. Ltd, India and is of analytical grade. Oxalic acid (99.8%) was used for the standardization of the NaOH and supplied by Merck Pvt. Ltd., India. Phenolphthalein solution (pH range 8.2 to 10.0) was used as an indicator for titration and was obtained from Merck Pvt. Ltd., India. The initial concentration of succinic acid was varied from 0.14mol/kg to 0.5mol/kg to obtain the equilibrium data. TOA was used at 0.57mol/kg as a basis of active diluents in the reactive extraction. Physical extraction

was also done by using these diluents. TOA concentration was varied from 0.11mol/kg to 0.57mol/kg by keeping succinic acid concentration constant at 0.5mol/kg.

2.2 Experimental procedures

The equal amount (15ml) of aqueous phase (SA+ water) and organic Phase (Extractant + diluent) were charged into a 100 ml Erlenmeyer flask. For efficient extraction, magnetic stirrer was used for phase mixing. The mixing of two immiscible phases at constant temperature were carried out by stirring with a magnetic bar at 1000 rpm for 2 hr. After each extraction batches centrifugation was followed for the clear separation of two phases. The mixed phases were centrifuged at 5000 rpm for 15 min. The two clear phases of organic and aqueous phases were obtained in the centrifuge tube and these two phases were separated by using micropipette. Samples of each phase were taken for the analysis for the concentrations of succinic acid.

The trace amount of water present in the organic phase were quantify by Karl-Fischer titrator. Both HPLC and titration with NaOH methods were used to quantify the acid content in the aqueous phase. Before each titration, fresh NaOH was produced. Using phenolphthalein as an indicator, the concentration of succinic acid was titrated with 0.05 N NaOH.

HPLC system (Agilent 1260) was composed of the quaternary pump with a diode array detector. The sample was eluted by 0.00625M H2SO4 solution endowing at a rate of 1.0 ml. min^{-1} in a reversed-phase C-18 column (4 mm ID × 125 mm in length). SA was identified at a wavelength of 210 nm. The preceding methods' findings were compared with a margin of error of less than 2%. A standard calibration graph was obtained by running different dilution of the standard SA, for the quantification of acid in the aqueous phase, that is presented in fig. 1. The values of R^2 close to approximately 0.99 are appearing negligible deviation within the result. The data presented in this paper is from an HPLC system. A mass balance was used to determine the acid content in the organic phase.

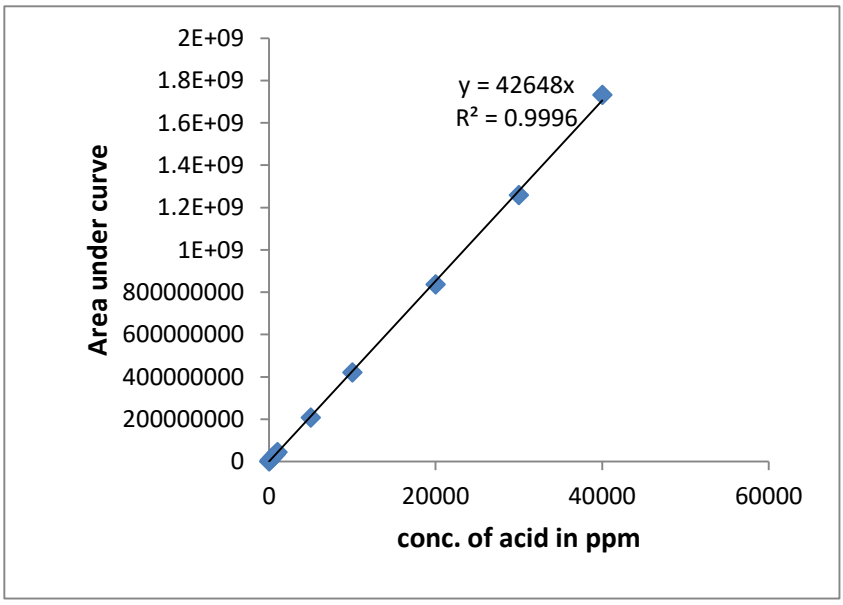

Fig 1. Standard calibration curve of succinic acid

3. Results and Discussion

Based on the experimentation carried out, the performance of the three diluents under study along with TOA was evaluated. The various parameters studied include concentration of TOA, concentration of diluents, extraction extent, distribution coefficients and degree of extraction. A chemical equilibrium study was carried out initially to establish extraction equilibrium for TOA and diluents for extraction of succinic acid under standard temperature and pressure conditions. [T= 25°C , P= 1atm]

3.1. Chemical equilibria study

As extraction proceeds, acid from the aqueous phase gets reacts with the amines and forms reaction complex. This reaction complex of succinic acid-TOA is soluble in organic phase. At quilibrium the distribution coefficient (K_D) is the ratio of concentration acid in the organic phase ($\overline{C_A}$) to the concentration of acid in the aqueous phase (C_A) and is given as [18],

$$K_D = \frac{\overline{C_A}}{C_A} \tag{1}$$

Benzyl alcohol is an aromatic alcohol. It is a useful diluent due to its high polarity. The extraction of SA was performed using TOA in the active diluents like benzyl alcohol, 2-Octanol, and 1-Decanol. Here in this study polar diluents were used because its forms hydrogen bond to extract SA. The effect of diluent on distribution of acid observed in Figure 2. The initial concentration was ranges from 0.14 mol/kg to 0.5 mol/kg.

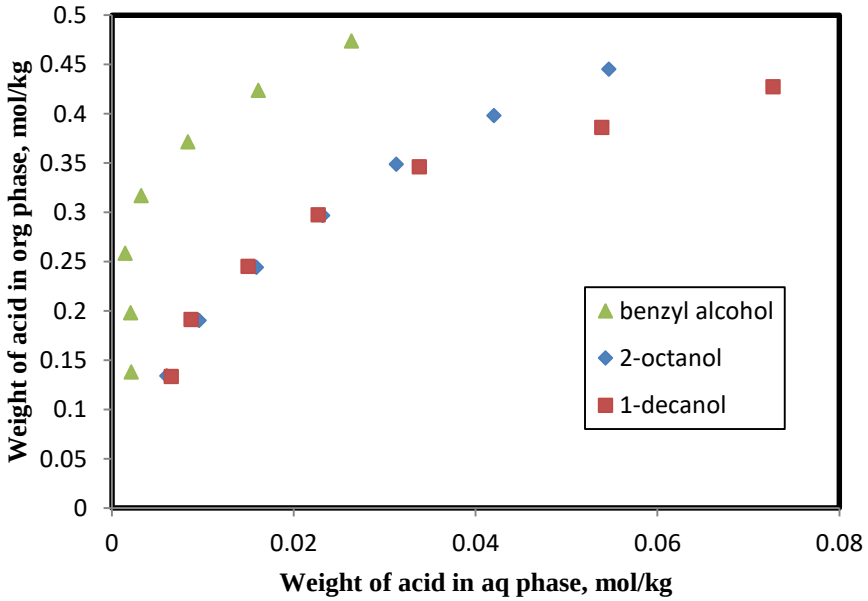

Figure 2. Chemical equilibria for extraction of succinic acid using aliquat TOA in different diluent at room temperature

Figure 2. shows the chemical equilibrium distribution coefficient of SA by using TOA with given diluents. Benzyl alcohol gives a higher distribution coefficient as compare to 1-decanol and 2-octanol. The highest value of K_D was obtained 178 for benzyl alcohol at initial succinic acid concentration 0.26 mol/kg. For 2-octanol and 1-decanol the highest K_D value was obtained 23.19 and 21.51 respectively at initial acid concentration 0.14 mol/kg. For all these batches of the initial concentration of TOA maintained at 0.57 mol/kg.

3.2. Effect of diluent on distribution coefficient

Experiments were also carried out to study the physical extraction as well as effect of TOA concentration on K_D was also observed for extraction of SA. In physical extraction, the highest K_D was obtained for benzyl alcohol that is 0.7 but it was very less as compared to the K_D of TOA-benzyl alcohol mixture. Also the K_D of 2-octanol and 1-decanol for physical extraction was 0.28 And 0.13 respectively. Figure 3. shows that as increase in the TOA concentration from 0.11 to 0.57 mol/kg, the K_D also increase.

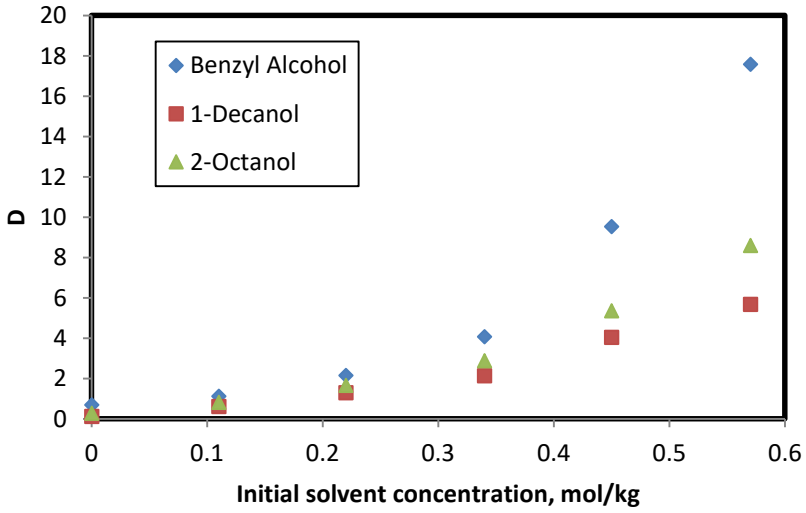

Figure 3. Effect of the initial concentration of TOA on the distribution coefficient and the distribution coefficient of succinic acid by physical extraction.

3.3. Effect of diluent on degree of extraction

Extraction Efficiency or Degree of Extraction (E) is defined as the ratio of succinic acid concentration in organic phase to the sum of acid concentration in the organic and aqueous phase and is defined as [18],

$$\%E = \frac{\overline{C_A}}{C_A^0} \times 100 \qquad (2)$$

Where, $\overline{C_A}$ is the concentration succinic acid is in the organic phase, C_A^0 is the initial acid concentration. The extraction efficiency is also defined in the terms of K_D [18],

$$\%E = \frac{(K_D \times 100)}{(1+K_D)} \quad (3)$$

Figure 4. shows that, increase the concentration of SA in the aqueous phase, the $\%E$ decreases. The highest $\%E$ obtained at the initial acid concentration of 0.26 mol/kg is 99.44%. For all acid concentrations above 90% efficiency was obtained. The highest extraction efficiency for 2-octanol and 1-decanol by using TOA was 95.70 and 95.64% respectively for the initial acid concentration of 0.14 mol/kg.

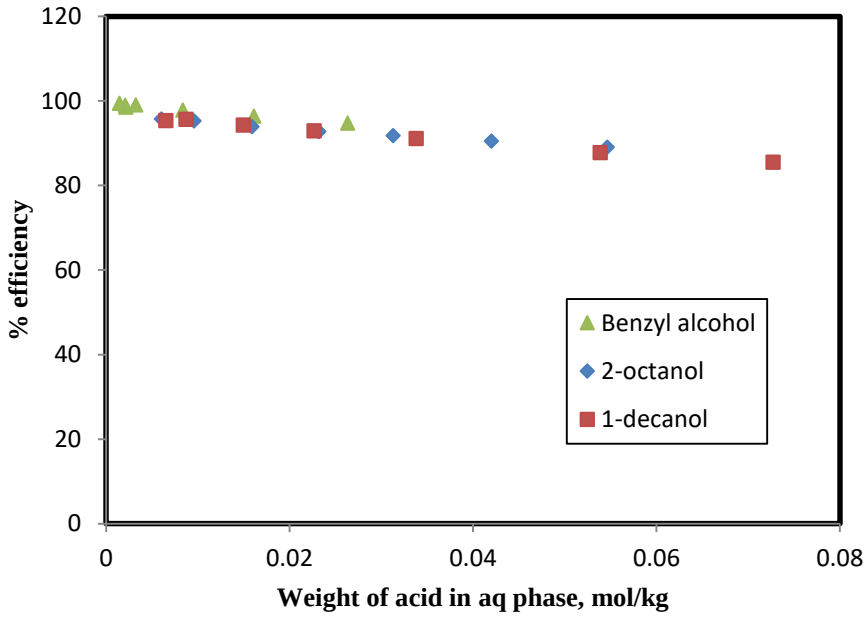

Figure 4. Degree of extraction for the extraction of succinic acid using 20% TOA in Benzyl alcohol, 2-octanol, and 1-decanol

3.4. Effect of initial concentration of TOA on degree of extraction

As stated in the literature, the solvent concentration affects the extraction efficiency. To authenticate this statement, experiments were performed by changing initial concentrations of TOA were employed for the SA extraction.

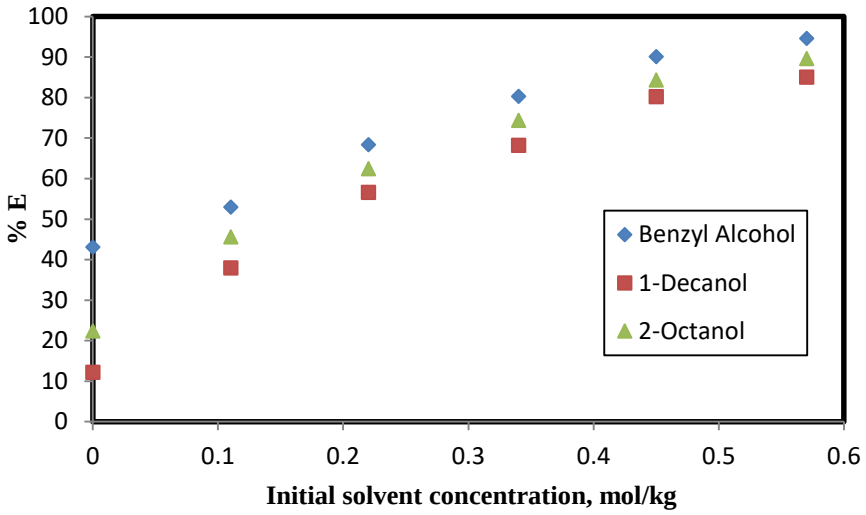

Figure 5. Effect of initial concentration of TOA on degree of extraction

Figure 5. shows that the effect of initial TOA concentration on $\%E$. Increase in the TOA concentration from 0.11 to 0.57mol/kg, the $\%E$ was also increased. For physical extraction by using benzyl alcohol, 1-octanol, and 2-decanol, the $\%E$ was obtained 43.05, 22.37, and 12.2 respectively.

3.5. Effect of diluent on equilibrium complexation constant

The initial concentration of solvent in the organic phase plays an important role in the extraction process. As we have seen with an increase in solvent concentration, the extraction efficiency was also increased. But at a higher concentration of tertiary amine dissolved in the organic phase, the third phase may be formed. It must be avoided in an extraction process [10].

Loading factor (z) shows the extent to which the organic phase can be loaded with succinic acid concentration. It is the ratio of the concentration of succinic acid in the organic phase to the initial amine concentration. Loading is defined as follows [19],

$$z = \frac{\overline{C_A}}{C_S^0} \tag{4}$$

Where $\overline{C_A}$ is the concentration of acid in the organic phase and C_S^0 is the initial concentration of amine in the organic phase. The value of z is less than 0.5 then (1:1) acid-amine complex to be formed and hence no overloading. The measure of the strength of interaction between acid-amine to form complex is called as equilibrium complexation constant and it is defined as [19],

$$\frac{z}{(1-z)} = K_E \times C_A \tag{5}$$

Where K_E is the equilibrium complexation constant. When the value of z is greater than 0.5 then (2:1) acid-amine complex is formed in the organic phase. And is defined as [19],

$$\frac{z}{(2-z)} = K_{E(2:1)} \times C_A^2 \tag{6}$$

When the graph was plotted z/(1-z) vs. weight of acid in aqueous phase it gives the value of equilibrium complexation constant. Figure 6. shows equilibrium complexation constants for extraction of succinic acid using TOA in the different diluents. The mixture of TOA in benzyl alcohol gives the highest K_E value was 572 kg/mol. The highest K_E value for TOA in 2-octanol and 1-decanol was 65 and 58 respectively.

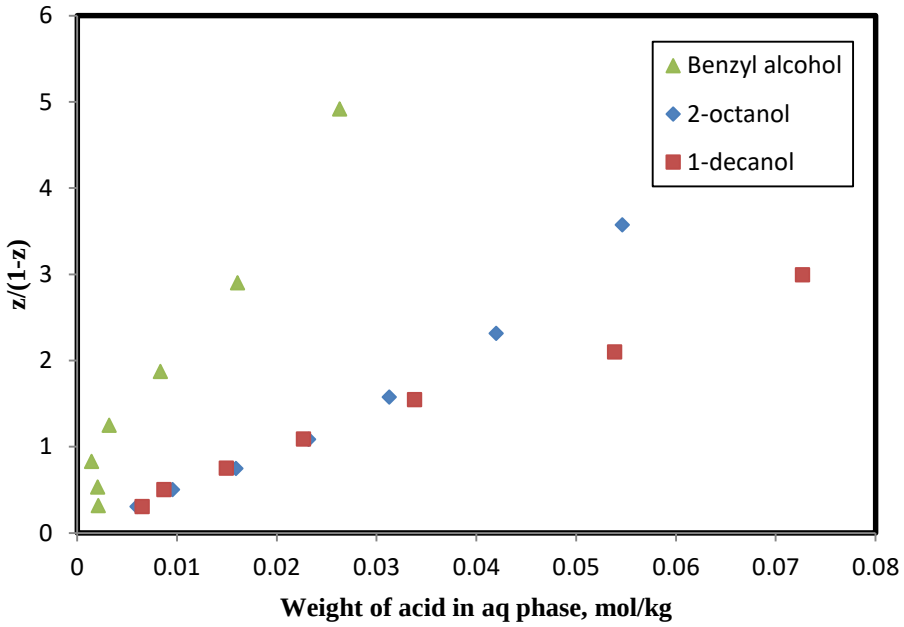

Figure 6. Equilibrium complexation constants for extraction of succinic acid using TOA in different diluent

Figure 2. shows the impact of extractant concentration (% TOA) on the chemical equilibrium. TOA is insoluble in the aqueous phase, so it is chosen for extraction. The TOA having sufficiently high extraction efficiency; nevertheless, to lower its viscosity (8.3 mPa.s) and specific gravity (0.809) it must used with diluents. It was discovered that as the concentration of TOA rises, so does the degree of extraction. Chemical extraction employing TOA in diluents produces significant improvements when compared to the results of physical extraction. The overall distribution coefficient trends follow (TOA + benzyl alcohol) > (TOA + 2-octanol) > (TOA + 1-decanol).

4. Conclusions

Reactive extraction is an optimal choice to conventional methods in the downstream process for the separation of succinic acid from fermentation broth. In the reactive extraction, aliphatic amines perform better as compare to other extractants used for recovery of succinic acid. Along with the aliphatic amines, the polar diluents like benzyl alcohol, 2-octanol, and 1-decanol ultimately affect the extraction efficiency of acid

1. The distribution coefficient for the various system was studied. When benzyl alcohol, 2-octanol, and 1-decanol are used as diluents with TOA as extractant it gives a higher distribution coefficient up to 178 for benzyl alcohol, 22.29 for 2-octanol, and 21.98 for 1-decanol.

2. The highest extraction efficiency was obtained 99.44% for benzyl alcohol, 95.70% for 2-octanol, and 95.64% for 1-decanol.
3. It was concluded that benzyl alcohol performance better as compare to other diluents with TOA as an extractant and the sequence of extraction power was noted benzyl alcohol > 2-octanol > 1-decanol.
4. As the increase in the initial concentration of TOA from 0.11-0.57 mol/kg, the extraction efficiency get increases. The TOA concentration above 0.57mol/kg, leading to the third phase formation.
5. When the TOA used with the benzyl alcohol having the initial concentration of 0.57 mol/kg, and the initial concentration of acid was at 0.26 mol/kg, it gives the best result with an extraction efficiency of 99.44%.

Nomenclature

C_A^0 – Initial concentration of succinic acid (mol/kg)

C_S^0 - Initial concentration of TOA (mol/kg)

C_A - Concentration of succinic acid in aqueous phase (mol/kg)

$\overline{C_A}$ – Concentration of succinic acid in organic phase (mol/kg)

C_S - Concentration of TOA in aqueous phase (mol/kg)

$\overline{C_S}$ - Concentration of TOA in organic phase (mol/kg)

E – Degree of extraction (%)

K_D - Distribution coefficient of succinic acid

K_E – Equilibrium complexation constant (kg/mol)

z - Loading factor

Subscript-

A - Acid

S - Solvent

D - Diluent

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