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Selective Pertraction of Carboxylic Acids Obtained by Citric Fermentation

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ABSTRACT

Pertraction through liquid membranes is one of the most recent liquid–liquid extraction techniques that could be applied for separation of biosynthetic products. This article describes facilitated pertraction has been used for selective separation of citric, malic, and succinic acids from a mixture. The separation equipment included a U-shaped cell containing 1,2-dichloroethane as a liquid membrane and Amberlite LA-2 as a carrier. The experimental data indicated that malic and succinic acids can be initially selectively separated from citric acid at an equimolecular ratio between the carrier and these acids. Then, for a selective

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separation of malic acid from succinic acid, a carrier molar concentration inside the liquid membrane equal to that of malic acid in the feed phase was required. The favorable effect of carrier concentration on separation selectivity was enhanced by the modification of aqueous phases pH and mixing intensification.

Key Words: Facilitated pertraction; Liquid membrane; Citric acid; Malic acid; Succinic acid; Amberlite LA-2; Mass flow; Permeability factor; Selectivity factor.

INTRODUCTION

Extraction using liquid membranes, called pertraction, has been studied since the 1980s and is one of the most advantageous techniques of separation at the present, with important applications on biosynthetic products separation (antibiotics, amino acids, and carboxylic acids), as well as on metals recovery from hydrometallurgical and nuclear industry wastes. This separation method consists of the transfer of a solute between two aqueous phases of different pH, which are separated by a solvent and carrier layer.

Commonly, liquid membranes can be obtained either by emulsification, when its stability is poor, or by including the solvent in a hydrophobic porous polymer matrix.[1–4] Moreover, the liquid membranes are obtained using pertraction equipment of special construction that allow separation and easy maintenance of the three phases without adding surfactants (free liquid membranes).[4–6]

Compared to conventional liquid–liquid extraction, the pertraction offers the following advantages:[1,4,7]

- The quantity of solvent used is small, because of its continuous regeneration.
- The loss of solvent during extraction and transport process is reduced.
- As long as the pH gradient between the two aqueous phases is maintained, there is the possibility of solute transport against its concentration gradient.

The pertraction efficiency could be significantly enhanced by adding of a carrier in the liquid membrane, such as organophosphoric compounds, long chain amines, or crown-ethers. The separation process is facilitated pertraction.

Citric acid is one of the widely used carboxylic acids, having multiple applications in chemical, pharmaceutical, food, and cosmetic industries.

This compound is mainly obtained through a fermentation process by *Aspergillus niger* cultivated on molasses.[8–10] Due to the presence in the final broth of other carboxylic acids, especially malic and succinic acids as secondary metabolic products, the separation and purification technology of citric acid is quite complicated complicate. Thus, the citric acid represents about 80–95% from total organic acids in the broth at the end of fermentation, its concentration being of 50 g/L. The rest are secondary acids, their concentration reaching 4 g/L.[8]

On an industrial scale, the separation and purification of citric acid consist of carboxylic acid precipitation as calcium salts, solubilization of calcium citrate by heating the solution, and citric acid release by treating with sulfuric acid.[8,9] This technology needs a high amount of raw materials and energy consumption and produces large amounts of calcium sulfate as the by-product, without leading to high-purity citric acid.

For these reasons, the possibility of selective separation of carboxylic acids from fermentation broths by reactive extraction with Amberlite LA-2 was analyzed in previous studies.[11,12] The reactive extraction of carboxylic acids with Amberlite LA-2 occurs by means of an interfacial chemical reaction with hydrophobic compounds formation.[11–13] The structures of the formed compounds depend on the molar ratio between the extraction system components. The reactive extraction mechanism can be generally expressed by the following interfacial equilibrium:

$$m\mathrm{R(COOH)}_{n\mathrm{(aq)}} + p\mathrm{A}_{\mathrm{(o)}} \rightleftarrows [\mathrm{R(COOH)}_n]_m \cdot \mathrm{A}_{\mathrm{p\,(o)}}$$

where $n = 2$ for malic and succinic acids and $n = 3$ for citric acid. A is the extractant of amine type, m and p are the moles of acid, respectively, and amine participating at the interfacial reaction.

For a constant value of the extractant concentration, the structure of the formed compound is determined by the level of the carboxylic acid concentration. Therefore, the reactive extraction could occur by means of the following possible mechanisms:[11–13]

a. For a molar ratio $m:p$ below 1, the type of interfacial reaction product is $\mathrm{R(COOH)}_2 \cdot \mathrm{A}_2$ for malic and succinic acids and $\mathrm{R(COOH)}_3 \cdot \mathrm{A}_3$ for citric acid.
b. For a molar ratio $m:p$ nearly 1, the extraction system components react in a equimolecular proportion forming: $\mathrm{R(COOH)}_\mathrm{n} \cdot \mathrm{A}$.
c. At high initial concentration of the organic acids, a stable emulsion of high acidic adducts concentration can appear in nonpolar diluents especially (the third phase).[13] In this case, the structure of the formed acidic adduct is $[\mathrm{R(COOH)}_n]_m \cdot \mathrm{A}$.

The previous results indicated that the proposed mechanisms are valid for malic and succinic acids, the structure of acidic adduct formed in the case c being of $[R(COOH)_2]_2 \cdot A$ type. The reactive extraction mechanism of citric acid with Amberlite LA-2 is different, the separation occurring only by the interfacial reaction type described by mechanism b for entire domain of acid concentrations in aqueous phase. Thus, the reactive extraction of citric acid with Amberlite LA-2 is based on $R(COOH)_3 \cdot A$ formation at the interface. The modification of the citric acid extraction mechanism compared with those for malic and succinic acids could be the result of the citric acid size, which generates steric hindrances between the molecules constituting the carrier–acid complex.[11] This phenomena was observed too in the case of reactive extraction of others high-molecular weight compounds, like penicillins G and V, with Amberlite LA-2.[13–15]

Owing to the differences between the extraction mechanisms, acidity of these carboxylic acids and hydrophobicity of the compounds formed with the extractant, the selective separation of citric acid from the malic and succinic acids by reactive extraction with Amberlite LA-2 was possible.[11] Thus, if the value of the molar ratio between secondary acids and Amberlite LA-1 is 1, the malic and succinic acids can be selective extracted, the raffinate phase containing only citric acid.

In this work, we studied the possibility of selective separation of citric, malic, and succinic acids using facilitated pertraction with Amberlite LA-2, a technique that combines the advantages of reactive extraction with those of transport through liquid membranes.

MATERIALS AND METHOD

The following materials were used: 1,2-dichloroethane ($\geq$99%) (Aldrich) as solvent, Amberlite LA-2 (Sigma Chemie GmbH) as carrier, citric acid anhydrous ($\geq$99.5%) (Fluka), malic acid ($\geq$99%) (Fluka), succinic acid ($\geq$99%) (Fluka), and sodium hydroxide pellets ($\geq$98%) (Fluka) added in the stripping solution.

The experiments were carried out using pertraction equipment that allows obtaining and easily maintaining the free liquid membrane. The pertraction cell consists of a U-shaped glass pipe having an inner diameter of 45 mm and a total volume of 400 mL, the volume of each compartment being equal (Fig. 1).

The aqueous solutions are independently mixed by means of double blade stirrers with 6-mm diameter and 3-mm height, having a rotation speed between 0 and 800 rpm. To reach high diffusional rates through the solvent layer, the organic phase was mixed with a stirrer of the same design, at a

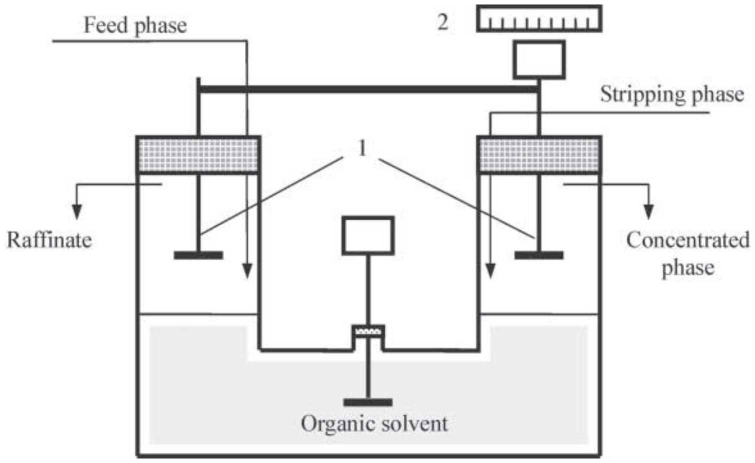

Figure 1. Pertraction cell (1-blade stirrers, 2-tachometer).

constant rotation speed of 500 rpm. The area of mass transfer surface, both for extraction and for re-extraction, was of $1.59 \times 10^{-3}\,\mathrm{m}^2$. The interfaces between the phases remained flat and, hence, the interfacial area constant, for the entire rotation speed domain used.

The experiments were carried out in a continuous system, at the steady-state conditions, the aqueous solutions being separately fed with a volumetric flow of 2.9 L/hr.

The liquid membrane phase consisted of a solution of 0- to 0.4-M Amberlite LA-2 as carrier dissolved in 1,2-dichloroethane. The feed phase contained a solution of citric, malic, and succinic acids. The characteristics of the pertracted acids are given in Table 1.

The carboxylic acids initial concentrations in the feed phase varied between 15 and 50 g/L (7.8 to 26×10^{-2} M) for citric acid, 2.5 and 10.5 g/L (1.9 to 7.8×10^{-2} M) for malic acid, respectively, between 2.5 and 9.2 g/L (2.1 to 7.8×10^{-2} M) for succinic acid. The stripping phases

Table 1. Acid values of pertracted carboxylic acids at 25°C.[16]

Carboxylic acid	k_1	k_2	k_3
Succinic acid	6.9×10^{-5}	2.4×10^{-6}	—
Malic acid	4.0×10^{-4}	8.9×10^{-6}	—
Citric acid	8.7×10^{-4}	1.8×10^{-5}	4.0×10^{-6}

consisted of solutions of sodium hydroxide of different pH values, varied between 8 and 12.

The feed solution pH adjustment was been made with a solution of 5% sulfuric acid or 5% sodium hydroxide, depending on the desired pH value, namely between pH = 2 and 6. The stripping solution pH value was corrected with a 5% sodium hydroxide solution. pH values were determined using a digital pH meter C831 type Consort. The pH values of the two aqueous phases were registered throughout each experiment and any pH change was recorded.

The evolution of pertraction was followed by means of carboxylic acids mass flows, permeability, and selectivity factors. The acids mass flows through liquid membrane were measured by HPLC analysis for the two aqueous phases using a high-pressure liquid chromatograph (Model 1090, Hewlett Packard) with a Waters μ Bondapak C18 column (3.9×200 mm) and an UV detector at 215 nm. The mobile phase was a phosphate buffer (pH = 2.5). Its flow was 0.6 mL/min. For the calculation of carboxylic-acid concentration in the solvent layer, mass balance was used. Samples removal was carried out from the aqueous phases evacuation outlet. Each experiment was carried out three or four times, for identical conditions, to calculate the average value of the studied parameter used. The maximum experimental error was $\pm 2.45\%$.

RESULTS AND DISCUSSION

Generally, pertraction is strongly influenced by the pH gradient between the aqueous phases, carrier concentration in liquid membrane, and phases mixing intensity. For the pertraction of carboxylic acids obtained by citric fermentation, the pH gradient between the feed and stripping phases induces a significant influence both on the efficiency of extraction and re-extraction and on the transport rate through the solvent layer. As shown in Fig. 2, reduction of the feed phase pH and the increase of the stripping phase pH, therefore, increased the pH gradient and led to the increase of acid mass flows.

It can be observed that the order of pertraction efficiency increase is as follows:

succinic acid < citric acid < malic acid

In the case of a pertraction from a mixture, the dependence of mass flows of these compounds on the pH gradient has to be correlated with their acidity, because the acidity controls the rate of interfacial reactions between solute and carrier. Thus, the obtained order is the result of higher acidity of citric and

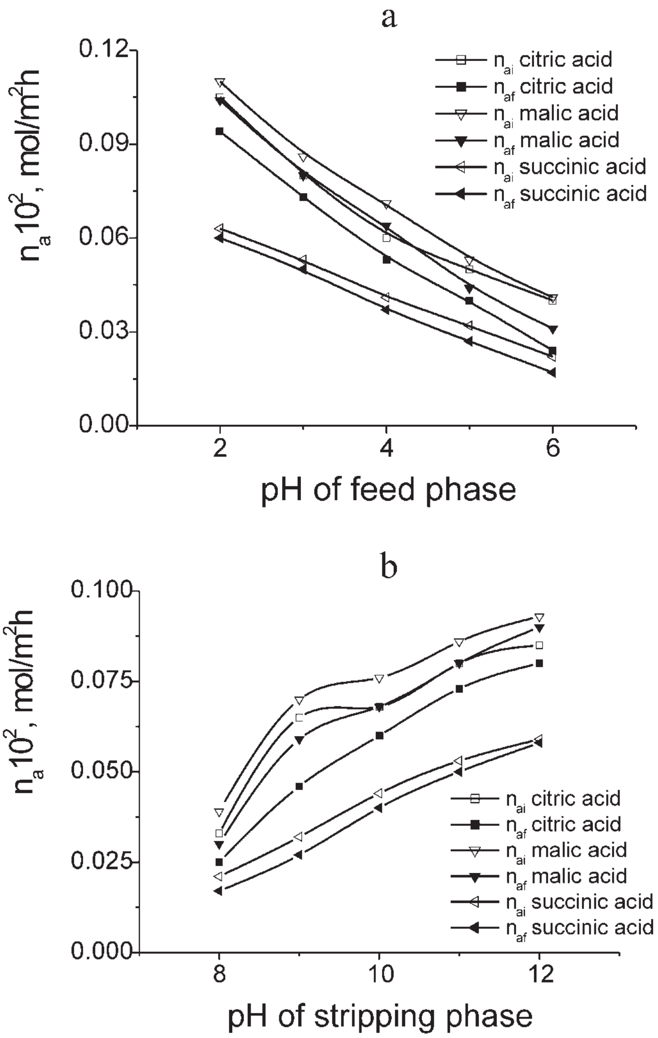

Figure 2. Influence of pH values of feed and stripping phases on citric, malic, and succinic acids mass flows [citric acid concentration in feed phase = 7.8×10^{-2} M, malic acid concentration in feed phase = 7.8×10^{-2} M, succinic acid concentration in feed phase = 7.8×10^{-2} M, carrier concentration = 0.3 M, rotation speed = 500 rpm; (a) pH of stripping phase = 11, and (b) pH of feed phase = 3].

malic acids, on the one hand, and of superior hydrophobicity of the malic acid–Amberlite LA-2 complex.[11]

To convey the capacity of a solute transfer in such separation systems, the permeability factor, P, has been defined in previous studies as the ratio between the final (overall) mass flow and the initial mass flow of carboxylic acid:[7]

$$P = \frac{n_{a_f}}{n_{a_i}} \tag{1}$$

Figure 3 indicates that the permeability factor tends to 1 with the increase of the pH gradient, therefore, the approach between the acid extraction and re-extraction yields.

Moreover, the values of permeability factors suggest an inverse proportionality between the transport capacity of liquid membrane and the acidity of transferred solute, the order of permeability factors decrease being:

succinic acid $>$ malic acid $>$ citric acid

This order could be explain by the similar variation of the rate of interfacial reaction between the acid–carrier compound and sodium hydroxide, the increase of acidity leading to the appearance of a kinetic resistance to the re-extraction process.

Concentration of Amberlite LA-2 inside of the liquid membrane induces a different influence on pertraction efficiency of the carboxylic acids. As it was stated for the reactive extraction of citric, malic, and succinic acids with Amberlite LA-2, the difference of carrier influence is due to the difference of acid mechanisms extraction, as well as to the difference on solutes acidity and on hydrophobicity of the extracted compounds.[11,12] As can be seen from Fig. 4, by increasing the carrier concentration, the malic acid, succinic acid, and citric acid are successively pertracted.

The succinic acid was extracted after the Amberlite LA-2 concentration exceeded the value stoichiometric needed for interfacial reaction with malic acid, respectively, after it exceeds the molar ratio between carrier and malic acid of 1 (the molar ratios were calculated as the ratio between the molar concentrations of acids in the feed phase and Amberlite LA-2 molar concentration in membrane phase). The citric acid was extracted for a carrier concentration level higher than that corresponding to an equimolecular ratio with malic and succinic acids. Below the carrier concentrations that allow the reactive extraction of succinic and citric acids, their pertraction is possible only by physical solubilization in 1,2-dichloroethane, but the acid mass flows are very low. These results underline the major influence of the Amberlite LA-2 concentration inside the liquid membrane on pertraction selectivity.

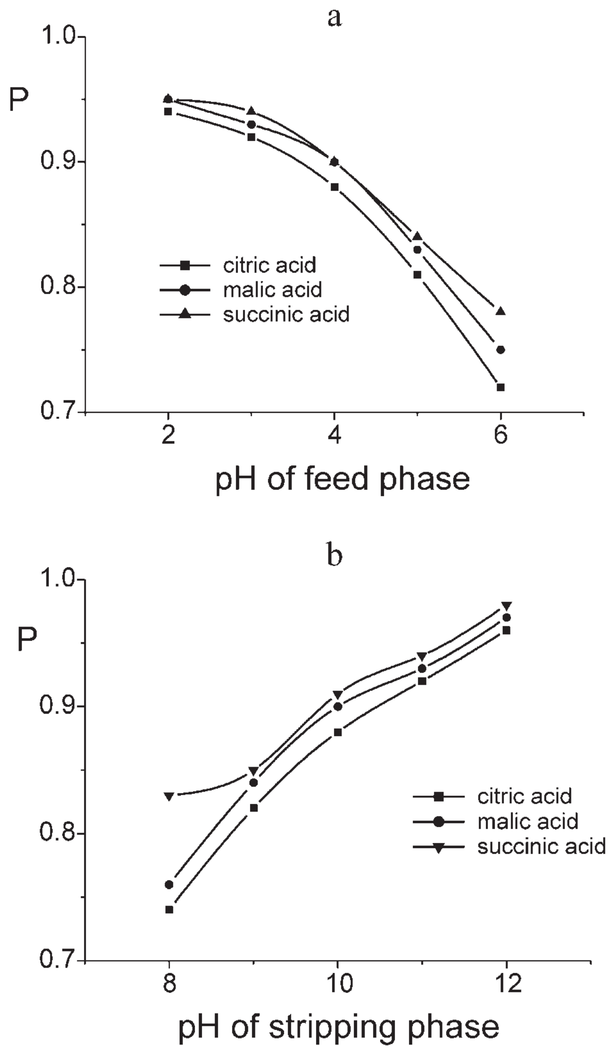

Figure 3. Influence of pH values of feed and stripping phases on citric, malic and succinic acids permeability factors [citric acid concentration in feed phase = 7.8×10^{-2} M, malic acid concentration in feed phase = 7.8×10^{-2} M, succinic acid concentration in feed phase = 7.8×10^{-2} M, carrier concentration = 0.3 M, rotation speed = 500 rpm; (a) pH of stripping phase = 11, and (b) pH of feed phase = 3].

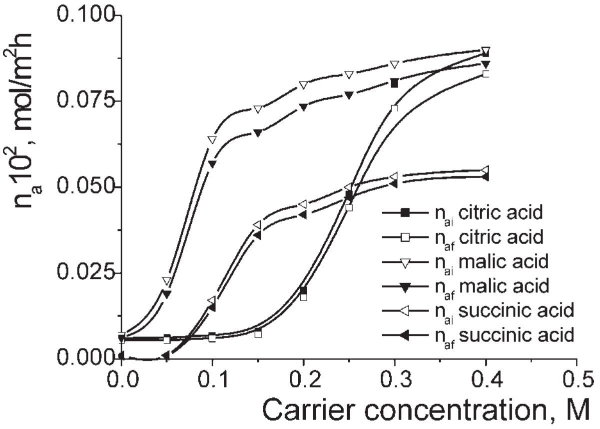

Figure 4. Influence of carrier concentration on citric, malic, and succinic acids mass flows (citric acid concentration in feed phase = 7.8×10^{-2} M, malic acid concentration in feed phase = 7.8×10^{-2} M, succinic acid concentration in feed phase = 7.8×10^{-2} M, rotation speed = 500 rpm, pH of feed phase = 3, and pH of stripping phase = 11).

The acid permeability factors had a different evolution. Thus, they initially decreased from a value corresponding to the absence of Amberlite LA-2 in the organic solvent to a minimum value for a concentration of 0.05-M Amberlite LA-2 and finally increased concomitantly with the carrier concentration (Fig. 5).

This variation could be the result of the changes in the relative rate of the interfacial chemical reactions. In the absence of the carrier, the extraction and transport of the solute through the liquid membrane occurs by physical process of solubilization only, the limiting steps of the overall separation process being of diffusional type. Adding Amberlite LA-2 in 1,2-dichloroethane results in a change of separation mechanism. Due to chemical reaction between carboxylic acid and carrier at the feed phase–solvent interface, as well chemical reaction between acid–carrier compound and sodium hydroxide at the solvent–stripping phase interface, additional limiting steps of kinetic type appeared. Moreover, as to the re-extraction process, the carboxylic acids do not attend in free acid form but, in combination with carrier, the rate of sodium salt formation was diminished. Consequently, comparing to physical extraction, the final mass flow was smaller, initially.

The mixing intensification of the two aqueous phases determined the transfer acceleration for all studied carboxylic acids, as the result of the diminution

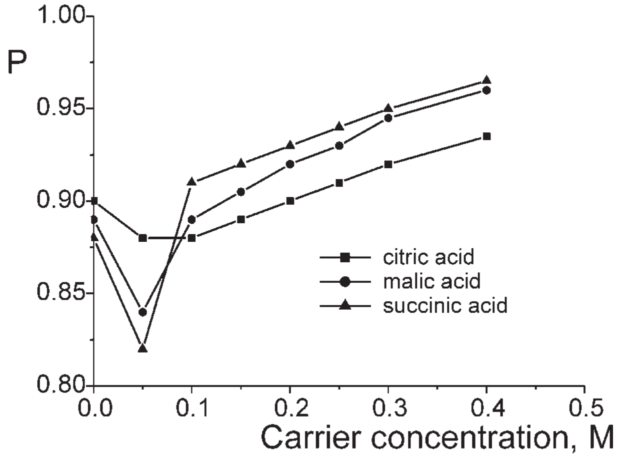

Figure 5. Influence of carrier concentration on citric, malic, and succinic acids permeability factors (citric acid concentration in feed phase = 7.8×10^{-2} M, malic acid concentration in feed phase = 7.8×10^{-2} M, succinic acid concentration in feed phase = 7.8×10^{-2} M, rotation speed = 500 rpm, pH of feed phase = 3, and pH of stripping phase = 11).

of resistance to the diffusion through boundary layers at separation interfaces, this evolution being recorded for permeability factors too (Figs. 6 and 7).

The dependence of acid mass flows on rotation speed suggests that the overall separation process can be controlled by diffusion or chemical reactions. The increasing domain of mass flows indicates that the pertraction occurs in diffusional regime, the extent of this domain being correlated with solute acidity. Therefore, the pertraction is diffusional limited below 700 rpm rotation speed value for citric and malic acids, respectively, below 600 rpm for succinic acid, and over these values, the chemical reactions become the limiting step.

The increase of permeability factors with rotation speed intensification indicates a stronger influence of mixing on final mass flow, due to the more accentuate resistance to the diffusion through stripping phase, as the result of a larger sizes of sodium salt molecules compared with free acids molecules from the feed phase.

These results suggest the possibility to selective pertraction of malic and succinic acids, the citric acid remaining in the raffinate phase. To confirm this hypothesis and to establish the required conditions for reaching a high selectivity of separation, the influences of pH gradient between the aqueous phases,

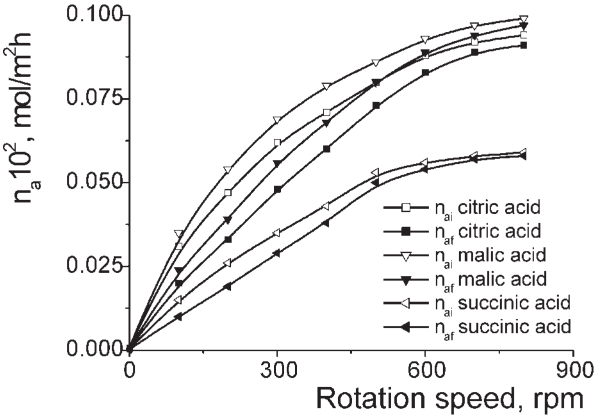

Figure 6. Influence of rotation speed on citric, malic, and succinic acids mass flows (citric acid concentration in feed phase = 7.8 × 10^{-2} M, malic acid concentration in feed phase = 7.8 × 10^{-2} M, succinic acid concentration in feed phase = 7.8 × 10^{-2} M, carrier concentration = 0.3 M, pH of feed phase = 3, and pH of stripping phase = 11).

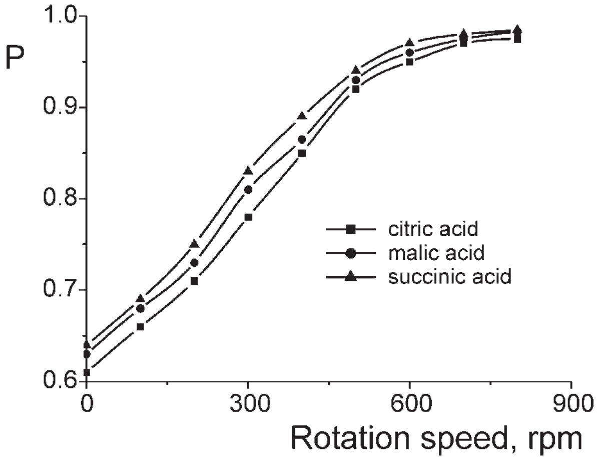

Figure 7. Influence of rotation speed on citric, malic, and succinic acids permeability factors (citric acid concentration in feed phase = 7.8 × 10^{-2} M, malic acid concentration in feed phase = 7.8 × 10^{-2} M, succinic acid concentration in feed phase = 7.8 × 10^{-2} M, carrier concentration = 0.3 M, pH of feed phase = 3, and pH of stripping phase = 11).

carrier concentration, and mixing intensity on pertraction selectivity were been studied.

The selectivity of pertraction was described by means of the selectivity factor, defined for separation of malic and succinic acids from citric acid as:

$$S = \frac{n_{\mathrm{a_f.malic.acid}} + n_{\mathrm{a_f.succinic.acid}}}{n_{\mathrm{a_f.citric.acid}}} \tag{2}$$

and for separation of malic acid from succinic acid as:

$$S_1 = \frac{n_{\mathrm{a_f.malic.acid}}}{n_{\mathrm{a_f.succinic.acid}}} \tag{3}$$

As it can be observed from Fig. 8, the reduced pH gradient leads to increased selectivity factors S and S_1, but this effect magnitude is rather different. Modification of the pH value of the feed phase induces a stronger effect on separation selectivity of secondary carboxylic acids from citric acid, while the modification of stripping phase pH exhibits a more pronounced effect on separation selectivity of malic acid from succinic acid.

These variations are due to the different ionization of the carboxylic acids by modifying pH of aqueous solutions, the efficiency of extraction and transport of corresponding ionic species through liquid membrane being different. Thus, it can be concluded that the selectivity of separation of malic and succinic acids from citric acid could be enhanced by increasing the pH values of both aqueous phases, and that of separation of malic acid from succinic acid by carrying out the pertraction at neutral domain of pH.

The decisive influence of carrier concentration on pertraction selectivity is underlined by the dependence between the selectivity factors and this parameter (Fig. 9).

Similar to the variation of acid mass flows with carrier concentration, the experimental data indicate that the maximum selectivity both for separation of secondary carboxylic acids from citric acid and for separation of malic acid from succinic acid, is reached for an equimolecular ratio between Amberlite LA-2 and the extracted acids. Furthermore, about a sevenfold increase in the selectivity factors can be achieved by optimization of the carrier concentration in comparison with optimization by modification of aqueous phase pH.

The effect of mixing intensity on selectivity factors S and S_1 is different. From Fig. 10, it can be seen that the selectivity of separation of malic and succinic acids from citric acid is not influenced by rotation speed value. However, the selectivity of malic acid from succinic acid separation is amplified by mixing intensification. These variations confirm the previous results that indicated a diffusional resistance more accentuated in the case of malic acid pertraction compared with that of succinic acid.

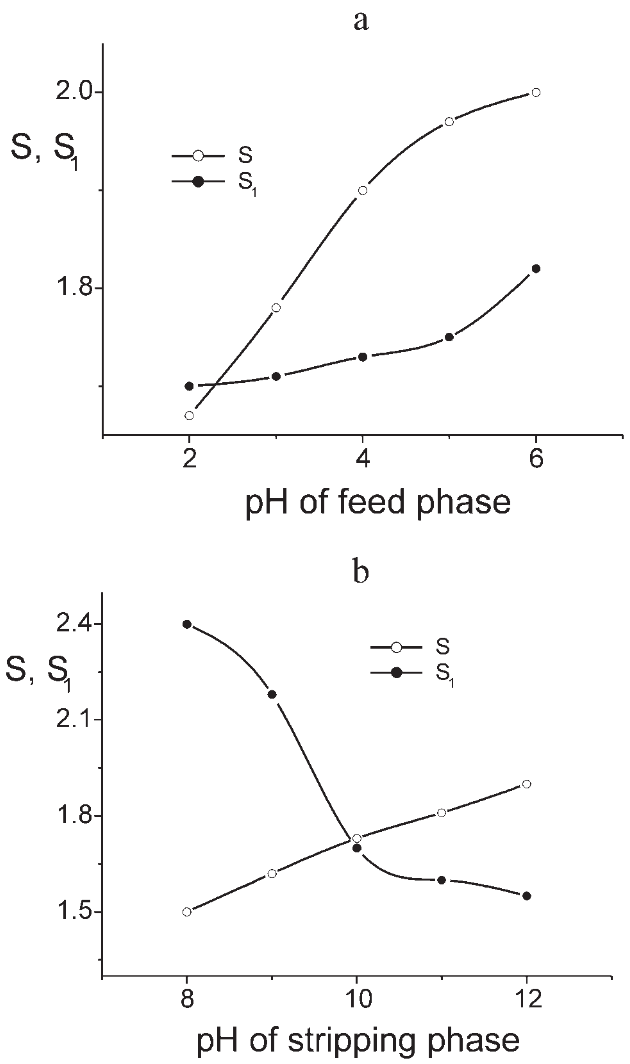

Figure 8. Influence of pH values of feed and stripping phases on selectivity factors [citric acid concentration in feed phase = 7.8×10^{-2} M, malic acid concentration in feed phase = $7.8 \times {}^{-2}$ M, succinic acid concentration in feed phase = 7.8×10^{-2} M, M, carrier concentration = 0.3 M, rotation speed = 500 rpm; (a) pH of stripping phase = 11, and (b) pH of feed phase = 3].

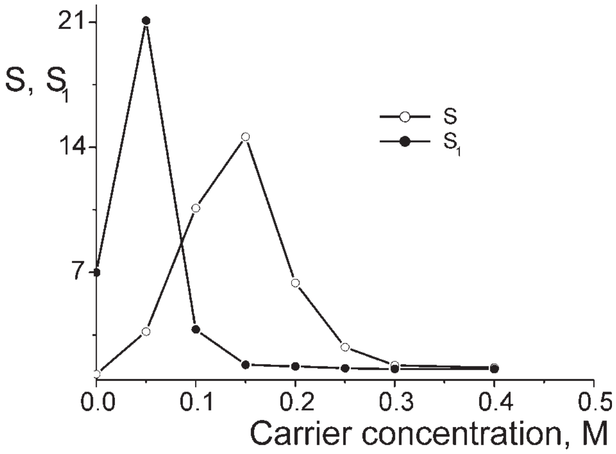

Figure 9. Influence of carrier concentration on selectivity factors (citric acid concentration in feed phase = 7.8 × 10^{-2} M, malic acid concentration in feed phase = 7.8 × 10^{-2} M succinic acid concentration in feed phase = 7.8 × 10^{-2} M, rotation speed = 500 rpm, pH of feed phase = 3, and pH of stripping phase = 11).

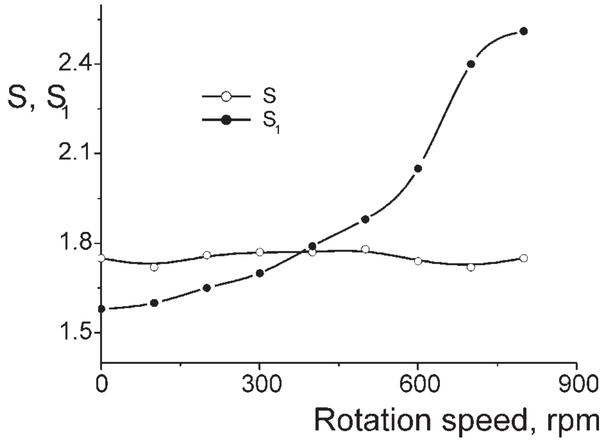

Figure 10. Influence of rotation speed on selectivity factors (citric acid concentration in feed phase = 7.8 × 10^{-2} M, malic acid concentration in feed phase = 7.8 × 10^{-2} M, succinic acid concentration in feed phase = 7.8 × 10^{-2} M, carrier concentration = 0.3 M, pH of feed phase = 3, and pH of stripping phase = 11).

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Therefore, although the separation of malic and succinic acids from citric acid is not influenced by mixing intensity, the increase of rotation speed leads to the increase of acid mass flows through liquid membrane and to the enhancement of separation selectivity of malic acid from succinic acid.

To verify these conclusions, the first step the pertraction of citric, malic, and succinic acids from a mixture similar to that obtained by citric fermentation was performed. The concentrations of the carboxylic acids in the feed solution were as follows: 50 g/L (0.26 M) citric acid, 2.5 g/L (2.1×10^{-2} M) malic acid, respectively, and 2.5 g/L (1.9×10^{-2} M) succinic acid. In the second step, the malic acid was pertracted from a mixture containing 2.5 g/L (2.1×10^{-2} M) malic acid and 2.5 g/L (1.9×10^{-2} M) succinic acid. In both cases, the pertraction was carried out using the separation conditions that offer maximum selectivity and a high rate of transport through liquid membrane. Thus, the selective pertraction of the secondary acids from the mixture of the three acids was performed at a carrier concentration of 0.04 M, rotation speed of 500 rpm, pH of feed phase of 4, and pH of stripping phase of 11. Then, the selective pertraction of malic acid from the mixture with succinic acid was performed at a carrier concentration of 0.018 M, rotation speed of 700 rpm, pH of feed phase of 4, and pH of stripping phase of 8. The obtained results are given in Tables 2 and 3.

It can be observed that by combining the favorable effects of pertraction parameters, superior values of selectivity factors were obtained. Consequently, the facilitated pertraction of carboxylic acids obtained by citric fermentation allows a high selectivity of separation and constitutes an advantageous alternative to the techniques applied at the present for citric acid separation from fermentation broths.

CONCLUSION

The studies on facilitated pertraction of citric, malic, and succinic acids through a liquid membrane of 1,2-dichloroethane and Amberlite LA-2 as a

Table 2. Selective separation of malic and succinic acids from citric acid.

Citric acid (mol/m^2 hr)		Malic acid (mol/m^2 hr)		Succinic acid (mol/m^2 hr)		
$n_{ai} \times 10^2$	$n_{af} \times 10^2$	$n_{ai} \times 10^2$	$n_{af} \times 10^2$	$n_{ai} \times 10^2$	$n_{af} \times 10^2$	S
0.45	0.29	5.8	4.8	2.7	2.3	24.5

Note: Carrier concentration = 0.04 M, rotation speed = 500 rpm, pH of feed phase = 4, and pH of stripping phase = 11.

Table 3. Selective separation of malic acid from succinic acid.

Malic acid (mol/m^2 hr)		Succinic acid (mol/m^2 hr)		
$n_{ai} \times 10^2$	$n_{af} \times 10^2$	$n_{ai} \times 10^2$	$n_{af} \times 10^2$	S_1
5.2	3.7	0.1	0.078	47.5

Note: Carrier concentration = 0.018 M, rotation speed = 700 rpm, pH of feed phase = 4, and pH of stripping phase = 8.

carrier underlined the major influences of process variables (the pH gradient between feed and stripping phases, carrier concentration in organic layer, and mixing intensity of aqueous phases) on separation efficiency and selectivity. Thus the following conclusions can be drawn:

1. The preliminary studies concerning the influence of separation conditions on pertraction of these carboxylic acids from a mixture indicated the possibility of selective separation of malic and succinic acids, the citric acid remaining in the raffinate phase. The malic acid can be furthermore selective separated from the stripping phase.
2. The modification of pH value of feed phase induces a stronger effect on separation selectivity of secondary carboxylic acids from citric acid, while the modification of stripping phase pH exhibits a more pronounced effect on separation selectivity of malic acid from succinic acid.
3. The maximum selectivity of malic and succinic acids separation from citric acid can be reached for an equimolecular ratio between the carrier and the separated acids. Similar, for a selective separation of malic acid from succinic acid a carrier concentration inside the liquid membrane equal to that of malic acid in the feed phase is required.
4. The rotation speed value does not influence the separation selectivity of secondary carboxylic acids from citric acid, but its acceleration induces a favorable effect on the separation of malic acid from succinic acid.

The results obtained by cumulating the favorable effects of separation conditions on selective pertraction of carboxylic acids obtained by citric fermentation underlined that the proposed technique represents an advantageous alternative to the separation technology applied on an industrial scale.

NOTATIONS

k_1, k_2, k_3	Acid values at 25°C (—)
n_a	Mass flow of carboxylic acid (mol/m^2 hr)
n_{ai}	Initial mass flow of carboxylic acid (mol/m^2 hr)
n_{af}	Final (overall) mass flow of carboxylic acid (mol/m^2 hr)
P	Permeability factor
S	Selectivity factor for separation of malic and succinic acids from citric acid (—)
S_1	Selectivity factor for separation of malic acid from succinic acid (—)

Subscript

aq	Aqueous phase
o	Organic phase

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