REACTIVE EXTRACTION OF SUCCINIC ACID BY USING ALIQUAT 336 IN DIFFERENT DILUENTS

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ABSTRACT

Reactive extraction of succinic acid from fermentation broth is an important process because of its number of uses in food, pharmaceutical and chemical industry. There are number of techniques available like distillation, sorption, adsorption, membrane separation, dialysis, electrodialysis and extraction to recover the succinic acid from fermentation broth. Among these processes reactive extraction should gives high selectivity and recoverability. In the present work extraction of succinic acid by using aliquat 336, a quaternary amine in different diluents like benzyl alcohol, 2-octanol and 1-decanol was studied. The experiments were carried out at various concentrations of succinic acid and aliquat 336. The acid concentration was varied from 0.14 to 0.5mol/kg by keeping aliquat 336 concentrations constant at 0.5mol/kg. After that aliquat concentration was varied from 0.1 to 0.5mol/kg at constant acid concentration 0.5mol/kg. The physical extraction was also carried out by using these diluents. The parameters such as distribution coefficient, extraction efficiency, loading ratio and equilibrium complexation constant were studied. The order of degree of extraction was found to be benzyl alcohol > 2-octanol > 1-decanol.

Keywords – Benzyl Alcohol, Distribution Coefficient, Extraction Efficiency, Reactive Extraction, Succinic Acid

I. INTRODUCTION

Succinic acid is also known as butanedoic acid or amber acid. It is a four carbon dicarboxylic acid having the molecular formula $C_4H_6O_4$.[1] It is an intermediate in the tricarboxylic acid during the anaerobic metabolism, being the end product of anaerobic metabolism.[2] The commercial succinic acid is mainly produced by petroleum. The chemical process on maleic anhydried which obtained by petroleum is used for the

production of succinic acid. The main disadvantage of this process is high conversion cost which limits the use of succinic acid for a wide range of application.

The new process for the production of succinic acid by using various bacteria in the fermentation broth has been investigated. The most widely used bacteria are *Anaerobiospirillum succiniproducens*, *Actinobacillus Succinogenes*, *Mannhei succiniciproducers* MBEL 55E and recombinant *Escherichia coli* recombinant.[1] These microorganisms possess the ability to convert various carbon sources into succinic acid.[3]

There are various process was developed for recovery of succinic acid from fermentation broth like ultrafiltration, precipitation, electrolysis, extraction, sorption and ion exchange. Among these separation processes reactive extraction is a cost saving and environmentally friendly process.[4] So the reactive extraction is mostly used for the carboxylic acid extraction from the aqueous fermentation broth.[5-13] The main advantage of this method is no byproduct formation and solvent can be reused for the extraction. Reactive extraction gives the higher extractability than other process.

Reactive extraction of succinic acid from fermentation broth by using various extractants and diluents were studied. The extractants such as phosphorus-boned oxygen donor extractant and high molecular weight aliphatic amines are used for extraction.[14] Long-chain aliphatic amines such as Amberlite LA-2, tri-n-octylamine and aliquat 336 are most widely used for the carboxylic acid extraction.[15] Although, the amines has good extractability for carboxylic acid, they always used in the form of solution with diluents which lowers the viscosity and corrosive properties of extractant. There are mainly two types of diluent polar and non polar diluent. Among these polar diluent enhance the extracting power of amines more than the non polar diluents. The polar diluents include alcohol, ketone and chlorinated hydrocarbon.[14]

B. V. Babu et. al. studied that the reactive extraction of propionic acid by using aliquat 336, a quaternary amine dissolved in a diluents like 1-decanol and n-dodecane. He found that with increase in the 1-decanol concentration in diluents, the distribution coefficient increases. The maximum distribution coefficient obtained was 6.4.[16]

Yavuz Selim Asci studied that the reactive extraction of succinic acid by using Amberlite LA-2, a secondary amine in various diluents likes cyclohexane, iso-octane, MIBK, 1-octanol, 2-octane, toluene and hexane. He was found that extraction increase with increase in amine concentration for all diluents and 1-octanol gives highest distribution coefficient.[17]

The aim of this study is to show the effect of various polar diluent such as benzyl alcohol, 2-octanol and 1-decanol on the extraction efficiency. The quaternary amine i. e. aliquat 336 was used with these diluent. The effect of succinic acid concentration as well as the amine concentration on the distribution coefficient was studied. The comparison between physical extraction and reactive extraction were done. The parameters such as distribution coefficient, extraction efficiency, loading ratio of amine and equilibrium complexation constant was studied.

II. MATERIALS AND METHOD

2.1 Materials

Aliquat 336 (Methyltricaprylammonium chloride), a quaternary amine , is a mixture of C_8-C_{10} with a minimum assay of 80% and with molecular weight of 404.16 g/mol and density of 0.884 g/cm^3. Succinic acid, with a minimum assay 99.5% from Himedia Laboratories Pvt. Ltd. India is a dicarboxylic acid. The diluents used were such as Benzyl alcohol from Spectrochem Pvt. Ltd. Mumbai, India, 1-Decanol from Himedia Laboratories Pvt. Ltd., India and 2-Octanol from Tokayo Chemicals Industry Co. Ltd, Japan are of the technical 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. Aliquat 336 was used at 0.5mol/kg as a basis of active diluents in the reactive extraction. Physical extraction was also done by using these diluents. Aliquat 336 concentration was varied from 0.1mol/kg to 0.5mol/kg by keeping succinic acid concentration constant at 0.5mol/kg.

2.2 Experimental procedure

Equal volumes of aqueous and organic phase were taken in a 100 ml erlemeyer flask. The extraction experiments were carried out by stirring the solution for two hour at 1000rpm. The two phases were separated by using centrifuge at 5000rpm for 15min. Then the phases were separated by using micropipette. The sample of each phases were taken for analysis.

The succinic acid concentration in aqueous phase was determined by HPLC analysis as well as titration with NaOH. In HPLC analysis, 0.0062M H_2SO_4 was used as a mobile phase and C18 column was used for analysis. In titration 0.05N NaOH was used for titration with phenolphthalein as an indicator. The water content in the organic phase was determined by using Karl-Fischer instrument. The acid concentration in organic phase was calculated by mass balance.

III. RESULTS AND DISCUSSION

3.1 Effect of diluents on distribution coefficient

The distribution coefficient is the ratio of concentration of acid in organic phase to the concentration of acid in aqueous phase. It is defined as,

$$K_D = \frac{C_A}{C_A} \quad (1)$$

The reactive extraction of succinic acid from aqueous fermentation broth by using a quaternary amine, aliquat 336 in different diluent was studied. The active diluents such as benzyl alcohol, 2-octanol and 1-decanol were used along with the aliquat 336 as extractant for the study. Fig.1 shows the equilibrium distribution of succinic acid in organic and aqueous phase. The initial succinic acid concentration was varied from 0.14mol/kg

to 0.5mol/kg by keeping concentration of aliquat 336 constant at 0.5mol/kg. Benzyl alcohol gives the higher distribution coefficient than 2-octanol and 1-decanol. The maximum distribution coefficient was obtained 0.89 at initial acid concentration 0.5mol/kg along with benzyl alcohol as diluent. 0.66 and 0.44 was the highest distribution coefficient for 2-octanol and 1-decanol respectively. It was observed that with increase in the initial concentration of succinic acid distribution coefficient were also increases.

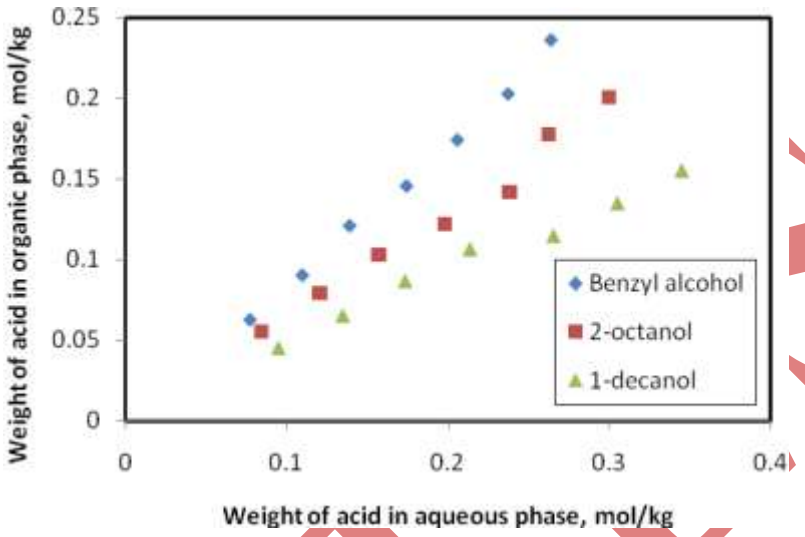

Fig. 1 Chemical equilibria for extraction of succinic acid using aliquat 336 in different diluent at room temperature

The physical extraction of succinic acid was also done by using these diluents. The maximum distribution coefficient obtained at initial concentration of succinic acid 0.5mol/kg was 0.747 by using benzyl alcohol as extractant. The highest distribution coefficient was obtained for 2-octanol and 1-decanol was 0.288 and 0.147 which is very low as compare to reactive extraction.

The initial concentration of aliquat 336 varied from 0.1mol/kg to 0.5mol/kg by keeping succinic acid concentration constant at 0.5mol/kg was studied. Fig.2 shows that with increase in the aliquat 336 concentration, the distribution coefficient was also increases for all diluents.

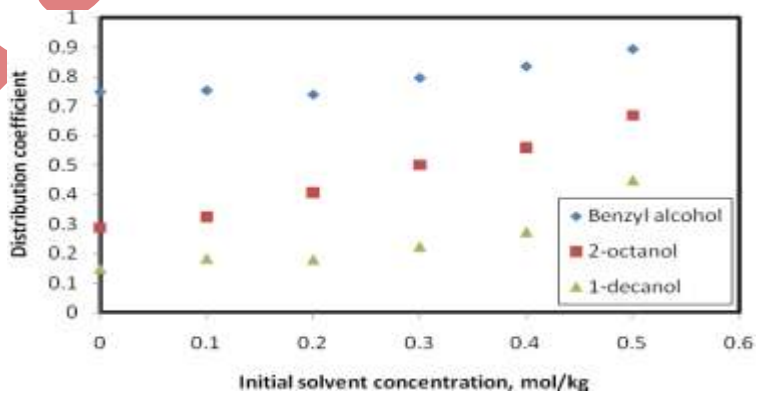

Fig. 2 shows the effect of initial concentration of aliquat 336 on distribution coefficient and the distribution coefficient of succinic acid by physical extraction.

3.2 Effect of diluent on Extraction efficiency

The extractability of the system is defined in the terms of extraction efficiency which is also called degree of extraction. Extraction efficiency is the ratio of succinic acid concentration in organic phase to the total acid concentration. It is defined as follows,

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

Where, $\overline{C_A}$ is the acid concentration in organic phase and C_A^0 is the total acid concentration. The extraction efficiency is also defined in the terms of distribution coefficient. It is given as,

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

Fig. 3 shows the extraction efficiency of succinic acid by using these three diluents. The highest extraction efficiency obtained at initial succinic acid concentration 0.5mol/kg was 47.15% along with benzyl alcohol as diluent. The maximum extraction efficiency was obtained 40.28% and 33.18% for 2-octanol and 1-decanol. As increase in the initial concentration of succinic acid, the extraction efficiency was approximately constant for all these diluents.

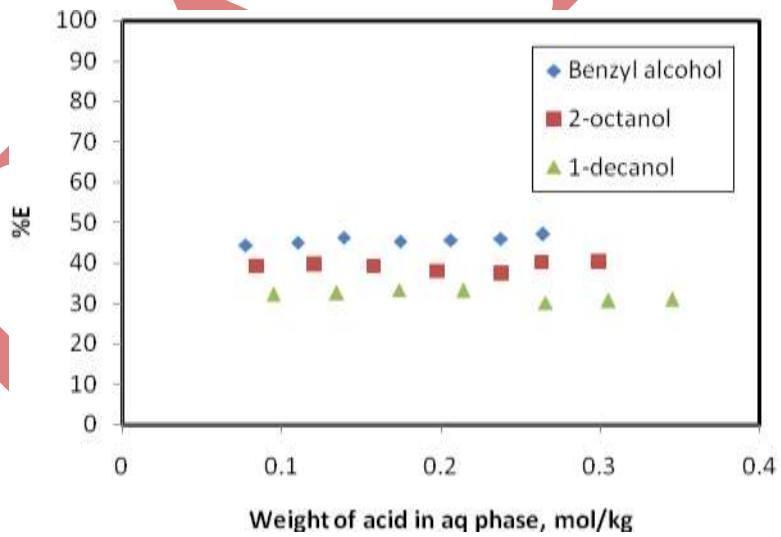

Fig. 3 Degree of extraction for extraction of succinic acid using 20% aliquat 336 in Benzyl alcohol, 2-octanol and 1-decanol

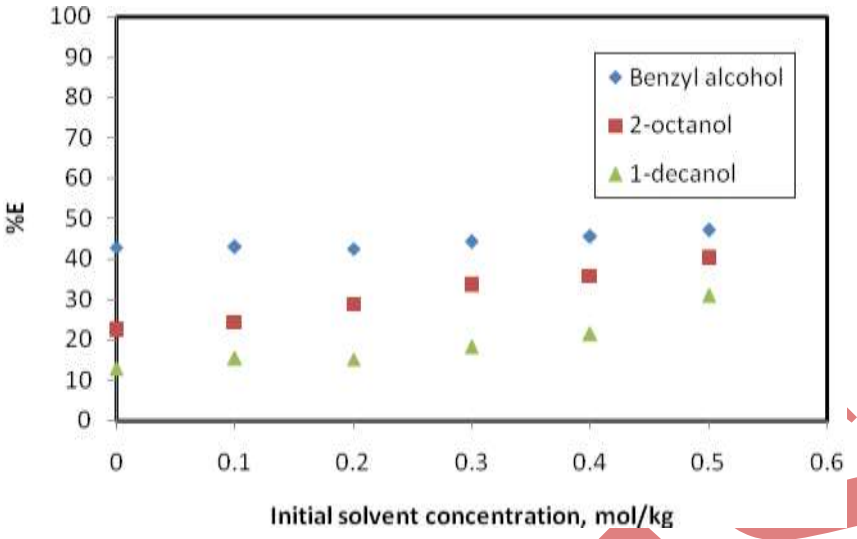

Fig. 4 The effect of initial concentration of aliquat 336 on Extraction efficiency

Fig. 4 shows the physical extraction of succinic acid by using only diluents as well as by changing the initial concentration of aliquat 336 in these three diluents. In the physical extraction the diluents was used as solvent, such as benzyl alcohol, 2-octanol and 1-decanol. The maximum extraction efficiency was obtained 42.78%, 22.37% and 12.87% for benzyl alcohol, 2-octanol and 1-decanol respectively. As increase in the initial concentration of aliquat 336 in diluent, extraction efficiency also increases.

3.3 Effect of diluent on Equilibrium complexation constant

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

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

$$z = \frac{[S]}{c_S^o} \tag{4}$$

TABLE 1. Chemical Equilibrium data for extraction of succinic acid using aliquat 336 in different diluent by varying acid concentration

Extractant	Diluent	C_S^0 mol/kg	C_A^0 mol/kg	K_D	%E	z	K_E kg/mol	pH
Aliquat 336	Benzyl alcohol	0.5	0.14	0.799	44.44	0.124	1.82	2.94
			0.2	0.816	44.95	0.179	1.99	2.69
			0.26	0.864	46.37	0.214	2.27	2.49
			0.32	0.831	45.39	0.29	2.34	2.47
			0.38	0.842	45.72	0.347	2.58	2.45
			0.44	0.851	45.98	0.404	2.86	2
			0.5	0.892	47.15	0.471	3.37	1.65
Aliquat 336	2-octanol	0.5	0.14	0.647	39.31	0.11	1.45	1.98
			0.2	0.652	39.48	0.157	1.54	1.93
			0.26	0.65	39.4	0.204	1.63	2.11
			0.32	0.614	38.04	0.243	1.62	2.14
			0.38	0.594	37.26	0.283	1.65	1.78
			0.44	0.674	40.28	0.354	2.08	2.01
			0.5	0.668	40.05	0.4	2.22	2.04
Aliquat 336	1-decanol	0.5	0.14	0.473	32.14	0.089	1.04	1.94
			0.2	0.482	32.53	0.13	1.10	1.91
			0.26	0.497	33.23	0.172	1.20	1.84
			0.32	0.496	33.18	0.212	1.26	1.82
			0.38	0.43	30.09	0.228	1.11	1.79
			0.44	0.441	30.6	0.269	1.20	1.76
			0.5	0.448	30.96	0.309	1.29	1.73

Where, $\overline{C_A}$ is the concentration of acid in organic phase and C_S^0 is the initial concentration of amine in 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,

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

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,

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

When the graph was plotted z/(1-z) vs. weight of acid in aqueous phase it gives the value of equilibrium complexation constant. Fig (5) shows equilibrium complexation constants for extraction of succinic acid using aliquat 336 in different diluent. The mixture of aliquat 336 in benzyl alcohol gives the highest K_E value was 3.37 kg/mol. The highest K_E value for aliquat 336 in 2-octanol and 1-decanol was 2.22 and 1.29 kg/mol respectively.

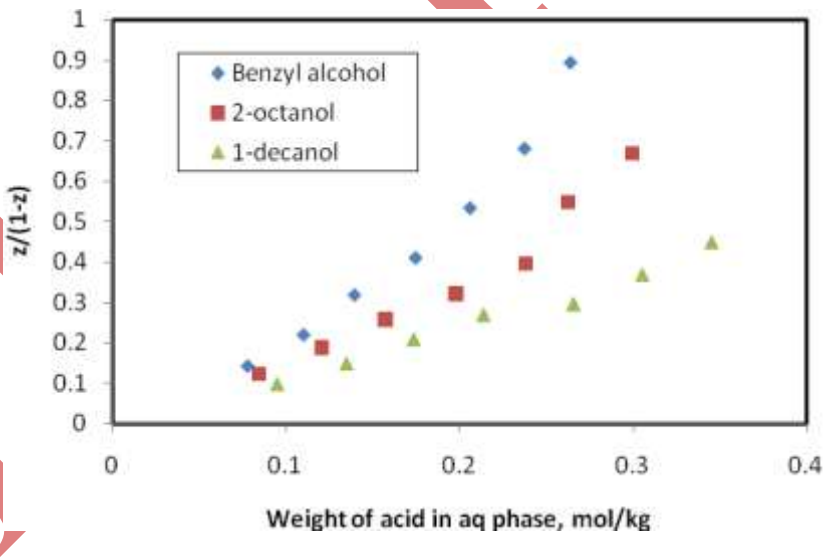

Fig. 5 shows equilibrium complexation constants for extraction of succinic acid using aliquat 336 in different diluent

TABLE 2. Chemical equilibrium data for extraction of succinic acid using aliquat 336 in different diluent at varying concentration of solvent

Extractant	Diluent	C_S^0 mol/kg	C_A^0 mol/kg	K_D	$\%E$	z	K_E kg/mol	pH
Aliquat 336	Benzyl alcohol	0	0.5	0.747	42.78	-	-	2.98
		0.1		0.752	42.94	2.14	8.82	2.5
		0.2		0.738	42.48	1.06	3.93	1.96
		0.3		0.794	44.28	0.73	2.10	1.88
		0.4		0.834	45.47	0.56	1.45	1.74
		0.5		0.892	47.15	0.47	3.37	1.65
Aliquat 336	2-octanol	0	0.5	0.288	22.37	-	-	2.25
		0.1		0.324	24.47	1.22	4.06	1.9
		0.2		0.406	28.88	0.72	6.88	1.81
		0.3		0.501	33.38	0.55	3.52	1.75
		0.4		0.559	35.85	0.44	2.43	1.75
		0.5		0.668	40.05	0.4	2.22	2.04
Aliquat 336	1-decanol	0	0.5	0.147	12.78	-	-	2.17
		0.1		0.182	15.4	0.77	7.93	1.92
		0.2		0.178	15.17	0.37	1.44	1.91
		0.3		0.223	18.24	0.3	1.06	1.78
		0.4		0.273	21.44	0.26	0.93	1.76
		0.5		0.448	30.96	0.3	1.29	1.73

IV. CONCLUSION

Reactive extraction is the efficient method for the recovery of succinic acid from aqueous fermentation broth. It gives the high distribution coefficient by using amines as extractant. When the quaternary amine, aliquat 336 was used for the extraction along with benzyl alcohol it gives the best result. The diluents such as benzyl alcohol, 2-octanol and 1-decanol were used for the study among these diluents benzyl alcohol gives the higher extraction efficiency up to the 47.15%. When 2-octanol and 1-decanol was used for the extraction of succinic acid along with the aliquat 336 it gives the highest efficiency up to 40.28% and 33.23% respectively. Reactive extraction gives the higher extractability than physical extraction. With increase in the initial concentration of aliquat 336 in organic phase, the extraction efficiency also increases.

Nomenclature

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

C_S^0 - Initial concentration of aliquat 336 (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 aliquat 336 in aqueous phase (mol/kg)

$\overline{C_S}$ - Concentration of aliquat 336 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

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