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STUDIES ON THE TRANSPORT OF INDOLE-3-ACETIC ACID THROUGH BULK LIQUID MEMBRANES

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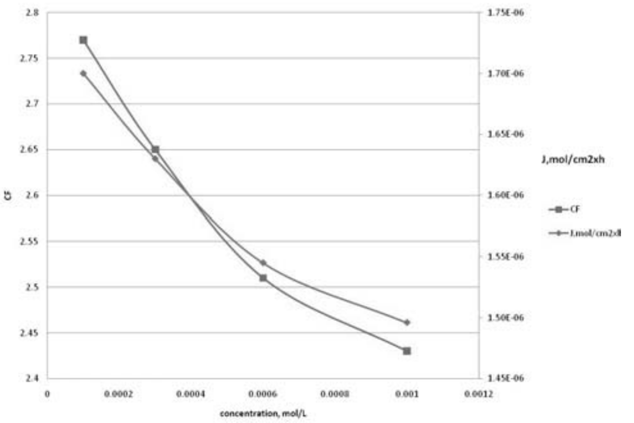
Recent research put in evidence that indole-3-acetic acid plays a major part as carriers for the indol derivates within biological fluids. In this study we present experimental data on the use of membranes in liquid bulk concentration processes of aqueous solutions of indole 3-acetic acid analytical purposes. Thus it was studied the influence of the operating parameters on the indole-3-acetic acid permeation through a membrane of chloroform containing as a carrier tributyl phosphate. There were studied operational parameters such as: the influence of the concentration of indole-3-acetic acid on feed phase, the concentration of reactive from stripping phase, the time transport and the presence of carrier tributyl phosphate in membrane phase. The assessment of the process of transport was done by determining the average flux and the concentration factor. It was obtained a recovery efficiency of the indole-3-acetic acid higher than 90% after a time of transport of 3-4 hours.



INTRODUCTION

Indole-3-acetic acid is a plant growth hormone with an important role in plant development. In plant organisms indole-3-acetic acid plant has role of carrier of mineral substances. This can be realized based on electrical potential gradient.[1-3]

The indole-3-acetic acid can be obtained in the biosynthesis of tryptophan. In recent years the separation and concentration of organic acids resulted by biosynthesis using liquid membrane technique has gained great interest. Using bulk liquid membranes in separation processes was imposed because of the advantages they present: high separation selectivity and efficiency, rapid mass transfer realized by using carriers as well without the use of such carriers, reduced number of steps necessary for separation, low consumption of materials and energy, reducing the time of separation as well as reducing solvent losses. Fundamental principles of transport process through liquid membrane are presented in several reference papers.[4,5] In field literature studies of separation of butyric acid,[6] of malic acid, citric, succinic[7] are reported. These articles studied the influence of process parameters such as: feed phase concentration, stripping phase concentration, the stirring speed of the phases. Was highlighted role of the pH gradient, and of hydrophobicity of acids studied in the selectivity membrane

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separation process.[7,8] Efficiency and selectivity of membrane separation process of organic acids can be much improved through the use of adequate carriers. For this purpose it was studied the role of carriers such as: Amberlite LA-2,[9] trioctylamina(TOA)[10], di-(2-ethylhexyl)phosphoric acid (D□EHPA)[11], N-metil-N, N, Ntrioctyloctan-1, ammonium chloride (Aliquate 336)[12] or phosphonium ionic liquid (IL) Cyphos IL-104.[13]

In this paper the results of studies conducted on the transport of indole-3-acetic acid through bulk liquid membranes are presented. The influence of process parameters on the average flux and the concentration factor is presented and there have been made some assessments on the kinetics of the pertraction process of indole-3-acetic acid for studied membrane system.[14]

EXPERIMENTAL

For the experimental study of the indole-3 acetic acid membrane transport analytical grade reagents were used and there were used without further purification. There reagents used were indole-3-acetic acid, hydrochloric acid, tributylphosphate, chloroform, sodium hydroxide provided by Merck.

The membrane system used consists of:

Feed phase: indole-3-acetic acid solution in the concentration range of 10^{-4} - 10^{-3} mol/L in the presence of hydrochloric acid concentration of 10^{-2} mol/L, (pH=2). Feed phase volume was 20 cm^3;

Membrane: tributyl phosphate solution concentration of 10^{-2} mol/L in chloroform; The volume of membrane was 50 cm^3;

Stripping phase: sodium hydroxide solution concentration of 10^{-2} - 10^{-1} mol/L; The volume of stripping phase was 7 cm^3, The stirring speed of the phases was of 180 rpm.

The chloroform used for membrane preparation was previously saturated with distilled water. The distilled water used to preparation of the feed phases was saturated in advance with chloroform. Transport experiments were realised in a wall in wall type transport cell presented in previous papers.[14]

The transport time was of 4 hours, at a stirring speed of the phases of 180 rot/min.

The analytical control was realized using a spectrophotometer LAMDA UV-VIS-NIR (Perkin Elmer Life and Analytical Sciences) at a specific wavelength λ = 280 nm for the feed phases of the studied system. The content of the indole-3-acetic acid from membrane was determined from the mass balance on the membrane system phases.

RESULTS AND DISCUSSION

In this paper are studied the influence of the operating parameters on the indole-3-acetic acid transport through bulk liquid membrane formed from chloroform with tributyl phosphate.

Were studied the influence of the concentration of indole-3-acetic acid in the feed phase, the concentration of NaOH in the stripping phase and the time of transport.

The assessment of the process was done by determining the average flux (J) and the concentration factor (CF) using the relationship:

$$J = \frac{V_{FR} \times C_{FR}}{A \times t} \qquad (1)$$

where noted:
J = average flux
V_{FR} = stripping phase volum, L
C_{FR} = concentration of the stripping phase, mol/L
A = area of interface membrane/stripping phase, cm^2
t = time of transport, h

$$CF = \frac{C_{FR,t}}{C_{FSo}} \qquad (2)$$

where:
CF = concentration factor
$C_{FR,t}$ = indole-3-acetic acid concentration in the stripping phase at the time „t"
C_{FS0} = initial concentration of indole-3-acetic acid in the stripping phase

Influence of the feed phase concentration

The influence of the concentration of indole-3-acetic acid in feed phase on average flux and the concentration factor at the next concentrations: 10^{-4} mol/L, $3x10^{-4}$ mol/L, $6x10^{-4}$ mol/L 10^{-3} mol/L. From Figure 1 it is established that there no major influences of the concentration in feed phase upon the average flux and the concentration factor. However the higher values of flux and of concentration factor can be obtained at low concentrations of indole-3-acetic acid. The result may be associated with a gradient of chemical potential higher in case of lower concentrations of indole-3-acetic acid.

Influence of the stripping phase concentration

The composition of stripping phase plays an important role in the decomplexation process at the interface membrane / stripping phase and transformation of the substrate in an inactive species for transport. Thus it was concluded that the concentration gradient of the substrate, as the driving force of transport, has minimal effect (Fig. 2). For an uphill transport it is required to be used a suitable stripping agent. As stripping agent used there was used a NaOH solution. It was determined the average flux at two concentrations of NaOH 10^{-2} mol/L and 10^{-1} mol/L. The experimental data are presented in the Fig. 2.

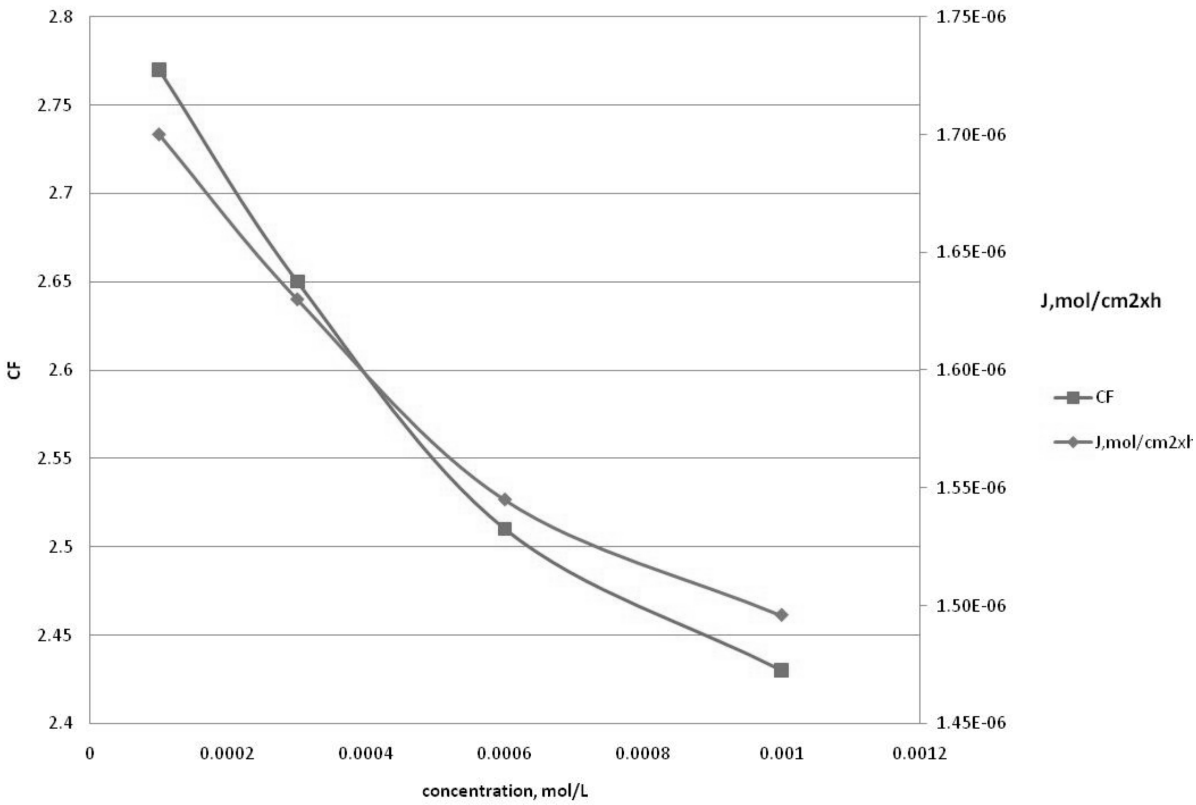

Fig. 1 – The effect of indol-3-acetic acid (IAA) concentration from the feed phase on the flux (J) and the concentration factor (CF). Experimental conditions: feed phase: indol-3-acetic acid 10^{-4} – 10^{-3} mol/L, membrane: solution of tributyl phosphate 10^{-2} mol/L in chloroform, stripping phase: 10^{-2} mol/L NaOH solution, transport time 4 hours, stirring speed: 180 rot/min.

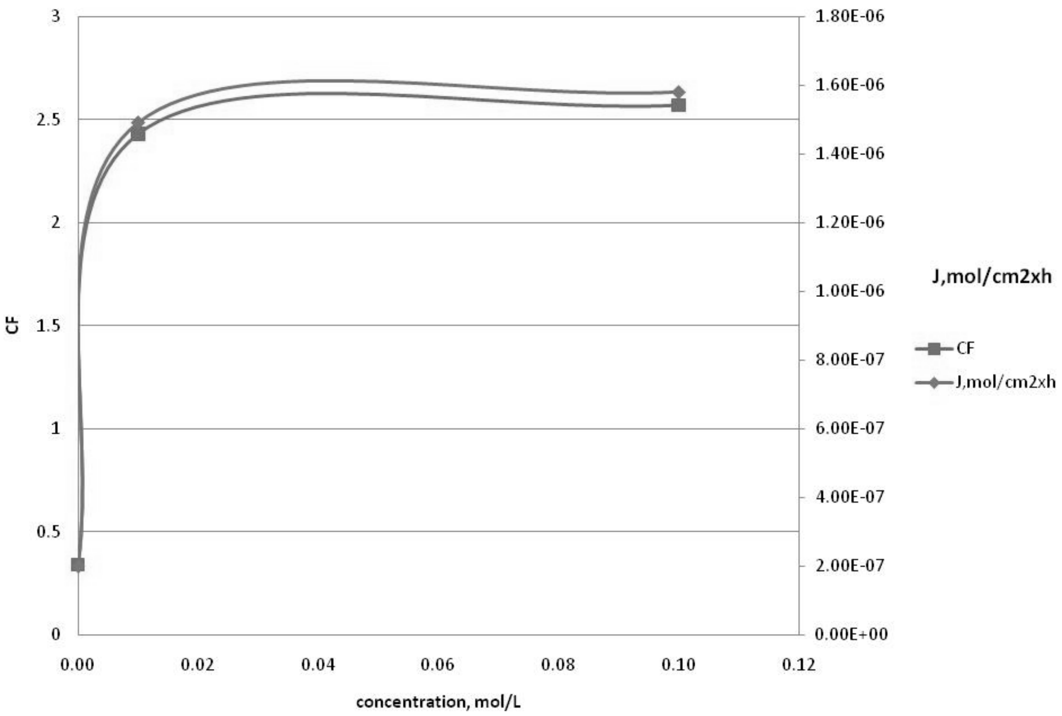

Fig. 2 – The effect of sodium hydroxide (NaOH) concentration from the stripping phase the average flux (J) and the concentration factor (CF). Experimental conditions: feed phase: indol-3-acetic acid $3x10^{-4}$ mol/L, membrane: solution of tributyl phosphate 10^{-2} mol/L in chloroform, stripping phase: 10^{-2} – 10^{-1} mol/L NaOH solution, transport time 4 hours, stirring speed: 180 rot/min.

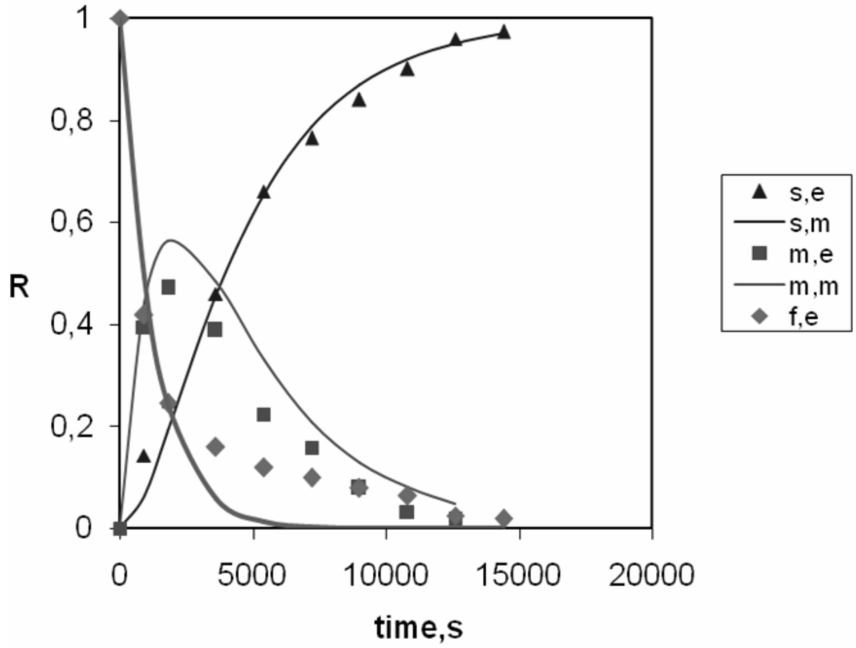

Fig. 3 – The variation of reduced concentrations of indole-3-acetic acid (IAA) in timeExperimental conditions: feed phase: indol-3-acetic acid 10^{-4} mol/L, membrane: solution of tributyl phosphate 10^{-2} mol/L in chloroform, stripping phase: 10^{-2} mol/L NaOH solution, transport time 4 hours, stirring speed: 180 rot/min.

It was observed that the average flux increases with the increasing of NaOH concentration from stripping phase. These results can be correlated with the transport mechanism of indole-3-acetic acid that supposes a neutralization reaction at the interface membrane /the stripping phase. Increasing the concentration of NaOH shifts the equilibrium from neutralization of the indole acetic acid in the direction of forming one inactive species at transport.

Influence of the transport time

Studying in time the transport process of indol-3-acetic acid we can conclude that this occurs through a series of reactions that correspond to consecutive first-order kinetics according to the scheme:

Trimiteti formula 3 (3)

where k_1 si k_2 represent pseudo-first-order apparent membrane entrance and exit rate constants [s^{-1}]. This kinetic model described by differential equations:

$$\frac{dR_{FP}}{dt} = -k_1 R_{FP} = J_{FP} \tag{4}$$

$$\frac{dR_M}{dt} = -k_1 R_{FP} - k_2 R_M \tag{5}$$

$$\frac{dR_{SP}}{dt} = -k_1 R_M = J_{SP} \tag{6}$$

in which J_{FP} si J_{SP} represent the flux at the entrance and exit out of membrane and R_{FS}, R_M si R_{FR} represent low concentrations in the three phases of membrane system calculated with relations:

$$R_{FS} = \frac{C_{FS}}{C_0} \tag{7}$$

$$R_M = \frac{C_M}{C_0} \tag{8}$$

$$R_{FR} = \frac{C_{FR}}{C_0} \tag{9}$$

R_{FS}, R_M, R_{FR} represent the reduced concentrations of indole-3- acetic acid in feed phase, the membrane and the stripping phase at the time "t".
C_{FS}, C_M, C_{FR} 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 these equations are obtained relationships:

$$R_{FP} = e^{-k_1 t} \tag{10}$$

$$R_M = \frac{k_1}{k_2 - k_1}\left(e^{-k_1 \cdot t} - e^{-k_2 \cdot t}\right) \qquad (11)$$

$$R_{SP} = 1 + \frac{1}{k_1 - k_2}\left(k_2 e^{-k_1 \cdot t} - k_1 e^{-k_2 \cdot t}\right) \qquad (12)$$

Correlating experimental data with the kinetic model described by these equations were obtained the results shown in Figure 3.

As it can be observed we obtained a good correlation of the experimental data with kinetic model of the consecutive first-order reaction which directs further studies towards improving this kinetic model.

CONCLUSIONS

In this paper it was studied the influence of operational parameters on the average flux from membrane in the transport process of the indole-3-acetic acid. In the studied concentration range the highest medium flux values are obtained by concentration 10^{-4} mol/L indole-3-acetic acid feed phase and 10^{-1} mol/L NaOH stripping phase. There were made assessments on a transport kinetic model of indole acetic acid that correspond to the consecutive first-order reaction that can be developed into further study.

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REFERENCES

1. P. J. Davies, “Plant Hormones, Biosynthesis, Signal Transduction, Action”, Kluwer Academic Publisher, Springer Netherlands, 2004, p. 1-9, 451-484.
2. S. Vantu, “Culturi de celule şi ţesuturi vegetale în bioteh.”, Ed. Univ. „Al. I. Cuza”, Iaşi, 2005, p. 1-180.
3. E. A. Şerban, I. Diaconu, C. Mirea, E. Ruse and G. Nechifor, *Rev. Chim.(Bucharest)*, **2016**, *67*, 638-642.
4. V.S. Kislik, “Liquid Membranes: Principles and Applications in Chemical Separations and Wastewater Treatment”, Elsevier B.V., The Netherlands, 2010, p. 11-29.
5. M. Mulder, “Basic Principles of Membrane Technology”, Kluwer Academic Publishers, Norwell, 1992, p. 1-20.
6. S. Schlosser and E. Sabolová, *Chem. Papers,* **1999**, *53*, 403 - 411.
7. D. Cascaval and A. I. Galaction, *St. Cerc. St. CICBIA*, **2010,** *11*, 129-160.
8. I. Zaharia, I. Diaconu and G. Nechifor, *U.P.B. Sci. Bull., Series B*, **2012**, *74*, 1454-2331.
9. A.I. Galaction, A. S. Bompa, L. Kloetzer and D. Cascaval. *Solvent Extr. Ion Exc.,* **2015**, *33*, 313-328.
10. A. Kaur and D. K. Vohra, *Indian J. Chem. Technol.,* **2010,** *17,* 33-138.
11. I. Zaharia, I. Diaconu, E. Ruse and G. Nechifor, *Rev. Chim.(Bucharest)*, **2014**, *65*, 1256-1259.
12. I. Zaharia, H.Y. Aboul-Enein, I. Diaconu, E. Ruse, A. A. Bunaciu and G. Nechifor, *J. Iran. Chem. Soc.,* **2013,** *10,* 1129-1136.
13. J. Martak, S. Schlosser and M. Blahusiak, *Chem. Pap.,* **2011**, *65*, 603-607.
14. C. M. Mirea, I. Diaconu, E. A. Şerban, E. Ruse, G. Nechifor, *Rev. Chim.(Bucharest)*, **2016**, *67*, 838-841.