Kinetic Aspects of Transport *para*-aminophenol through Agitated Bulk Liquid Membrane

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This paper presents experimental results regarding the transport through agitated bulk liquid membrane of para-aminophenol, a highly toxic chemical reagent. The influence of a group of carriers para-tert-butyl-calix[n]arenes (n=4,6,8) in the transport of para-aminophenol through a chloroform membrane was studied. In the presence of the carrier an increase of the efficiency transport takes place. Thus the transport efficiency increases from 26% without carrier to over 73% in the presence of the carrier para-tert-butyl-calix[8]arene. Assessing the kinetic parameters of transport process (entry and exit flow through the membrane, mass transfer coefficients), it was established that the transport efficiency increases in the order: para-tert-butyl-calix[4]arene < para-tert-butyl-calix[6]arene < para-tert-butyl-calix[8]arene. Also it has been observed an increase of exit flow from the membrane and also for mass transfer coefficients.

Keywords: para-aminophenol, para-tert-butyl-calix[n]arene, kinetic model

Organic compounds with phenolic structures are products commonly found in industrial aqueous waste and are the most common forms of chemical pollutants from industrial wastewater. More than that, because of their toxicity to microorganisms in high concentrations, the state of degradation is limited [1, 2].

Aminophenols are considered a special class of pollutants because of high toxicity at low concentrations.

Almost all aminophenols and their derivatives are toxic and carcinogenic for the organisms. It is know that *para*-aminophenol can produce the increase of human body temperature but also show chronic effects on aquatic organisms similar to the toxicity of phenol and aniline, the limit being 50 ppb in drinking water and sea water [3]. It is reported that *para*-aminophenol presents significant nephrotoxic and teratogenic effects [4]. Is a toxic compound, irritable to eyes, skin and respiratory system, which can cause irreversible damage to blood and kidneys.

Para-aminophenol is used to obtain azo, sulfur, acid wool and leather dyes. From medical point of view, it is used to produce paracetamol and other drugs [5 - 8]. It also presents applications as a photodeveloper, in the rubber and petroleum additives [9].

Due to its using as an important intermediary in different processes the water pollution degree has grown [10 - 14]. Therefore its removal from wastewater is a very important activity with direct applications in environmental protection.

For this purpose many studies designed to remove or treat the waste water of aminophenols were realized [15 - 18]. Such studies have been performed for the treatment of *para*-aminophenol with granular sludge in methanogenic conditions at a temperature of 30°C, under stirring over a period of 150 days. Biodegradability test was performed by measuring the methane gas composition. It was found that methanogenic bacteria led to complete mineralization of *para*-aminophenol [18].

Oxidative methods have frequently been used to treat wastewater containing aminophenol. The use of hydrogen peroxide in the presence of Fe^{2+}, has reduced the content of *para*-aminophenol in aqueous medium at a rate of 98% to 99,5% [17]. Very good results were obtained in the case of oxidation with hydrogen peroxide using the enzyme as a catalyst; degradation was virtually complete, up to CO_2 and H_2O [19].

A special focus was put on the use of methods of separating *para*-aminophenols from different aqueous systems.

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 [20].

Treatment of wastewater using emulsion or supported liquid membranes, is an intense process, with a huge application potential but is still under development [21, 22].

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 [23].

Because of instability of these membranes, the literature does not show very many applications of liquid membranes [24, 25], 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 [26, 27].

In this context, in this work we studied the transport of *para*-aminophenol through bulk liquid membrane focusing on the role of transporters *para*-tert-butyl-calyx[n]arenas [28-32].

Experimental part

Reagents

All reagents used in transport experiments were of analytical grade and were used without further purification. HCl and *para*-aminophenol were purchased from Merck. The feed/donor (d) source and receiving/acceptor (a) phase were prepared using distilled water saturated in membrane solvent. The feed source is an aqueous solution of *para*-aminophenol 10^{-3} mol/L. The receiving phase (acceptor aqueous phase) consists of a 10^{-2}mol/L solution of HCl (*p*H=2). The membrane (m) is prepared from a

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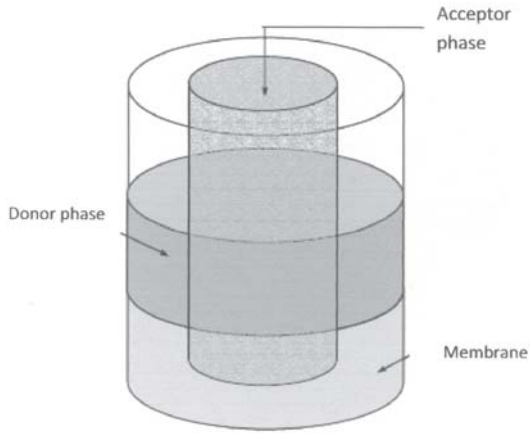

Fig. 1. Experimental device used for transport

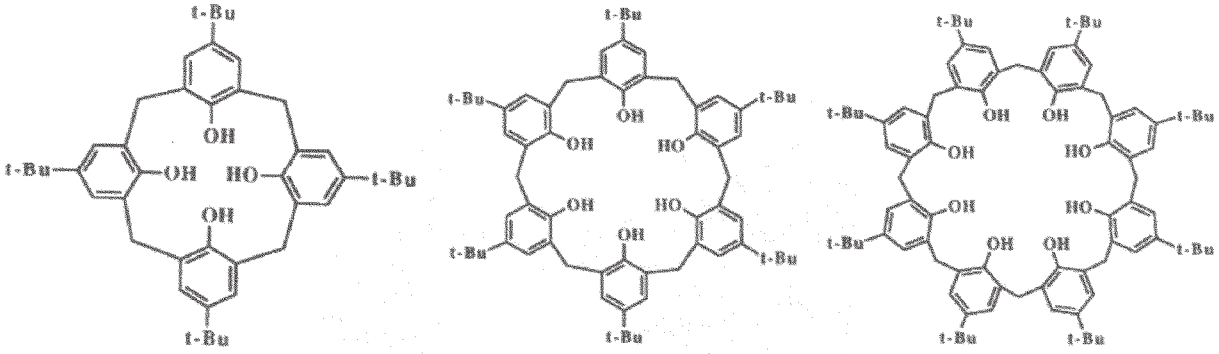

Fig. 2. The structure of *para*-tert-butyl-calix[n]arene, n = 4,6,8

liquid chlorinated organic solvents saturated with distilled water. The chloroform membrane contains different transporters: *para*-tert-butyl-calix [n]arene, n=4,6,8, in concentration of 10^{-2} mol/L, of Flucka origin.

Apparatus

Para-aminophenol compound content from the aqueous phases was determined using a spectrophotometer LAMBDA 750 (Perkin Elmer Co). The analysis of *para*-aminophenol content was performed at characteristic wavelength (λ =317 nm). *Para*-aminophenol compound content from the membrane is determined by mass balance of the three phases of the membrane system.

Procedure

The transport experiments were realized in a wall in wall type transport cell presented in figure 1.

As it can be observed from the figure, at the base of the transport cell is a membrane with a higher density than water. In the outer tube is the feed/donor source, and in the inner tube is the receiving/acceptor phase. Because the volume of acceptor phase is lower than the volume of the donor phase together with the transport a concentration of the transported compound is performed.

The transport stirring speed used during the experiments was 180 rot/min, and the transport time 3 h. Temperature was 25±1°C.

Results and discussions

Neutral molecules can pass through a membrane according to their solubility in the organic membrane. The solubility in the membrane can often be improved by using a carrier.

Therefore in this work we studied the transport of *para*-aminophenol in the presence of type carriers *para*-tert-butyl-calix[n]arene (n=4,6,8)(fig. 2). The experimental results obtained at transport of *para*-aminophenol in the presence of carriers are illustrated in figure 3.

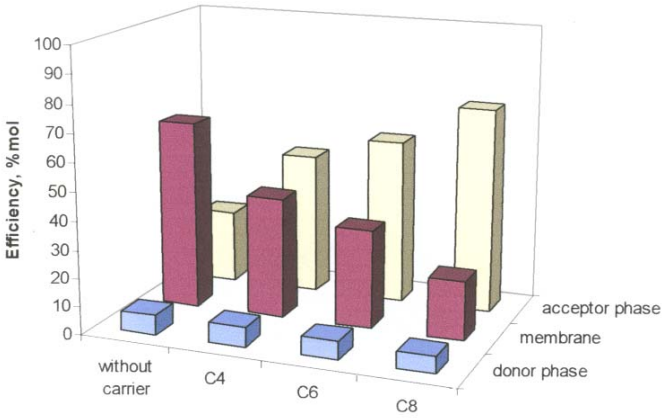

Fig. 3. The results obtained at assisted transport of *para*-aminophenol
Donor phase: 20 cm^3 *para*-aminophenol solution (10^{-3} mol/L), Membrane: 50 cm^3 organic solvent: chloroform and carrier C4 (*para*-tert-butyl-calix[4]arene), C6 (*para*-tert-butyl calix[6]arene), C8 (*para*-tert-butyl-calix[8]arene) 10^{-2} mol/L, Acceptor phase: 7 cm^3 solution HCl 10^{-2} mol/L.

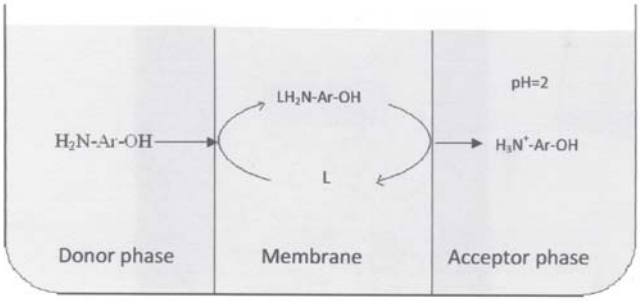

Fig. 4. The mechanism of transport of *para*-aminophenol through chloroform membrane that contains *para*-tert-butyl-calix[n]arene (L) transporter

As it can be observed transport efficiency has improved in the presence of carrier. Therefore the transport efficiency was increased from 26% to over 73%. The best results were achieved when using carrier *para*-tert-butyl-calix[8]arene. The experimental results can be correlated with the capacity of *para*-tert-butyl-calix[n]arenas to complex neutral melecules thus increasing the transport species permeability through membrane. These observations are validated by the transport mechanism illustrated in figure 4.

Para-aminophenol molecular form penetrates the membrane and comes across transporter molecule that complex according to the equilibrium (1).

$$(H_2N\text{-}Ar\text{-}OH)_m + (L)_m \rightleftharpoons ([LH_2N\text{-}Ar\text{-}OH])_m \quad (1)$$

where L – represents *para*-tert-butyl-calix[n]arenas

Then the complex molecule [LH_2N-Ar-OH] diffuses through the membrane and it will decompose at the membrane-acceptor phase interface where the following equilibrium takes place (2):

$$(LH_2N\text{-}Ar\text{-}OH)_m + H_3O^+ \rightleftharpoons (H_3N^+\text{-}Ar\text{-}OH)_a + L_m + H_2O \quad (2)$$

The literature [32] shows that, the complex of *para*-aminophenol and *para*-tert-butyl-calix[n]arene is based on the formation oh hydrogen bonds between OH groups of *para*-tert-butyl-calix[n]arene and the amino group of *para*-aminophenol in which organic substrate is outside the cavity of *para*-tert-butyl-calix[n]arene. It is observed the transport efficiency increases in the following order: *para*-tert-butyl-calix[4]arene < *para*-tert-butyl-calix[6]arene < *para*-tert-butyl-calix[8]arene coresponding to the increase of cavity size.

From the kinetic point of view the transport of a solute through bulk liquid membrane takes place according to a consecutive irreversible first order chemical reaction (3)[33 – 42]:

$$S_{aq,d} \xrightarrow{k_1} S_{org,m} \xrightarrow{k_2} S_{aq,a} \quad (3)$$

where:

$S_{aq,d}$ – represents *para*-aminophenol neutral molecule in donor phase (feed phase);

$S_{org,m}$ – represents *para*-aminophenol neutral molecule in membrane phase;

$S_{aq,a}$ - represents *para*-aminophenol neutral molecule in acceptor (receiving phase);

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

The variation in time of *para*-aminophenol concentration was determined in both aqueous phases: in the donor phase (C_d) and in the acceptor phase (C_a). The concentration in the membrane phase (C_m) was determined from the phases material balance. For practical reasons, were used undimensional reduced concentrations (R), defined by the equations:

$$R_d = \frac{C_d}{C_{d_0}} \quad (4)$$

$$R_m = \frac{C_m}{C_{d_0}} \quad (5)$$

$$R_a = \frac{C_a}{C_{d_0}} \quad (6)$$

where:

C_d, C_m, C_a – represents *para*-aminophenol concentration from donor phase, membrane phase and acceptor phase, mol/L;

C_{do} - *para*-aminophenol initial concentration from donor phase.

The material balance regarding the reduced concentrations can be expressed as:

$$R_d + R_m + R_a = 1 \quad (7)$$

Kinetic scheme of the equation (3) for consecutive first-order reactions can be described by the following equations:

$$\frac{dR_d}{dt} = -k_1 R_d \equiv J_d \quad (8)$$

$$\frac{dR_m}{dt} = -k_1 R_d - k_2 R_m \quad (9)$$

$$\frac{dR_a}{dt} = -k_1 R_m \equiv J_a \quad (10)$$

where: J_d, J_a – represent entry and exit flow from membrane.

When $k_1 \neq k_2$ and integrating equations 8-10 the following expressions, which define the low concentrations of the three phases of the membrane system, are obtained:

$$R_d = e^{-k_1 \cdot t} \quad (11)$$

$$R_m = \frac{k_1}{k_2 - k_1}(e^{-k_1 \cdot t} - e^{-k_2 \cdot t}) \quad (12)$$

$$R_a = 1 + \frac{1}{k_1 - k_2}(k_2 e^{-k_1 \cdot t} - k_1 e^{-k_2 \cdot t}) \quad (13)$$

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

Kinetic parameters k_1 and k_2 are obtained by fitting equations (11) – (13) to the experimental results.

When $dRm/dt = 0$ it can be determined the maximum value of reduced concentration from membrane R_m^{max} characteristic for the dependence $R_m = f(t)$.

$$R_m^{max} = \left(\frac{k_1}{k_2}\right)^{-\frac{k_2}{k_1 - k_2}} \quad (14)$$

And also it may determine the relative value of maximum time using equation (15):

$$t_{max} = \frac{\ln(k_1 / k_2)}{k_1 - k_2} \quad (15)$$

Taking the first order differential equations (11)-(13) at $t = t_{max}$ may be obtained the maximum flow value.

$$\left.\frac{dR_d}{dt}\right|_{max} = -k_1 \left(\frac{k_1}{k_2}\right)^{-k_1/(k_1 - k_2)} \equiv J_d^{max} \quad (16)$$

$$\left.\frac{dR_m}{dt}\right|_{max} = 0 \quad (17)$$

$$\left.\frac{dR_a}{dt}\right|_{max} = -k_2\left(\frac{k_1}{k_2}\right)^{-k_2/(k_1-k_2)} \equiv J_a^{max} \quad (18)$$

It can be observed that at $t = t_{max}$ a steady state is achieved because the *para*-aminophenol concentration in the membrane does not change with time (17) and the entrance (J_d^{max}) and exit (J_a^{max}) fluxes are equal but of opposite sign:

$$-J_d^{max} = J_a^{max} \quad (19)$$

Pseudo-first-order apparent membrane entrance and exit rate constants are closely related to the apparent mass transfer coefficients through the following relations:

$$k_1 = k'_d \frac{A_d}{V_d} \quad (20)$$

$$k_2 = k'_a \frac{A_a}{V_m} \quad (21)$$

where:

k'_d, k'_a - the apparent mass transfer coefficients, cm/s;

A_d, A_a - the interface area donor phase/membrane and respectively membrane/ acceptor phase, cm^2;

V_d, V_m - the volume of donor phase and respectively acceptor phase, cm^3.

Equations 20 and 21 indicate that the apparent pseudo-first-order apparent membrane entrance and exit rate constants depend on the interface area and volume of donor phase and of the liquid membrane. Therefore, the values of pseudo-constants k_1 and k_2 can not be used to compare different membrane systems.

The experimental results obtained show that R_d decreases exponentially with time while R_a simultaneously increase and R_m has different maximum times (fig. 5 - 7). Therefore, in the case of *para*-aminophenol transport using *para*-tert-butyl-calix[n]arene as carrier a concentration in the membrane is observed for *para*-tert-butyl-calix[4]arene. Curves with the model time dependence (continuous lines) are in agreement with experimental data. However there are some discrepancies between experimental data and those of the model, but the correlation coefficient for all time dependences $R=f(t)$ is higher than 0.98. Kinetic parameters of the model are presented in table 1.

According to table 1, it is observed that the maximum entry and exit flux from the membrane as well as the apparent pseudo-first-order apparent membrane entrance and exit rate constants vary in direction *para*-tert-butyl-calix[4]arene < *para*-tert-butyl-calix[6]arene < *para*-tert-butyl-calix[8]arene. Therefore the transport efficiency

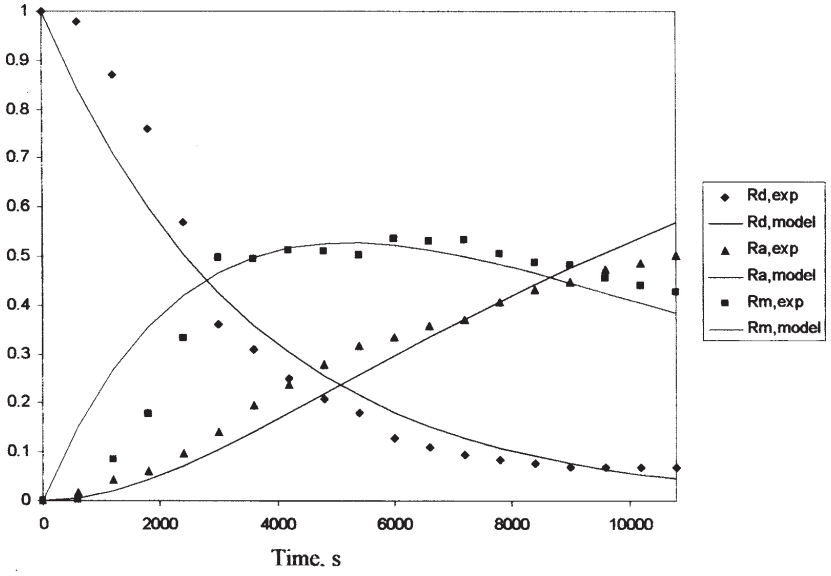

Fig 5. Time dependence of Rd, Rm, Ra for *para*-aminophenol transport using carrier *para*-tert-butyl-calix[4]arene. Feed source: 20 cm^3 *para*-aminophenol solution (10^{-3} mol/L), Membrane: 50 cm^3 chloroform with *para*-tert-butyl-calix[4]arene 10^{-2} mol/L, Receiving phase: 7 cm^3 solution HCl 10^{-2} mol/L.

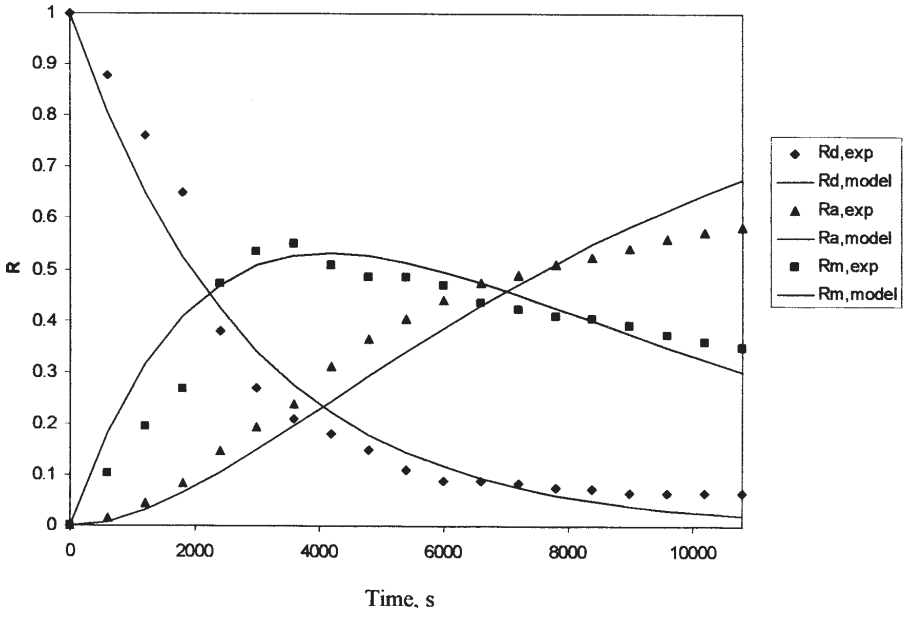

Fig. 6. Time dependence of Rd, Rm, Ra for *para*-aminophenol transport using carrier *para*-tert-butyl-calix[6]arene. Feed source: 20 cm^3 *para*-aminophenol solution (10^{-3} mol/L), Membrane: 50 cm^3 chloroform with *para*-tert-butyl-calix[6]arene 10^{-2} mol/L, Receiving phase: 7 cm^3 solution HCl 10^{-2} mol/L.

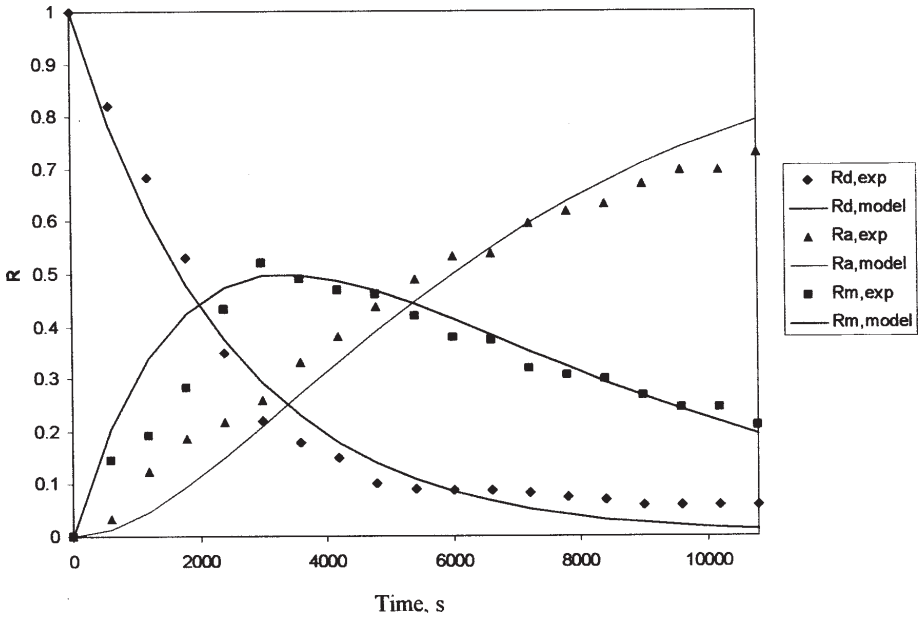

Fig 7. Time dependence of Rd, Rm, Ra for *para*-aminophenol transport using carrier *para*-tert-butyl-calix[8]arene. Feed source: 20 cm^3 *para*-aminophenol solution (10^{-3} mol/L), Membrane: 50 cm^3 chloroform with *para*-tert-butyl-calix[8]arene 10^{-2} mol/L, Receiving phase: 7 cm^3 solution HCl 10^{-2} mol/L.

increases in the presence of *para*-tert-butyl-calix[n]arenas in the following order: *para*-tert-butyl-calix[4]arene < *para*-tert-butyl-calix[6]arene < *para*-tert-butyl-calix[8]arene.

The apparent pseudo-first order constant of entry and exit from the membrane can be used to determine the apparent mass transfer coefficients.

The contact area between donor phase and the membrane is 51.0250 cm^2, and between membrane phase and acceptor phase is: 9.3886 cm^2. The donor phase volume is 20 cm^3 and the acceptor phase volume is 7 cm^3. Apparent mass transfer coefficients are presented according to the carrier used at transport, in table 2.

The studied carriers increase mass transfer coefficient of organic substrate, *para*-aminophenol, at membrane system interfaces. The largest contribution was obtained for *para*-tert-butyl-calix[8]arene carrier.

Table 1

KINETIC PARAMETERS OF *para*-AMINOPHENOL ASSISTED TRANSPORT USING *para*-TERT-BUTYL-CALIX[n]ARENE CARRIER

Compound/parameter	k_1, s^{-1}	k_2, s^{-1}	R_m^{max}	t_{max}, s	J_d^{max}, s^{-1}	J_a^{max}, s^{-1}
para-tert-butyl-calix[4]arene	$2.84 \cdot 10^{-4}$	$1.22 \cdot 10^{-4}$	0.53	5195	$-6.49 \cdot 10^{-5}$	$6.49 \cdot 10^{-5}$
para-tert-butyl-calix[6]arene	$3.57 \cdot 10^{-4}$	$1.51 \cdot 10^{-4}$	0.53	4169	$-8.05 \cdot 10^{-5}$	$8.05 \cdot 10^{-5}$
para-tert-butyl-calix[8]arene	$4.09 \cdot 10^{-4}$	$2.05 \cdot 10^{-4}$	0.49	3385	$-1.024 \cdot 10^{-4}$	$1.024 \cdot 10^{-4}$

Table 2

APPARENT MASS TRANSFER COEFFICIENTS IN THE CASE OF *para*-AMINOPHENOL ASSISTED TRANSPORT USING *para*-TERT-BUTYL-CALIX[n]ARENE CARRIER.

Compound/parameter	k_1, s^{-1}	k_2, s^{-1}	k_d' cm/s	k_a', cm/s
para-tert-butyl-calix[4]arene	$2.84 \cdot 10^{-4}$	$1.22 \cdot 10^{-4}$	$1.11 \cdot 10^{-4}$	$6.54 \cdot 10^{-4}$
para-tert-butyl-calix[6]arene	$3.57 \cdot 10^{-4}$	$1.51 \cdot 10^{-4}$	$1.40 \cdot 10^{-4}$	$8.05 \cdot 10^{-4}$
para-tert-butyl-calix[8]arene	$4.09 \cdot 10^{-4}$	$2.05 \cdot 10^{-4}$	$1.60 \cdot 10^{-4}$	$1.09 \cdot 10^{-3}$

Conclusions

In the case of compounds with low transport efficiency, the efficiency can be improved by introducing a carrier. Due to the interaction of carrier with phenolic compound, the solubility of phenolic derivate increases in the membrane and results in increasing of the transport efficiency. As a result the transport efficiency of *para*-aminophenol increased from 26% without carrier to over 73% in the presence of the carrier *para*-tert-butyl-calix[8]arene. The transport efficiency increases in the order: *para*-tert-butyl-calix[4]arene < *para*-tert-butyl-calix[6]arene < *para*-tert-butyl-calix[8]arene. In the same direction it has been observed an increase of exit flux from the membrane. This idea is confirmed by a proportional increase of apparent mass transfer coefficients.

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