Mechanisms evaluation and characterization of butanol concentration using pervaporation

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ABSTRACT

Pervaporation (PV) is a membrane-based process. The liquid feed remains in contact with the active part of the membrane, which selectively transports components to its another side. Many different models can describe this phenomenon, but usually a number of simplifications have to be made. This is because several elements of mass transfer process should be taken into account. The presented work discusses all transport mechanisms, which occur in the vacuum PV. The authors recommend the semi-empirical approach, which allows predicting effects of PV process, basing on the experimental data and the component activity. As an example, the separation of butanol from acetone-butanol-ethanol-water solutions is presented. Additionally, a resistance of the mass transfer process through the commercial (PERVAP 4060) membrane is considered. According to calculations, the highest mass transfer resistances were estimated for butanol and ethanol. The enrichment factor of membranes was also shown. Butanol concentration increased 16-fold in refer to their concentration in the feed.

Keywords: Semi-empirical model; Pervaporation; Biobutanol

1. Introduction

Chemical and petrochemical industries search for alternative separation methods. Nowadays, pervaporation (PV) is considered to be a promising separation technique for organic–organic [1] and organic-inorganic liquid mixtures [2], as it provides high efficiency in separating azeotropes, close-boiling mixtures, isomers and heat-sensitive compounds [3].

PV is a membrane-based process for selective separation of one or more compounds using an appropriate membrane. In this process (Fig. 1), the feed (ABE – water mixture) is split into the enriched permeate and the retentate depleted of the separated component. Because of the lower pressure on the permeate side, the permeate is received in vapor form [4].

The selective mass transfer through the membrane is based on the membrane-compound interactions [5]. Both chemical nature and structure of the material forming the active layer are key factors for membrane performance determination [6,7]. Despite the advantages of PV [8,9] and other hybrid processes involving PV [10] over non-pervaporative processes, a mathematical description of the mass transfer is required.

2. Concentration profiles

To obtain an analytical description of the PV process, it is necessary to consider all constituent phenomena and processes.

As an example, pervaporative separation of the acetone-butanol-ethanol-water system is examined. Pressure, temperature and concentration profiles of butanol are presented in Fig. 2. Similar profiles can be obtained for any system and any hydrophobic membrane.

Due to the feed flow along the membrane, a polarization layer is created. Its thickness depends on Reynolds number
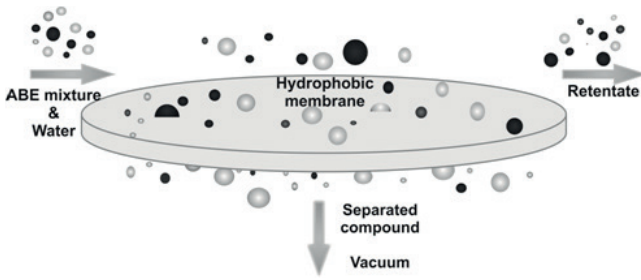
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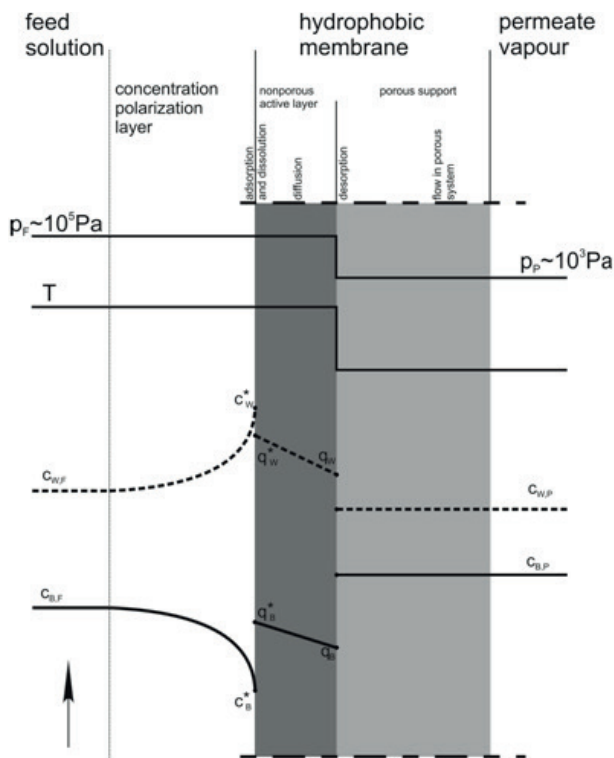
Fig. 1. The scheme of pervaporation process.

Fig. 2. The scheme of concentration profiles through the membrane (B – butanol, W – water).

Note: c_{iF} is component concentration in the feed [$g_{component}/cm^3_{feed}$]; c_{iP} is component concentration in the permeate [$g_{component}/cm^3_{permeate}$]; c^*_i is equilibrium component concentration near the active layer on the feed side [$g_{component}/cm^3_{feed}$]; q^*_i is equilibrium component concentration in the polymer (active layer), on the active layer side [$mg_{component}/g_{polymer}$]; q_i is component concentration in the polymer, on the active layer-support layer border [$mg_{component}/g_{polymer}$].

calculated for the boundary layer. Consequently, a change in the component concentration near the membrane surface appears. Concentrations of acetone, butanol and ethanol decrease when compared with water because of the hydrophobic nature of the membrane.

An adsorption process takes place on the membrane surface, and it is accompanied by swelling, which occurs due to the solvent penetration into the active layer of the membrane. Next, multicomponent diffusion through the active layer takes place as a result of the difference in chemical potential. The components change their state into vapor, but it is still questionable whether this phenomenon happens [11] inside or
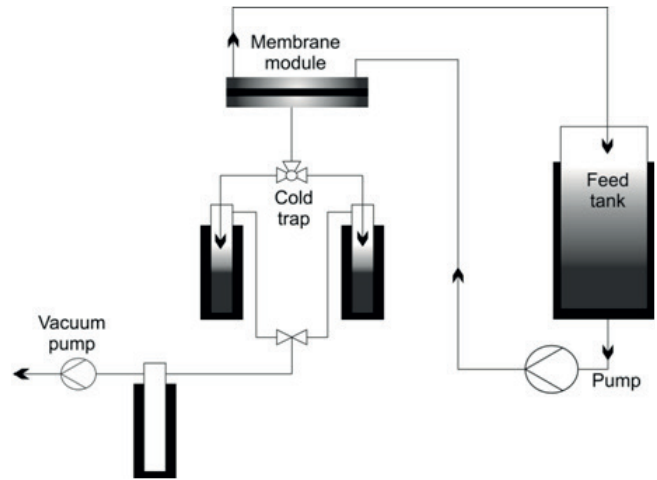

Fig. 3. The scheme of pervaporation laboratory setup.

on the low pressure side of the active layer. Afterwards, the permeate is desorbed due to the low pressure on the opposite side of the active layer. Finally, the vaporous permeate flows through the porous support layer and condenses in a cold trap.

In order to describe and predict mass transfer effects during PV, additional experiments are required to obtain coefficients necessary for description of all constituent phenomena and processes.

PV involves not only mass but also heat transfer through the membrane. The physical change from liquid to vapor requires energy. Therefore, in order to keep the temperature constant, heat exchangers are frequently added to the system on the feed side.

The number of studies devoted to PV do not provide mathematical models able to explain all related phenomena and processes. Usually, many simplifications are proposed. Several different models have been used to describe mass transfer through a PV membrane. The Table 1 classified all possible approaches to modeling of PV in three basic types: theoretical, semi-empirical [12,13], which is based on the solution-diffusion mechanism [14–17], and experimental (empirical).

The main aim of mathematical modeling is to simulate the process and compare experimental results with calculated data. It also allows predicting process conditions, which can differ from experimental ones, and design the large-scale PV units.

In this work, the semi-empirical approach was taken into account. PV process was characterized using experimental data.

3. Materials and methods

The diagram of the experimental setup is presented in Fig. 3. For the PV tests, a hydrophobic composite membrane PERVAP 4060 (supplied by Sulzer) with PDMS based active layer was used. The membrane was cut into circular samples of 8 cm diameter and placed in the module cell. The aqueous feed contained three organic components, that is, acetone, n-butanol and ethanol (Chempur) in the ratio of 3:6:1. The butanol concentration in the feed was

Table 1
Mass transfer models used in pervaporation [11]

Theoretical	Semi-empirical	Empirical	Mass transfer mechanism
UNIFAC Molecular simulations for sorption	Solubility parameter theory Flory-Huggins UNIQUAC ASOG-FV Entropic-FV Modified NRTL ENSIC	Langmuir and Henry's law isotherms	Sorption
Free volume Dual sorption Molecular simulations for diffusion	—	Empirical diffusion coefficients	Diffusion
Stephan-Maxwell theory Pseudophase-change solution-diffusion model	Solution-diffusion model Semi-empirical model after Meyer-Blumenroth Q_i model Process-specific permeability functions Thermodynamic of irreversible processes (TIP) Pore-flow model	Empirical model by Franke	Transmembrane mass transfer

1.5, 3 and 5 wt.%. The PV process was carried out at the feed flow rate of 20 dm^3 h^{-1}, permeate pressure of 10 mbar and temperatures of 29°C, 37°C and 50°C. The permeate was collected in a cooled trap (at predetermined time intervals) using liquid nitrogen and the retentate was recycled to the feed vessel.

Gas chromatography (GC) was used to measure compositions of permeate and retentate and methanol was added to the sample as a tracer. In order to exclude an influence of the sample preparation on the analytical results, all concentrations measurements were repeated three times. The analytical error was found to be approximately equal to 0.75%.

4. Results and discussion

The mass flux of the selected component is described by Eq. (1).

$$J_i = \frac{\rho_i \, \Delta a_i}{R_{Ti}} \tag{1}$$

where R_{Ti} is total mass transfer resistance of component i [s cm^{-1}]; ρ_i is component i density [kg m^{-3}]; Δa_i is difference in component i activity.

The change of activity in the solution on both membrane sides is expressed by the following equation:

$$\Delta a_i = \gamma_{iP} \cdot x_{iP} - \gamma_{iF} \cdot x_{iF} \tag{2}$$

where γ_{iP}, γ_{iF} are activity coefficients of component i in the permeate and the feed, respectively; x_{iP}, x_{iF} are mole fraction of component i in the permeate and the feed, respectively.

Table 2
G_{ij} parameter used to activity coefficients determination

	Acetone	Butanol	Ethanol	Water
Acetone	1.0000	0.6776	0.9039	0.8840
Butanol	1.2380	1.0000	0.8802	0.8639
Ethanol	0.8590	1.0883	1.0000	0.9959
Water	0.6484	0.5391	0.6342	1.0000

Table 3
τ_{ij} used to determine activity coefficients

	Acetone	Butanol	Ethanol	Water
Acetone	0	1.2971	0.3367	0.4110
Butanol	–0.7117	0	0.4253	0.4876
Ethanol	0.5068	–0.2820	0	0.0139
Water	1.4443	2.0596	1.5181	0

The non-random two-liquid model (NRTL) was used to calculate the component activity as a function of both, solution composition and temperature. NRTL equation coefficients, which describe binary interactions between molecules, are known for the feed and the permeate [18,19]. Hence, Eqs. (3)–(5) allow calculating activity coefficients.

All calculations were conducted with the use of MATLAB software. Binary parameters a_{ij}, b_{ij} and c_{ij} can be found in literature [20]. Exemplary values of G_{ij} and τ_{ij} at 50°C, used to determine activity coefficients, are presented in Tables 2 and 3.
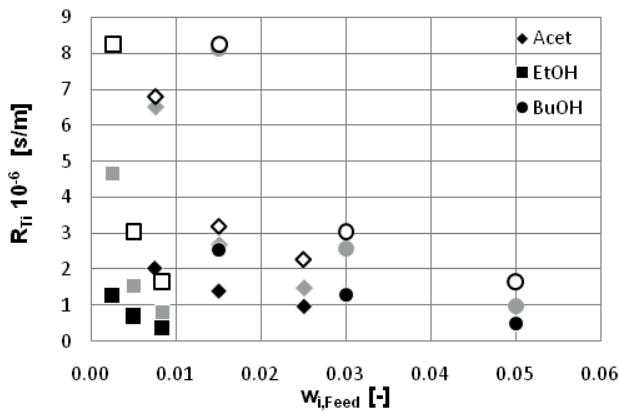
Fig. 4. Total mass transfer resistance in relation to the component concentration in the feed (black = 50°C; grey = 37°C; white = 29°C).
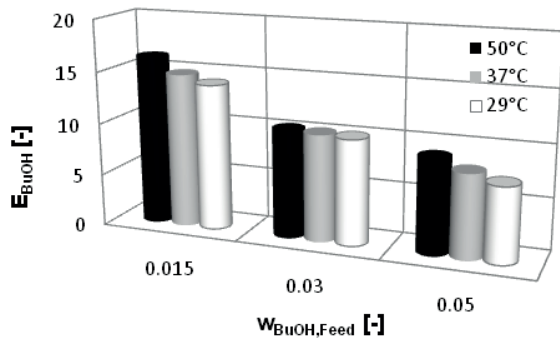

Fig. 5. Enrichment factor in relation to the component concentration in the feed.

$$\ln \gamma_i = \frac{\sum_{j=1}^{n} \tau_{ji} x_j G_{ji}}{\sum_{k=1}^{n} x_k G_{ki}} + \sum_{j=1}^{n} \frac{x_j G_{ij}}{\sum_{k=1}^{n} x_k G_{kj}} \left[\tau_{ij} - \frac{\sum_{m=1}^{n} \tau_{mj} x_m G_{mj}}{\sum_{k=1}^{n} x_k G_{kj}} \right] \tag{3}$$

where:

$$G_{ij} = \exp\left(-c_{ij} \ddot{A}_{ij}\right) \tag{4}$$

$$\tau_{ij} = a_{ij} + \frac{b_{ij}}{T} \tag{5}$$

Performance of the PV membrane can be characterized by enrichment factors (E_i) calculated for individual components, which may be expressed by Eq. (6).

$$E_i = \frac{w_{ip}}{w_{iF}} \tag{6}$$

where w_i is mass fraction of component "i" in the permeate "P" and feed "F", respectively.

Total mass transfer resistances R_{Ti} for individual components were calculated using Eq. (1). According to Fig. 4, R_{Ti} decreases, when the concentration of component i in the feed increases. Additionally, the comparison of R_{Ti} values for the same concentration of component i in the feed proves that the mass transfer resistance decreases with temperature increase.

Using the experimental results and subsequent calculations, the enrichment factors were estimated. Fig. 5 shows the results obtained for different temperatures and butanol feed concentrations. The highest (16-fold) increase was recorded, when butanol concentration in the feed was equal to 1.5 wt.%.

5. Conclusions

The paper presents the constituent mass transfer mechanisms occurring in the complex PV process and proposes the use of the semi-empirical NRTL model to activity coefficients determination. Specifically, it describes the separation of acetone, butanol and ethanol from aqueous solutions.

During the experimental work, the recovery was performed at different temperatures and different concentrations of butanol in the feed. As a result, the total mass transfer resistance through the PERVAP 4060 membrane was calculated, due to which efficiency of PV membranes towards the preferentially transferred components could be estimated. The lowest value of the parameter was observed for ethanol at 50°C, while the highest for butanol was at 29°C. Hence, the efficiency of the process clearly depends on both process temperature and feed composition.

Therefore, more effort is needed to model the diffusivity through polymeric membranes. The better understanding of the PV process will improve its large-scale design and operation.

Symbols

c_{iF}	—	Component concentration in the feed, $g_{component}/cm^3_{feed}$
c_{iP}	—	Component concentration in the permeate, $g_{component}/cm^3_{permeate}$
c_i^*	—	Equilibrium component concentration near the active layer on the feed side, $g_{component}/cm^3_{feed}$
q_i^*	—	Equilibrium component concentration in the polymer (active layer), on the active layer side, $mg_{component}/g_{polymer}$
q_i	—	Component concentration in the polymer, on the active layer-support layer border, $mg_{component}/g_{polymer}$
R_{Ti}	—	Total mass transfer resistance of component, i, s cm^{-1}
ρ_i	—	Component i density, kg m^{-3}
Δa_i	—	Difference in component i activity, –
γ_{iP}, γ_{iF}	—	Activity coefficients of component i in the permeate and the feed, respectively, –
x_{iP}, x_{iF}	—	Mole fraction of component i in the permeate and the feed, respectively, –

τ_{ij} — NRTL binary parameter, –
G_{ij} — Gibbs free energy, NRTL binary parameter, J
a — Activity, NRTL binary parameter, –
b — NRTL binary parameter, –
c_{ij} — Concentration, NRTL binary parameter, –
J_i — Permeate flux of component i, kg $(m^{-2}h)^{-1}$

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