APPLICATION OF TOPOLOGICAL INDICES FOR DESCRIPTION OF PERTRACTION IN AN AGITATED BULK LIQUID MEMBRANE SYSTEM

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Abstract

The pertraction of benzoic acid in a bulk liquid membrane (BLM) was investigated. The effect of membrane solvent and presence of carrier (tri-n-octylphosphine oxide TOPO) was examined. The liquid membrane was composed of hexane, heptane, octane, nonane, decane or dodecane. The results of experiments indicated that some selected topological indices of the membrane components can be used for quantitative description of linear correlation between fluxes and structure of organic solvent.

1. INTRODUCTION

Benzoic acid is used as a chemical raw material (production of phenol, sodium and potassium benzoates), and in food industry as a preservative in foodstuff [1,2]. Because of the industrial importance of benzoic acid, knowledge on its pertraction in a bulk liquid membrane (BLM) system is necessary for developing some new membrane and extraction processes.

Graph theory is a part of mathematics, and has been applied to solve various problems in synthetic chemistry, quantum chemistry, chemical kinetics, phase equilibrium, chemical information storage, etc. [3]. Graphs in chemistry can be divided into the two categories: (i) structural graphs, and (ii) reaction graphs. The chemical behavior of a compound is dependent upon the structure of its molecules. Quantitative structure-activity relationship (QSAR) studies and the quantitative structure - property relationship (QSPR) studies are the typical areas of chemical research that focuses on the nature of this dependency. The quantitative relationships are the mathematical models that either enable the prediction of a continuous variable (e.g. boiling point) or classification of a discrete variable (e.g. sweet/bitter, toxic/non-toxic) from structural parameters. Topological indices such as molecular connectivity, polarizability, etc. can be easily calculated solely from the molecular structure.

The liquid membranes (LM) are frequently used in the transport and

separation of organic acids [4-6], but there are no data concerning pertraction of benzoic acid in the LM systems. The aim of this study was to evaluate the relationship between fluxes and the type of organic solvent (with and without TOPO as a carrier) in the pertraction of benzoic acid in BLM. Tri-*n*-octylphosphine oxide (TOPO) has been used in the extraction or pertraction of carboxylic acids, because of its chemical stability, high boiling point and low solubility in water [7].

2. EXPERIMENTAL

The bulk liquid membrane experiments were carried out in a glass H-type cell (Fig. 1). Solutions in the cell were stirred with two Teflon-coated magnetic bars (325 rpm). The membrane phase was mixed with two mechanical stirrers. 190 cm^3 solution of benzoic acid (2.0 g/l, P.O.Ch. Gliwice) was used as the feed phase, 190 cm^3 solution of distilled water was used as the stripping phase. The liquid membrane was composed of 50 cm^3 solution of hexane, heptane, octane, nonane, decane or dodecane (Fluka) or from these solvents and TOPO (0.05 M). The contact areas (f/LM and LM/s interfaces) were 17 cm^2. The concentration of benzoic acid in the aqueous phases was determined conductometrically (Elmetron CX-721 Multimeter).

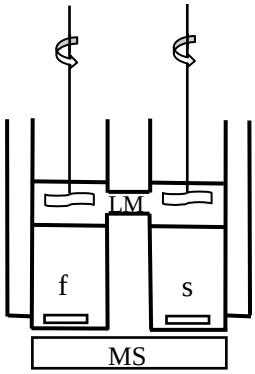

Fig. 1. Scheme of laboratory bulk liquid membrane pertractor:
f- feed phase, LM- liquid membrane, s – stripping phase, MS – magnetic stirrer.

3. CALCULATIONS

The pertraction of benzoic acid in the laboratory pertractor, occurs under non-stationary conditions. Therefore, nonlinear equations, Eq.(1) and (2) were applied for fitting the experimental results:

$$c(t) = \left(a \cdot b + c \cdot t^{d}\right)\left(b + t^{d}\right)^{-1} \tag{1}$$

for the blank system, and

$$c(t) = a + b \cdot t + c \cdot t^2 + d \cdot t^3 + e \cdot t^4 \tag{2}$$

for the system with TOPO as the carrier of benzoic acid. The fluxes, *J(t)*, were calculated by differentiating the curve-fit functions Eqs.(1, 2):

$$J(t) = \frac{V}{A} \cdot \frac{dc(t)}{dt} \tag{3}$$

where V denotes volume of the stripping solution, A – the interphase contact area. The plot of $J(t)$ vs. t exhibits a maximum characterized by J_{max}. Moreover, the influence of the carrier on the pertraction can be estimated by calculating the facilitation factors (*FF*) as a ratio of the flux in the system with liquid membrane containing the carrier ($J_{carrier}$) and the flux in the blank system (J_{blank}):

$$FF = J_{carrier}/J_{blank} \tag{4}$$

Six topological indices have been used in description of the correlation between fluxes and structure (composition) of organic solvent i.e.: connectivity index chi-0 (Chi0), Harrary index (H), reciprocal distance Randić-type index (RDChi), reciprocal hyper-detour index (Rww), first Zagreb index (ZM1), and superpendentic index (SPI).

4. EXPERIMENTAL RESULTS

Typical experimental results corresponding to the system with hexane as the liquid membrane phase and 0.05 M TOPO in hexane are presented in Fig. 2.a and 2.b, respectively.

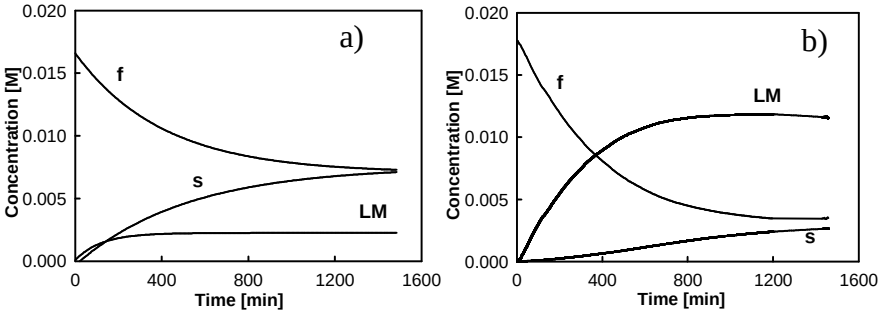

Fig. 2. Experimental results for benzoic acid pertraction in the bulk liquid membrane containing hexane (a) and 0.05 M TOPO in hexane (b) as the liquid membrane: f-feed phase, LM- liquid membrane phase, s – stripping phase

The results indicated that, in the system with a carrier, the concentration of benzoic acid (in the form of complex with TOPO) in the liquid membrane is much higher than the observed for the blank system.

Some selected topological indices (calculated from the chemical structure of the solvent) were applied to describe the solvent structure – BLM properties (flux) relationship by the chemometric methods. The results of simple linear regression for connectivity index Chi0 are presented in Fig.3.

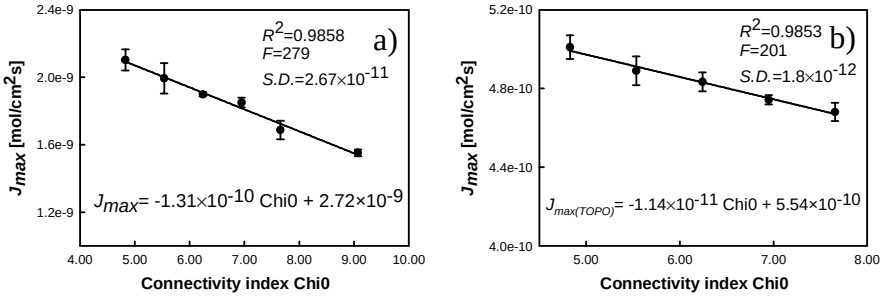

Fig. 3. Correlation between fluxes of benzoic acid vs. connectivity index Chi0 of organic solvent in bulk liquid membrane: system without carrier (a), 0.05 M TOPO as a carrier (b)

Statistical validity of the correlation was estimated using the determination coefficient (R^2) and test function F of Snedecor-Fisher (F-statistics). The characteristics of simple linear regression are collected in Tab.1.

Tab.1. Linear correlations between fluxes (J_{max}) of benzoic acid and topological indices of organic solvent in bulk liquid membrane

Topological index	Correlations	R^2	F
connectivity index (Chi0)	$Jmax \cdot 10^{10}$= -1.31·Chi0+27.2	0.9858	279
	$J_{max(TOPO)} \cdot 10^{10}$= -0.114·Chi0+5.54	0.9853	201
Harrary index (H)	$J_{max} \cdot 10^{10}$= -0.604·H+24.8	0.9854	270
	$J_{max(TOPO)} \cdot 10^{10}$= -0.053·H+5.34	0.9841	186
reciprocal distance Randic-type index (RDChi)	$J_{max} \cdot 10^{10}$= -6.11·RDChi+31.3	0.9866	295
	$J_{max(TOPO)} \cdot 10^{10}$= -0.519·RDChi+5.87	0.9878	243
reciprocal hyper-detour index (Rww)	$J_{max} \cdot 10^{10}$= -0.518·Rww+24.6	0.9850	264
	$J_{max(TOPO)} \cdot 10^{10}$= -0.0457·Rww+5.32	0.9853	201
first Zagreb index (ZM1)	$J_{max} \cdot 10^{10}$= -0.231·ZM1+25.1	0.9858	279
	$J_{max(TOPO)} \cdot 10^{10}$= -0.0201·ZM1+5.35	0.9852	200
superpendentic index (SPI)	$J_{max} \cdot 10^{10}$= -1.967·SPI+27.1	0.9862	287
	$J_{max(TOPO)} \cdot 10^{10}$= -0.1642·SPI+5.51	0.9897	288

In all the calculated linear equations, the quality of correlation is satisfactory. The results indicate that linear regression can be used for description of correlation between selected topological indices and fluxes of benzoic acid in BLM system with and without TOPO as the carrier.

The results of calculated $FF<1$ (hexane 0.238, heptane 0.245, octane 0.254, nonane 0.256, decane 0.277) indicate that the stable chemical complex between extractant and benzoic acid in the liquid membrane is formed.

3. CONCLUSIONS

From presented results one can conclude that the topological indices derived from the molecular structure of solvents can be correlated with the fluxes of benzoic acid in the BLM system. A simple linear model is sufficient to describe the fluxes as the function of topological indices (descriptors) of an organic solvent. The relationships found can be used for prediction of benzoic acid fluxes, for instance in the case of isooctane the calculated flux is $J_{max} = 1.71\times10^{-9}$ and the one observed experimentally equals to $1.77(\pm0.16)\times10^{-9}$ mol/cm^{2}s.

The application of topological indices, calculated solely from molecular structure, is advantageous when compared with the application of physicochemical descriptors (boiling point etc.) which must be determined experimentally.

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