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THE TRANSPORT OF 3-AMINOPHENOL THROUGH BULK LIQUID MEMBRANE IN THE PRESENCE OF ALIQUAT 336

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In this paper the transport behavior through an organic membrane, chloroform, of 3-aminophenol in the presence of Aliquat 336 was investigated. The influence of 3-aminophenol concentration in the feed source, the influence of HCl concentration in the receiving phase and the transport time were studied. It was established the mechanism transport of 3-aminophenol in the presence of Aliquat 336. The process takes place with an efficiency of over 98%, when the concentration of 3-aminophenol in the feed source is 10^{-3} mol/L, the concentration of HCl in the receiving phase is 1 mol/L and the transport time is 24 hours.

The transport takes place with higher yields of 90% when the concentration of hydrochloric acid in the receiving phase is 1- 10^{-1} mol/L and the m-aminophenol concentration in the feed source varies in the range 10^{-4} – 10^{-3} mol/L. The necessary time to obtain transport yields vary between 8 – 24 hours, depending on the aminophenol concentration in the feed source.

Keywords: 3-aminophenol, bulk liquid membrane, Aliquat 336, assisted transport

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1. Introduction

Besides phenols, amino phenols are products frequently encountered in industrial aqueous wastes and are among the most common forms of chemical pollutants. They are considered a special class of pollutants due to high toxicity at low concentrations. Due to the high toxicity of these compounds in the surrounding environment and low biodegradability, US and European Environmental Protection Agency's (EPA and EEA), have included these compounds on the priority lists of pollutants, that need to be carefully monitored in wastewaters.

The frequency of these compounds in the environment is related to their use in many areas such as manufacture of explosives, the manufacture of pharmaceuticals, pesticides and pigments.

The main use of amino phenols is in the synthesis precursors. Both 2-aminophenol and 4-aminophenol are strong reducing agents and are used as a photographic developing agent under the name of Atomal, Ortal (2-aminophenol) and Activol, Azol (4-aminophenol). 4-Aminophenol is used to obtain azo and sulfuric dyes, used for wool and leather treatment. From a health perspective it is used for manufacture of paracetamol and other drugs. The oxalate salts of 4-aminophenol can be used as corrosion inhibitors in paints [1] or as anticorrosion-lubricating agents in two-cycle engine fuels [2]. 2-Aminophenol is a main intermediate in the synthesis of heterocyclic systems used as antiallergic agents[3] and inflammation inhibitors[4] such as oxyquinolines, phenoxazines and benzoxazoles. The main use of 3-aminophenol is as an

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intermediate in the manufacture of 4-amino-2-hydroxybenzoic acid, drug against tuberculosis [5]. It can also be used in the manufacture of hair dyes in cosmetic industry.

Removal of these compounds from wastewaters is a very important activity. For this purpose many studies designed to remove or treat the waste water of amino phenols were realized [6-8]. One of the studies consisted in treating aminophenol with granular sludge in methanogenic conditions at a temperature of 30^0C, under stirring over a period of 150 days. The methanogenic bacteria led to complete mineralization of amino phenols [9]. Another method for removing of aminophenol represents the application of the oxidative method with H_2O_2 /Fe^{2+} [10] or with hydrogen peroxide, using enzymes as catalysts [11]. Another method of removing industrial waters aminophenol is the activated carbon adsorption [12].

Classical methods for selective separation of organic compounds, such as fractional distillation, solvent extraction processes and others, involve considerable costs of energy and large amounts of waste [13].

Treatment of wastewater using emulsion or supported liquid membranes is an intense process, with a huge application potential but is still under development [14, 15].

These liquid membranes can be used as a viable alternative, because they involve low energy consumption, high sensitivity and rapid extraction with high efficiency due to the large contact surface for the mass transfer [16].

Because of the instability of these membranes, the literature does not show very many applications of liquid membranes [17, 18], despite multiple uses available, both at laboratory, but also at pilot and industrial scale. Liquid membranes are considered a promising alternative technology for separation of pharmaceutical importance [19-21]

In this context, in this paper we followed the transport of 3-aminophenol through bulk liquid membrane using Aliquat 336 as carrier.

2. Experimental

All reagents used in the experimental study are of analytical grade. Aminophenol and carrier Aliquat 336 were purchased from Flucka. Chloroform (Merck), used as the membrane, was saturated with distilled water. Distilled water was previously saturated with chloroform and used in the preparation of feed source and receiving phase. To prepare the receiving phase was used hydrochloric acid purchased from Merck. Sodium hydroxide (Merck) was used for pH correction of feed source. The experimental membrane system was: - *feed source* (FS) formed from m-aminophenol solution of concentration 10^{-4} – 10^{-3} mol/L in the presence of NaOH concentration 10^{-2} mol/L required to achieve an alkaline pH. The feed source volume was of 20 cm^3;

- *receiving phase* (RP) is a solution of HCl concentration 1 – 10^{-1} mol/L. The receiving phase volume was 7 cm^3;

- *membrane* is a solution of Aliquat 336 (methyltrioctylammonium chloride, $R_{1,8,8,8}N^+Cl^-$) concentration of 10^{-2} mol/L in chloroform. The membrane volume was 50 cm^3.

For the transport experiments was used a wall in wall type cell presented in figure 1:

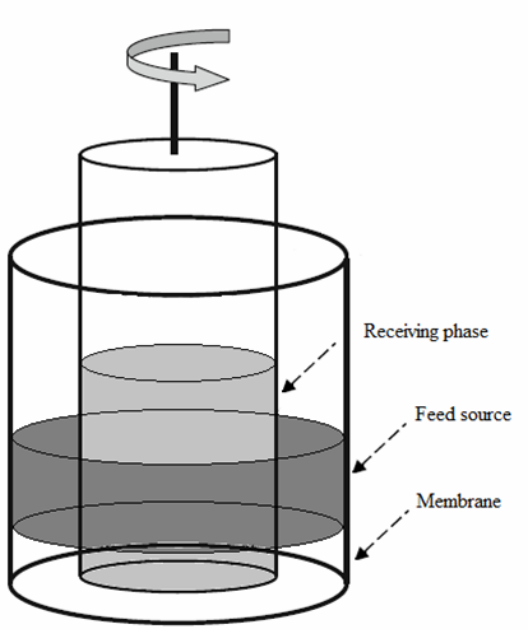


Figure 1.Experimental device used for transport

At the basis of the cell is located the chloroform membrane. The feed source is above the membrane, between the inner and exterior tube and the receiving phase is in the inner tube. Because the receiving phase has a smaller volume than the feed source, together with organic substrate transport from the feed source into the receiving phase its concentration takes place also. Analytical control of the process was performed by molecular absorption spectrometry using a UV spectrometer GBC Cintra. m-Aminophenol in aqueous solution shows an absorption band at λ = 292nm (for the feed source) and λ = 271nm (for the receiving phase). The content of m-aminophenol in the membrane was determined from mass balance.

3. Results and discussion

Aminophenols generally are compounds with amphoteric character due to the presence of two functional groups –OH (with acid character) and –NH_2 (basic character). In aqueous solution these compounds participate in proton exchange equilibrium, controlled equilibrium by the pH:

$$-C_6H_4\text{-}NH_2 + H_3O^+ \leftrightarrow HO\text{-}C_6H_4\text{-}NH_3^+ + HOH$$
$$HO\text{-}C_6H_4\text{-}NH_2 + HOH \leftrightarrow {}^-O\text{-}C_6H_4\text{-}NH_2 + H_3O^+$$

Based on this equilibrium are defined the acidity constants:

$$K_{a_1} = \frac{[HO-C_6H_4-NH_2][H_3O^+]}{[HO-C_6H_4-NH_3^+]} \quad (1)$$

$$K_{a_2} = \frac{[{}^-O-C_6H_4-NH_2][H_3O^+]}{[HO-C_6H_4-NH_2]} \quad (2)$$

In the case of m-aminophenol pKa_1= 4,17 and pKa_2= 9,87. Formation degrees of these chemical species can be evaluated with relationships (3) – (5):

$$\alpha_0 = \frac{1}{1+10^{pK_{a_2}-pH}+10^{pK_{a_1}+pK_{a_2}-2pH}} \quad (3)$$

$$\alpha_1 = \frac{1}{1+10^{pK_{a_1}-pH}+10^{pH-pK_{a_2}}} \quad (4)$$

$$\alpha_2 = \frac{1}{1+10^{pH-pK_{a_1}}+10^{2pH-pK_{a_1}-pK_{a_2}}} \quad (5)$$

where α_0, α_1, α_2 is the formation degree of species: $^{-}O\text{-}C_6H_4\text{-}NH_2$, $HO\text{-}C_6H_4\text{-}NH_2$, $HO\text{-}C_6H_4\text{-}NH_3^+$ in the solution of m-aminophenol. With these relations was obtain the speciation diagram shown in figure 2:

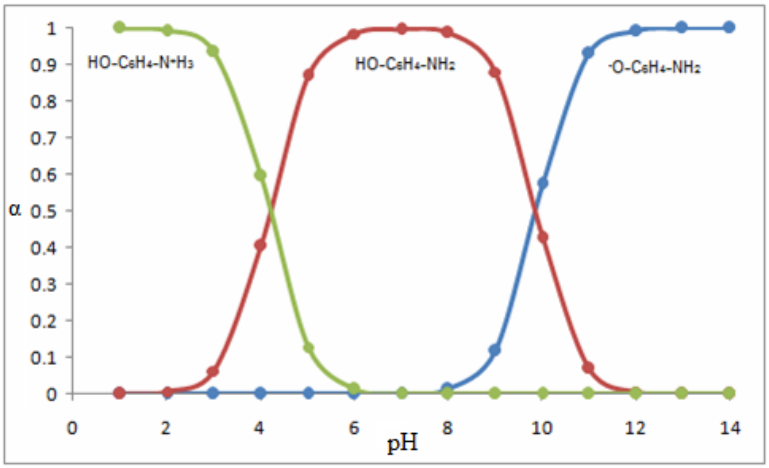


Figure 2.The speciation diagram of m-aminophenol function of pH

It is found that at pH=12 in aqueous solution predominates the anionic form ($^{-}O\text{-}C_6H_4\text{-}NH_2$) at a rate of 99,26%. In these pH conditions, the feed source, containing m-aminophenol is possible that at chloroform membrane interface, in which was dissolved Aliquat 336, to form an ion pair type, complex soluble in chloroform. The complex formed between Aliquat 336 and the anionic form ($^{-}O\text{-}C_6H_4\text{-}NH_2$), crosses the chloroform membrane and at the receiving phase interface, which contains hydrochloric acid, it decomposes. It is obtained a compound $HO\text{-}C_6H_4\text{-}NH_3^+Cl^-$ soluble in the receiving phase and insoluble in the chloroform membrane, therefore inactive for transport. At the same time carrier regeneration takes place and resumes a new transport cycle. This transport mechanism is shown in figure 3:

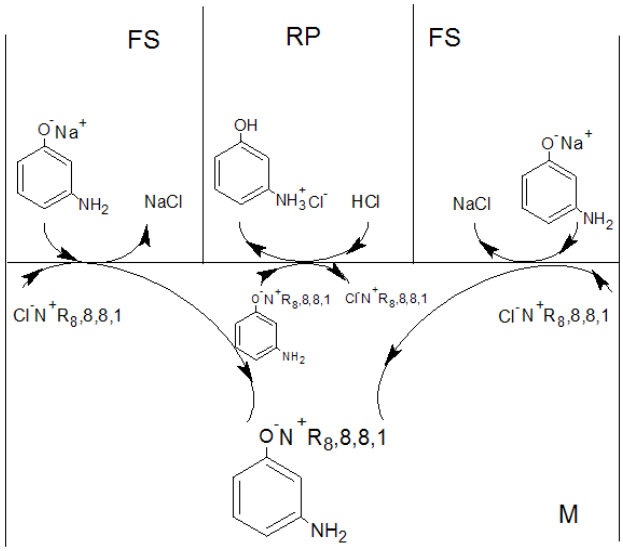


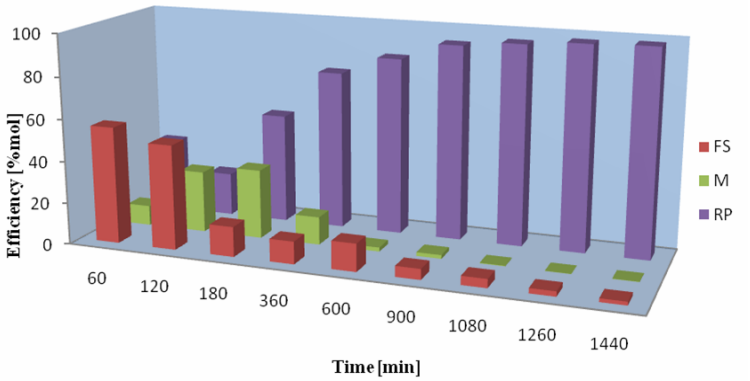
Figure 3.Transport mechanism of m-aminophenol transport through bulk liquid membrane

Experimental studies took into account the influence of experimental parameters such as: influence of the hydrochloric acid concentration in receiving phase, influence of the organic substrate in feed source, influence of the transport time. Assessing the influence of the first two parameters was performed following the distribution of organic substrate in the phase's membrane system during the transport process. For these purposes was used the relationships:

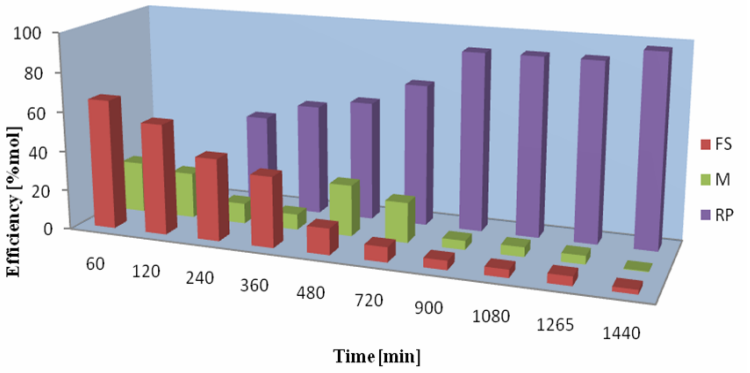
$$\%moli = \frac{V_{Faq} \cdot C_{Faq}}{V_{FS_0} \cdot C_{FS_0}} \cdot 100 \quad (6)$$

where:
%moli = molar percentage in phases membrane system
V_{Faq} = aqueous phase volume, L
C_{Faq}= aqueous phase concentration, mol/L
V_{FS0} = initial feed source volume, L
C_{FS0} = initial feed source concentration, mol/L
m-Aminophenol molar percentage of membrane was calculated from mass balance.

Influence of hydrochloric acid concentration in the receiving phase.



a)



b)

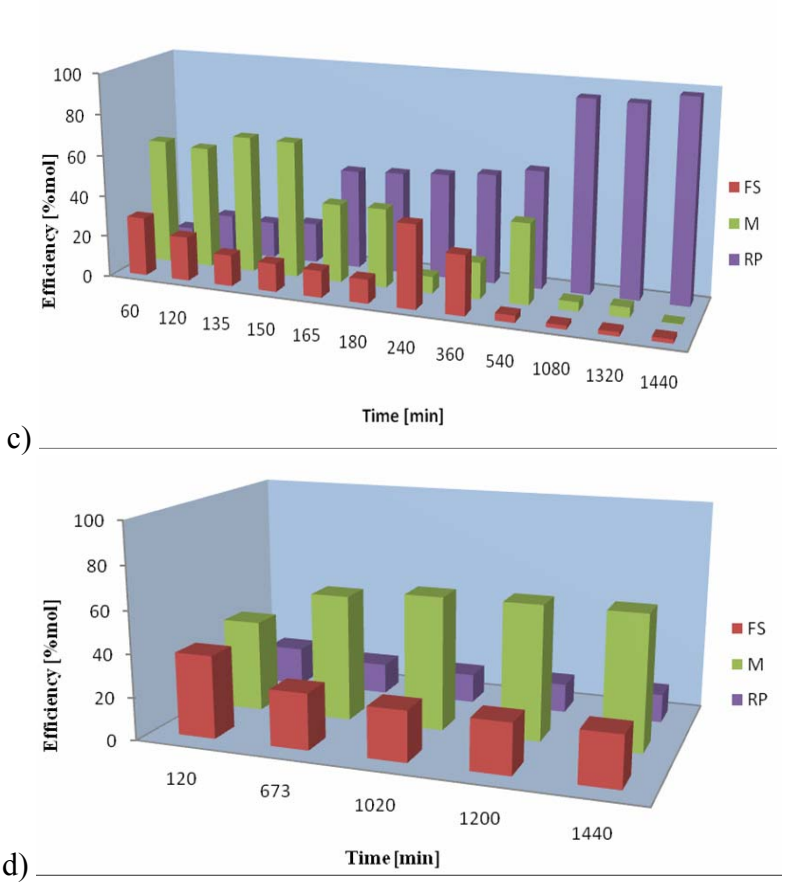


Figure 4.Influence of HCl concentration in receiving phase on the m-aminophenol transport process Feed source: $C_{initial,\ m\text{-}aminophenol} = 10^{-3}$ mol/L (pH = 2); Liquid membrane: [Aliquat 336] = 10^{-2} mol/L, in chloroform; Receiving phase: [HCl] = 1 mol/L (a), $5x10^{-1}$ mol/L (b), 10^{-1} mol/L (c), 10^{-2} mol/L (d); Transport time – 24 hours.

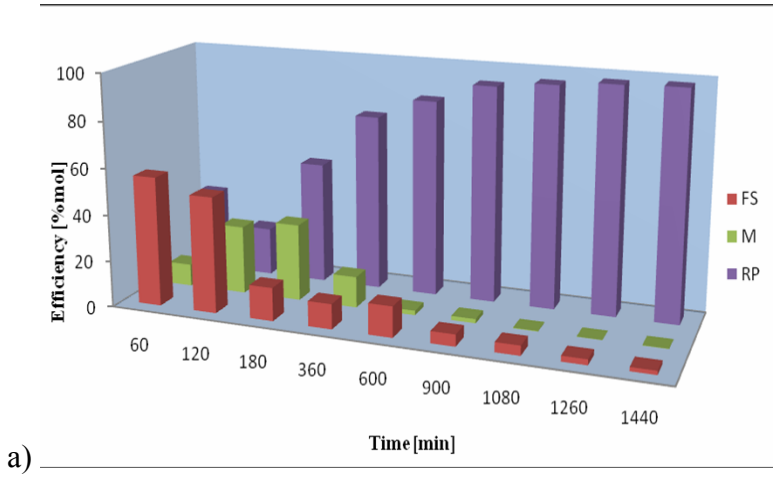
Being a transport reaction in the receiving phase, the hydrochloric acid concentration in this phase of the membrane system is a very important factor for transport efficiency. The influence of hydrochloric acid concentration in the receiving phase on concentration range 1 – 10^{-2} mol/L was studied. During this study, the initial m-aminophenol concentration was 10^{-3} mol/L (pH = 12) and carrier concentration, Aliquat 336, was 10^{-2} mol/L. Experimental results are shown in figures 4(a, b, c, d):

Experimental data obtained have shown that the transport process follows with efficiency of over 90% for HCl concentration in the range of 1 mol/L – 10^{-1} mol/L. At HCl concentration of 10^{-2} mol/L, in the receiving phase, the transport process practically does not take place, at this HCl concentration, an extraction in the membrane phase takes place with efficiencies of more than 60%.

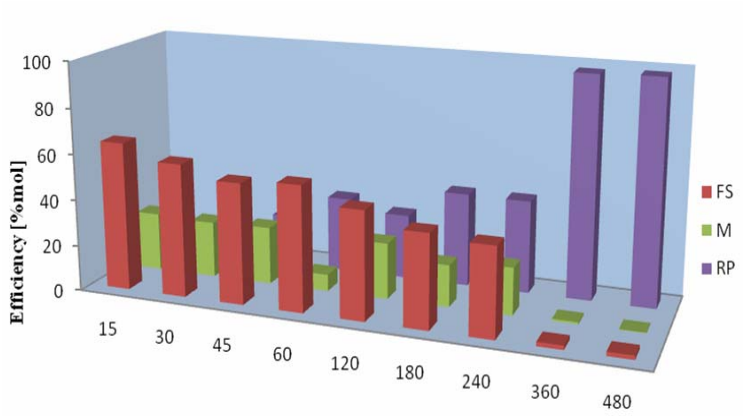
Influence of initial m-aminophenol concentration in the feed source.

Was studied the influence of m-aminophenol concentration in the feed phase for the following concentrations: 10^{-4}, $5x10^{-4}$ and 10^{-3} mol/L. pH = 12 of the feed source was determined to be optimal based on speciation diagram. The hydrochloric acid concentration in the receiving phase was 1 mol/L and carrier concentration in the membrane was 10^{-2} mol/L. Experimental results are shown in figures 5(a, b, c).

It is found that the transport efficiency is influenced by the initial m-aminophenol concentration. The influence of this parameter is reflected in the required time to achieve a maximum transport yield. Generally, at lower m-aminophenol concentration, the required time to obtain efficiency of 90% is less than 8 – 12 hours (for the initial m-aminophenol concentration of $5x10^{-4}$, 10^{-4} mol/L) compared to 24 hours at the initial m-aminophenol concentration of 10^{-3} mol/L.



a)



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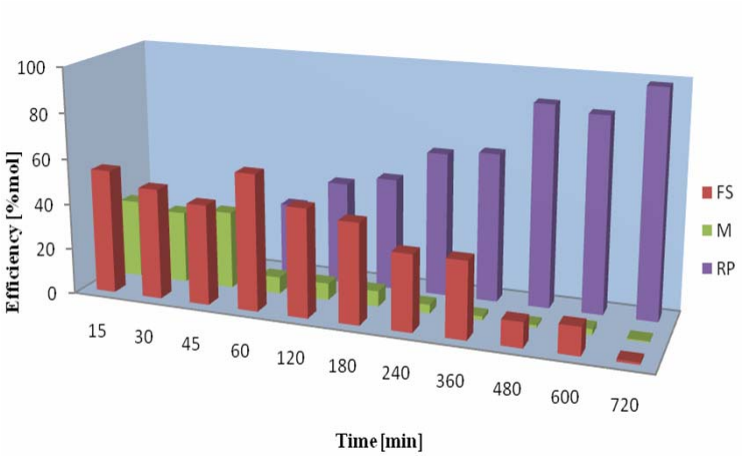


c)

Figure 5.Influence of initial m-aminophenol concentration in feed source on the transport process Feed source: $C_{initial,\ m\text{-}aminophenol} = 10^{-3}$ mol/L (a), $C_{initial,\ m\text{-}aminophenol} = 5x10^{-4}$ mol/L (b), $C_{initial,\ m\text{-}aminophenol} = 10^{-4}$ mol/L (c); Liquid membrane: [Aliquat 336] = 10^{-2} mol/L, in chloroform; Receiving phase: [HCl] = 1 mol/L; Transport time – 24 hours.

Influence of transport time

Time analysis of m-aminophenol transport process showed that mass transfer in membrane systems studied takes place following the kinetic law of consecutive first order I chemical reaction according to the kinetic scheme:

$$(HO\text{-}C_6H_4\text{-}NH_2)_{FS} \xrightarrow{k_1} (HO\text{-}C_6H_M\text{-}NH_2)_M \xrightarrow{k_2} (HO\text{-}C_6H_4\text{-}NH_2)_{RP}$$

where: k_1, k_2- represents pseudo-first-order apparent membrane entrance and exit rate constants, s^{-1}.

Pseudo-first-order apparent membrane entrance and exit rate constants can be determined by the equations that describe the time variation of reduced concentrations:

$$R_{FS} = e^{-k_1 \cdot t} \tag{7}$$

$$R_M = \frac{k_1}{k_2 - k_1}(e^{-k_1 \cdot t} - e^{-k_2 \cdot t}) \tag{8}$$

$$R_{RP} = \frac{1}{k_1 - k_2}(k_2 e^{-k_1 \cdot t} - k_1 e^{-k_2 \cdot t}) \tag{9}$$

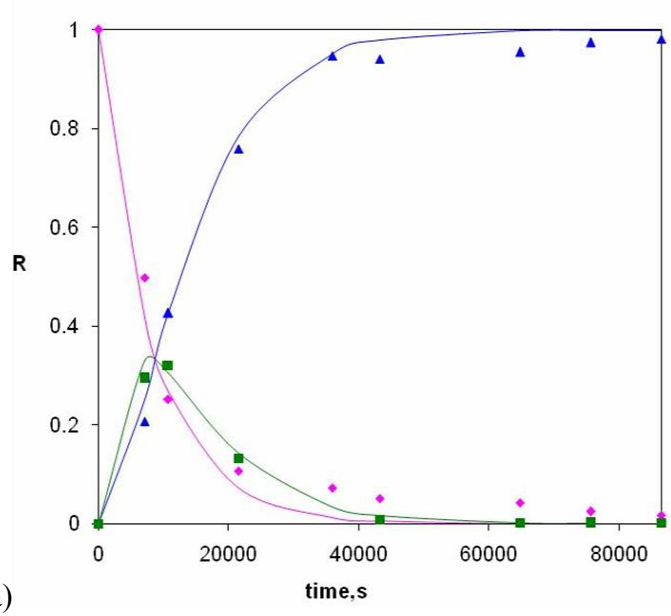
where R_{FS}, R_M and R_{RP} are reduced concentrations defined by relations:

$$R_{FS} = \frac{C_{FS}}{C_{FS_0}} \tag{10}$$

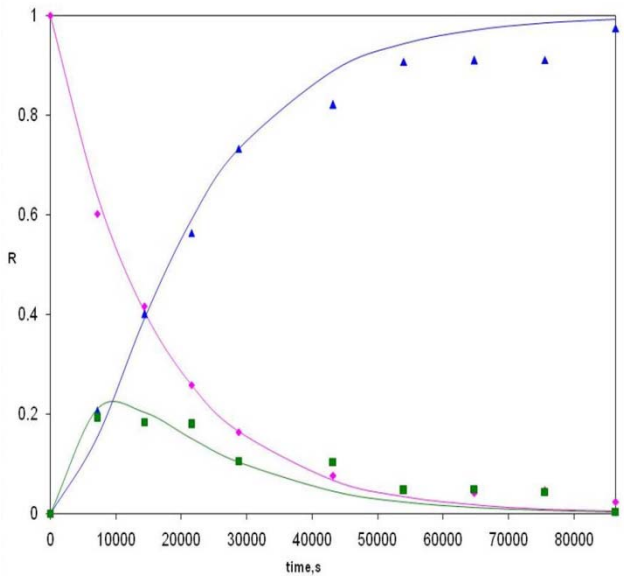
$$R_M = \frac{C_M}{C_{FS_0}} \tag{11}$$

$$R_{RP} = \frac{C_{RP}}{C_{FS_0}} \tag{12}$$

Diagrams, presented in figure 6 (a, b, c, d), show a good correlation between experimental data and consecutive first order I reactions model.



a)



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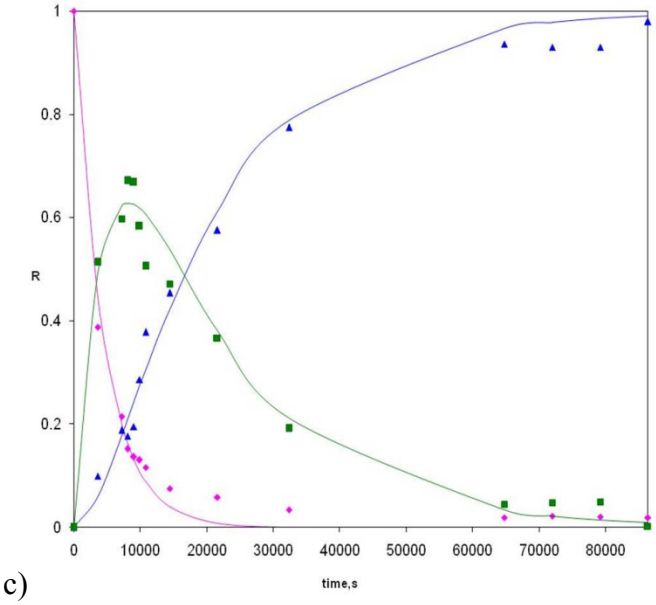
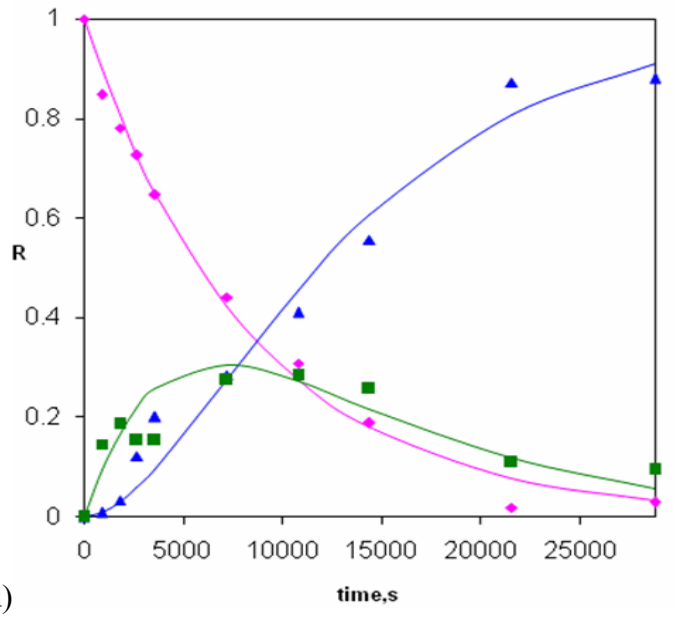


c)



d)

Figure 6.Dependence of reduce concentrations R_{FS}, R_M R_{RP}, in time for m-aminophenol transport using Aliquat 336 as carrier
Solid line-model;
a) Feed source (●): $C_{initial,\ m\text{-}aminophenol} = 10^{-3}$ mol/L (pH = 2); Liquid membrane (■): [Aliquat 336] = 10^{-2} mol/L, in chloroform; Receiving phase (▲): [HCl] = 1 mol/L
b) Feed source (●): $C_{initial,\ m\text{-}aminophenol} = 10^{-3}$ mol/L (pH = 2); Liquid membrane (■): [Aliquat 336] = 10^{-2} mol/L, in chloroform; Receiving phase (▲): [HCl] = $5x10^{-1}$ mol/L
c) Feed source (●): $C_{initial,\ m\text{-}aminophenol} = 10^{-3}$ mol/L (pH = 2); Liquid membrane (■): [Aliquat 336] = 10^{-2} mol/L, in chloroform; Receiving phase (▲): [HCl] = 10^{-1} mol/L
d) Feed source (●): $C_{initial,\ m\text{-}aminophenol} = 5x10^{-4}$ mol/L (pH = 2); Liquid membrane (■): [Aliquat 336] = 10^{-2} mol/L, in chloroform; Receiving phase (▲): [HCl] = 1 mol/L

The correlation coefficient for all dependences R=f(t) has values greater than 0,98. Values of pseudo rate constants according to the operational parameters are listed in table 1:

Table 1.Values of kinetic parameters k_1, k_2 to m-aminophenol transport in the presence of Aliquat 336 as carrier

Operational parameters	$k_1, s^{-1}x10^{-4}$	$k_2, s^{-1}x10^{-4}$
a)Feed source: $C_{m\text{-}aminophenol}= 10^{-3}$mol/L, Membrane: [Aliquat 336] = 10^{-2} mol/L in chloroform, Receiving phase:[HCl] = 1mol/L	1,24	1,49
b)Feed source: $C_{m\text{-}aminophenol}= 10^{-3}$mol/L, Membrane: [Aliquat 336] = 10^{-2} mol/L in chloroform, Receiving phase: [HCl] = $5x10^{-1}$ mol/L	0,63	1,55
c)Feed source: $C_{m\text{-}aminophenol}= 10^{-3}$ mol/L, Membrane: [Aliquat 336] = 10^{-2} mol/L in chloroform, Receiving phase: [HCl] = 10^{-1} mol/L	2,24	0,57
d)Feed source: $C_{m\text{-}aminophenol}$ = $5x10^{-4}$ mol/L, Membrane: [Aliquat 336] = 10^{-2} mol/L in chloroform, Receiving phase: [HCl] = 1mol/L	1,20	1,71

The data presented in table 1 show that the values of pseudo rate constants do not vary significantly according to the feed source concentration and receiving phase concentration.

4. Conclusions

In this paper are presented the experimental results obtained from m-aminophenol transport through organic chloroform membrane.

The influence of important operational parameters of the transport process efficiency, such as m-aminophenol concentration in the feed source, HCl concentration in the receiving phase, transport time, was studied.

Transport takes place with higher yields of 90% when the concentration of hydrochloric acid in the receiving phase is $1\text{-}10^{-1}$mol/L and the concentration of m-aminophenol in the feed source varies in range 10^{-4}- 10^{-3} mol/L.

The time required to obtain high yields of transport depends on the concentration of m-aminophenol in the feed source and varies between 8 – 24 hours.

The transport takes place following the kinetic law of consecutive first order I reactions. The kinetic parameters determined (pseudo rate constants k_1 and k_2) does not significantly vary according to the feed source concentration and receiving phase concentration.

Acknowledgments

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