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A Review: Reactive Extraction of Succinic Acid form Aqueous Solution Using Different Extractant

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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, electro dialysis and extraction to recover the succinic acid from fermentation broth. Among these processes reactive extraction should give high selectivity and recoverability. This review is based on different extractants used for the reactive extraction of succinic acid from aqueous solution. Various extractants are studied along with diluents.

Keywords: Succinic acid, Reactive extraction, Extractants, Diluents

Introduction:

Succinic acid a dicarboxylic acid having the molecular formula $C_4H_6O_4$, is an intermediate in the tricarboxylic acid cycle and also as one of the fermentation products of anaerobic metabolism. It has been widely used in the agriculture, food and pharmaceuticals. As, the importance of succinic acid for biodegradable polymers has increased, the biological production by fermentation has been focused as an alternative to petrochemical-based processes. Sang Yup Lee, et. al. have been studied many different microorganisms like *Actinobacillussuccinogenes*, *Anaerobiospirillumsucciniciproducens*, *Mannheimiasucciniciproducens*and recombinant *Escherichiacoli* [1,2].

Marcio de Barros studied that biotechnological production of succinic acid by *Actinobacillus Succinogenes* using different substrate. The various substrate like glucose, sugar cane molasses, xylose, glycerol P.A. and glycerol were used as substrate in the fermentation broth for the production of succinic acid. The fermentation broth was maintained at 37˚C, agitated at 150rpm in different time period using free cell. They observed that glycerol is a best substrate it produce succinic acid up to 1.62 g/L in 48 hours of fermentation[3].

There are various methods for recovery of succinic acid from fermentation broth like precipitation, sorption and ion exchange, electrodialysis and extraction. Among these methods the reactive extraction was the best method[4].Reactiveextraction is the receiving increasing attention for the recovery of carboxylic acids from fermentation broth or dilute aqueous streams because of its various advantageslike cost saving and energy effective down streaming over conventional and other recovery methods [5].

Reactive extraction is a separation process using the reactions between extractants and the materials extracted. The extractant in the organic phase reacts with the material in the aqueous phase and the reaction complexes formed are then solubilized in the organic phase. Extractants such as hydrocarbon, phosphorous, and aliphatic amine extractants are mainly used in the reactive extraction of carboxylic acids. [6]

This review is mainly based on different types of extractants used for the extraction of succinic acid from the aqueous solution and the comparison study of their extraction efficiency along with distribution coefficient. The various extractants are classified below.

Extractants in Reactive Extraction

There are three categories of extractants used in reactiveextraction. These are extraction by solvation withcarbon-bonded oxygen-bearing extractants, salvation with phosphorous-bonded oxygen-bearing extractants,and proton transfer or ion-pairing formation with highmolecular weight aliphatic amines and their salts [7].Since phosphorous and amine extractants have beenmainly used in the recovery of carboxylic acids, onlythese extractants are discussed here.

Phosphorous-bonded Oxygen Donor Extractants

These extractants contain a phosphoryl group that is a stronger Lewis base than carbon-bonded oxygen donor extractants. The extractants belonging to this group is more water-immiscible and extractable than carbon-bonded oxygen donor extractants.For example, trioctyl phosphine oxide (TOPO) and tributylphosphate (TBP). If the alkoxy groups in TBP are substituted by alkyl groups, then the Lewis basicity is increased through inductive effects. This is also the case with TOPO. Due to its higher basicity, it produces higher distribution coefficients. However, the extractabilities of these extractants for carboxylic acids have influenced not only their basicities but also other factors such as the properties of the diluent, acid, and pH. Although the extractabilities of these extractants are lower than those of aliphatic amine extractants, they are adaptive for extractive-fermentation because of their low toxicity as regards on the viability of the fermentation microbe.

Extraction of succinic acid using phosphonium-based ionic liquids(ILs).

In this work Filipe S. Oliveira et. al. tested the efficiency of hydrophobic ionic liquids, namely phosphonium-based to extract succinic acid from dilute aqueous solution, as model systems for the use of ionic liquids to extract bioproducts from fermentation broth. The phosphonium-based extractant used for the study such as Tetradecyltrihexylphosphonium Chloride
[P66614][Cl],Tetradecyltrihexylphosphoniumdecanoate [P66614][Dec],
Tetradecyltrihexylphosphoniumbisphosphinate
[P66614][Phos]. They showed that phosphonium-based ILs were better extractant of short chain organic acids from aqueous dilute solution than the organic solvents. The maximum partition coefficient and extraction efficiency was ontained 20.9 and 89% respectively. The extraction efficiency of the three phosphonium-based ILs showed different behaviors to succinic acid. Neverthless, [p66614][Phos] IL showed the best extraction performance for the succinic acid [8].

High Molecular Weight Aliphatic Amines and Their Salts

The extraction of proton-bearing organic and inorganiccompounds from aqueous media by long chainaliphatic amines and their salts dissolved in a waterimmiscibleorganic solvent is one of the newest developmentsin separation technology. The fundamentaldifference between oxygen- and nitrogen-bearing basicextractants in the extraction of carboxylic acids is thebehavior of the acid proton during the transfer from anaqueous to an organic solution. In the systems withoxygen-bearing extractants, whether carbon, phosphorous,or sulfur bound, the acid strength in the aqueoussolution and that of the hydrogen bond in the organicsolution are the measures of extractability. In contrast,the acid extracted into an amine-containing organicphase is no longer regarded as an acid but as ammoniumsalt. It is thus the extent of the ion pair associationbetween the alkylammoniumcation and the acidradical that is the measure of extractability, or moreprecisely, the stability of the organic phase species [7].

To increase the extraction yield and the selectivity of the liquid–liquid extraction of organic acids from an aqueous phase, many authors propose the use of amines as reactive components, dissolved in water immiscible organic solvents. Amines offer a high affinity to react with negatively charged molecules because of their high basicity (electron donor). Therefore they are suitable for the extraction of organic acids such as succinic acid. The amine reacts with the succinic acid molecules at the interface between the aqueous and the organic phase leading to the formation of amine-acid–complexes. These complexes are solubilized into the organic phase. The mechanismconsists in proton transfer or ion pair formation depending on the type of amine and the organic solvent.

High Molecular Weight Secondary Amines

Reactive extraction of succinic acid by using Amberlite LA-2 in various diluents

Yavuz Selim Ascı and Ismail Incı studied the extraction equilibria of succinic acid in the solution of Amberlite LA-2, a secondary amine, in seven individual diluents at a temperature of 298.15K. the diluents used for this study was cyclohexane, iso-octane, MIBK, 1-octanol, 2-octanone, toluene, hexane. Among these diluents best result was obtained for the mixture of Amberlite LA-2 and 1-octanol.

The highest distribution coefficient and exraction efficiency obtained to extract succinic acid by using mixture of Amberlite LA-2 and 1-octanol was 91.244 and 98.19% respectively. The maximum extraction efficiency for diluents used at the maximum Amberlite L-2 (0.93 mol.L-1) concentration are determined as 1-octanol> 2-octanone >MIBK >toluene >Iso-octane >hexane >cyclohexane [9].

High Molecular Weight Tertiary Amines

Reactive extraction of succinic acid with tripropylamine (TPA) in various diluents

The tripropylamine (TPA) was used as the extraction agent for the reactive extraction of succinic acid in various alcohol diluents.In this study, extraction characteristics of succinic acid by using TPA/various diluents were investigated. The distribution coefficient and the extraction efficiency increase with increase of TPA concentration. And the extractability decreases in the order 1-butanol > 1-hexanol > 1-octanol. In the loading analysis of extractant, the loading value decreases with increasing of carbon chain length of alcohols[10].

Reactive extraction of succinic acid by using TOA in various diluents

Reactive extraction of succinic acid by using Tri-n-octylamine (TOA) in different diluents such as benzyl alcohol, 2-octanol and 1-decanol were studied. succinic acid extraction along with TOA as extractant it gives higher distribution coefficient up to 178 for benzyl alcohol, 22.29 for 2-octanol and 21.98 for 1-decanol. The highest extraction efficiency was obtained 99.44% for benzyl alcohol, 95.70% for 2-octanol and 95.64% for 1-decanol. It was conclude that benzyl alcohol is the best diluent for the extraction of succinic acid along with TOA as extractant and the order of extraction power was found to be benzyl alcohol > 2-octanol > 1-decanol [11].

Reactive Extraction of Succinic Acid Using Tridodecylamine dissolved in MIBK

Ismail Inci was investigate the extractability of succinic acid by tridodecylamine dissolved in MIBK. They studied that there is only a very slight effect, if any, of temperature in the range of 20-90°C on the distribution of succinic acid. The chemical equilibrium distribution coefficients were measured at 25°C for various concentrations of tridodecylamine in MIBK. The maximum distribution coefficient and extraction efficiency was obtained upto 13.238 and 93% respectively. They also determine kinetics of extraction of succinic acid by tridodecylamine in MIBK [12].

Reactive Extraction of Succinic Acid Using Mixed Tertiary Amine

Reactive extraction of succinic acid was carried out by using TPA/TOA (Tripropylamine/ Trioctylamine) extraction agent. The maximum distribution coefficient was obtained at 8:2 weight ratio of TPA/TOA. Its extraction efficiency was above 90% at the 3.9 wt% of succinic acid in aqueous solution. The ratio of TPA and TOA was varied from 0.2 to 0.8 weight ratio to obtain the equilibrium data for the range of concentration of succinic acid obtained from fermentation broth [13].

Equilibrium Studies on Reactive Extraction of Succinic Acid from Aqueous Solution with Tertiary Amines

Yeon Ki Hong studied the reactive extraction of succinic acid from aqueous solution with various tertiary amines such as Tripropylamine (TPA), Tributylamine (TBA), Tripentylamine (TPeA) and Trioctylamine (TOA) dissolved in 1-octanol(active diluent) and n-heptane (inactive diluent) has been studied. In reactive extraction with tertiary amines in 1-octanol, the extractability and loading is proportional to the chain length of amine. That is loading value is decreases in the order TOA>TPeA>TBA>TPA. It is due to increase in basicity with chain length of amine. However by using inactive diluents for reactive extraction of with tertieary amines, the contrary results were obtained [14].

Reactive extraction of succinic acid using various tertiary amines dissolved in 1-octanol and n-heptane.

Yeon Ki Hong Studied the reactive extraction of succinic acid by using various tertiary amines such as Tripropylamine (TPA), Tributylamine (TBA), Tripantylamine (TPeA) and Trioctylamine (TOA) in diluents such as 1-octanol (active diluent) and n-heptane (inactive diluent). It is the function of chain length of the tertiary amine. In the tertiary amine extractant in 1-octanol, the extractability of tertiary amines was proportional to their chain length. But in n-heptane, the extractabilities of tertiary amines decresed with their chain length. It was found that the difference of extractability in 1-octanol and in n-heptane was mainly due to the different degree of intermolecular hydrogen bondingof succinic acid with the polarity of diluents. The maximum extraction efficiency was obtained for the reactive extraction of succinic acid by using tertiary amines in 1-octanol was about 88% and in n-heptane 55%. So it was conclude that the intermolecular hydrogen bonding played an important role in determining the stoichiometries of acid-amine complex [15].

High Molecular Weight Quaternary Amines

Reactive extraction of succinic acid by using Aliquat 336 in various diluents

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 [16].

Table 1. represents chemical equilibrium data for the extraction of succinic acid using different extractant and diluents discussed above.

Conclusion:

Reactive extraction is a promising alternative to conventional methods for the recovery of succinic acid from fermentation broth.Phosphorous and amine extractants have been mainly used in the recovery of succinic acid. It has been reported that aliphatic amines are the best extractant for the recovery of succinic acid from aqueous solution. When benzyl alcohol was used as diluent for the extraction of succinic acid extraction along with TOA as extractant it gives higher distribution coefficient up to 178 and the highest extraction efficiency was obtained 99.44% for benzyl alcohol. It was conclude that TOA is the best extractant for the extraction of succinic acid along with benzyl alcohol as diluent. Secondary and tertiary amines gives the best results for the extraction of succinic acid from aqueoussolution.

Table 1:Chemical equilibrium data for extraction of succinic acid using different extractant.

Extractant	Diluents	Initial Extractant Concentration (mol/Kg)	Initial Succinic Acid Concentration (mol/Kg)	Distribution Coefficient (K_D)	Extraction Efficiency (%E)
Phosphorous-bonded Oxygen Donor Extractants					
[P_{66614}][Cl]	-	0.5	0.05	8.5	89.5
[P_{66614}][Dec]	-	0.5	0.05	4.2	80.8
[P_{66614}][Phos]	-	0.5	0.05	8.6	89.6
High Molecular Weight Secondary Amines					
Amberlite LA-2	Cyclohexane	0.93	0.47	10.021	90.93
	Iso-octane	0.93	0.47	13.91	93.29
	MIBK	0.93	0.47	45.09	98.92
	1-octanol	0.93	0.47	91.24	98.19
	2-octanone	0.93	0.47	54.32	94.39
	Toluene	0.93	0.47	16.809	91.84
	hexane	0.93	0.47	11.25	90.93
High Molecular Weight Tertiary Amines					
Tripropylamine (TPA)	1-butanol	1.0	0.5	3.5	78
	1-hexanol	1.0	0.5	2.4	70
	1-octanol	1.0	0.5	3	68
Tributylamine(TBA)	1-octanol	0.5	0.5	10	91
Tripentylamine (TPeA)	1-octanol	0.5	0.5	5	82
Trioctylamine (TOA)	**Benzyl alcohol**	**0.57**	**0.26**	**178**	**99.44**
	1-octanol	0.5	0.5	26	96
	2-octanol	0.57	0.14	23.19	95.7
	1-decanol	0.57	0.2	21.98	95.64
Tridodecylamine	MIBK	1.0	0.6	13.238	93
TPA/TOA (8:2)	1-octanol: n-heptane	1.0	-	70	98
High Molecular Weight Quaternary Amines					
Aliquate 336	Butyl alcohol	0.5	0.5	0.89	47.15

	2-octanol	0.5	0.5	0.668	40.05
	1-decanol	0.5	0.26	0.497	33.23

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