Pertraction of Acetaminophen through Bulk Liquid Membranes

Kinetic aspects

IOANA DIACONU[1]*, CRISTINA MONICA MIREA[1,2], ECATERINA ANCA SERBAN[1], ELENA RUSE[1], GHEORGHE NECHIFOR[1]

[1] University Politehnica Bucharest, Faculty of Applied Chemistry and Materials Science, Department of Analytical Chemistry and Environmental Engineering, 1-7 Polizu Str., 011061, Bucharest, Romania,

[2] Arcuda Laboratory, Water Quality Service, Joita, 103997, Giurgiu, Romania

In the present paper a model for the pertraction of acetaminophen through bulk liquid membrane based on consecutive irreversible first order reactions was studied. The membrane system consisted in: feed phase- an aqueous solution of acetaminophen at different concentrations, membrane- a solution of tri-n-butyl phosphate in chloroform, stripping phase- an aqueous solution of NaOH. Under this model the fallowing kinetic parameters were assessed: the maximum reduced concentration in the membrane and the time when this concentration is obtained, the membrane entrance and exit flux, as well as apparent mass transfer coefficients. The influence of acetaminophen concentration from the feed phase upon these parameters was investigated

Keywords: bulk liquid membrane, pertraction, acetaminophen, kinetic model

Membranes, depending on their morphology, divide in to two major categories: liquid membranes or solid membranes (polymeric) [1]. Liquid membranes were intensively studied since their discovery by Li [2] at the separation of chemical species such as: metal ions [3, 4], nitrophenols [5-8], active principles from drugs [9-14] or amino-acids [15, 16] in scientific purpose or at their removal and recovery from waste waters. Three types of liquid membranes: liquid membranes, emulsion liquid membranes and supported liquid membranes are known. The most intensively used types of membrane by a large number of scientists due to the simplicity in operation are the bulk liquid membranes [17]. This type of membranes is preferred due to multiple advantages such as: high separation selectivity, fast mass transfer that can take place in the presence of carriers, facilitated transfer that is in favor of product concentration, the fact that you do not need an expensive pretreatment concentration before the membrane transport and also a high energetic efficiency [18, 19]. A liquid membrane can be easily obtained by dissolving the carrier into the membrane matrix [1]. In this case the carrier plays an important role for expressing the permselectivity of the membrane. Several carriers can be used such as: di-(2-ethylhexyl) phosphoric acid (D2EHPA), trioctylphosphine oxide (TOPO) and N-Methyl-N,N,N-trioctyloctan-1-ammonium chloride (Aliquate 336). A carrier often used in the membrane transport is tri-n-butyl phosphate (TBP). TBP has been showed to be an effective carrier for the separation and purification of a number of metals and organic acids due to its excellent chemical stability, high boiling point and low solubility in water [20].

The description of the pertraction through bulk liquid membranes is very useful because of the necessity to determine physical and chemical parameters that can explain the laboratory experiments or that can be used to design a pilot or industrial pertraction process [6]. A common mathematical model used by many researchers to describe the pertraction through bulk liquid membrane is the model of consecutive irreversible first order reactions. A characteristic of this model is that when the time is tending to infinity the concentration in feed and membrane tends to zero, while the concentration in the stripping phase tends to a limiting value depending on the initial concentration in feed phase [21-31].

Acetaminophen or paracetamol as it is commonly known is used as an antipyretic and a drug used for headache and minor pains relief [32] and it is used as a major ingredient in numerous cold and flu remedies [33]. Ingestion of an overdose of acetaminophen can cause hepatic necrosis or renal failure [34].

In the present study the influence of the feed phase concentration upon the pertraction kinetic parameters was investigated.

Experimental part

Reagents and apparatus

All the reagents used were analytically grade and were used without further purification. Acetaminophen was purchased from China. The feed phase was formed 20 cm^3 of 10^{-4}- 10^{-2} mol/L aqueous solution of acetaminophen. As liquid membrane was used a solution of TBP dissolved in chloroform, saturated previously with water. The volume of the membrane was of 50cm^3. The NaOH was used to prepare the aqueous stripping phase. The volume of the stripping phase was of 7 cm^3. Chloroform and NaOH were purchased from Merck. Distilled water used to prepare the feed and the stripping phases was previously saturated with chloroform.

The transport experiments were realized in a wall in wall type of cell presented in previous papers [7, 9]. The transport experiments were realized at room temperature ($t=22\pm1^oC$) with a stirring speed of 180 rot/min. At the end of the transport the content of acetaminophen in the aqueous phases was analyzed using a LAMBDA 45 Perkin Elmer spectrometer. The content of acetaminophen was realized at characteristic wavelength for acetaminophen in aqueous phases at $\lambda=241$ nm for the feed phase and at $\lambda=256$ nm for the stripping phase. The content of acetaminophen from the membrane phase was

* *email: diaconuioana12@yahoo.com*

determined using the mass balance of the three phases of the membrane system.

Results and discussions

The behaviour of acetaminophen (A) through bulk liquid membranes demonstrated that the pertraction process from a feed phase (FP) through an organic membrane (M) into a stripping phase (SP) takes place according to a consecutive irreversible first order chemical reaction according to the kinetic scheme [21-30]:

$$A_{FP} \xrightarrow{k_1} A_M \xrightarrow{k_2} A_{SP} \quad (1)$$

described by the equations:

$$R_{FP} = e^{-k_1 \cdot t} \quad (2)$$

$$R_M = \frac{k_1}{k_2 - k_1}(e^{-k_1 \cdot t} - e^{-k_2 \cdot t}) \quad (3)$$

$$R_{SP} = 1 + \frac{1}{k_1 - k_2}(k_2 e^{-k_1 \cdot t} - k_1 e^{-k_2 \cdot t}) \quad (4)$$

where:

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

R_{FP}, R_M and R_{SP} represent the un-dimensional reduced concentrations from the feed phase, membrane and stripping phase and are calculated with the fallowing relationships:

$$R_{FP} = \frac{C_{FP} \cdot V_{FP}}{C_{FP_0} \cdot V_{FP_0}} \quad (5)$$

$$R_M = \frac{C_M \cdot V_M}{C_{FP_0} \cdot V_{FP_0}} \quad (6)$$

$$R_{SP} = \frac{C_{SP} \cdot V_{SP}}{C_{FP_0} \cdot V_{FP_0}} \quad (7)$$

where:

C_{FP}, C_M, C_{SP} represents the feed phase, membrane and stripping phase concentration, mol/L,

C_{SP0}, represents the initial concentration from the feed phase, mol/L,

V_{FP}, V_M, V_{SP} represents the feed phase, membrane and stripping phase volume, cm^3.

The pseudo-first-order apparent membrane entrance and exit rate constants can be correlated with the mass transfer coefficient using the relationships (8, 9):

$$k_1 = k'_{FP} \frac{A_{FP}}{V_{FP}} \quad (8)$$

$$k_2 = k'_{SP} \frac{A_{SP}}{V_M} \quad (9)$$

where:

k'_{EP} and k'_{SP} represent the apparent mass transfer coefficients, cm/s.

A_{FP}, A_{SP} represent the area of the interface feed phase|membrane and the area of the interface membrane|stripping phase, respectively, cm^2.

V_{FS}, V_M represent the feed phase and membrane volume, respectively, cm^3.

The maximum solute concentration in the membrane is calculated from the dependence $R_m = f(t)$ when $dR_m/dt = 0$.

$$R_M^{max} = \left(\frac{k_1}{k_2}\right)^{-\frac{k_2}{k_1 - k_2}} \quad (10)$$

$$t_{max} = \frac{\ln\left(\frac{k_1}{k_2}\right)}{k_1 - k_2} \quad (11)$$

where:

R_M^{max}- maximum solute concentration in the membrane

t_{max} - time when maximum solute concentration in the membrane is obtained

Pseudo-first-order apparent membrane entrance and exit rate constants can be used at the determination of the maximum flux according to the equation (10):

$$J_{max} = -k_1\left(\frac{k_1}{k_2}\right)^{-\frac{k_1}{k_1 - k_2}} = k_2\left(\frac{k_1}{k_2}\right)^{-\frac{k_2}{k_1 - k_2}} = -J_{SP\,max} = J_{RP\,max} \quad (12)$$

where:

J_{SPmax} = membrane entrance flux

J_{RPmax} = membrane exit flux

The experimental data demonstrated a good correlation with the kinetic model proposed according to figure 1, the correlation coefficient being higher than 0.99 for all the presented dependences.

The solid lines in figure 1 represent the values the reduced concentrations calculated using relationships 2-4. These data were obtained using the fallowing conditions: feed phase-20 cm^3 solution of acetaminophen 10^{-4} mol/L, membrane-50 cm^3 solution of TBP 10^2 mol/L in chloroform, stripping phase-7 cm^3 NaOH 1 mol/L. At higher concentration of acetaminophen in the feed phase some discrepancies between the model and the experimental data were observed, but the correlation coefficient was higher 0.98.

The kinetic parameters were assessed by varying the acetaminophen concentration from the aqueous feed phase. The effect of acetaminophen concentration from

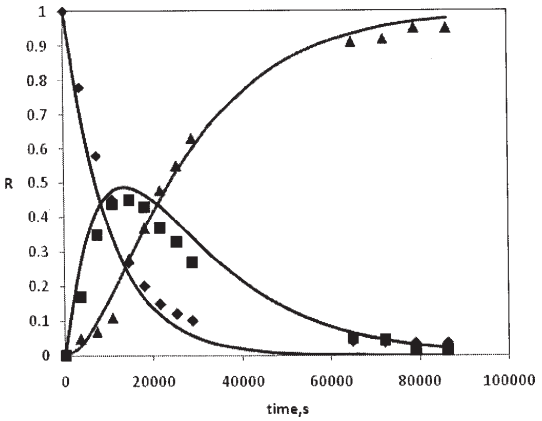

Fig. 1. Time depending variation of the acetaminophen reduced concentration in the phases of the membrane system feed phase(♦): 25cm^3 solution of acetaminophen 10^{-4} mol/L, membrane(■): 50 cm^3 solution of TBP 10^2 mol/L in chloroform, stripping phase(▲): 7 cm^3 NaOH 1 mol/L; continuous line represents the values calculated using the kinetic model, transport - 24 h

Concentration of acetaminophen in feed phase, mol/L	R_{max}	t_{max}	J_{FP}max x10^5,s^{-1}	J_{SP}max x10^5,s^{-1}	k'$_{FP}$ x105, cm/s	k'$_{SP}$ x10^3, cm/s
10^{-4}	0.48	3h 28 min	2,73	-2,73	6.71	1,05
4x10^{-4}	0,61	5h 15 min	1,36	-1,36	3,40	0,72
10^{-3}	0,70	8h 20 min	0.47	-0.47	1,38	0.43

Table 1
KINETIC PARAMETERS OBTAINED AT THE FACILITATED TRANSPORT OF ACETAMINOPHEN WHEN USING TBP AS CARRIER

the aqueous feed phase upon its transport through an organic bulk liquid membrane was realized using the following concentration of acetaminophen: 10^{-4}, 4 x10^{-4}, 10^{-3} mol/L.

The kinetic parameters depend on the concentration of the acetaminophen from the aqueous feed phase. In the studied concentration range the values of the kinetic parameters decrease with the increase of the concentration of acetaminophen.

Conclusions

The transport of acetaminophen through an organic bulk liquid membrane can be assessed using a kinetic pertraction model described by consecutive irreversible first order reactions. Kinetic parameters such as maximum solute concentration in the membrane, time when maximum solute concentration in the membrane is obtained, membrane exit flux, membrane entrance flux and mass transfer coefficient. A correlation between the studied kinetic parameters and the concentration of acetaminophen from aqueous feed phase was established.

Acknowledgement: The work has been funded by the Sectoral Operational Programme Human Resources Development 2007-2013 of the Ministry of European Funds through the Financial Agreement POSDRU/159/1.5/S/132395.

Reference

1.TSUJIMOTO, H., YOSHIKAWA, M. J. Membr. Sci., 445, 2013, p. 8
2.N.N. Li, Separating Hydrocarbons with Liquid Membranes, United States Patent, 3410794, 1968.
3.OLTEANU, C., SZCZEPANSKI, P, ORBECI, C.. LICA, C. G, COSTACHE, L., DIACONU, I, Rev. Chim.(Bucharest), **64**, no. 9 ,2013,p. 925
4.MATEESCU, M., NECHIFOR, A. C., PACURARIU, L, BUNGHEZ , I.R.. Rev. Chim. (Bucharest), **64**, no. 5, 2013, p. 468
5.DIACONU, I., ABOUL-ENEIN, H.Y., AL-OMAR, M.A., NECHIFOR, G., RUSE, E., BUNACIU, A.A. EFTIMIE TOTU, E. , Arabian. J. Chem. 4, no. 1, 2011, p. 99
6.SZCZEPA SKI, P., DIACONU, I, Separ. Sci. Technol., 47, no. 12 , 2012, p. 1725
7.DIACONU, I., GÎRDEA, R, CRISTEA, C., NECHIFOR, G., RUSE, E., EFTIMIE TOTU, E., Rom. Biotech.Lett., 15, no. 6, 2010, p. 5703.
8.DIACONU, I., RUSE, E., EFTIMIE TOTU, E. NECHIFOR, G, Rev. Chim.(Bucharest), **61**, no. 8, 2010, p. 718
9.ZAHARIA, I., ABOUL-ENEIN, H.Y., DIACONU, I., RUSE, E. BUNACIU, A.A., NECHIFOR, G., J. Iran. Chem. Soc., 10, no. 6, 2013, p. 1129
10.ZAHARIA, I., DIACONU, I., NECHIFOR, G., U.P.B. Sci. Bull., Series B, Vol. 74, no. 2, 2012 , p. 61
11.LEE, S. C., Chem. Eng. J., 79, no. 1, 2000, p. 61
12.GHOSH, R., J. Membr. Sci., 344, no. 1, 2009, p. 107
13.MATSUMOTO, M., OHTANI, T., KONDO, K., J. Membr.Sci., 289, no. 1, 2007, p. 92
14.GUMI, T., FERREIRA, Q., MC VIEGAS, R., CRESPO, J.G., COELHOSO, I. M., PALET. C., Separ. Sci. Technol., 40, no. 4 , 2005, p. 773
15.STANCU, A.D., HILLEBRAND, M., TABLET, C., MUTIHAC, L., J. Incl. Phenom. Macrocyclic Chem., 78, no. 1-4 (2014): 71-76.
16.MUTIHAC, L., BUSCHMANN, H.J., MUTIHAC, R. C., SCHOLLMEYER, E., J. Incl. Phenom. Macrocyclic Chem., 51, no. 1-2, 2005, p. 1
17.CHANG, S. H., TENG, T. T., NORLI, I., Chem. Eng. J., 173, no. 2, 2011, p. 352
18.SINGH, R., MEHTA, R., KUMAR, V., Desal., 272, no. 1, 2011, 170
19.REDDY, T. R., RAMKUMAR, J., CHANDRAMOULEESWARAN, S., REDDY, A. V. R., .J. Membr.Sci., 351, no.1, 2010, p. 11
20.ZHANG, W., LIU, J., REN, Z., WANG, S., DU, C., MA., J., Chem. Eng. J., 150, no. 1, 2009, p. 83
21. MUTHURAMAN, G., IBRAHIM, M., J. Ind. Eng. Chem., 19, no. 2, 2013, p. 444
22.JAFARI, S., YAFTIAN, M.R., PARINEJAD, M., Sep. Purif. Technol.,70, no. 1, 2009, p. 118
23. MADAENI, S. S., ISLAMI, N. ,J. Chin. Chem. Soc., 60, nr. 5, o2013, p.559
24. WEIDONG, Z., LIU, J., REN, Z., WANG, S., DU, C., MA, J., Chem. Eng. J., 150, no. 1, 2009, p. 83
25. GRANADO-CASTRO, M. D., GALINDO-RIA O, M. D., DOMINGUEZ-LLEDO, F. C., DÍAZ-LÓPEZ, C., GARCÍA-VARGAS, M., Anal. Bioanal. Chem., 391, no. 3, 2008, p. 779
26. GUBBUK, I. H., GUNGOR, O., ALPOGUZ, H. K., ERSOZ, M., YILMAZ, M., Desal. , 261, no. 1, 2010, p. 157
27. LEÓN, G., GUZMÁN, M. A., Desal. Water Treat., 13,no. 1-3, 2010, p. 267
28.LEON, G., GUZMÁN, M. A. Desal, 184, no. 1, 2005, p. 79
29. ALPOGUZ, H. K., MEMON, S., ERSOZ, M., YILMAZ, M. Sep. Sci. Technol., 39, no. 4, 2005, p. 799
30. ALPAYDIN, S., YILMAZ, M., ERSOZ, M., Sep. Sci.Technol., 39, nr. 9, 2005, p. 2189
31. KOTER, S., SZCZEPA SKI, P., Chem. Pap., 65, no. 5, 2011, p. 584-595.
32.MASLARSKA, V., TENCHEVA, J., Int. J. Pharm. Sci., 5, 2013, p. 417
33.BEHERA, S., GHANTY, S., AHMAD, F., SANTRA, S., BANERJEE, S., J Anal Bioanal Tech., 3, no. 151, 2012, p. 2
34.AL-SHWAIYAT, M. K. EA., Jordan J. Chem., 8 no.2, 2013, p. 79

Manuscript received: 30.10.2014