Evaluation of Kinetic Parameters at the Transport of Indole-3-acetic Acid Through Bulk Liquid Membranes

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Indole-3-acetic acid is a growth phytohormone considered the most important representative of auxin class. This paper presents the assessment of some kinetic parameters in the process of transport of indole-3-acetic acid taking into consideration the kinetic model of consecutive irreversible first order reactions. It was pursued the influence upon the process of parameters such as: feed phase concentration, stripping phase concentration in the presence of two type carriers: tributyl phosphate (TBP) and trioctylphosphine oxide (TOPO). Depending on these transport parameters were calculated kinetics parameters such as: pseudo-first-order apparent membrane entrance and exit rate constants, the maximum flux at the entrance and exit out of the membrane. The highest values of the transport flux is obtained in the presence of carrier trioctylphosphine oxide (TOPO) at the concentration in the feed phase of 10⁻⁴ mol/L indole-3-acetic acid and a concentration of 10⁻⁵ mol/L NaOH in the stripping phase.

Keywords: indole-3-acetic acid, bulk liquid membrane, tributyl phosphate (TBP), trioctylphosphine oxide (TOPO), kinetic model

The use of the bulk liquid membranes has been applied in many fields of research, due to their ability to transport certain compounds of interest, such as: analytical chemistry, organic chemistry and inorganic chemistry; biomedicine, pharmaceutical industry, chemical industry, biotechnology, environmental protection, as well as in wastewater treatment. Separation, removal or recovery of organic compounds, toxic metals and products of fermentation were realized using the system of de transport through liquid membranes [1-10].

Currently, liquid membranes are used for the transport and separation of cations [2, 5, 28], anions [2,19], isomers [2, 35], amines [20], organic acids [4-19, 21-24], drugs [3, 12,17,19], amino acids [10], vitamins [13,22-23], antibiotics [21, 24] (products of biosynthesis in group), etc.

The use of liquid membranes offers a viable alternative to extraction solvent processes due to the selectivity and application on diluted solutions. The main advantage of using liquid membranes is related to obtaining a high flux of transport compared with other types of membranes (e.g. polymer membranes, inorganic membranes or hybrid organic-inorganic membranes) due to large diffusion coefficients [1-4].

Bulk liquid membranes technology is increasingly due to its advantages in fundamental (basic) research as it can be shown in the large number of articles published about the selective separation of organic acids such as: indole-3-acetic acid [16], benzoic acid [7,9], para-aminobenzoic acid [21-22], acetzalic acid [17], amino-acezalic acid [17], salicylic acid [17], butyric acid [6], propionic acid [22,27], pantothenic acid [21-24], cinnamic acid [21], succinic acid [21, 24, 26], folic acid [21-24], lauric acid [25], phenol [15], para-nitrophenol [4], para-aminophenol [14], gentamicin and codeine etc. [3-24]

The transport and separation of organic acids through liquid membranes occurs following a chemical potential gradient. The dissociation constant (pKa), the initial pH of the aqueous solutions, the solubility of the solute in the aqueous phases and in the membrane solvent are important parameters in membrane transport processes of organic acids.

Operational parameters that usually influence significantly the efficiency of the transport are: the transport time, the feed phase concentration, nature and stripping phase concentration [17].

The efficiency and selectivity of liquid membrane transport processes is greatly enhanced through the use of appropriate carriers. For transport and separation of organic acids most used carriers are: tributyl phosphate (TBP), trioctylphosphine oxide (TOPO), triocylamine (TOA), Amberlite LA-2 and De-(2-ethylhexyl)phosphoric acid (D-EHPA), triocyl methyl ammonium chloride (Aliquate 336) and Alamine 336 [4-35].

The transport and separation studies through liquid membrane of organic acids are important parameters that characterize the transport of indole-3-acetic acid through bulk liquid membranes is realized.

Experimental part

Materials and method

Reagents and equipment

For the transport experiments performed all the reagents used were analytically grade and were used without further purification. The indole-3-acetic acid was purchased from Merck. Hydrochloric acid necessary for preparation of the
feed phase and sodium hydroxide necessary for preparation of the stripping phase were purchased from Merck.

In the transport studies were used as carriers: tri-n-butylphosphate (TBP) and trioctylphosphine oxide (TOPO) both purchased from Merck. The chloroform used as a solvent for the membrane was purchased from Sigma-Aldrich.

The membrane system consists from:

- Feed phase: solution of indole-3-acetic acid in the concentration range of 10^{-4} - 10^{-3} mol/L in the presence of hydrochloric acid concentration of 10^{-2} mol/L, at pH=2. Feed phase volume was 20 cm³;
- Membrane: chloroform in which one of the carriers was dissolved, tributyl phosphate solution at the concentration of 10^{-2} mol/L or trioctylphosphine oxide solution at the concentration of 10^{-2} mol/L. The membrane volume was 50 cm³;
- Stripping phase: sodium hydroxide solution in the concentration range of 10^{-2} - 10^{-1} mol/L. The stripping phase volume was 7 cm³.

For the preparation of the feed phase and of the stripping phase was used saturated distilled water with chloroform and for membrane preparation was used chloroform saturated with water. The experiments of transport were realized in a wall in wall type transport cell presented in previous papers [12, 14-19]. The working temperature was room temperature (22 ± 2°C) at a stirring speed of the phases of 180 rot/min. At the end of transport experiments the content of the indole-3-acetic acid was analyzed through molecular absorption spectrometry in the UV range. Thus a spectrophotometer LAMDA UV-Vis-NIR (Perkin Elmer Life and Analytical Sciences) was used. Indole-3-acetic acid presents a characteristic absorption band at a wavelength \( \lambda = 280 \text{ nm} \) both for acid and alkaline medium corresponding to content in the feed phase and the stripping phase.

The content of the indole-3-acetic acid from membrane phase was assessed from the mass balance of the three phases of the membrane system.

**Results and discussions**

Assessing in time of the reduced concentrations of indole-3-acetic acid demonstrated that its pertraction through bulk liquid membrane transport system is realized after a kinetic model of consecutive irreversible first order reactions according to the equation (1):

\[
(IAA)_{FP} \xrightarrow{k_1} (IAA) \xrightarrow{k_2} (IAA)_{SP}
\]

where \( k_1 \) and \( k_2 \) represent pseudo-first-order apparent membrane entrance and exit rate constants, s⁻¹;

According to this model kinetic the variation in time of reduced concentrations respects relationships:

\[
\frac{dR_{FP}}{dt} = -k_1 R_{FP} = J_{FP}
\]  \hspace{1cm} (2)

\[
\frac{dR_{ML}}{dt} = -k_2 R_{FP} - k_1 R_{ML} = J_{ML}
\]  \hspace{1cm} (3)

\[
\frac{dR_{SP}}{dt} = -k_1 R_{ML} = J_{SP}
\]  \hspace{1cm} (4)

where:

\( J_{FP}, J_{ML}, J_{SP} \) represent the flux at the entrance and exit out of membrane, mol/cm² s;

\( R_{FP}, R_{ML}, R_{SP} \) represent reduced concentrations in the three phases of membrane system calculated with relations:

\[
R_{FP} = \frac{C_{FP}}{C_0}
\]  \hspace{1cm} (5)

\[
R_{ML} = \frac{C_{ML}}{C_0}
\]  \hspace{1cm} (6)

\[
R_{SP} = \frac{C_{SP}}{C_0}
\]  \hspace{1cm} (7)

\( C_{FP}, C_{ML}, C_{SP} \) represent concentrations of the indole-3-acetic acid in feed phase, the membrane and the stripping phase at the time \( t \), in mol/L;

\( C_0 \) represent initial concentration in the feed phase, in mol/L.

By integrating the equations 2-4 are obtained the variation functions of reduced concentrations in time described by equations 8-10.

\[
R_{FP} = e^{-k_1 t} R_{FP0}
\]  \hspace{1cm} (8)

\[
R_{ML} = \frac{k_2}{k_2 - k_1} (e^{k_1 t} - e^{k_2 t})
\]  \hspace{1cm} (9)

\[
R_{SP} = 1 + \frac{1}{k_1 - k_2} (e^{k_2 t} - k_1 e^{k_1 t})
\]  \hspace{1cm} (10)

Through the fitting of equations 8-10 with the experimental data pseudo-first-order apparent membrane entrance and exit rate constants \( k_1 \) and \( k_2 \) are obtained. From the dependence \( R_m = f(t) \) one can determine the maximum concentration of indole-3-acetic acid from the membrane. This maximum amount at the concentration of indole-3-acetic acid concentration in the membrane, \( R_{\text{max}} \), is obtained when then \( dR_m/dt=0 \). Thus it results:

\[
R_{\text{max}} = \left( \frac{k_2}{k_2 - k_1} \right) \frac{1}{k_1 - k_2}
\]  \hspace{1cm} (11)

The time at which is obtained the maximum of concentration from solute in membrane can be assessed with equation (12):

\[
t_{\text{max}} = \ln \left( \frac{k_1}{k_2} \right)
\]  \hspace{1cm} (12)

At \( t = t_{\text{max}} \), a maximum value of the flux at the entrance and exit out of membrane is obtained and can be described by the equations (13) and (14):

\[
\frac{dR_{FP}}{dt} \bigg|_{t_{\text{max}}} = -k_1 \left( \frac{k_1}{k_2} \right) \frac{1}{(k_2 - k_1)} J_{FP}\text{max}
\]  \hspace{1cm} (13)

\[
\frac{dR_{SP}}{dt} \bigg|_{t_{\text{max}}} = -k_2 \left( \frac{k_1}{k_2} \right) \frac{1}{(k_2 - k_1)} J_{SP}\text{max}
\]  \hspace{1cm} (14)

It is observed that the flux at the entrance and exit out of membrane are equal but the by contrary sign to. At the same time in the membrane at \( t = t_{\text{max}} \) is obtain a stationary status because:

\[
\frac{dR_{ML}}{dt} \bigg|_{t_{\text{max}}} = 0
\]  \hspace{1cm} (15)

The experimental data obtained, presented in the figures 1 and 2 demonstrate a good correlation of the transport process of indole-3-acetic acid with the kinetic model of consecutive first order reactions.
**Working conditions**

Feed phase (d): indole-3-acetic acid solution at concentration $3 \times 10^{-4}$ mol/L in the presence of hydrochloric acid concentration of $10^{-2}$ mol/L; Membrane (m): tributyl phosphate solution concentration of $10^{-2}$ mol/L in chloroform; Stripping phase (a): sodium hydroxide solution at concentration of $10^{-2}$ mol/L; $R$: represent the reduced concentrations.

**Influence of the feed phase concentration**

The influence of the concentration of indole-3-acetic acid from the feed phase was studied in the range $10^{-4}$ - $10^{-3}$ mol/L indole-3-acetic acid. The experiments were realized at pH=2 considered as optimum based on speciation diagrams presented in a previous paper [12; 14-19]. The concentration of sodium hydroxide in the stripping phase was of $10^{-2}$ mol/L. The kinetic parameters were calculated: $k_1$, $k_2$, $R_{m}^\text{max}$, $t_{\text{max}}$, $J_d^\text{max} \cdot 10^4$, $J_a^\text{max} \cdot 10^4$ and the values obtained are presented in tables number 1 and 2.

It finds that in the field of studied of variation of the concentrations indole-3-acetic acid does not show a significant influence upon the studied kinetic parameters.

![Fig. 1. The experimental results obtained at the pertraction of indole-3-acetic acid](image1)

![Fig. 2. The experimental results obtained to pertraction of indole-3-acetic acid](image2)

<table>
<thead>
<tr>
<th>Concentration of indole-3-acetic acid, mol/L</th>
<th>$k_1 \cdot 10^4$ s$^{-1}$</th>
<th>$k_2 \cdot 10^4$ s$^{-1}$</th>
<th>$R_{m}^\text{max}$</th>
<th>$t_{\text{max}}$, s</th>
<th>$J_d^\text{max} \cdot 10^4$ mol/cm$^2$/s</th>
<th>$J_a^\text{max} \cdot 10^4$ mol/cm$^2$/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^{-4}$</td>
<td>7.258</td>
<td>1.891</td>
<td>0.6232</td>
<td>2499</td>
<td>-1.1790</td>
<td>1.1790</td>
</tr>
<tr>
<td>$3 \cdot 10^{-4}$</td>
<td>5.618</td>
<td>2.146</td>
<td>0.5514</td>
<td>2770</td>
<td>-1.1846</td>
<td>1.1846</td>
</tr>
<tr>
<td>$6 \cdot 10^{-4}$</td>
<td>5.121</td>
<td>1.4355</td>
<td>0.6093</td>
<td>3450</td>
<td>-0.8747</td>
<td>0.8747</td>
</tr>
<tr>
<td>$10^{-3}$</td>
<td>5.227</td>
<td>1.8252</td>
<td>0.5686</td>
<td>3092</td>
<td>-1.0379</td>
<td>1.0379</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Concentration of indole-3-acetic acid, mol/L</th>
<th>$k_1 \cdot 10^4$ s$^{-1}$</th>
<th>$k_2 \cdot 10^4$ s$^{-1}$</th>
<th>$R_{m}^\text{max}$</th>
<th>$t_{\text{max}}$, s</th>
<th>$J_d^\text{max} \cdot 10^4$ mol/cm$^2$/s</th>
<th>$J_a^\text{max} \cdot 10^4$ mol/cm$^2$/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^{-4}$</td>
<td>10.6356</td>
<td>2.4114</td>
<td>0.6496</td>
<td>1803</td>
<td>-1.5620</td>
<td>1.5620</td>
</tr>
<tr>
<td>$3 \cdot 10^{-4}$</td>
<td>7.0080</td>
<td>1.2686</td>
<td>0.6853</td>
<td>2977</td>
<td>-0.8694</td>
<td>0.8694</td>
</tr>
<tr>
<td>$6 \cdot 10^{-4}$</td>
<td>11.3508</td>
<td>1.2680</td>
<td>0.7390</td>
<td>2173</td>
<td>0.9626</td>
<td>0.9626</td>
</tr>
<tr>
<td>$10^{-3}$</td>
<td>9.0386</td>
<td>1.1575</td>
<td>0.7394</td>
<td>2607</td>
<td>-0.8559</td>
<td>0.8559</td>
</tr>
</tbody>
</table>
Experimental data obtained highlight higher values of the rate constants at the interface feed phase - membrane than those at interface membrane - stripping phase. The maximum fluxes at the entrance and exit out of membrane are of the same order of size all on range of concentration of indole-3-acetic acid variation.

**Influence of the stripping phase concentration**

In the stripping phase was used a sodium hydroxide solution at the concentrations in the range of $10^{-2}\text{ mol/L} - 10^{-1}\text{ mol/L}$. In the feed phase was used indole-3-acetic acid solution at the concentration $10^{-3}\text{ mol/L}$ at pH=2 obtained with hydrochloric acid. The kinetic parameters obtained in case of using of two carriers are presented in table 3 and 4.

It finds that a tendency of growth of the maximum fluxes at the entrance and exit out of membrane with increasing concentration of sodium hydroxide by stripping phase. Variation of the concentrations of sodium hydroxide does not reflect a significant variation on rate constants.

**Influence of the carrier**

It was studied the transport of indole-3-acetic acid in the presence of two carriers generally used in the membrane transport of organic acids: tributylphosphate (TBP) and trioctylphosphine oxide (TOPO). Optimal concentration of carrier was of $10^{-2}\text{ mol/L}$ [36]. Analyzing the data presented in table 1-4 is found that in the presence carrier trioctylphosphine oxide (TOPO) the rate constants at interface feed phase| membrane have the highest values. The two carriers tributylphosphate and trioctylphosphine oxide do not have important influence upon the other studied kinetic parameters.

**Conclusions**

In the present paper was studied the transport of indole-3-acetic acid from straining phase on some kinetic parameters, namely: $k_1$, $k_2$, $k_3$, $t_{\text{app}}$, $J_{\text{m}}^\text{max}$, $J_{\text{g}}^\text{max}$. The concentration of indole-3-acetic acid in feed phase does not significantly influence the values of kinetic parameters studied.

Increased concentration of sodium hydroxide from stripping phase is reflecting into a slight tendency of increase of maximum fluxes. The influence of the carrier was observed in the value of pseudo-first-order apparent membrane entrance rate constants rate. These have the highest values in case of trioctylphosphine oxide carrier.

**References**

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