BOND-GRAPH DESCRIPTION AND SIMULATION OF MEMBRANE PROCESSES: DEPENDENCE OF ABLM EFFICIENCY ON LIQUID MEMBNE VOLUME

Romuald WÓDZKI, Piotr SZCZEPAŃSKI

Nicolaus Copernicus University, Faculty of Chemistry, 7 Gagarin Str.,
87-100 Toruń, Poland

Abstract

Network thermodynamic analysis was used for bond-graph representation of simple pertraction in the agitated bulk liquid membrane. The output flux dependence on the membrane volume was analysed and compared with the same dependence observed experimentally for pertraction of benzoic acid.

1. INTRODUCTION

This contribution concerns the simplest case of the pertraction process which is represented by a sequence of extraction-diffusion-re-extraction steps, i.e. the liquid membrane transport occurring according to a solution-diffusion mechanism. The effectiveness of such a process is represented by a flux of target species from the aqueous feed solution, through the hydrophobic liquid membrane, into the receiving solution. This flux depends on many factors of very different nature. e.g. the properties of the liquid membrane components, configuration of the membrane, (BLM, ELM, SLM) and respective operational parameters. From this reason, output fluxes reported in literature as the most characteristic property of LMs are completely incomparable, especially in the case of agitated bulk liquid membranes (ABLM) of different volumes. To solve this problem by modeling in the framework of thermodynamic network analysis (TNA) it is required to formulate: (*i*) the phenomenological model, (*ii*) compartmental model, (*iii*) network model, (*iv*) mathematical description (set of ordinary coupled differential equations). Generally, variables such as diffusion coefficients rate constants for interfacial processes and typical operational conditions (concentrations, volumes, etc.) should be taken into account in the mathematical model. To characterize the flux vs. ABLM volume dependence, the system operating under stationary, pseudostationary and nonstationary conditions was studied. The results of calculations are compared with the experimental study of the pertraction of benzoic acid.

2. TNA MODEL

The process occurs in the closed system composed of two external solutions of finite volumes (V_f, V_s), i.e. feed (*f*) and stripping solution (*s*). The solutions are separated by ABLM of volume V_m, with contact area *A*, and thickness of diffusion layers (l_i, $i=f,s,m$). The feed solution contains *S* substance which can permeate from the aqueous solution into the membrane phase and then it diffuses through the liquid membrane with its own diffusion coefficient equal to D_m. The diffusion coefficients in the aqueous diffusion layers are equal to D_f and D_s for the feed and receiving solution, respectively. The interfacial layers are divided into f_n, and s_n diffusion sub-layers. Consequently, ABLM is characterized by m_n diffusion sub-layers and one large central volume (m_c, sink phase) with convective transport. The detailed scheme of the compartmental model is presented in Fig.1

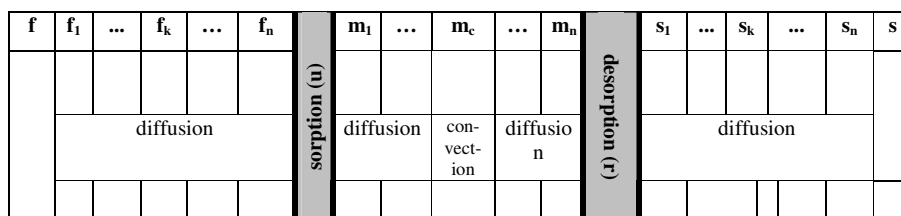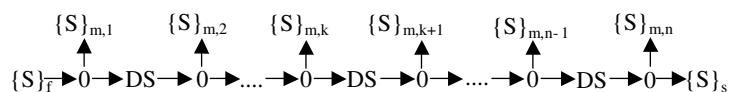| f	f_1	...	f_k	...	f_n	sorption (u)	m_1	...	m_c	...	m_n	desorption (r)	s_1	...	s_k	...	s_n	s
			diffusion				diffusion		con-vect-ion		diffusion				diffusion			

Fig. 2. Compartmental model of the solution-diffusion pertraction

Under nonstationary state conditions, the S substance permeates with different rates from one volume element to another and can be accumulated in the respective volumes acting as a capacitor {S}. All the processes of accumulation and diffusion can be represented by basic thermodynamic network analysis in the bond-graph version [1,2]. The overall bond-graph for the studied phenomena can be synthesized using basic network thermodynamics in the simplified version proposed by Schnakenberg [3,4]. According to this approach, the permeation of *S* through the membrane from the first m_1 to the last m_n layer is represented by a series of diffusion bond-graphs in the form:

$$\{S\}_{m,1} \quad \{S\}_{m,2} \quad \{S\}_{m,k} \quad \{S\}_{m,k+1} \quad \{S\}_{m,n-1} \quad \{S\}_{m,n}$$

$$\{S\}_{\overline{f}} \rightarrow 0 \rightarrow DS \rightarrow 0 \rightarrow .... \rightarrow 0 \rightarrow DS \rightarrow 0 \rightarrow .... \rightarrow 0 \rightarrow DS \rightarrow 0 \rightarrow \{S\}_s$$

To simplify final description, an equivalent graph module for membrane diffusion (MD) is introduced:

Analogous bond graphs and modules can be applied to describe diffusion phenomena in the interfacial layers of the aqueous feed (FD) and stripping (SD) solution:
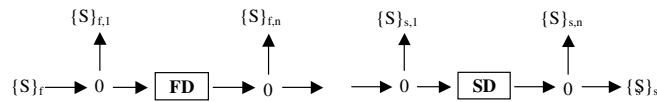
For modeling the interfacial phenomena (uptake and release of S substance), it was assumed that these processes are represented by unimolecular reversible reactions with respective bond graphs:

u – uptake:

r – release:
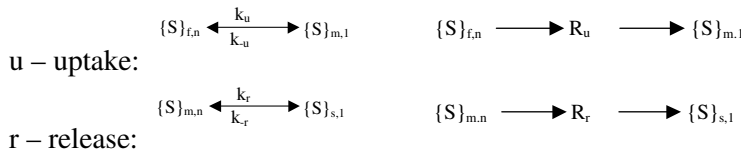
The above networks can be added using 0-junctions (described by KCL-Kirchhoff current law). Thus, the final network for pertraction is represented by a linear network of all the above specified local bond-graphs:
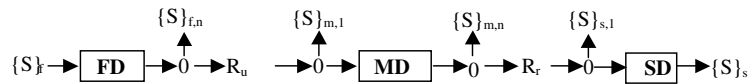
The mathematical description, according to the pertraction bond-graph, involves the definition of time dependence of all the local capacitances (mol/cm^{3}s) along diffusion pathways. The local input and output flows (N, mol/s) are defined using phenomenological linear transport equation (from k sub-layer to $k+1$ sub-layer):

$$N_{k \rightarrow k+1} = D_{i=f,s,m} A([S]_k - [S]_{k+1})/l_i \text{ (mol/s)}$$

The uptake and release flows are described by kinetic equations:

$$N_u = k_u A\left([S]_{fn} - [S]_{m1}/\alpha_u\right) \qquad N_r = k_r A\left([S]_{mn} - [S]_{s1}\alpha_r\right)$$

where k (cm/s) and α denote kinetic constants and equilibrium distribution coefficients for S (between the membrane and aqueous phase).

The set of differential equations describing the dynamic properties of the membrane system and its other characteristics are listed in Tab.1. The

model was formulated for 10 sub-layers in each of diffusion layer in the feed, stripping and liquid membrane phase, i.e $f_n=s_n=10$, $m_n=20$. This value was established after detailed analysis described elsewhere [5].

Table 1. Mathematical model and data for calculations

FEED SOLUTION (*f*): mol/cm^{3}s	MEMBRANE (*m*): mol/cm^{3}s
$d[S]_f/dt= -N_{f\rightarrow f1}/V_f$ $d[S]_{fk}/dt= (N_{fk-1\rightarrow fk}- N_{fk\rightarrow fk+1})/V_{fk}$ $d[S]_{f10}/dt= (N_{f9\rightarrow f10}- N_u)/V_{f10}$ $k=2\ldots9$	$d[S]_{m1}/dt= (N_u- N_{m1\rightarrow m2})/V_{m1}$ $d[S]_{mk}/dt= (N_{mk-1\rightarrow mk}- N_{mk\rightarrow mk+1})/V_{mk}$ $d[S]_{m10}/dt= (N_{m9\rightarrow m10}- N_{m10\rightarrow mc})/V_{m10}$ $d[S]_{mc}/dt= (N_{m10\rightarrow mc}- N_{mc\rightarrow m11})/V_{mc}$ $d[S]_{m11}/dt= (N_{mc\rightarrow m11}- N_{m11\rightarrow m12})/V_{m11})$ $d[S]_{mk}/dt= (N_{mk-1\rightarrow mk}- N_{mk\rightarrow mk+1})/V_{mk}$ $d[S]_{m20}/dt= (N_{m19\rightarrow m20}- N_r)/V_{m20}$ $k=2\ldots9; 11\ldots19$
STRIPPING SOLUTION (s): mol/cm^{3}s	DEFINITIONS
$d[S]_{s1}/dt= (N_r- N_{s1\rightarrow s2})/V_{s1}$ $d[S]_{sk}/dt= (N_{sk-1\rightarrow sk}- N_{sk\rightarrow sk+1})/V_{sk}$ $d[S]_{s10}/dt= (N_{s9\rightarrow s10}- N_{s10\rightarrow s})/V_{s10}$ $d[S]_s/dt= (N_{s10\rightarrow s})/V_s$ $k=2\ldots9$	$V_{f0}=V_f-l_fA$, $V_{s0}=V_s-l_sA$, $V_{mc}=V_m-2l_mA$, cm^3 $V_{fk}=l_{fi}A$, $V_{sk}=l_{si}A$, $V_{mk}=l_{mi}A$, cm^3 $l_{fi}=l_f/f_n$, $l_{si}=l_s/s_n$, $l_{mi}=2l_n/m_n$, cm $N_{output}=N_{s10\rightarrow s}$, mol/s $J_{output}=N_{output}/A$, mol/ cm^{2}s
DATA FOR CALCULATIONS:	INITIAL CONDITIONS (*t*=0)
$V_f=100$; $V_s=100$, $V_m=0.02-1000$, cm^3 $l_f=0.001$, $l_s=0.001$, $l_m=0.001$, cm $A=10$ cm^2 $\alpha_u=1000$, $\alpha_r=1000$ $k_u= 1\times10^{-2}$, $k_r= 1\times10^{-9}$ cm/s $D_f= 1\times10^{-5}$, $D_s=1\times10^{-5}$, $D_m=1\times10^{-9}$, cm^2/s	$S_f=0.1$, $S_s=0$, $S_m=0$, mol/dm^3

3. EXPERIMENTAL

3.1. Benzoic acid pertraction

To verify the results of theoretical calculations and to formulate a mathematical relationship between the maximum flux and liquid membrane volume some experiments were carried out. The scheme of the pertractor is presented in Fig. 5, together with respective experimental conditions
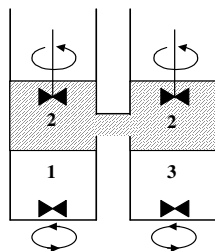

Fig. 2. Scheme of pertractor; 1- feed solution, 2- agitated bulk liquid membrane, 3- stripping solution.

EXPERIMENTAL CONDITIONS:

Solutions (t=0):
1: feed- aqueous solution of 2g benzoic acid/dm^3, 375 rpm; 2: membrane, octane, 20 rpm; 3: stripping solution- distilled water (*t*=0), 375 rpm

Initial conditions:
$c_f = 0.0164$ mol/dm^3, $c_s=0$, $c_m=0$

Parameters:
$A=17$ cm^2, $\alpha_u\approx1.4$, $\alpha_r\approx1.4$,
$V_f =V_s =190$ cm^3, $V_m =40 - 200$ cm^3, $T=25^{o}$C,

4. RESULTS AND DISCUSSION

The results of calculations (Berkeley Madonna v.8, Runge-Kutta method) concerning different experimental conditions are presented in Fig. 3 and 4. Stationary state conditions were established by setting constant concentrations of the feed and stripping phase in time. The pseudostationary conditions were characterized by the constant feed concentration and time dependent stripping solution concentration. The nonstationary conditions, as in real pertraction experiments, were represented by time dependent feed and stripping solutions concentrations.
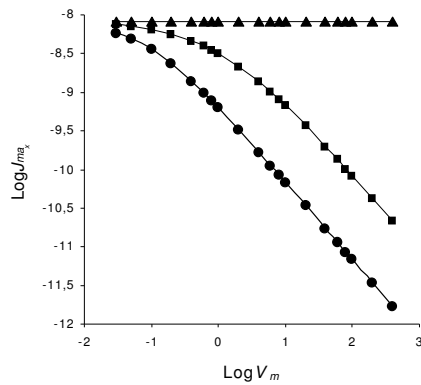

Fig. 3. Dependence of calculated maximum flux (J_{max} mol/cm^{2}s) on volume of agitated bulk liquid membrane: (▲) stationary, (■) quasi-stationary, (●) nonstationary state transport conditions.
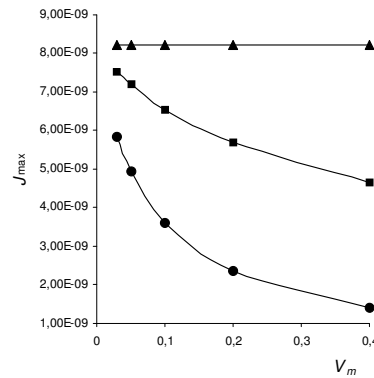
Fig. 4. Extrapolation of nonstationary (●) and quasi-stationary (■) fluxes to steady state values (▲).

According to the results presented in Fig.3, the fluxes observed under stationary conditions do not depend on the ABLM volume. The respective curves (in Fig.3) for non-stationary and quasi stationary conditions are nonlinear indicating strong dependence on the ABLM volume. For non-stationary conditions this dependence is described by a nonlinear equation:

$$\log J_{max} = a_0 + a_1 \log V_m + a_2 \left(\log V_m \right)^2 + a_3 \left(\log V_m \right)^3 \cdots\cdots$$

Qualitatively, the same dependence as in Fig.3 was observed for experimental data presented in Fig. 5 which are well described ($r^2=0.97$) by the following regression function:

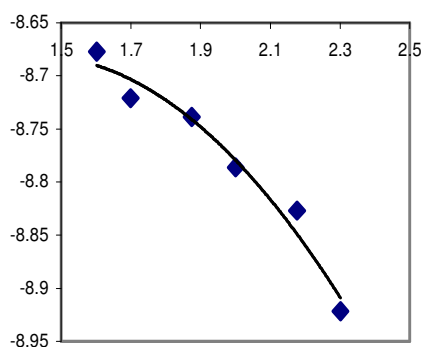$$\log J_{max} = 9.2805 + 0.843 \log V_m + -0.2962 \left(\log V_m \right)^2$$

Fig. 5. Dependence of experimental maximum flux (J_{max} mol/cm^{2}s) on volume of agitated bulk liquid membrane

The maximum flux was calculated from experimental data c_S=f(t) according to the previously described method [6]

The results of calculations allow to conclude that only the stationary flux can be evaluated as a representative and unique quantity for describing transport properties of the agitated bulk liquid membrane system. However, such conditions are very difficult to maintain in practice. To obtain comparable and reliable characteristics for pertraction processes when realized in the systems of limited volumes, the results should be extrapolated to infinitely small or other standardized volume of the membrane, according to plots in Fig. 4.

5. CONCLUSIONS

■ Characteristics of pertraction in the agitated bulk liquid membrane system depend on the overall liquid membrane volume, i.e. they can be described using log(flux) vs. log(V_m) polynomials

■ It was demonstrated by comparing the results of calculations under stationary, quasi-stationary and non-stationary conditions that only maximum fluxes for the experimental systems with $V_m \rightarrow 0$ can be compared with the stationary results.

■ The results of experiments are in qualitative accordance with the calculated dependence of fluxes on liquid membrane volume.

REFERENCES

[1] G. Oster, A. Perelson, A. Katchalsky, *Quart. Rev. Biophys.,***6**, 1973, 1.
[2] H. Paytner, *Analysis and Design of Engineering Systems*, MIT, Cambridge Mass., 1961.
[3] J. Schnakenberg, *Thermodynamic Network Analysis of Biological Systems*, Springer-Verlag, Berlin, Heidelberg, 1977, 4-65.
[4] R. Wódzki, G. Szczepańska, P.Szczepański, *Sep. Purif. Technol*., **36**, 2004, 1
[5] R. Wódzki, P. Szczepański, R. Pawłowski*, Bond-graph description and simulation of membrane processes. 3. Diffusion phenomena in a compartmental system, *Proc. XXIII Int. Symp. Ars Separatoria 2008*, S. Koter, I. Koter (Eds.), Toruń 2008, 306-310
[6] P. Szczepański, *Sep. Purif. Technol.*, **71**, 2010, 121