



# A novel simple and efficient procedure for the pervaporation transport study of binary mixtures through polymeric membranes: tested systems propanol isomers–water–polyethylene membrane



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## ABSTRACT

A novel simple and efficient procedure for the study of binary mixtures pervaporation transport through polymer membranes is reported. The basic idea is a gradual increase of one component concentration in the feed mixture instead of time-consuming repetitive measurements of several solutions of different compositions. Presented procedure called "component addition method" allows obtaining the required experimental data much faster and easier. The study of the transport behavior of propanol isomers (propan-1-ol and propan-2-ol)/water mixtures during the pervaporation through a polyethylene membrane was performed using the proposed novel method. The effects of temperature, feed composition and the shape of the isomer molecules were investigated. Higher temperature effect on pervaporation transport of propan-2-ol was registered. Lower mass fluxes and diffusion coefficients of propan-2-ol for all experimental temperatures were found; the reason may be the more branched molecular structure. With respect to the feed composition, an interesting trend of propanols transport parameters were obtained; increasing water content in the feed caused the slight diffusion coefficient increase and the mass flux decrease for both isomers; however, in the concentration range 30–70 wt% the flux decrease was slower than in other regions.

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## 1. Introduction

Pervaporation belongs to the efficient membrane processes for liquid separation that have gained increasing interest in many fields in the past decades. The fundamentals and application aspects of this perspective technology were summarized in several reviews [1–10].

Compared to conventional processes such as distillation or adsorption, pervaporation is considered an effective, energy saving and environmentally friendly technology for separations which are difficult to achieve, e.g., separation of azeotropic and close-boiling liquid mixtures, isomers or heat-sensitive compounds [6,11].

The three major areas of pervaporation application are (i) dehydration of organic solvents including bioalcohols [6–13]; (ii) recovery of organic compounds from aqueous solutions (e.g., removal of volatile organic compounds, recovery of aroma, and recovery of biofuels from fermentation broth) and (iii) separation of organic mixtures [6–9] (polar/non-polar, e.g. methyl *tert*-butyl ether (MTBE)/methanol, aromatic/aliphatic, e.g., benzene/*n*-hexane, aromatic/alicyclic, e.g. benzene/cyclohexane, and isomers, e.g., *p*-xylene, *m*-xylene, and *o*-xylene).

A large amount of work has been carried out on dehydration of alcohols by pervaporation, mostly focused on ethanol/water and propan-2-ol/water systems [6–9,14]. A comprehensive review of polymeric membranes for pervaporation was published by Shao and Huang [9]; the authors provided an overview on the potential of pervaporation for separating liquid mixtures focusing on alcohol and solvent dehydration. The review prepared by Chapman et al. [7] complements this area with detailed look at hydrophilic pervaporation; both polymeric and inorganic membranes are examined and dehydration of alcohols such as ethanol and propan-2-ol is covered in depth.

The aim of the present work is a detailed study of pervaporation transport of propanol isomers (propan-1-ol and propan-2-ol) through a homogenous polyethylene membrane at various compositions of alcohol and water in feed mixtures as a model system for an application test of a novel efficient procedure named "component addition method" allowing much faster and easier data collection. The effects of temperature, water content, and molecular structure of permeating species on the permeation transport have been investigated.

A similar study dealing with pervaporation of butanol isomers was already performed [15]. However, the data were investigated by the "classical method", using several mixtures of different alcohol contents. This method was rather laborious and time-consuming.

Thus in this work a rapid method based on a gradual increase of propanol concentration in the feed was described and used for

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## Nomenclature

$A_{12}, A_{21}$	adjustable parameter of van Laar equation
$a$	activity (–)
$c$	concentration of molecules (mol/m <sup>3</sup> )
$c_1$	steady state concentration of vapor in feed (mol/m <sup>3</sup> )
$c_2$	steady state concentration of vapor on permeate side membrane (mol/m <sup>3</sup> )
$c_s$	equilibrium sorption of component in the membrane (kg/m <sup>3</sup> )
$D$	diffusion coefficient (m <sup>2</sup> /s)
$D_{\text{eff}}$	effective diffusion coefficient (m <sup>2</sup> /s)
$E_D$	diffusion activation energy (kJ/mol)
$E_j$	apparent activation energy (kJ/mol)
$E_p$	permeation activation energy (kJ/mol)
$\Delta H_S$	enthalpy of solution (kJ/mol)
$\Delta H_v$	molar enthalpy of vaporization (kJ/mol)
$J$	permeation flux (mol/m <sup>2</sup> s)
$J_0$	pre-exponential factor (mol/m <sup>2</sup> s)
$J_{\text{max}}$	permeation flux in steady state (mol/m <sup>2</sup> s)
$m_s$	relative equilibrium sorption of component in the membrane (kg/m <sup>3</sup> Pa)
$l$	thickness of the membrane (m)
$p$	pressure (Pa)
$P$	membrane permeability (mol/m s Pa)
$R$	perfect gas constant (J/mol K)
$S$	solubility coefficient (mol/m <sup>3</sup> Pa)
$T$	temperature (K)
$t$	time (s)
$x$	the space coordinate (m)
$x_1, x_2$	mole fractions (–)
$\gamma_1, \gamma_2$	activity coefficients (–)
$\gamma_1^\infty, \gamma_2^\infty$	activity coefficients at infinitive dilution (–)

efficient and prompt acquisition of transport parameters, mass fluxes, and diffusion coefficients in a wide feed concentration range for different operating temperatures in order to promptly evaluate and compare the transport of both isomers in a membrane.

## 2. Theory

The solution-diffusion model [16,17] is generally accepted one for the mass transport description through dense polymeric membranes. According to this model the transport through homogeneous membrane consists of three fundamental processes: the solution of molecules in the upstream membrane surface, the diffusion of the dissolved species across the membrane, and the desorption of the permeated species in the vapor form at the downstream membrane side. The diffusion through the membrane is the slowest step therefore it is considered as the rate-limiting step of the process.

Diffusion coefficients  $D$  in polymeric membranes are usually determined by matching the time course of the permeate flux or from particular points of this curve [18–25].

Fitting of the experimental time course of the permeate flux through the polymeric membrane during dynamic permeation measurement by numerical solution of Fick's second law (Eq. 1) published by Carslaw and Jaeger [18] for unsteady dimensionless flux  $J/J_{\text{max}}$  of permeate at given initial and boundary conditions (Eqs. 2 and 4) was used for evaluation of the diffusion coefficient [15,26–30].

$$\frac{\partial c}{\partial t} = D \left( \frac{\partial^2 c}{\partial x^2} \right) \quad (1)$$

$$0 < x < l \quad t = 0 \quad c = 0 \quad (2)$$

$$x = 0 \quad t \geq 0 \quad c = c_1 \quad (3)$$

$$x = l \quad t \geq 0 \quad c = c_2 = 0 \quad (4)$$

Combined solution of Fick's first and second laws assuming constant diffusion coefficient leads to the following final equation (Eq. 5), for details see [15,26–30].

$$\frac{J}{J_{\text{max}}} = 1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp \left( -\frac{Dn^2\pi^2 t}{l^2} \right) \quad (5)$$

where  $J_{\text{max}}$  is the flux in the steady state of pervaporation,  $t$  is the time and  $l$  is the thickness of the polymeric membrane (negligible compared to other dimensions of the membrane).

## 3. Experimental

### 3.1. Materials and chemicals

The polymeric membrane used in this study was a high-pressure, low density polyethylene BRALEN FB2-30, in the form of a film, a commercial product supplied by Slovnaft, a.s., Slovak Republic. The polymer density was  $\rho = (919 \pm 2)$  kg/m<sup>3</sup> at 298.15 K, an average degree of crystallinity was 45.5% and the polymer glass transition temperature  $T_g$  was  $-120$  °C. The thickness of the polyethylene film was about 50  $\mu\text{m}$ .

Polyethylene is a raw material for plastics industry. It has a broad spectrum of use, such as foil, plastic containers, pipes, cable sheathing, various parts in the construction, sporting needs, households, etc. The polyethylene membrane characterized by good homogeneity and low swelling rate in contact with alcohols was selected as an appropriate test membrane material in this work; and its easy availability was another crucial aspect.

Propanol isomers, propan-1-ol, (NPA) and propan-2-ol, (IPA) of analytical grade with purity 99% purchased from Lachema Neratovice, Czech Republic, were used to mix with water to prepare the feed binary mixtures. Nitrogen used as a sweeping gas in pervaporation process was purchased from Linde Technoplyn, Czech Republic, in purity 99.99%.

Table 1 compares physicochemical properties of propanol isomers discussed in this study and data informed about their binary azeotropes formed with water.

### 3.2. Experimental setup

#### 3.2.1. Pervaporation transport of pure propanol isomers

Pervaporation experiments were performed according to the procedure described in detail elsewhere [15,27]. The schematic experimental setup in sweeping gas arrangement is depicted in Fig. 1. Briefly, the pervaporation cell with the membrane (the effective membrane area 380 mm<sup>2</sup>) was immersed in a thermostated vessel containing a feed solution. The upstream face of the membrane was in contact with the liquid feed and the downstream face was swept by the nitrogen. The permeate concentration on the downside of the membrane was maintained very low due to a high flow rate (100 mL/min) of nitrogen. The permeate was transported by a sweeping gas to a Flame Ionization Detector (FID).

The value of the FID signal was recorded throughout the experiment, from the beginning (the immersion of the cell with the membrane in the feed solution) to the steady state of the pervaporation process. The fluxes in the steady state of the transport process were calculated from the plateau of the FID signal record, which is the maximal level of the FID signal. The diffusion coefficients were calculated from the time dependency of the FID signal, the data evaluation was described in Section 2.

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