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A. Manzak[a]; O. Tutkun[a]
[a] Department of Chemistry, Sakarya University, Adapazarı, Turkey

Online publication date: 08 July 2010

To cite this Article Manzak, A. and Tutkun, O.(2005) 'Extraction of Citric Acid Through an Emulsion Liquid Membrane Containing Aliquat 336 as Carrier', Separation Science and Technology, 39: 10, 2497 — 2512

To link to this Article: DOI: 10.1081/SS-120037391

URL: http://dx.doi.org/10.1081/SS-120037391

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SEPARATION SCIENCE AND TECHNOLOGY
Vol. 39, No. 10, pp. 2497–2512, 2004

Extraction of Citric Acid Through an Emulsion Liquid Membrane Containing Aliquat 336 as Carrier

A. Manzak* **and O. Tutkun**

Department of Chemistry, Sakarya University, Adapazarı, Turkey

ABSTRACT

The extraction of citric acid from aqueous solutions through an emulsion liquid membrane containing Aliquat 336 carrier was studied. For the emulsions to be functionally stable, it was necessary to select suitable combinations of surfactants and internal stripping reagents. A quaternary amine, trioctylmethylammonium chloride (TOMAC), commercially known as Aliquat 336, was used as a complexing reagent for the extraction of citric acid from aqueous solutions, using sodium carbonate solutions as the internal stripping reagent. A nonionic surfactant, Span 80, was utilized to stabilize the emulsion. A mixture of STA90 NS, dominantly of paraffinic origin, and xylene was used as a diluent. Such parameters that affect the rate of extraction of citric acid, like surfactant concentration, initial feed pH, concentration of feed solution, carrier concentration, and stripping reagent concentration, were examined

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*Correspondence: A. Manzak, Department of Chemistry, Sakarya University, Adapazarı 54100, Turkey; E-mail: manzakaynur@hotmail.com.

DOI: 10.1081/SS-120037391 0149-6395 (Print); 1520-5754 (Online)
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experimentally. Under the conditions studied, it was found that it is possible to extract about 90% of the acid from the relatively concentrated feed solutions of 10% (w/v).

Key Words: Emulsion liquid membrane; Citric acid; Quaternary amine; Aliquat 336; Solvent extraction; Span 80.

INTRODUCTION

When they used for the production of organic acids, aerobic fermentation processes are the most interesting products that can be made from a biomass. Recently, extractive recovery of carboxylic acids from dilute, aqueous solutions, such as fermentation broth and wastewater, which have acid concentrations lower than 10%, has received an increasing attention.[1 – 14]

The classical method for recovering various carboxylic and hydroxycarboxylic acids from fermentation broth or aqueous streams is a common precipitation process. This method of recovery is costly and unfriendly to the environment. Because of their hydrophilic nature, the hydroxycarboxylic acids are poorly extractable by common organic solvents when applied to dilute solutions. Therefore, for their recovery from aqueous solutions, reactive extraction by a suitable extractant has been considered to be a promising alternative to the conventional process.[4,5,15] The phosphorus-based, oxygen-bearing extractants and high molecular weight aliphatic amines were proposed as the most suitable extractants.[4,5,7,8,15 – 18]

A significant amount of work has been reported on the extraction equilibrium of carboxylic acids extraction with tertiary and quaternary amines such as tri-*n*-octylamine (TOA), trilaurylamine, Alamine 336, and Aliquat 336.[4,6 – 9,11 – 14,19] Extraction of organic acids with the phosphorus-based, oxygen-bearing extractants, such as tri-*n*-octylphosphine oxide (TOPO) and tri-*n*-butylphosphate (TBP), has been also studied.[6,14,19,20]

Many factors have important influences on the extraction characteristics—the nature of the acid extracted, concentrations of the acid and extractant, and the type of diluent used.[7] Primary amines are too soluble in water to be used with aqueous solutions. Secondary amines are subjected to amide formation upon regeneration by distillation. Consequently, long-chain amines have received the most attention. Quaternary amines also have higher distribution factors.[6,7]

In the extraction of carboxylic acids with long-chain tertiary amines, dissolved in organic diluents, a third phase (a second organic phase) between the organic and aqueous phases may form at higher acid concentrations in the organic phase. Similar to amine extraction of other acids and their salts,

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the region of average organic phase compositions in which formation of third phase takes place depends strongly on the nature of the diluent. On the other hand, in the organic phase, paraffinic, inert diluents, limit the solvent capacity by the third-phase formation at higher acid concentrations.[21] However, if a mixture of an inert diluent and an active, solvating modifier is used, increasing the modifier concentration in the binary diluent tends to suppress the third phase formation.[22] The aromatic hydrocarbons have a greater solvency for the amine–acid complex than the parafinic complex.[4]

Since conventional precipitation is a complex process, solvent extraction and a liquid membrane process have been proposed as alternatives to the conventional precipitation processes. Moreover, these techniques have the advantages of continuously removing the acid from the fermentation broth and keeping the acid concentration to a low level. Recently, in situ extractive fermentation processes, in which organic acids are simultaneously recovered during the production of the fermentation broth, have attracted great attention from the points of view of suppression of the product inhibition and increasing the reactor efficiency.[23]

Citric acid and its alkaline salts (citrates) are widely used in pharmaceuticals and cosmetics. Citric acid is also added to other pharmaceuticals as an antioxidant to improve flavor and maintain the stability of the active ingredients.

Today, citric acid is produced almost exclusively by fermentation of the fungus *Aspergillus niger* using either surface or submerged cultures. Complex raw materials, often molasses, are used.

Liquid membrane is certainly a promising method for the separation and concentration of such species from aqueous streams because it combines the extraction and stripping processes.[10,24–38]

Liquid membranes utilize a water-immiscible phase into which a component from an aqueous solution (preferably) is distributed. In this sense, it is similar to solvent extraction, and much of the theory in that field can be applied. However, unlike solvent extraction, there is no stage in which the water-immiscible phase comprises a marked part of the separated component (A). Instead, it forms a thin membrane through which A transfers from one aqueous phase (feed) to another (stripping solution or product phase). As stated by Pellegrino and Noble,[28] the extraction chemistry involved in liquid membrane transport is essentially the same as that found in solvent extraction, but the overall transport is governed by kinetic rather than equilibrium parameters. The solvent extraction process, however, requires larger volumes of solvent inventory and equipment, and thus higher investment costs. One disadvantage of the system is swelling due to water transport from the external phase (feed) to the internal phase (product), resulting in a decrease in the degree of solute concentration achieved inside the membrane.[39]

In the present work, the application of the emulsion type of liquid membrane technique to the separation and enrichment of citric acid from aqueous solutions were studied experimentally with parameters as surfactant concentration, feed concentration and pH, carrier concentration, and stripping reagent concentration.

EXPERIMENTAL

Materials

Diluent used as the membrane phase was STA90 NS, which is an aliphatic mixture, a product of ExxonMobil. The carrier, Aliquat 336, a quaternary amine (trioctylmethylammonium chloride, TOMAC) was kindly received from Henkel Corporation, Germany. The surfactant, Span 80 (sorbitan monooleate) reagent grade, was purchased from Fluka and used as the emulsion stabilizer. Citric acid (Merck, citric acid monohydrate cryst., extra pure) was used as received to prepare the feed solutions of various pH and concentrations. The feed solution pH was adjusted by adding either NaOH or H_2SO_4 solution.

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Method

The liquid membranes, consisted of a carrier, a surfactant, and a diluent. The surfactant was Span 80 and used as the emulsion stabilizer. The diluent was STA90 NS, a mixture of predominantly aliphatic origin. A water-in-oil (W/O) emulsion was made by dropwise addition of Na_2CO_3 solutions (50 mL) to the organic membrane solution (40 g), stirred at 2000 rpm for 30 min at ambient temperature of $20^\circ C \pm 1^\circ C$. The phase ratio of the membrane phase to the internal phase was 1 : 1. The membrane solutions were prepared as required. All the membrane compositions were on mass basis; feed and stripping solutions were prepared in w/v basis. The resulting emulsion was then dispersed in a 600-mL baffled beaker that contained the citric acid solution to be extracted. The two-phase system was stirred by a variable speed mixer (Ultra Turrax, IKA, Germany) equipped with a turbine-type Teflon impeller.

The dispersed globules were typically about 1 mm in size. Samples of approximately 2 mL of the feed phase were taken periodically for analysis. Extraction rates were measured by analyzing the feed phase citric acid concentrations. At the end of each run, the emulsion was recovered and subsequently broken into its constituent organic and aqueous phases using a high-voltage splitter with niobium electrodes.

Analysis of citric acid samples was performed by high-performance liquid chromotography (HPLC) by the help of Shimadzu (Tokyo, Japan) organic acid column. Aqueous phase pH measurements were determined with a Schott model CG840 pH meter (Germany). All extraction experiments were carried out batchwise and at the ambient temperature of 20°C ± 10°C. All aqueous solutions were prepared using deionized water. The details of the experimental procedure were reported elsewhere.[40]

RESULTS AND DISCUSSION

Effect of External Phase pH on Extraction of Citric Acid

The effect of hydrogen ion concentration was examined by varying the initial pH of the external phase 1 through 4. The feed solution (initial citric acid concentration of 10% w/v or 0.520 M) had a pH of 1.5 and the adjustments in pH were made by adding either NaOH or H_2SO_4 solutions. All the other operating parameters were held constant. Figure 1 shows the effect of the initial pH of the external phase on the rate of extraction.

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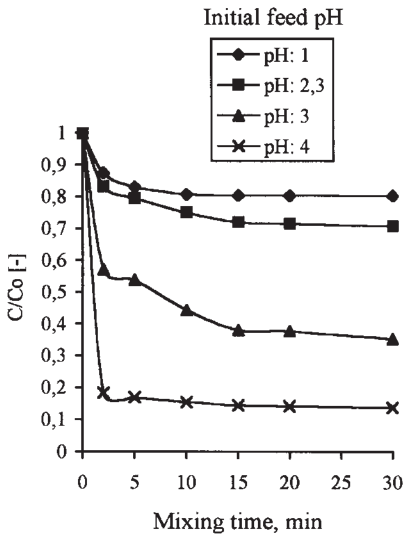

Figure 1. The effect of initial pH in the external phase on the extraction of citric acid [diluent: 85% w/w (80% STA90 NS + 20% xylene); surfactant: 10% w/w Span 80; Aliquat 336: 5% w/w; external phase concentration: 10% w/v citric acid; stripping phase: 50 mL of 10% w/v (Na_2CO_3) mixing speed: 300 rpm; treatment ratio (V_F/V_E): 2/1; phase ratio (V_s/V_m): 1/1]. V_F, V_E, V_s, and V_m: volumes of the external, emulsion, stripping, and membrane phase, respectively.

Citric acid (H_3A) is a trivalent acid. Its dissociation can be described by the stepwise reactions:

$$H_{4-i}A^{1-i} \rightleftarrows H^+ + H_{3-i}A^{i-} \quad (i = 1, 2, 3) \tag{1}$$

characterized by the stepwise dissociation constants $K_{a,i}$

$$K_{a,i} = \frac{[H^+][H_{3-i}A^{i-}]}{[H_{4-i}A^{1-i}]} \quad (i = 1, 2, 3) \tag{2}$$

The corresponding values of $pK_{a,i}$, reported elsewhere,[41] where 3.1, 4.8, and 6.4, respectively.

The concentrations of dissociated ($H_{3-i}A^{i-}$) and undissociated acids were calculated in the initial feed solutions for the measured pH values, as shown in Table 1. From Table 1, the concentrations of dissociated and undissociated acids are affected by the concentration of hydrogen ion (H^+) or pH. At low pH values, or high H^+ ion concentrations, the acid present in the aqueous phase is mainly in the undissociated form (Table 1). On the contrary, at high pH values, the acid present in the aqueous phase is mainly in the dissociated form. The degree of dissociation of the citric acid at pH = 1 ranges from 0.74% to 88.1% at pH = 4, as may be seen from Table 1. All the initial pH values were below the first $pK_{a,1}$ value, except for pH = 4, which is the just below the second $pK_{a,2}$ value. Figure 1 indicates that the rate of extraction enhances as the pH increases since the dissociation of the acid has been increased. This is also in agreement with the findings of Yang et al.[8] Since Aliquat 336 is composed of an organic cation associated with a chloride ion, it can function as an ionexchange reagent under both acidic and basic conditions, as stated elsewhere.[42] However, Yang et al. argue that extractant regeneration by stripping might be diffucult for Aliquat 336 in solvent extraction. In fact, this was not the case in this study, as observed in Fig. 1. Though the extraction chemistry involved in liquid membrane transport is similar to

Table 1. The dissociated and undissociated citric acid concentrations, that are calculated in the initial feed concentrations, $[H_3A]_0$, all are given in mol/L.

pH	$[H^+]$	$[H_3A]_0$	$[H_3A]$	$[H_2A^-]$	$[HA^{2-}]$	$[A^{3-}]$	Degr. of diss[a] (%)
1	0.100	0.520	0.516	0.00385	6.55E − 3	2.62E − 12	0.740
2.3	0.005	0.520	0.453	0.0673	2.28E − 4	1.82E − 08	12.9
3	0.001	0.520	0.298	0.222	3.77E − 4	1.51E − 06	42.7
4	0.0001	0.520	0.062	0.458	7.80E − 2	3.12E − 04	88.1

[a] Degree of dissociation of the acid (%).

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that in solvent extraction, the overall transport is governed by the kinetic rather than equilibrium parameters.[28]

In this study, no attempt was made to measure the time dependence pH of the feed solutions, for that requires a much higher amount of samples to be taken. It would cause a disruption in the experiments. However, during the trial runs, one such run was carried out. The results are given in Table 2. For solutions of citric acid between 5% and 10% w/v the initial pH ranges from 1.9 to 1.5, respectively. From Table 2, it is seen that the external phase pH gradually increased during extraction, though a sharp decrease in pH initially occurred. The emulsion globules appeared to be very stable, therefore, the pH increase observed in the feed phase, as shown in Table 2, could be attributed to the progressive removal of the acid from the external phase.

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Effect of Surfactant Concentration

The concentration of Span 80 in the membrane phase was varied to examine the effect of the surfactant concentration on the rate of extraction, as shown in Fig. 2. The extraction rate was found to increase with an increase in Span 80 concentration. The results show that increasing the concentration improved emulsion stability and increased the extraction efficiency, η.

$$\eta = 1 - \frac{C}{C_0} \tag{3}$$

where C_0 and C are the concentrations of the citric acid, initial and actual, respectively. The similar trend was obtained by Boey et al[25] in the liquid membrane extraction of citric acid with Alamine 336, a tertiary amine.

Table 2. The variation of external phase pH with time; min.

	$t = 0$	2	5	10	15	20	30
pH	4.0	2.6	2.7	2.8	2.8	2.8	2.9
C/C_0	1.000	0.482	0.250	0.194	0.166	0.143	0.140

Notes: Diluent: 83% w/w (80% STA90 NS + 20% xylene); surfactant: 12% w/w Span 80; Aliquat 336: 5% w/w; initial external phase pH : 4; initial external phase concentration: 10% w/v citric acid; stripping phase: 50 mL of 10% w/v (Na_2CO_3); mixing speed: 300 rpm; treatment ratio (V_F/V_E): 2/1; phase ratio (V_s/V_m): 1/1. V_F, V_E, V_s, and V_m: volumes of the external, emulsion, stripping, and membrane phases, respectively.

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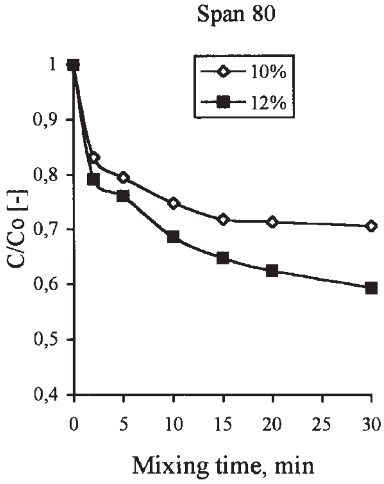

Figure 2. The effect of surfactant (Span 80) concentration on the rate of extraction [diluent: 83–85% w/w (80% STA90 NS + 20% xylene); Aliquat 336: 5% w/w; external phase concentration: 10% w/v citric acid; initial pH of external phase: 2.3; stripping phase: 50 mL of 10% w/v (Na_2CO_3); mixing speed: 300 rpm; treatment ratio (V_F/V_E): 2/1; phase ratio (V_s/V_m): 1/1]. V_F, V_E, V_s, and V_m: volumes of the external, emulsion, stripping, and membrane phase, respectively.

Effect of External Phase Concentration

The effect of the external phase concentration of citric acid on extraction is shown in Fig. 3. The citric acid concentrations in the external phase were varied from 2% w/v (or 0.104 M) to 10% w/v (or 0.520 M). It may be observed from Fig. 3 that when the citric acid concentration in the external phase is decreased, there is a significant increase in the rate of extraction. While 50% of the citric acid is extracted within 15 min for a feed concentration of 5% w/v, almost all of the citric acid is extracted during same period of time for feed concentration of 2% w/v. The concentrations of acid dissociated (mainly consisting of H_2A^-) at the initial feed pH of 2.3 were calculated to be of 0.0135, 0.0337, and 0.0673 M for the initial feed concentrations $[H_3A]_0$ of 2%, 5%, and 10% w/v, respectively. The higher the concentration is, the higher driving force for the citric acid transfer and, thus, the higher the acid extraction rate is.

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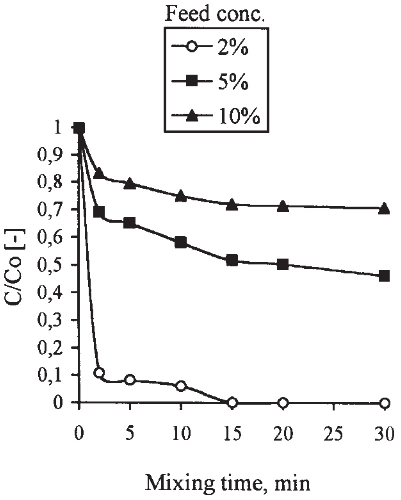

Figure 3. The effect of external phase concentration on the rate of extraction [diluent: 85% w/w (80% STA90 NS + 20% xylene); surfactant: 10% w/w Span 80; Aliquat 336: 5% w/w; initial pH of external phase: 2.3; stripping phase: 50 mL of 10% w/v (Na_2CO_3); mixing speed: 300 rpm; treatment ratio (V_F/V_E): 2/1; phase ratio (V_s/V_m): 1/1]. V_F, V_E, V_s, and V_m: volumes of the external, emulsion, stripping, and membrane phase, respectively.

Effect of Carrier Concentration

In practice, the surfactant Span 80 has been found to have the most satisfactory results with the carrier (Aliquat 336) concentration of 5–10% by weight of the membrane phase giving the required complexing ability, coupled with very good emulsion stability. The initial exraction rate of citric acid is slightly higher for 7% and 10% w/w Aliquat 336 than for 5% w/w, as shown in Fig. 4. However, the rate of extraction generally appears to be comparable, within the range of experimental error. This could be attributable to a permeation process controlled by the diffusion in the stagnant film of the aqueous feed phase, as reported by Alguacil et al.[43]

Effect of Stripping Reagent Concentration

Figure 5 shows the effect of increasing the concentration of sodium carbonate (Na_2CO_3) used as the internal phase stripping reagent. Increasing the

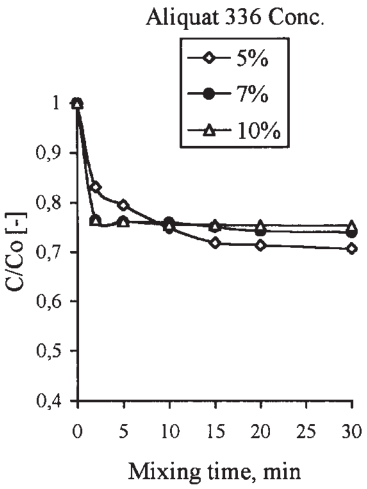

Figure 4. The effect of carrier (Aliquat 336) concentration on the extraction rate [diluent: 85% w/w (80% STA90 NS + 20% xylene); surfactant: 10% w/w Span 80; initial pH of external phase: 2.3; external phase concentration: 10% w/w citric acid; stripping phase: 50 mL of 10% w/v (Na_2CO_3); mixing speed: 300 rpm; treatment ratio (V_F/V_E): 2/1; phase ratio (V_s/V_m): 1/1]. V_F, V_E, V_s, and V_m: volumes of the external, emulsion, stripping, and membrane phase, respectively.

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concentration from 10% to 20% (w/v) leads to an improvement of about 40% in the final yield of extraction. The results in Fig. 5 show that excellent kinetics and final yield of citric acid extraction could be achieved using 20% w/v Na_2CO_3 solutions as the stripping reagent. When Na_2CO_3 solution was used as the internal aqueous solution, the pH in the stripping solution was higher than that in the feed solution. The driving force for extraction is the difference in pH between the internal and external phases. Citrate anions are extracted into the organic phase through the interface between the feed solution and membrane phase. They are then stripped into the internal phase through the interface between the membrane and internal phases. The overall driving force in pH for citric acid transfer with a 20% w/v Na_2CO_3 solution is higher than that with 10% w/v solution, thus the higher rate of extraction.

Extraction Mechanism

Boey et al.[25] proposed a mechanism for the liquid membrane extraction of citric acid with Alamine 336, a tertiary amine. They observed the CO_2

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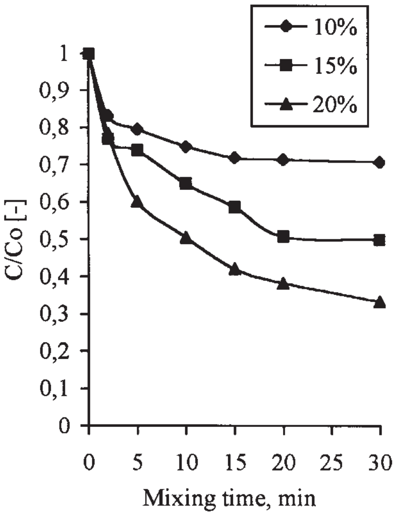

Figure 5. Effect of stripping reagent concentration on the rate of extraction [diluent: 85% w/w (80% STA90 NS + 20% xylene); surfactant: 10% w/w Span 80; Aliquat 336: 5% w/w; external phase concentration: 10% w/v citric acid; initial pH of external phase: 2.3; mixing speed: 300 rpm; treatment ratio (V_F/V_E): 2/1; phase ratio (V_s/V_m): 1/1]. V_F, V_E, V_s, and V_m: volumes of the external, emulsion, stripping, and membrane phase, respectively.

formation and found that the external phase became very gaseous between the first 3–10 min of adding the emulsions. This was also observed by Manzak[44] for citric acid extraction with Alamine 336.

The formation of CO_2 for the citric acid using Aliquat 336, a quaternary amine, was also observed, similarly to the observations of Boey et al.[25] From the experimental observations, an extraction mechanism, similar to that of Boey et al.[25] may be proposed.

The steps of the proposed transport mechanism are as follows (Fig. 6):

a. In the extraction step, the quaternary amine reacts with the citric acid to form a citrate-amine complex at the interface between the external and membrane phases:

$$\underset{\text{Aliquat 336}}{6CH_3R_3N^+Cl^-_{(org)}} + \underset{\text{citric acid}}{2C_6H_5O_{8(aq)}} \longrightarrow \underset{\text{citrate-amine complex}}{2(CH_3R_3N)_3C_6H_5O_{7(org)}} + 6H^+ + 6Cl^- \qquad (4)$$

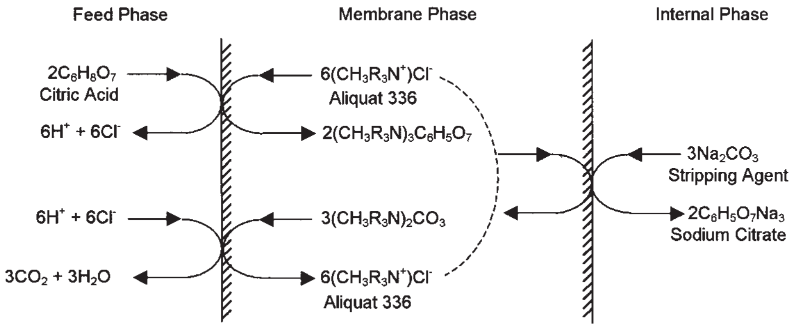

Figure 6. Schematic mechanism of citric acid extraction and stripping by quaternary amine (TOMAC) and sodium carbonate.[25]

where the subscripts (aq) and (org) designate species in the aqueous and organic phases, respectively.

b. Transport of the citrate-amine complex (amine salt) followed by stripping at the interface between the membrane and internal phases: after the citrate-amine complex has diffused across the membrane, the complex reacts with the stripping solution (Na_2CO_3) at the membrane–stripping phase interface. The citrate ions are stripped from the organic carrier solution into the stripping phase by the following reaction.

$$\underset{\text{citrate-amine complex}}{2(CH_3R_3N)_3C_6H_5O_{7(org)}} + \underset{\text{sodium carbonate}}{3Na_2CO_{3(aq)}} \longrightarrow \underset{\text{amine carbonate}}{3(CH_3R_3N)_2CO_{3(org)}} + \underset{\text{sodium citrate}}{2C_6H_5O_7Na_{3(aq)}} \tag{5}$$

c. Transport of the amine carbonate with CO_2 disengagement and quaternary amine regeneration at the interface between the membrane and external phases:

$$\underset{\text{amine carbonate}}{3(CH_3R_3N)_2CO_{3(org)}} + 6H^+_{(aq)} + 6Cl^-_{(aq)} \longrightarrow \underset{\text{Aliquat 336}}{6CH_3R_3N^+Cl^-_{(org)}} + 3CO_2 + 3H_2O \tag{6}$$

The amine carbonate then diffuses back to the membrane–external phase interface, where the carrier (quaternary amine) regenerates with a CO_2 disengagement.

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CONCLUSION

The following conclusions can be drawn from the experimental work carried out on the liquid membrane extraction of citric acid from the aqueous solutions using Aliquat 336 as carrier and sodium carbonate as the stripping reagent.

1. As the initial pH of external phase ranged from 1 to 4, the degree of the acid dissociation increased from 0.74% to 88.1%. The extraction efficiency of citric acid increased as much 65%, that is, the extent of extraction increases, while the pH of the feed phase increases, regarding the relatively concentrated citric acid solutions of 10% (w/v). This further supports the view that Aliquate 336 is composed of an organic cation associated with a chloride ion. It can function as an ion-exchange reagent.[8,42]
2. The concentration of the carrier, trioctylmethylammonium chloride (TOMAC, commercially known as Aliquate 336), does not affect the extraction rate significantly, as the concentration ranged from 5% to 10% (w/w). This could be attributable to a permeation process controlled by the diffusion in the stagnant film of the aqueous feed phase, as reported by Alguacil et al.[43]
3. As the concentration of stripping reagent, Na_2CO_3 increases from 10% to 20% w/v, there is an increase of about 40% in the overall extraction efficiency.
4. The extraction efficiency of citric acid decreases with an increase in the external phase concentrations. Almost 100% extraction of citric acid, with the external phase concentration of 20% w/v, is possible within 15 min.
5. A transport mechanism for the liquid membrane extraction of citric acid, similar to that of Boey et al.,[25] which involves salt formation with the quaternary amine carrier, followed by the formation of amine carbonate during the stripping process and subsequent release of CO_2 in the external phase, has been proposed.

Some researchers[6,8] state that extractant regeneration by stripping may be difficult using Aliquat 336 as carrier, because of higher distribution factors for the solvent extraction of carboxylic acids. However, this would not apply to liquid membranes, combining the processes of extraction, diffusion, and stripping in a single step, since the overall transport is governed by kinetic rather than equilibrium parameters, as stated by Pellegrino and Noble.[28] This view has been further supported experimentally in this study.

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ACKNOWLEDGMENT

The authors express their sincere gratitude to ExxonMobil Co., Belgium, for supplying the solvent STA90 NS, and to Henkel Co., Germany for the carrier Aliquat 336.

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