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Facilitated Pertraction of p-Aminobenzoic Acid with Amberlite LA-2 in Presence of 1-Octanol

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p-Aminobenzoic acid has been facilitated pertracted with Amberlite LA-2 dissolved in dichloromethane, using a U-shaped pertraction cell which allows obtaining the free liquid membrane. The pertraction has been a carrier out in the presence of 1-octanol added in the liquid membrane. The addition of the alcohol led to the increase for up to 3 times of the acid initial and final mass flows, this effect being directly related to the process variables (pH-gradient between the aqueous phases, carrier and alcohol concentrations inside the membrane phase, mixing intensity). But, the influence of 1-octanol on the transport capacity of the pertraction system was negative, its addition inducing the accumulation of PABA in the liquid membrane, and requiring the reevaluation and optimization of the acid reextraction from the membrane phase to the stripping one.

Keywords 1-octanol; Amberlite LA-2; facilitated pertraction; mass flow; p-aminobenzoic acid; permeability factor

INTRODUCTION

Pertraction, defined as the extraction and transport through liquid membranes, is rather a new separation technique and consists of the transfer of a solute between two aqueous phases of different values of pH or other properties, these phases being separated by a solvent layer of various sizes (1–3). The pertraction efficiency and selectivity could be significantly enhanced by adding a carrier in the liquid membrane, such as organophosphoric compounds, long-chain amines or crown-ethers etc., the separation process being called facilitated pertraction or facilitated transport (3–8).

The liquid membranes can be obtained either by emulsification, but their stability is poor and need surfactants for enhancing it (1,2,4,8–10), by including the solvent in a hydrophobic porous polymer matrix (1,2,4,11–14), or by using pertraction equipments of special construction, which allow to separate and easily maintain the three phases without the addition of surfactants (free liquid membranes) (3,6,15–17).

Compared with the physical or reactive liquid-liquid extraction, the use of pertraction reduces the loss of solvent during the separation cycle, needs a small quantity of solvent and carrier, owing to their continuous regeneration, and offers the possibility to transport the solute against its concentration gradient, as long as the pH-gradient between the two aqueous phases is maintained (1–4).

Besides the separation conditions, the pertraction mechanism and, implicitly, its performance are controlled by the solute and carrier characteristics, respectively by their ability to form products soluble in the liquid membrane, as well as by the physical properties of the liquid membrane. Because the facilitated pertraction is the development of the reactive extraction, it requires the adjustment such that the extraction process conditions fit to its specific ones.

In many processes of acids reactive extraction, the formation of "the third phase" has been observed. This phase consists of a stable emulsion with high amount of acids or acid-extractant adducts, being insoluble both in the organic phase and in the aqueous one (6,18,19). This phenomenon is more important for the extraction systems containing extractants of amine type and solvents with low polarity and leads to the increase of the separation duration simultaneously with the diminution of its efficiency. The formation of the third phase can be avoided by addition of a "phase modifier" in the organic solvent. Generally, this compound is an alcohol with an aliphatic chain with at least 8 carbon atoms and modifies the polarity of the solvent, promoting the breakage of the stable emulsion and its content solubilization (18–20).

Because the facilitated pertraction performance is directly related to the reactive extraction mechanism and efficiency, the addition of the phase modifier into the membrane phase is expected to induce an important effect

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on the solute extraction and transport through the liquid membrane. But, although this effect could be favorable for the solute extraction from the feed phase to the membrane one, its overall influence on the pertraction process could be different.

p-Aminobenzoic acid (PABA), also called vitamin B_{10} or factor R, was found to be part of the folic acids. Because it is a component of the pteroylglutamate, it is considered to act as provitamin for some bacteria and growth factor for some superior animals, and in the human body it possesses the capacity to synthesize folates. PABA is used in cosmetics as an additive in sunscreen lotions. The medical applications are for skin protection against vitiligo, sclerodermy, and male infertility treatment. It is also used in diagnostic tests for the state of the gastrointestinal tract. Although this compound is not considered an essential nutrient, it is included in vitamin B or multivitamins supplements (21).

The most recent methods for PABA production are the chemical synthesis using methyl-4-formylbenzoate as the starting material (22) or biosynthesis by mutant strains of *E. coli* (23). In both cases the separation stages are complex and require the consumtion of a large amount of energy and materials.

Due to the insolubility of PABA in organic solvents immiscible with water, its separation by physical extraction is impossible. The previous studies indicated that its extraction became possible by adding into the solvent of an extractant which could react with this acid, leading to the formation of a hydrophobic compound. Owing to the chemical structure of PABA which contains an acidic group, $-COOH$, and a basic one, $-NH_2$, the reactive extraction has been performed by using extractants of aminic and organophosphoric acid types, namely Amberlite LA-2 (lauryl-trialkyl-methylamine) and di-(2-ethylhexyl) phosphoric acid (D2EHPA), respectively (24). Because the formation of the third phase has been observed during the reactive extraction of PABA, the mechanisms and, consequently, the factors which control the mechanisms of acid extraction with the two extractants in presence of 1-octanol as phase modifier have been investigated in the former studies (24). Therefore, it was concluded that the addition of 1-octanol induces the increase of the extraction efficiency, the most important influence being recorded for the solvent with the lowest dielectric constant. Moreover, the addition of 1-octanol influenced the mechanism of the interfacial reaction between the solute and the extractant, by controlling the number of extractant molecules participating to the interfacial product formation (24).

On the basis of the previous investigations on the reactive extraction of PABA in presence of the phase modifier, the aims of this paper are to study the facilitated pertraction of this acid using a liquid membrane containing 1-octanol and to analyze comparatively the influences of the process parameters (pH gradient between the feed and stripping phases, carrier concentration, mixing intensity) on the separation performances for the pertraction systems with and without 1-octanol.

MATERIALS AND METHOD

The experiments have been carried out using the pertraction equipment that allows obtaining and easily maintaining the solvent layer between the two aqueous phases (free liquid membrane). The pertraction cell has been described in the previous papers and consists of a U-shaped glass pipe having an inner diameter of 45 mm and a total volume of 450 ml, the volume of each compartment being 150 ml (3,6).

The aqueous solutions are independently mixed by means of double blade stirrers with a 6 mm diameter and a 3 mm height, having a rotation speed between 0 and 800 rpm. In order to reach high diffusional rates through the solvent layer, the organic phase has been mixed with a similar stirrer, at a constant rotation speed of 500 rpm. The area of mass transfer surface, both for extraction and for re-extraction, was of $1.59 \times 10^{-3}\,m^2$. The interfaces between the phases remained flat, and hence the interfacial area constant, for the entire rotation speed domain used. The aqueous solutions have been separately fed with a volumetric flow of 2.1 l/hr. The pertraction has been carried out at 25°C.

The liquid membrane phase consisted of dichloromethane ($\geq$99%) (Aldrich) in which has been dissolved the most efficient carrier according to the previous results on the reactive extraction of PABA, namely Amberlite LA-2 (Sigma Chemie GmbH) (24). The carrier concentration varied between 0 and 80 g/l (0.21 M Amberlite LA-2). 1-Octanol (dielectric constant of 10.3 at 25°C (26)) has been added into the membrane phase, its concentration varying between 5 and 20% vol.

The feed phase was an aqueous solution of 5 g/l PABA (3.65×10^{-2} M) ($\geq$99%) (Merck). The pH-value of the feed phase varied between 2 and 7. The pH adjustment of the feed phase has been made with a solution of 3% sulfuric acid or 3% sodium hydroxide, a function on the prescribed pH-value. The stripping phase consisted of a solution of sodium hydroxide with pH = 8–12.

The pH-values of both aqueous phases have been determined using a digital pH-meter of HI 213 (Hanna Instruments) type and have been recorded throughout each experiment. Any pH change was recorded during the pertraction experiments.

The pertraction process has been analyzed by means of PABA initial and final mass flows and permeability factor. The initial mass flow represents the solute mass flow from the feed phase to the liquid membrane, while the final (overall) mass flow the mass flow from the liquid membrane to the stripping phase:

$$n_i = \frac{Q \cdot (C_{Fi} - C_{Fo})}{A} \qquad (1)$$

$$n_f = \frac{Q \cdot C_S}{A} \qquad (2)$$

The permeability factor conveys the capacity of a solute transfer through the liquid membrane, and has been defined as the ratio between the final mass flow and the initial mass flow of the solute (6).

These parameters have been calculated by determining the acid concentrations in the feed and stripping phases and by applying the mass balance for the pertraction system. PABA concentrations have been measured by the spectrophotometric technique, using a spectrophotometer of CAMSPEC M550 type. The absorption of the aqueous solutions has been determined at 267 nm (25).

RESULTS AND DISCUSSION

The facilitated pertraction is strongly influenced by the pH-gradient between the feed and stripping phases, as well as by the carrier concentration inside the liquid membrane. In the case of separation of PABA, the influence of the pH-gradient is amplified by the ionization-protonation of this acid in the two aqueous phases, these processes controlling the efficiency of extraction and reextraction, as well as the rate of the solute transport through the liquid membrane.

From Fig. 1 it can be observed that the initial mass flow of PABA increases with the increase of the pH of the feed phase, pH_F, reaches a maximum value, and then decreases. This variation is the result of the mechanism of acid reactive extraction, which is based on the formation of a strong hydrophobic compound at the interface between the feed and membrane phases. According to the previous studies (24), the carboxylic group of the PABA is involved in the reactive extraction process with Amberlite LA-2 (Q). The interfacial interactions between the acid and the extractant could be of hydrogen bonding type with the undissociated carboxylic groups, or of the ionic type, if the acid dissociates in the aqueous solution:

$$H_2N\text{-}C_6H_4\text{-}COOH_{(aq)} + Q_{(o)} \rightleftharpoons H_2N\text{-}C_6H_4\text{-}COOH.Q_{(o)}$$

If dichloromethane is used as an extract phase (liquid membrane), each reactant participates with one molecule to the interfacial reaction (24).

The existence of the maximum of the initial mass flow is the result of PABA aminic group ionization at strong acidic pH-domain ($pK_{a1} = 2.50$ (26)), this phenomena limiting the extraction efficiency. On the other hand, the increase of the pH-value induces the dissociation of $-COOH$ group ($pK_{a2} = 4.87$ (26)) and, implicitly, the reduction of the extraction yield. Thus, as the result of the two contrary effects generated by the increase of pH_F, the optimum value of the feed phase pH for the reactive extraction of PABA from the feed phase to the liquid membrane with Amberlite LA- 2 in the presence of 1-octanol is 4. In the case of the facilitated pertraction of this acid using similar process conditions, but without 1-octanol in the liquid membrane, the optimum value of the feed phase pH was 3 (27). The extension of the pH_F-domain which corresponds to the positive influence of this parameter on the initial mass flow is due to the addition of the phase modifier inside the organic phase, which increases this phase polarity. Therefore, the dissociated PABA molecules from the feed phase are also partially solubilized in dichloromethane, leading to higher acid initial mass flows compared with those recorded for the pertraction system without alcohol.

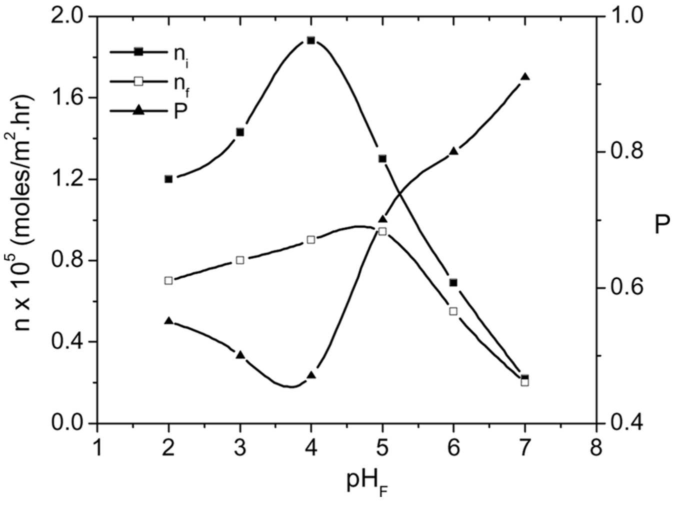

FIG. 1. Influence of pH_F on PABA mass flows and permeability factor ($pH_S = 10$, Amberlite LA-2 concentration = 40 g/l, 1-octanol concentration = 10% vol., rotation speed = 500 rpm).

The influence of the pH-value of the feed phase on PABA final mass flow is similar to that on the initial mass flows, owing to the direct dependence between the acid amounts extracted in the organic layer and those reextracted in the stripping phase (Fig. 1).

The permeability factor of PABA has a contrary evolution with the pH_F increase. This parameter initially decreases and reaches a minimum level at $pH = 4$, then increasing continuously (Fig. 1). For $pH_F < 4$, the increase of the amount of acid extracted in organic layer exceeds the increase of its final mass flow, due to the high and increasing initial mass flow. The influence of the feed phase pH on the permeability factor becomes positive for pH_F-values over 4, because the reduction of the initial mass flow exhibits a favorable effect on the permeability through the liquid membrane, due to the diminution of the amount of acid accumulated into the organic phase.

In order to quantify the effect of 1-octanol addition inside the liquid membrane on the initial and final mass flows, the factor F_N has been considered and defined as the ratio between the mass flows recorded in the presence and in the absence of alcohol (27). Similarly, the factor F_P has been calculated as the ratio between the permeability factors reached for liquid membrane with and without 1-octanol (27).

The dependence of the values of factors F_N and F_P on the feed phase pH, plotted in Fig. 2, suggests that the addition of 1-octanol exhibits two different effects. On the one hand, the factor F_N, calculated either for the initial mass flows or for the final ones, is greater than the unit for the entire considered pH_F-domain and increases with the increase of pH_F. Thus, for pH_F variation from 2 to 7, F_N increased from 1.5 to 2.9 for the initial mass flows, respectively from 1.2 to 2.4 for the final mass flows. These results are the consequence of the favorable effect of 1-octanol on the solubilization of PABA molecules, free or bounded to the carrier molecules, on the membrane phase. The increase of pH_F induces the dissociation of PABA in the feed phase, the presence of 1-octanol favoring the extraction also of the dissociated molecules of acid. The relative magnitude of the positive effect of alcohol addition is superior in the case of the initial mass flow, due to the supplementary kinetic resistance to the acid reextraction process from the membrane phase to the stripping solution.

On the contrary, the values of factor F_P are lower than 1 for the entire experimented domain of the feed phase pH, the increase of pH_F inducing the reduction of this factor (Fig. 2). In this case, the significant increase of the initial mass flow of PABA due to the addition of 1-octanol inside the liquid membrane exceeds the membrane capacity to transport the acid and to release it into the stripping phase.

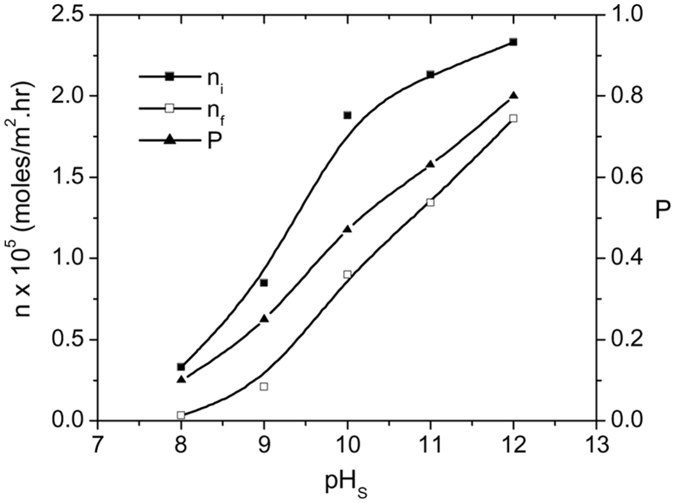

FIG. 3. Influence of pH_S on PABA mass flows and permeability factor ($pH_F = 4$, Amberlite LA-2 concentration = 40 g/l, 1-octanol concentration = 10% vol., rotation speed = 500 rpm).

According to the data given in Fig. 3, the increase of the stripping phase pH-value, pH_S, determines the significant increase of the initial and final mass flows of PABA, due both to the increase of the pH-gradient between the two aqueous phases and to the diminution of the kinetic resistance to PABA reextraction from the membrane phase.

The increase of pH_S promotes also the increase of the permeability factor of PABA, thus suggesting that at higher pH_S-values the acceleration of the reextraction rate becomes more important than that of the extraction rate (Fig. 3).

Similar to the influence of pH_F, the factors F_N are superior to 1 for all the considered pH_S-values, but the influence of pH_S has to be distinctly analyzed for the initial and, respectively, final mass flows ratios (Fig. 4). Thus, the factor F_N calculated as the ratio between the initial mass

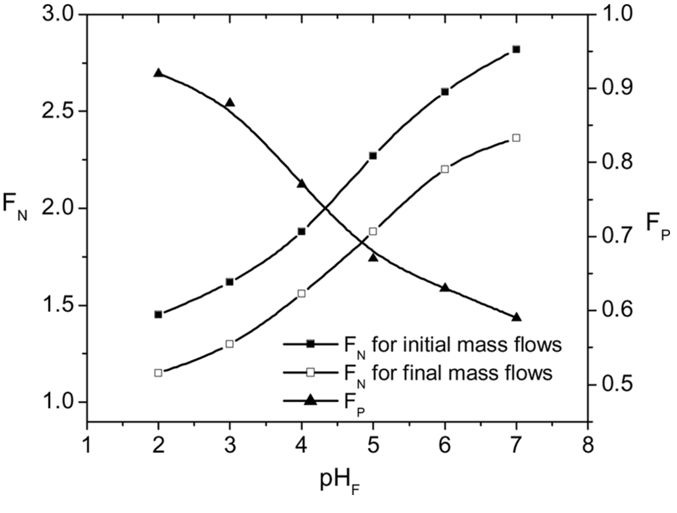

FIG. 2. Influence of pH_F on factors F_N and F_P ($pH_S = 10$, Amberlite LA-2 concentration = 40 g/l, rotation speed = 500 rpm; 1-octanol concentration = 10% vol.).

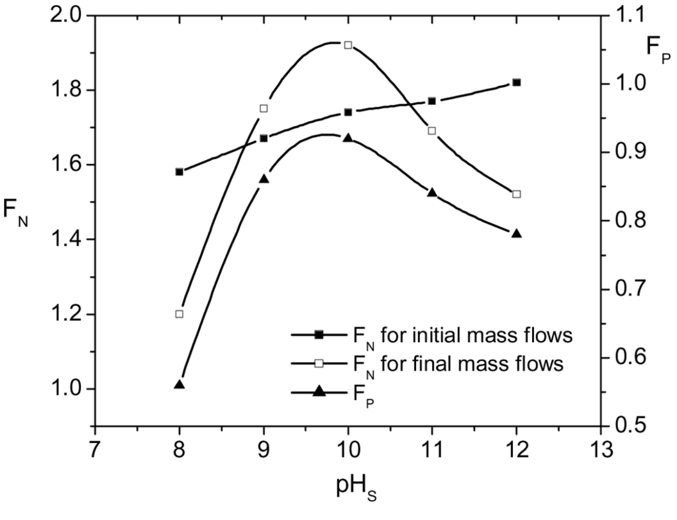

FIG. 4. Influence of pH_S on factors F_N and F_P ($pH_F = 4$, Amberlite LA-2 concentration = 40 g/l, rotation speed = 500 rpm; 1-octanol concentration = 10% vol.).

flows increases slowly with the increase of stripping phase pH, from 1.6 to 1.8. The variation of factor F_N related to the final mass flows with pH_S indicates its increase to a maximum level, corresponding to $pH_S = 10$, followed by its decrease. The maximum F_N (1.9) exceeds that obtained for the initial mass flows indifferent of pH_S-value, due to the more important influence of pH_S on the PABA reextraction step from the membrane phase. The value of the stripping phase pH of 10 could be associated with the maximum capacity of the liquid membrane to transport the acid from the feed phase to the stripping one. For pH_S values over 10, the acceleration of the reextraction rate does not sustain the higher value of the extraction rate reached by the addition of 1-octanol.

The variation of F_P follows that of F_N calculated for the final mass flows, the two factors being directly correlated. Moreover, for the entire investigated domain of stripping phase pH, the value of F_P was lower than 1 (maximum F_P is of 0.92), from the above discussed reasons.

As can be observed from Fig. 5, the increase of Amberlite LA-2 concentration into the liquid membrane induces the increase of the initial and final mass flows of PABA. The increase of mass flows is the result, on the one hand, of the increase of the concentration of one reactant (carrier) to the interface between the feed and membrane phases, and, on the other hand, to the accumulation of the interfacial compound inside the liquid membrane. Unlike the facilitated pertraction of PABA with Amberlite LA-2 in absence of 1-octanol (27), the influence of carrier concentration on the initial mass flow of solute is pronounced also for the carrier concentration levels over that corresponding to the formation of the hydrophobic compounds by the participation of one molecule of each reactant at the interfacial chemical reaction (15 g/l Amberlite LA-2 (27)). This variation is the result of the addition of the phase modifier inside the liquid membrane and, consequently, to the solubilization of the supplementary amount of free or complexed PABA molecules.

The variation of the final mass flow of carboxylic acid is similar to that of its initial mass flow.

Figure 5 indicates a particular dependence of the acid permeability factor on carrier concentration. Thus, this factor initially decreases from a value corresponding to the absence of Amberlite LA-2 in the organic solvent to a minimum value for the Amberlite LA-2 concentration of 5 g/l, and finally increases concomitantly with the carrier concentration. This variation could be the result of the changes in the relative rate of the interfacial chemical reactions. In the absence of the carrier (free pertraction), the extraction and transport of PABA through the liquid membrane occur by physical process of solubilization, the limiting steps of the overall separation process being only of diffusional type. The addition of Amberlite LA-2 in dichloromethane changes the separation mechanism. Due to the chemical reactions between the acid and carrier at the feed phase–liquid membrane interface and between the acid–carrier compound and sodium hydroxide at the liquid membrane–stripping phase interface, the additional limiting steps of kinetic type appeared. Moreover, because the acid participates mostly in its complexed form to the reextraction process, the rate of sodium salt formation is diminished. Consequently, comparing with the free pertraction, the final mass flow will be initially smaller.

The factors F_N are also over 1, but the increase of carrier concentration into the liquid membrane exhibits a negative influence. Therefore, Fig. 6 shows that, for Amberlite LA-2

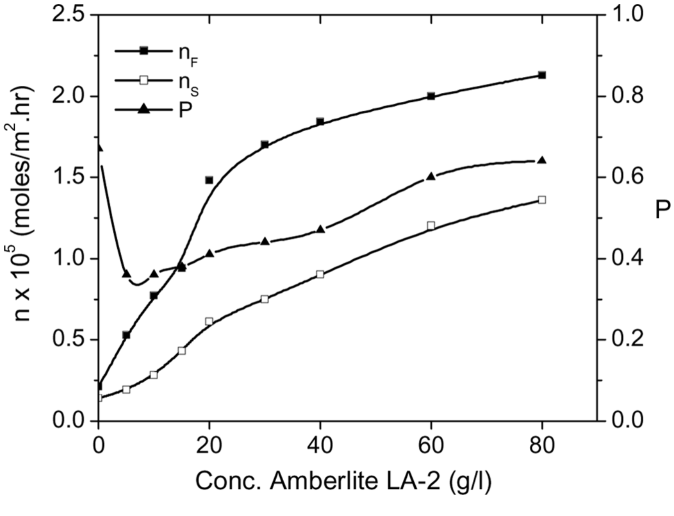

FIG. 5. Influence of carrier concentration on PABA mass flows and permeability factor ($pH_F = 4$, $pH_S = 10$, 1-octanol concentration = 10% vol., rotation speed = 500 rpm).

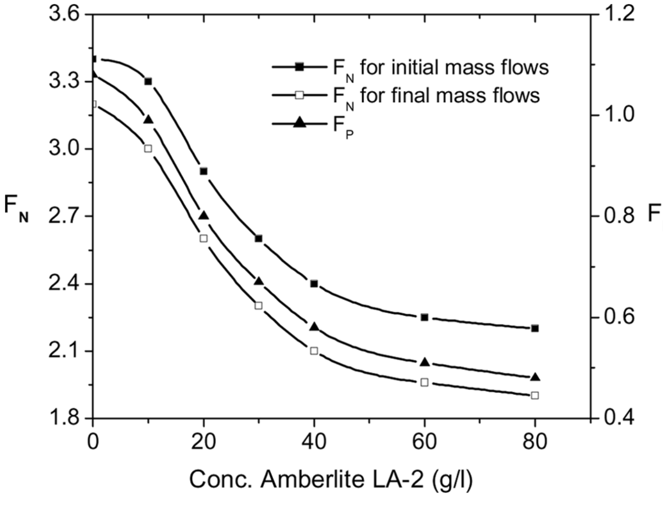

FIG. 6. Influence of carrier concentration on factors F_N and F_P ($pH_F = 4$, $pH_F = 10$, rotation speed = 500 rpm; 1-octanol concentration = 10% vol.).

concentration increases from 0 to 80 g/l, F_N decreases from 3.4 to 2.2 for the initial mass flows respectively, from 3.2 to 1.9 for the final mass flows. The obtained variation of the factor F_N can be explained by the diminution of the magnitude of carrier concentration influence in the presence of 1-octanol.

For the free pertraction, the factor F_P becomes higher than 1, thus underlining the positive effect of alcohol addition on the acid-free pertraction respectively, on its solubilization into the membrane phase and, implicitly, on its amount reextracted into the stripping solution. But, by adding Amberlite LA-2 and increasing its concentration, F_P decreases and becomes lower than the unit. Similar to the above-discussed effects, the increasing of the relative contribution of the physical co-extraction of PABA to its transport from the feed phase by 1-octanol addition leads to the overflow of the transport capacity of the liquid membrane and, consequently, to the solute accumulation inside the membrane phase.

The mixing intensity of the aqueous phases represents another important factor influencing the pertraction of the studied acid. Because the diffusion through the boundary layers formed at the two separation interfaces is an important limiting factor, the intensification of mixing leads to the significant increase of the initial and final mass flows of the acid, as the result of the diminution of the diffusion resistance (Fig. 7). Comparatively with PABA facilitated pertraction without 1-octanol (27), the acceleration of the rotation speed of the impellers induces a continuous positive effect on its mass flows in the presence of this alcohol, owing to the increase of the importance of physical processes of diffusion and solubilization.

The positive influence of the rotation speed on the permeability factor indicates a stronger influence of mixing on the final mass flow, due to the more accentuated resistance to the diffusion through the stripping phase, as the result of the sizes of sodium salt molecules from this phase, which are larger compared with the free acid molecules from the feed phase.

The effect of the aqueous phases' mixing intensity on the factor F_N is less important compared with those of the above analyzed factors. In both cases, corresponding either to the initial mass flows or to the final ones, the value of this factor is close to 1 for all experimented values of the rotation speed, because the mixing influences only the diffusion of the acid, free or as sodium salt, existing in the feed or the stripping phase. Similarly, the value of F_P remains below but nearly 1, from the above presented-reasons.

Due to its favorable effect on PABA extraction from the feed phase into the liquid membrane, the addition of 1-octanol in dichloromethane induces the increase of the initial and final mass flows of the acid (Fig. 8). Thus, for 40 g/l Amberlite LA-2 and alcohol concentration variation from 5 to 20% vol., the initial mass flow was amplified for about 1.4–2.2 times and the final mass flow for about 1.1–1.6 times compared with the corresponding mass flows in absence of 1-octanol (27). This effect is more significant for the initial mass flow, because the reextraction rate tends to its maximum level for the given experimental conditions.

For the same reason, the permeability factor is slowly increased from 0.4 to 0.7 by increasing the alcohol concentration inside the membrane phase.

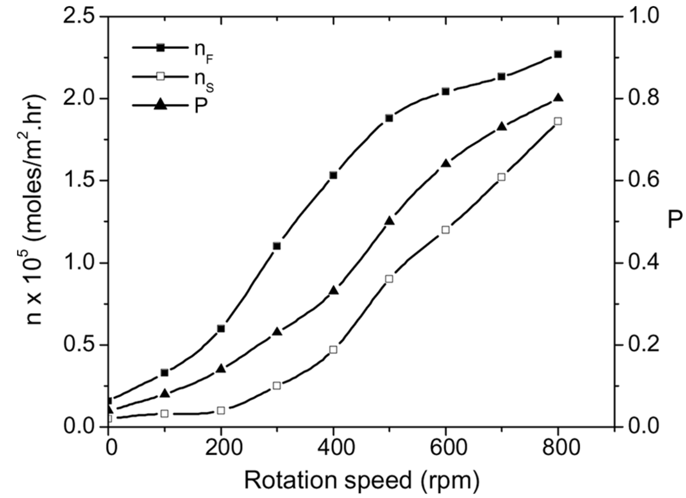

FIG. 7. Influence of mixing intensity on PABA mass flows and permeability factor ($pH_F = 4$, $pH_S = 10$, Amberlite LA-2 concentration = 40 g/l, 1-octanol concentration = 10% vol.).

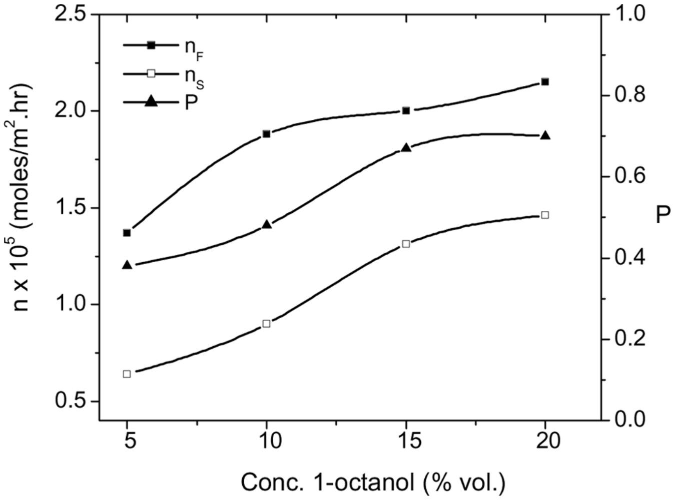

FIG. 8. Influence of 1-octanol concentration on PABA mass flows and permeability factor ($pH_F = 4$, $pH_S = 10$, Amberlite LA-2 concentration = 40 g/l, rotation speed 500 rpm).

CONCLUSIONS

The studies on facilitated pertraction with Amberlite LA-2 of PABA in presence of 1-octanol added into the membrane phase indicated the significant increase of the acid initial and final mass flows. Compared with the facilitated pertraction without alcohol, the acid mass flows have been amplified up to 3 times, but the magnitude of this effect has to be correlated with the pH-gradient between the feed and the stripping phase, and carrier and 1-octanol concentrations inside the liquid membrane and mixing intensity.

Contrary to this positive effect, the addition of 1-octanol induced the diminution of the permeability factor, because the extraction rate of PABA into the membrane phase exceeded that of reextraction from this phase, the transport capacity of the investigated pertraction system being limited. For this reason, the aim of the future studies is to optimize the reextraction process of the acid from the liquid membrane to the stripping phase.

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NOTATIONS

A	interfacial surface area (m^2)
C_{Fi}	PABA concentration at the feed phase inlet (moles/l)
C_{Fo}	PABA concentration at the feed phase outlet (moles/l)
C_M	PABA concentration in the liquid membrane (moles/l)
C_S	PABA concentration in the stripping phase (moles/l)
n	mass flow of acid (moles/m^{2}hr)
n_i	initial mass flow of acid (moles/m^{2}hr)
n_f	final (overall) mass flow of acid (moles/m^{2}hr)
P	permeability factor (–)
pH_F	pH-value of feed phase
pH_S	pH-value of stripping phase
Q	volumetric flow of the feed or stripping phase (l/hr)

subscript

aq	aqueous phase
o	organic phase

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