

Application of Reactive Extraction to Recovery of Carboxylic Acids

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Abstract Carboxylic acids are examples of compounds with wide industrial applications and high potential. This article presents the principles of reactive extraction along with the characteristics of tertiary amine extractants, while is given on considering the effect of the amine class and chain length. As such a brief overview the current research on reactive extraction, including the recovery of citric acid, selective amine-based extraction, and extractive fermentation is given. When discussing extractive fermentation, strategies for reducing solvent toxicity are also suggested based on specific examples. Finally, solvent regeneration and stripping of extracted acid are explained.

Keywords: amine, biocompatibility, carboxylic acids, extraction, toxicity

INTRODUCTION

Certain carboxylic acids have a variety of applications in industries producing food and pharmaceutical products, surfactants, detergents, and green solvent. Currently, carboxylic acids have become interesting as a raw material for biodegradable polymers. Plus the rise in petroleum costs, the large-volume production of carboxylic acids by fermentation has been the focus of new attention [1]. In the production of carboxylic acids by fermentation, free acid is required for the manufacture of commodities and specialty chemicals. Moreover, contaminating proteins and cell by-products need to be removed from the final product. Thus, to be cost effective, the separation process requires the removal of cells and protein-like impurities, concentration of salt, conversion of acid salts into free acids, and polishing of free acid to its required purity [2]. As such, the costs associated with product recovery, concentration, acidification, and purification have been very high in the past accounting for 60-70% of the product cost and making fermentation-based chemical technology impractical. account for 60-70% of the product cost [3].

Conventional Process for Recovery of Carboxylic Acids

The traditional product recovery method is based on precipitation of the insoluble calcium salt of carboxylic acids with $\text{Ca}(\text{OH})_2$ or CaCO_3 followed by reacidification with H_2SO_4 . The disadvantage of this process is handling large amounts of solid and slurry, and the production of equal amounts of calcium sulfate waste.

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Therefore, a separation process is required to eliminate the generation of calcium sulfate waste that includes solvent extraction and electrodialysis [4].

Another conventional process is liquid-liquid extraction in which a solute is transferred between an aqueous and water-immiscible organic phase based on the physical contact of the two phases. The phases are then separated, and the solute-rich phase is regenerated to recover the product. Extraction with conventional solvents, such as ether, is impractical for the recovery of most carboxylic acids because the low activity coefficient of the acid in the aqueous phase does not allow for a substantial transfer of the acid into the solvent.

Porous, solid sorbents with large surface areas, such as activated carbons and polymeric resins with functional groups, can be used in the recovery of carboxylic acids. Although the sorption process is effective, the limited capacity for the carboxylic acid on the solid surface is a disadvantage [5-7].

Membrane processes, such as electrodialysis, nanofiltration, and reverse osmosis, have been suggested as alternatives for the recovery of carboxylic acids, yet these methods are still in the early stage of development [8,9].

PRINCIPLES OF REACTIVE EXTRACTION

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 [10].

The following factors favor the use of extraction by

reversible chemical complexation over alternative methods [11]:

(1) The presence of functional groups in the solute capable of complexation. Acidic functional groups promote selectivity and increase the uptake capacity.

(2) Low solute concentration. With low solute concentrations there is a high driving force of free association sites on the complexing agent which is very favorable for extraction. Other separation processes do not have these advantages at low solute concentrations.

(3) Low activity of the solute in water. Because complexation can substantially lower the solute activity in the solvent phase, this produces a relative advantage over competing methods.

(4) Low volatility of solute. Complexation gains a relative advantage over distillation for non-volatile solutes.

(5) Low pH feedstream. Reversible complexation is driven by the amount of un-ionized acid in the solution and is thus favored at a low pH. The optimal pH for separation by complexation is related to the pK_A of the acid. Feed solutions with a low pH can have the disadvantage of promoting the extraction of other competing acids in multiple acid systems. At high pH values, where the acid is mostly dissociated, ion exchange can be more favorable. However, when considering that the optimum pH is near 5 in an acid fermentator, this can be troublesome for practical separation. Recently, the selective extraction of a specific acid from multiple acid systems have been carried out using the different degrees of dissociation of carboxylic acids based on their different pK_A 's [12,13]. Table 1 shows the pK_A values of various carboxylic acids.

(6) Regeneration of organic phase must be easy. Most liquid extractants are more easily regenerated than solid sorbents. Regeneration is required for recycling the complexing agent and the recovery of the product. The cost of the regeneration step is an important and determining factor in the economic viability of the separation.

Extractants in Reactive Extraction

There are three categories of extractants used in reactive extraction. These are extraction by solvation with carbon-bonded oxygen-bearing extractants, solvation with phosphorous-bonded oxygen-bearing extractants, and proton transfer or ion-pairing formation with high molecular weight aliphatic amines and their salts [14]. Since phosphorous and amine extractants have been mainly used in the recovery of carboxylic acids, only these extractants are discussed in the current article.

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, Fahim *et al.* [15] reported that for dilute acids, the dis-

Table 1. pK_A values of various carboxylic acids [5]

Carboxylic acids	pK_{A1}	pK_{A2}	pK_{A3}
Acetic acid	4.76	-	-
Propionic acid	4.87	-	-
Lactic acid	3.86	-	-
Oxalic acid	1.27	4.27	-
Malonic acid	2.83	5.70	-
Succinic acid	4.21	5.64	-
Phthalic acid	2.95	5.41	-
Citric acid	3.14	4.77	6.39

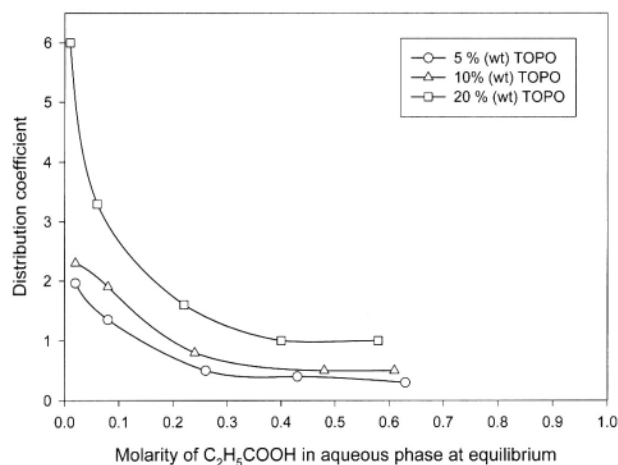


Fig. 1. Distribution coefficients of propionic acid extracted from water at 25°C to TOPO in hexane [15].

tribution coefficients for acetic and propionic acids are high in the reactive extraction by trioctyl phosphine oxide (TOPO) and tributylphosphate (TBP) dissolved in various diluents. In Fig. 1, the distribution coefficients of propionic acid extracted from water to TOPO in hexane are illustrated. 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 [15]. In general, the basicity of phosphoryl oxygen increases in the order: trialkyl phosphate $((RO)_3P=O)$, dialkyl phosphonate $((RO)_2P=O)$, alkyl dialkyl phosphinate $((RO)R_2P=O)$, and trialkyl phosphine oxide $(R_3P=O)$ [16]. 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. For example, Hano *et al.* reported that TOPO in hexane is the optimum extractant for *in-situ* extractive fermentation with *Rhizopus Oryzae* [17]. Solichien *et al.* found that TOPO/kerosene is the optimum extractant in membrane-based extractive fermenta-

tation for the production of propionic acid by *Propionibacterium acidipropionici* [18].

High Molecular Weight Aliphatic Amines and Their Salts

The extraction of proton-bearing organic and inorganic compounds from aqueous media by long chain aliphatic amines and their salts dissolved in a water-immiscible organic solvent is one of the newest developments in separation technology. The fundamental difference between oxygen- and nitrogen-bearing basic extractants in the extraction of carboxylic acids is the behavior of the acid proton during the transfer from an aqueous to an organic solution. In the systems with oxygen-bearing extractants, whether carbon, phosphorous, or sulfur bound, the acid strength in the aqueous solution and that of the hydrogen bond in the organic solution are the measures of extractability. In contrast, the acid extracted into an amine-containing organic phase is no longer regarded as an acid but as ammonium salt. It is thus the extent of the ion pair association between the alkylammonium cation and the acid radical that is the measure of extractability, or more precisely, the stability of the organic phase species [14]. The following reactions occur in the reactive extraction of carboxylic acids with tertiary amine extractants.

Dissociation of carboxylic acid :



Proton transfer to amine :



Recombination of ammonium salt :



Thus, the overall reaction can be given as follows:



In an acid-amine reaction, the stoichiometry of the acid and amine in the acid-amine complex varies with several factors, such as the property and concentration of amine, acid, and diluent.

In general, in an amine class there are primary, secondary, and tertiary amines. Ricker [19] studied the extraction of acetic acid by Amberlite LA-2 (secondary amine) in methyl isobutyl ketone (MIBK) and Alamine 336 (tertiary amine) in diisobutyl ketone. He reported that the extractability of the secondary amine was higher than that of the tertiary amine. However, secondary amines are subject to amine formation during regeneration by distillation. Therefore, tertiary amines have been used in the reactive extraction of carboxylic acids even though the extractabilities of tertiary amines are lower than those of secondary amines. In the case of primary amines, they are not applicable to the recovery of carboxylic acids because of their high water miscibility.

Generally, the basicities of tertiary amines are proportional to their chain length. However, the trend of extraction power is not always dictated by the basicity of a tertiary amine. For example, as seen in Fig. 2, the extraction power increases with the chain length of tertiary amines in an active diluent, such as 1-octanol,

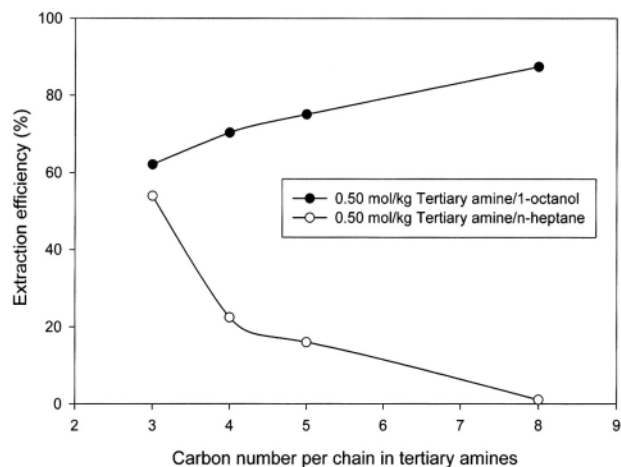


Fig. 2. Variation of extraction efficiency relative to the chain length of tertiary amines in reactive extraction of succinic acid [22].

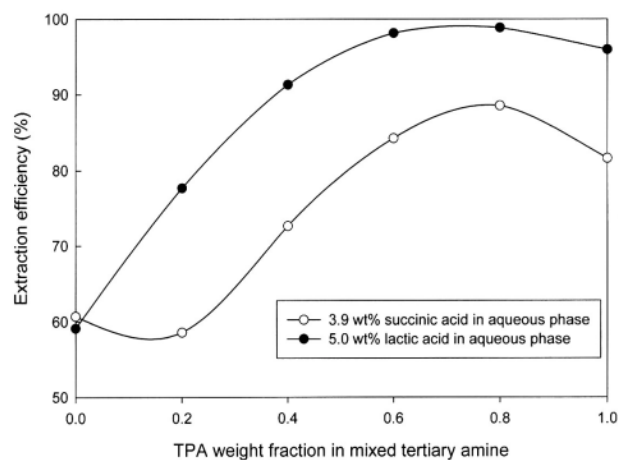


Fig. 3. Effect of tripropylamine composition in mixed tertiary amine composed of tripropylamine and trioctylamine on extraction efficiency [24,25] (1.0 mol/kg mixed tertiary amine dissolved in 3:7 (w/w) 1-octanol and *n*-heptane).

however, decreases with the chain length in an inactive diluent, such as *n*-heptane, in the reactive extraction of succinic acid [20-22]. This is because the more inert the diluent, the more favorable it is for polar complexes to form an aggregate, thereby shielding themselves from the nonpolar environment [23]. Based on these results, a mixed tertiary amine was developed. In general, a diluent mixed with an active and inactive diluent is used in reactive extraction to increase the efficiency of stripping. In most studies, only one kind of tertiary amine, such as TOA, has been used for reactive extraction in mixed diluents. However, when a mixed diluent such as 1-octanol/*n*-heptane is used in reactive extraction, a mixed tertiary amine composed of a relatively short chain tertiary amine and long chain tertiary amine provides a higher extraction efficiency than that with only one kind of tertiary amine [24,25]. Fig. 3 illustrates the

effect of the composition of tripropylamine on extraction efficiency. In addition, the selective extraction of succinic acid from a succinic and acetic acid aqueous mixture using a different basicity relative to the chain length of the tertiary amine has also been reported [26].

Diluents in Reactive Extraction

Although a tertiary amine has good extractability for carboxylic acids, it must always be used in the form of a solution in organic diluents due to its high viscous and corrosive properties. It has been found that diluents, especially those with functional groups, can significantly affect the extraction behavior of an amine. The properties of the diluents have an influence on the stoichiometry of the acid-amine complexes, the loading of the amine, as well as the third phase formation [27]. Diluents can be classified into active and inactive diluents.

Active Diluent

Active diluents have functional groups that enable a greater solvation of the acid-amine complex. This heading includes chlorinated hydrocarbon, ketone, alcohol and halogenated aromatic solvents. These diluents are a good solvating medium for an ion-pair, such as an acid-amine complex, because of their polar properties [23].

Inactive Diluent

This heading includes alkanes, benzene, and alkyl-substituted aromatics. Inactive diluents provide a very low distribution of the acid in the solvent phase, plus alkane, being nonpolar, provides for very little solvation of the polar complexes. Although inert diluents limit the solvating capacity of the third phase formation at higher acid concentrations in the organic phase, they are useful for the stripping step. In the stripping step, the equilibrium curve is shifted to the aqueous phase by increasing the concentration of the inert diluent in the mixed diluent, thereby re-extracting the extracted acid into the aqueous phase [28].

Criteria for Selection of Extractant

In general, the selection of the extractant is important for a reactive extraction process. The two most important characteristics are a high capacity for the product and a high selectivity for the product compared with water. These two requirements are represented by the distribution coefficient and separation factor [29]. The complexation between the extractant and the solute should also be strong enough to overcome the low activity of the solute in the aqueous phase, yet not so strong as to render regeneration difficult or impossible [11].

Among the various extractants for reactive extraction, tertiary aliphatic amines are widely used in the reactive extraction of carboxylic acids. Long chain aliphatic amines have a very low solubility for water without any loss of the extractant. They are also ther-

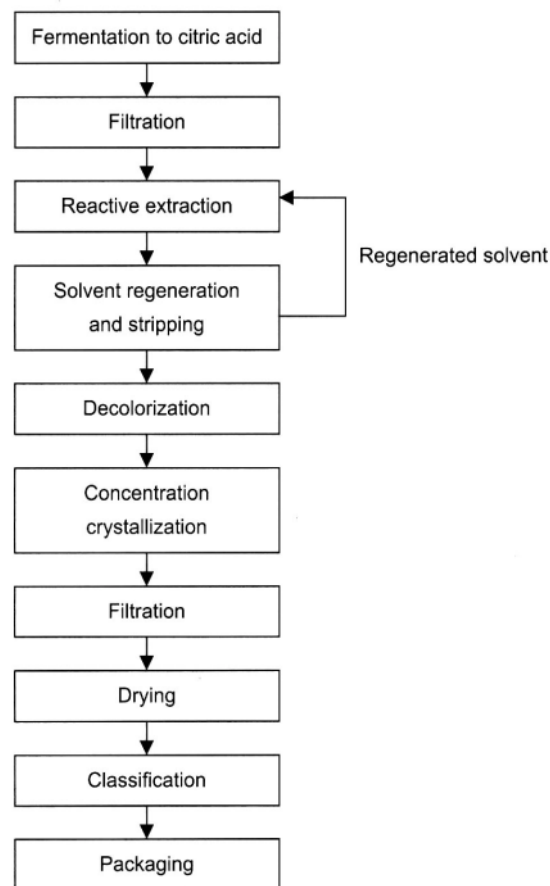


Fig. 4. Schematic diagram of reactive extraction process for citric acid [30].

mally stable, thereby, enabling regeneration by distillation. Tertiary amines are generally favored over secondary or primary amines. Primary amines are too soluble in water to be of practical use. Secondary amines potentially undergo amide formation with carboxylic acid, which causes a loss of both product and extractant. Longer chains reduce the molar concentration of the extractant available for complexation and increase the alkyl character of the solvent, thus reducing extraction [29].

In addition, other aspects such as biocompatibility and economics are also important in the selection of a solvent. Biocompatibility will be discussed later through several examples.

PRACTICAL APPLICATIONS

Amine-Based Recovery of Carboxylic Acids

One of the successful applications of amine-based extraction is the recovery of citric acid. Citric acid is the most versatile and widely used carboxylic acid in food, beverages, and pharmaceuticals [30]. It is produced by fermentation at a pH near the pK_{A1} of the acid ($pK_{A1} =$

3.14), where a substantial fraction of the acid exists in an undissociated form. Because the driving force for separation by reversible complexation is the undissociated form of the acid, reversible complexation is a practical method for recovering citric acid from fermentation media [31]. Commercially, amine-based extraction is used for the recovery of citric acid from a fermentation broth. The reactive extraction recovery process for citric acid is shown in Fig. 4. In this process, a mixture of tri-laurylamine, *n*-octanol, and C_{10} or C_{11} hydrocarbon is followed by the re-extraction of the citric acid from the solvent phase into water. Efficient citric acid extraction is achieved through a series of countercurrent steps that ensure the intimate contact of the aqueous and nonaqueous phases. When the transfer of the citric acid to the solvent phase is complete, the citric acid is re-extracted into water, also using a multistage countercurrent system. The two steps differ mainly in the temperature at which they are performed. Moreover, amine-based extraction has the advantage of minimal solid by products [30]. Bizek *et al.* [32] found that an undissociated as well as a dissociated form of citric acid is extracted in the recovery of citric acid when using trialkylamine dissolved in MIBK. This is a favorable result for the practical operation of the recovery of citric acid by amine-based extraction.

Recently, the amine-based extraction of lactic acid in a packed column was performed [33]. The application of columns for amine-based extraction provides for easy operation and a short operation time. In addition, the differential contacts in columns produce an easy phase separation and large interfacial area for mass transfer.

However, there are some limitations to the amine-based extraction of carboxylic acids. One of the limitations with amine extractants is the need for a low pH to convert the acid to its undissociated form for transfer to the solvent [4]. Generally, it has been reported that, except for the fermentation of citric acid, the operating pH in fermentation for carboxylic acids is at $\text{pH}=5-6$ (operating $\text{pH} > \text{pK}_A$). Accordingly, with an appropriate technique to overcome this pH limitation for acids other than citric acid, amine-based extraction has the potential to become an industrial-level recovery process for carboxylic acids from fermentation broth.

Selective Extraction of Specific Acid from Multiple Acid Systems

In the fermentation of a specific carboxylic acid, fermentation broths typically contain other carboxylic acids besides the main product. Yet, since most carboxylic acids are non-volatile, the fractionation of these acids is impossible by distillation.

For example, in a fermentation process with *Anaerobiospirillum succiniciproducens*, the maximum yield was determined as 0.99 succinic acid/g glucose consumed and the molar ratio of succinic acid and acetic acid was 1.9 [34]. It is well known that the presence of a by-product, such as acetic acid, can negatively affect the purification process and decrease the yield of the

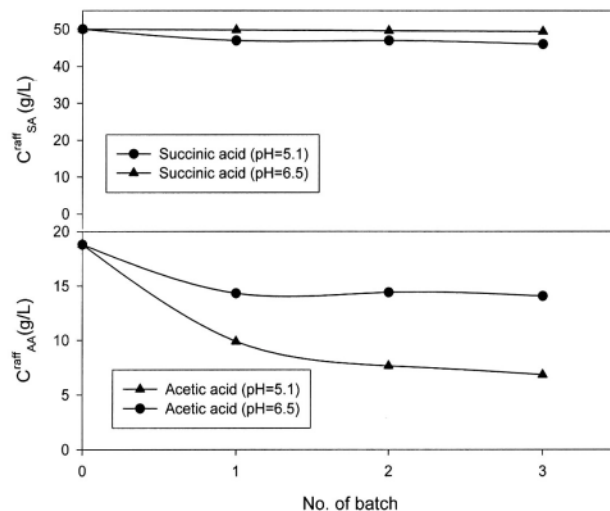


Fig. 5. Multiple extraction for removal of acetic acid from succinic and acetic acid aqueous solution [12] (0.25 mol/kg trioctylamine dissolved in 1-octanol).

fermentor. Therefore, a process for the removal of acetic acid from a fermentation broth should be developed for the economical purification of succinic acid as well as for a better fermentation performance. Jagirdar and Sharma recovered a variety of organic acids from aqueous acid mixtures with tri-*n*-octylamine in various water-immiscible solvents [35]. Siebold *et al.* [36] studied on the separation of lactic acid from citric acid and acetic acids by various extractants. When using Hostarex A337 dissolved in Cyanex 923/kerosene, they were able to separate citric acid from lactic and acetic acids, yet concluded that an optimized multistage extractor was required for the complete separation of these acids. Kirsh and Maurer studied the extraction characteristics of binary mixtures of citric, acetic, and oxalic acids in amine-based extraction. Husson and King investigated multiple-acid equilibria in ion-exchange adsorption and an equilibrium model [7]. Hong *et al.* selectively purified succinic acid from a binary mixture of succinic acid and acetic acid in the aqueous phase using different basicities relative to a variation in the chain length of tertiary amines [26]. Recently, the different extraction characteristics of carboxylic acids relative to pH enabled the selective extraction of acetic acid from a succinic/acetic acid aqueous mixture (Fig. 5). It was found that the mole ratio of succinic acid to acetic acid decreased to 6 [12].

Extractive Fermentation and Biocompatibility of Organic Phase

A variety of carboxylic acids can be produced by fermentation using various species of microbe, yet product inhibition limits the productivity of these fermentations. Thus extractive fermentation is a technique used to reduce end-product inhibition by removing the fermentation product *in situ* (Fig. 6). For extractive fer-

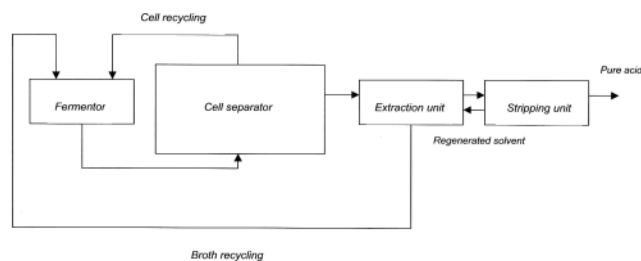


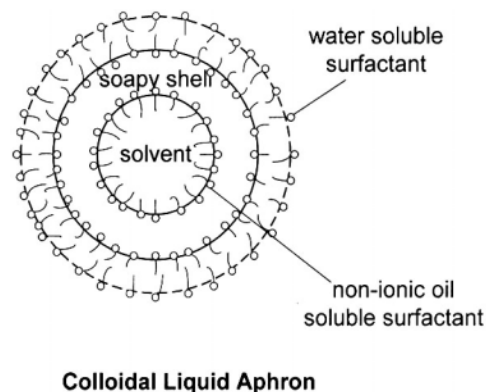
Fig. 6. Schematic diagram of extractive fermentation system [38].

mentation conditions, the fermentation broth is pumped continuously into a cell separator where the cells are separated and recycled into the fermentor. The filtrate is then transferred to an extraction unit in which the carboxylic acid is extracted. The aqueous phase containing a low concentration of carboxylic acid is recycled into the fermentor. The solvent phase rich in carboxylic acid is continuously transferred to a regeneration and stripping unit [38]. However, the limitations related to the development of extractive fermentation are solvent toxicity and poor extraction.

Most organic solvents are to a certain extent toxic to microorganisms. The presence of an organic solvent can damage the cell membrane, causing membrane rupture and metabolite leakage [39]. Osborne *et al.* found for various solvent-microorganism combinations that a critical solvent concentration in the cell membrane was reached, above which the cell membrane fluidity increased and cellular activity declined [40]. The solvent interacts with the cell by two routes: dissolution in the aqueous broth and direct contact of the cell with the water-immiscible solvent phase. The former is described by some as “molecular” toxicity, while the latter as “phase” toxicity [41]. Molecular toxicity usually causes less damage to the cell than does phase toxicity because the former is limited by the solvent solubility in the aqueous phase. Solvent-cell compatibility can be predicted by empirical methods such as the correlation between the solvent toxicity and the $\log P$ value of the solvent [42].

There are two ways to reduce solvent toxicity in an extractive fermentation process. One is replacement of the toxic solvent component with a nontoxic one. In this method, the identification of a nontoxic solvent is difficult and the extraction may be poor. For example, Tong *et al.* [43] investigated solvent screening for the extractive fermentation of lactic acid by *Lactobacillus rhamnosus*. They reported that TOMAC (Tri-*n*-octyl-methylammonium chloride) was highly toxic, and both butyl acetate and hexane exhibited some detrimental effects. However, they found that oleyl alcohol exhibited no toxicity, and selected TOMAC dissolved in oleyl alcohol (as low as 0.1 kmol/m^3) as the optimal solvent.

The second method is the addition of an immiscible, biocompatible component to the medium to entrap any toxic solvent that dissolves during the aqueous medium phase. Yabannavar and Wang were successful in per-



Colloidal Liquid Aphron

Fig. 7. Schematic diagram of CLAs [46].

forming extractive fermentation with *Lactobacillus delbrueckii*. They found that the immobilization of a solvent by κ -carrageenan significantly protected the cells from the immiscible solvent phase. Plus they reported that the toxic effect from the water soluble portion of the solvent was reduced by adding soybean oil. The supplementation soy oil to the encapsulated culture has been further tested in an attempt to reduce the diffusion of the extracting solvent into the κ -carrageenan beads used to immobilize the cells [44]. Tik *et al.* [45] immobilized the Alamine 336 in oleyl alcohol using sunflower oil in extractive lactic acid fermentation by *Lactobacillus delbrueckii*. A maximum total lactic acid concentration of 25.59 g/L was obtained with an oleyl alcohol solution containing 15% (v/v) Alamine 336 together with immobilized cells with 15% (v/v) sunflower oil. Hong *et al.* [46] immobilized the solvent using colloidal liquid aphrons (CLAs) in lactic acid production by *Lactobacillus rhamnosus*. As seen in Fig. 7, CLAs are micron-sized solvent droplets encapsulated by a thin aqueous film stabilized by surfactants. The use of CLAs facilitated both a reduction of toxicity and a fast rate of extraction. In addition to the above examples, a membrane contactor and liquid membrane can also be used as the method of toxicity reduction in fermentation microbe [47,48].

REGENERATION-SWING PROCESS

The most general approach for regeneration is the swing process, in which certain factors are altered so as to promote the back-extraction of a carboxylic acid from the extract into water. These swing variables involve the temperature and diluent composition.

Temperature Swing Regeneration

The complexation reactions between carboxylic acid and amine involve proton transfer or hydrogen-bonding formation and are normally exothermic. The formation of a complex makes the system more ordered and thus decreases the entropy. Therefore, as the temperature is

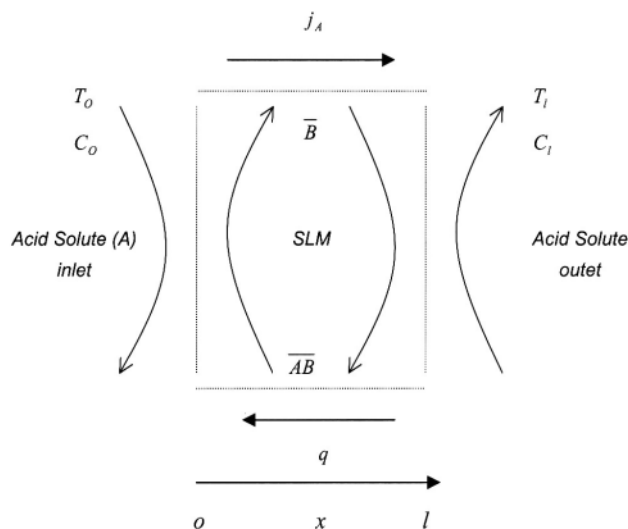


Fig. 8. Transport of acid solute from one phase to an other via flat unidirectional SLM by mass and heat exchange [51].

increased, the amount of carboxylic acid extracted decreases [49]. Baniel *et al.* [50] developed a process for citric acid recovery based on the shift of equilibrium relative to temperature. The acid is extracted at a low temperature, where the equilibrium favors the solvent phase, and then regenerated at a higher temperature, where the equilibrium favors the transfer of the acid to the aqueous phase. This is called TSR (Temperature-Swing-Regeneration) and is used commercially for the recovery of citric acid. Recently, Rockman *et al.* [51] developed a process incorporating temperature-swing regeneration for the recovery of carboxylic acids from an aqueous solution with a SLM (supported liquid membrane). They reported that the transport of carboxylic acid across a liquid membrane is facilitated by applying a temperature gradient between the feed and stripping phase. As shown in Fig. 8, the acid solute *A* in the left aqueous phase reacts quickly and reversibly with the complexing agent *B* in the membrane to form a complex *AB* at the SLM left boundary ($x=0$). *AB* now diffuses across the SLM to its right boundary ($x=l$). The reaction that previously occurred at the inlet is then reversed causing *AB* to decompose, stripping *A* into the right aqueous phase, and leaving the free *B* to diffuse back from right to left, thereby completing a full cycle.

Diluent Swing Regeneration

DSR (Diluent swing regeneration) is based on a shift in the equilibrium distribution of the acid from the aqueous phase to the organic phase between forward and back extraction caused by a change in the composition of the diluent with which the extractant is mixed [49,50,52]. This diluent composition swing facilitates the back extraction of the acid into an aqueous product phase. Some of the methods applied to accomplish this change in diluent composition have already been sum-

marized by Baniel *et al.* [50].

A diluent composition change can be combined with a temperature change to achieve a greater swing than its attainable with either approach alone, thereby producing a still greater overall concentrating effect [1]. Han and Hong [28] recommended the combination of the two processes is for the economic stripping of lactic acid. In their study, tri-*n*-octylamine dissolved in methylene chloride/*n*-hexane was used for the separation of lactic acid from an aqueous solution. The lactic acid in the organic phase was stripped by a simple distillation process at 50°C. In the stripping by simple distillation, TSR and DSR were both used because a change in the composition of the active diluent is related to an increase in temperature. The lactic acid was stripped in the reboiler, then methylene chloride was condensed and recovered from the condenser for reuse. In this stripping process, the stripped lactic acid was nearly pure [28,53].

CONCLUSION

There is still a considerable challenge related to lowering the costs of carboxylic acid recovery technology. Among the various recovery technologies of carboxylic acids, reactive extraction is perhaps most useful for improving the overall process economics. In particular, fermentation coupled with reactive extraction offers several advantages, such as a high product yield and the removal of by-products. However, the development of a solvent immobilization method and nontoxic solvent are still required for successful extractive fermentation. Recently, the use of solid sorbents bearing tertiary amine functional groups appears promising. Plus, the pH limitation must be overcome for a high separation efficiency.

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REFERENCES

- [1] King, C. J. (1992) Amine-based systems for carboxylic acid recovery. *CHEMTECH*. May: 285-291.
- [2] Zeikus, J. G., M. K. Jain, and P. Elankovan (1999) Biotechnology of succinic acid production and markets for derived industrial products. *Appl. Microbiol. Biotechnol.* 51: 545-552.
- [3] Baniel, A. M. and A. M. Eyal (1995) Citric acid extraction. *US Patent* 5,426,220.
- [4] Schügerl, K. (2000) Integrating processing of biotechnology products. *Biotechnol. Adv.* 18: 581-599.
- [5] Tung, L. A. and C. J. King (1994) Sorption and extraction of lactic and succinic acids at $\text{pH} > \text{pK}_{a1}$. 1. Factors Governing Equilibria. *Ind. Eng. Chem. Res.* 33: 3217-3223.
- [6] Dai, Y. and C. J. King (1996) Selectivity between lactic

- acid and glucose during recovery of lactic acid with basic extractants and polymeric sorbents. *Ind. Eng. Chem. Res.* 35: 1215-1224.
- [7] Husson, S. M. and C. J. King (1999) Multiple-acid equilibria in adsorption of carboxylic acids from dilute aqueous solution. *Ind. Eng. Chem. Res.* 38: 502-511.
- [8] Lee, E. G., S. H. Moon, and Y. K. Chang (1998) Lactic acid recovery using two-stage electro dialysis and its modelling. *J. Membr. Sci.* 145: 53-66.
- [9] Kim, Y. H. and S. H. Moon (2001) Lactic acid recovery from fermentation broth using one-stage electro dialysis. *J. Chem. Technol. Biotechnol.* 76: 169-178.
- [10] Hong, Y. K. and W. H. Hong (2000) Reactive extraction of succinic acid with tripropylamine (TPA) in various diluents. *Biopro. Eng.* 22: 282-284.
- [11] Tamada, J. A. (1989) *Extraction of Carboxylic Acids with Amine Extractants*. Ph. D. Thesis. Univ. of California at Berkeley, USA.
- [12] Hong, Y. K., B. S. Kim, and W. H. Hong (2001) Effect of pH on extraction characteristics of carboxylic acids and selective extraction from multiple acid systems. *Proceedings of Fall Meeting of KICChE*, 19-20 October Hanbat Univ, Taejon, Korea.
- [13] Hong, Y. K., W. H. Hong, and Y. K. Chang (2001) Effect of pH on the extraction characteristics of succinic and formic acids with tri-*n*-octylamine dissolved in 1-octanol. *Biotechnol. Bioprocess. Eng.* 6: 347-351.
- [14] Kertes, A. S. and C. J. King (1986) Extraction chemistry of fermentation product carboxylic acids. *Biotechnol. Bioeng.* 28: 269-282.
- [15] Fahim, M. A., A. Qader, and M. A. Hughes (1992) Extraction equilibria of acetic and propionic acids from dilute aqueous solution by several solvents. *Sep. Sci. Technol.* 27: 1809-1821.
- [16] Schügerl, K (1994) p. 77. *Solvent Extraction in Biotechnology*. Springer-Verlag, Berlin, Germany.
- [17] Hano, T., M. Mstumoto, M. Hirata, and S. Miura (1996) Extractive fermentation of lactic acid with *Rhizopus Oryzae* and *Lactobacillus rhamnosus*. *ISEC '96*. 1477-1452.
- [18] Solichien, M. S., D. O'Brien, E. G. Hammond, and C. E. Glatz (1995) Membrane-based extractive fermentation to produce propionic and acetic acids: Toxicity and mass transfer considerations. *Enzyme Microb. Technol.* 17: 23-31.
- [19] Ricker, N. L. (1978) *Recovery of Carboxylic Acids and Related Organic Chemicals from Wastewaters by Solvent Extraction*. Ph. D. Thesis. Univ. of California at Berkeley, USA.
- [20] Hong, Y. K. and W. H. Hong (2000) Separation characteristics of succinic acid in reactive extraction by using amine extractant. *Hwahak Konghak.* 38: 186-190.
- [21] Hong, Y. K. and W. H. Hong (2001) Performance improvement of succinic acid extraction by mixed tertiary amines. *6th World Congress of Chemical Engineering*. Melbourne, Australia, 23-27 September.
- [22] Hong, Y. K. and W. H. Hong (2000) Equilibrium studies on reactive extraction of succinic acid from aqueous solutions with tertiary amines. *Biopro. Eng.* 22: 477-481.
- [23] Tamada, J. A. and C. J. King (1990) Extraction of carboxylic acids by amine extractants. 2. Chemical interactions and interpretation of data. *Ind. Eng. Chem. Res.* 29: 1327-1333.
- [24] Hong Y. K. and W. H. Hong (1999) Reactive extraction of lactic acid with mixed tertiary amine extractants. *Biotechnol. Tech.* 13: 915-918.
- [25] Hong, Y. K. and W. H. Hong (2000) Extraction of succinic acid with 1-octanol/*n*-heptane solutions of mixed tertiary amine. *Biopro. Eng.* 23: 535-538.
- [26] Hong, Y. K., W. H. Hong, and H. N. Chang (2000) Selective extraction of succinic acid from binary mixture of succinic acid and acetic acid. *Biotechnol. Lett.* 22: 871-874.
- [27] Bizek, A., J. Honacek, R. Rericha, and M. Kousova (1992) Amine extraction of hydrocarboxylic acids. 1. Extraction of citric acid with 1-octanol/*n*-heptane solutions of trialkylamine. *Ind. Eng. Chem. Res.* 31: 1554-1562.
- [28] Han, D. H. and W. H. Hong (1996) Reactive extraction of lactic acid with trioctylamine/methylene chloride/*n*-hexane. *Sep. Sci. Technol.* 31: 1123-1135.
- [29] Kennedy, J. F. and J. M. S. Cabral (1993) *Recovery Processes for Biological Materials*. Wiley & Sons, NY, USA.
- [30] Blair, G. and P. Staal (1993) Citric acid. In: I. Kroschwitz and M. Howe-Grant (Eds.) *Kirk-Othmer Encyclopedia of Chemical Technology*. Wiley & Sons, NY, USA.
- [31] Husson, S. M. (1998) *Regeneration of Basic Adsorbents in the Recovery of Carboxylic Acids from Dilute Aqueous Solution and Multiple-Acid Equilibria in Adsorption of Carboxylic Acids from Dilute Aqueous Solutions*. Ph. D. Thesis. Univ. of California at Berkeley, USA.
- [32] Bizek, V., J. Horacek, M. Kousova, A. Heyberger, and J. Prochazka (1992) Mathematical model of extraction of citric acid with amine. *Chem. Eng. Sci.* 47: 1433-1440.
- [33] Han, D. H. and W. H. Hong (1998) Reactive extraction of lactic acid in a packed column. *Kor. J. Chem. Eng.* 15: 324-329.
- [34] Lee, P. C., W. G. Lee, S. Kwon, S. Y. Lee, and H. N. Chang (1999) Succinic acid production by *Anaerobiospirillum succiniciproducens*: Effects of the H₂/CO₂ supply and glucose concentration. *Enzyme Microb. Technol.* 24: 549-554.
- [35] Jagirdar, G. C. and M. M. Sharma (1980) Recovery and separation of mixtures of organic acids from dilute aqueous solutions. *J. Sep. Proc. Technol.* 1: 40-43.
- [36] Siebold, M., P. v. Frieling, R. Joppien, D. Rindfleisch, K. Schugerl, and H. Roper (1995) Comparison of the production of lactic acid by three different Lactobacilli and its recovery by extraction and electro dialysis. *Proc. Biochem.* 30: 81-95.
- [37] Kirsh, T. and G. Maurer (1997) Distribution of binary mixtures of citric, acetic, and oxalic acids between water and organic solutions of tri-*n*-octylamine. Part I. Organic solvent toluene. *Fluid Phase Equilib.* 131: 213-231.
- [38] Ye, K., S. Jin, and K. Shimizu (1996) Performance improvement of lactic acid fermentation by multistage extractive fermentation. *J. Ferment. Bioeng.* 81: 240-246.
- [39] Gu, Z., B. A. Glatz, and C. E. Glatz (1998) Propionic acid production by extractive fermentation. I. Solvent consideration. *Biotechnol. Bioeng.* 57: 454-461.
- [40] Osborne, S., J. Leaver, M. Turner, and P. Dunnill (1990) Correlation of biocatalytic activity in an organic-aqueous two-liquid phase system with solvent concentration in the cell membrane. *Enzyme Microbiol. Technol.* 12: 281-291.

- [41] Basettti, L. and J. Tramper (1994) Organic solvent toxicity in *Morinda citrifolia* cell suspension. *Enzyme Microb. Technol.* 16: 642-652.
- [42] Laane, C., S. Boeren, and K. Vos (1985) On optimizing organic solvents in multi-liquid-phase biocatalyst. *Trends Biotechnol.* 3: 251-252.
- [43] Tong, Y., M. Hirata, H. Takahashi, T. Hano, M. Mastomoto, and S. Miura (1998) Solvent screening for production of lactic acid by extractive fermentation. *Sep. Sci. Technol.* 33: 1439-1453.
- [44] Yabannavar, V. and D. I. C. Wang (1991) Strategies for reducing solvent toxicity in extractive fermentation. *Biotechnol. Bioeng.* 37: 716-722.
- [45] Tik, N., E. Bayraktar, and Ü.Mehmetoglu (2001) In situ reactive extraction of lactic acid from fermentation media. *J. Chem. Technol. Biotechnol.* 76: 764-768.
- [46] Hong, Y. K., D. W. Lee, P. C. Lee, W. H. Hong, and H. N. Chang (2001) Extraction of lactic acid with colloidal liquid aphrons and comparison of their toxicities with solvnets without surfactant on the viability of *Lactobacillus rhamnosus*. *Biotechnol. Lett.* 23: 983-988.
- [47] Solichien. M. S., D. O'Brien, E. G. Hammond, and C. E. Glatz (1995) Membrane-based extractive fermentation to produce propionic and acetic acids: Toxicity and mass transfer considerations. *Enzyme Microb. Technol.* 17: 23-31.
- [48] Tong, Y., M. Hirata, H. Takahashi, T. Hano, F. Kubota, M. Goto, F. Nakashio, and M. Mastomoto (1998) Extraction of lactic acid from fermented broth with microporous hollow fiber membranes. *J. Membr. Sci.* 143: 81-91.
- [49] Tamada, J. A. and C. J. King (1990) Extraction of carboxylic acids with amine extractants: 3. Effect of temperature, water coextraction, and process considerations. *Ind. Eng. Chem. Res.* 29: 1333-1338.
- [50] Baniel, A. M., A. M. Eyal, and K. Hajdu (1981) Recovery of acids from aqueous solutions. *U.S. Patent 4,275,234*.
- [51] Rockman, J. T., E. Kehat, and R. Lavie (1997) Thermally enhanced extraction of citric acid through supported liquid membrane. *AIChE J.* 43: 2376-2380.
- [52] Hong, Y. K., W. H. Hong, and T. H. Hong (1999) Separation characteristics of lactic acid by using mixed tertiary amine extractants. *Kor. J. Biotechnol. Bioeng.* 14: 566-571.
- [53] Han, D. H., Y. K. Hong, and W. H. Hong (2000) Separation characteristics of lactic acid in reactive extraction and stripping. *Kor. J. Chem. Eng.* 17: 528-533.

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