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A new method for estimation of the overall mass transfer coefficient in pertraction

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ABSTRACT

The pertraction of benzoic acid was studied in an agitated bulk liquid membrane system. The simultaneous effect of the operational parameters such as initial feed phase concentration (c_{f0}), bulk liquid membrane volume (V_{LM}) as well as a molecular descriptor (MD) which represent the organic solvent is discussed. The response surface methodology with a full factorial design and multiple linear regression analysis was applied for the description of the dependence of benzoic acid fluxes on selected parameters and descriptors.

It was experimentally confirmed that the response surface methodology enables the determination of the parameter which can be considered as the apparent overall mass transfer coefficient dependent on the volume of the liquid membrane and the liquid membrane solvent in the studied system.

It was additionally found that the extended linear regression models with two and/or three factor interaction terms describe over 99.5% of the total variance between the maximum output fluxes of benzoic acid and selected variables. To evaluate the prediction accuracy of the empirical regression models, the standard validation procedures were carried out. For example, the highest prediction accuracy (over 99.5%) was achieved in the case of the models involving three variables (c_{f0} and V_{LM} parameters and 3D Wiener index (W3D)), and additionally, two factor interaction terms ($c_{f0} \times V_{LM}$, $c_{f0} \times$ W3D, $V_{LM} \times$ W3D).

Alternatively, similar models with comparable prediction accuracy but exploiting the squared Moriguchi octanol–water partition coefficient (MLOGP2) or reciprocal hyper-detour index (R_{ww}) can be formulated. However, in this case, the models involves three factors interaction term ($c_{f0} \times V_{LM} \times$ MD).

1. Introduction

Transport in the liquid membrane systems can occur as the sequence of extraction, diffusion, and back-extraction processes, according to a simple solution–diffusion mechanism. The efficiency of pertraction processes as dependent on the fluxes can be influenced by a number of operational parameters such as the feed and stripping phase concentration, volume of the organic phase, agitation rates, etc. The primary aim of many experimental studies is to determine exactly the influence of these parameters and physicochemical features (e.g., diffusion coefficients, equilibrium constants, kinetic characteristics) of the system components on the overall pertraction rate (output flux). The quantitative description of such a dependence is usually derived from some theoretical models (Behr et al., 1985), the solution of which requires a number of exact values of such physicochemical quantities as: diffusion coefficients, the thicknesses of the diffusion layers in the aqueous and organic phases, the partition coefficients as well as the extraction and re-extraction rate constants. Frequently, the accessibility of these quantities in databases is limited or their experimental determination is difficult and

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requires the application of advanced adjusting procedures (Koter et al., 2013). The respective equations usually take into account the effect of only one parameter (one variable models) on the fluxes (Matsumoto et al., 1998). Moreover, their form also depends on certain assumptions (such as a slow (or fast) interfacial reaction, the presence of water diffusion layers only, steady state, a linear concentration gradient, etc.) which should be fulfilled by the described transport system (Danesi et al., 1981).

An alternative way to formulate a mathematical model for predicting an object response (e.g., membrane system fluxes) on its descriptors is the application of chemometric modeling and the use of resulting empirical models, the form of which is not based on physical chemistry. In the chemometric terminology (Lattore, 1984), one can state that the response of the modeled object is dependent on the values of the carefully selected explanatory variables. This carefulness requires the control of the statistical significance of variables and a model validation procedure. Note that empirical chemometric models are widely applied in the response surface methodology (Myers et al., 2009) as well as used in the Quantitative Structure-Property Relationships (QSPR) or Quantitative Structure-Activity Relationships (QSAR) analysis (Todeschini and Consonni, 2000). Obviously, in order to formulate a correct chemometric model, the methods of experimental design must be applied. In such a case, all explanatory variables should be independent, i.e., the plan of experiments should be orthogonal. If these variables are highly correlated (e.g., collinearity is high) the assessment of significant effect on the dependent variable (model response) becomes difficult or impossible.

There are many methods for planning experiments among which full (or fractional) factorial, simplex, Plackett–Burman, Taguchi, central composite, Box–Behnken designs can be mentioned (Brereton, 2003) as most frequently applied. However, there are only a few examples of their application for the description of transport phenomena as mediated by liquid membranes. For instance, Kargari et al. (2006) applied the Taguchi method for the optimization of process parameters in the extraction of gold (III) ions by an emulsion liquid membrane (ELM) system. The Box–Behnken experimental design was used to optimize lactic acid extraction by ELM in a mixed flow reactor (Thakur et al., 2008), and to optimize the chosen key variables for the extraction of chromium in ELM (Rajasimman et al., 2009). The factorial experimental design was used by Chimuka et al. (2003) to optimize the pertraction procedure of uranium with the use of a supported liquid membrane (SLM). The screening factor experimental design was applied to determine the model and the optimal values for Zn^{2+} pertraction in ELM (Valenzuela et al., 2005) whereas Doehlert's and full factorial designs were used for the optimization of the biogenic amines pertraction through a SLM (Romero et al., 2002). Moreover, a central composite design was employed to study the influence of several operational parameters on lactic acid pertraction efficiency in ELM (Chanukya et al., 2013).

The above examples show that the response surface methodology lead to the empirical models usually applied for the process optimization without obtaining the physicochemical parameters characterizing the process. Therefore, in this work an attempt made to physicochemically interpret the empirical model slope will be presented. According to the response surface methodology, in this paper, a step-by-step method of empirical regression models building for the maximum output flux (J_{max}) correlation observed in the pertraction system with the initial feed phase concentration (c_{f0}), liquid membrane volume (V_{LM}), and the liquid membrane solvent (described by MD) is presented. Such a model can be used to predict the simultaneous effect of c_{f0}, V_{LM}, and MD on the maximum output flux in the agitated bulk liquid membrane system operating under non-stationary conditions and to estimate the overall mass transfer coefficient.

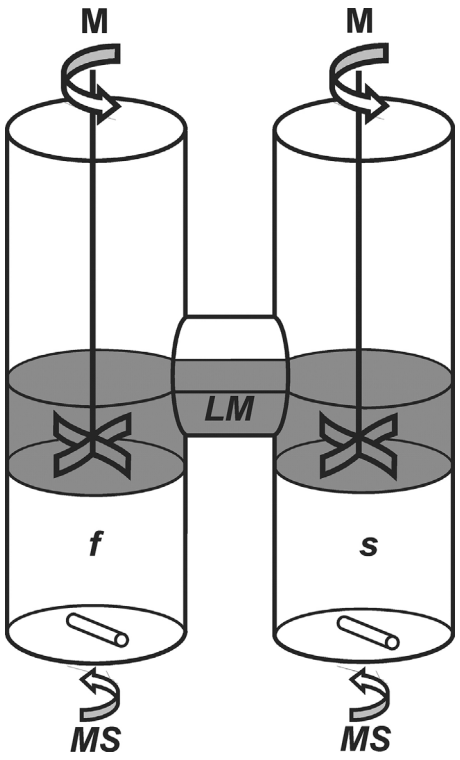

Fig. 1 – The scheme of the experimental agitated bulk liquid membrane system; f—feed phase, LM—liquid membrane phase, s—stripping phase, MS—magnetic stirrer, M—mechanical stirrer.

2. Experimental

The pertraction experiments were performed in the agitated bulk liquid membrane system, ABLM, (Fig. 1) at the temperature of $25 \pm 0.5\,^{\circ}C$. The system was composed of the aqueous feed and receiving solution with the volume of 190 cm^3, and the organic phase with the volume varying in the range from 50 cm^3 to 150 cm^3. The concentration of benzoic acid (pure p.a., P.O.Ch., Gliwice) in the feed phase was changed from 0.0041 mol/dm^3 to 0.0229 mol/dm^3. As the receiving phase (at $t = 0$), twice-distilled water was used. The liquid membrane phase was composed of hexane, heptane, octane, nonane, or decane as the organic solvent (pure p.a., P.O.Ch., Gliwice). The feed and receiving solution were stirred with two Teflon-coated magnetic bars (325 rpm). The liquid membrane phase was intensively agitated with two mechanical stirrers (30 rpm). The contact areas between the feed and the liquid membrane or the liquid membrane and the receiving solution were 17 cm^2 each. An Elmetron CX-721 Multimeter, equipped with a conductometric cell was applied for the benzoic acid concentration analysis.