

SIMULATION OF THE PERVAPORATION PROCESS FOR SEPARATING ORGANIC MIXTURES USING SOLUTION-DIFFUSION MODEL

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Abstract

Simulation results for the separation of the system methyl acetate-water using the pervaporation process were obtained. The solution-diffusion model proposed by Kataoka et al. (1991) was used. The transport parameters used in the mathematical model were obtained from the experimental data presented by Kujawski (2000). A general equation expressing the permeate composition as a function of the feed composition was developed. It was observed that, for the membrane studied, which is selective to methyl acetate, the permeate flux for this component increases, increasing its feed composition, however the separation factor decreases. The permeate flux decreases increasing the permeate side pressure. It can be concluded that the model represents quite well the experimental data. Moreover, the simulator developed shows robustness for evaluating new systems to be separated what represents a useful tool in process assessment.

Keywords

Pervaporation, Azeotropic Mixtures, Simulation, Membranes, solution-diffusion model.

Introduction

Pervaporation operation is a separating technique based on a material selective transport through a non-porous membrane followed by evaporation of the permeate. This phase change is usually obtained through vacuum at the membrane downstream side. The swollen permselective film usually works as a thin solvent layer, and the permeate composition is mainly determined by the preferential solvation of the barrier material (González and Uribe, 2001). This process can be effective for separating azeotropic mixtures. However, for large scale plants, it needs to be well understood and the variables must be well adjusted for the success of the operation.

Pervaporation differs from other membrane processes by the change of phase that occurs on the permeate side. Another important characteristic of this process is that the permeate flow is relatively low. Thus, the process becomes attractive, when small amounts of material are to be removed of the liquid phase. For this, it is necessary that

the membrane presents elevated selectivity in relation to the component to be removed (Cunha et al., 1998).

On the other hand, removal of organics from aqueous solutions is of particular interest mainly for wastewater treatment. For that and, also, considering the azeotropic behavior of the mixture, the separation of the system methyl acetate-water is being considered in this work.

The modelling developed by Kataoka et al. (1991) (with other kind of system) was used to build up a simulator, which was used to carried out the studies. The system considered here was studied experimentally by Kujawski (2000), using a PDMS ZSM-5 zeolite filled (PERVAP-1070) membrane. So, the intention in this work is to apply the model and the simulator for this system, in order to study better the main variables influencing the performance of the process and to optimize it.

Furthermore, an equation relating the permeate to feed compositions was developed in such a way to facilitate the

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interpretation of selectivity and of azeotropic point breaking.

At this point, it is convenient to mention that the work of Kataoka et al. (1991) is based on the system ethanol-water and, so, the developments claimed in this work are not found in the open literature and its originality is concerned with the application of a known model in a new system and its validation with available experimental data. This is crucial to evaluate the potentials of the model, of the simulator and of the membrane. Additionally, it is important to have a tool to assess new applications.

Pervaporation Model

Several empirical equations have been developed to calculate the diffusion coefficient used in the solution-diffusion mechanism, from simple linear equation to exponential models. Those equations try to describe the relationship between the diffusion coefficient and the concentration, as the exponential model of six coefficients studied by Brun et al. (1985).

The solution diffusion mechanism presented by Kataoka et al. (1991) was used in this work. The model relates the permeate flux behavior as a function of feed composition. The model assumes that the membrane pressure gradient varies linearly according to:

$$P^m = P_1 + \frac{z}{\ell}(P_2 - P_1) \quad (1)$$

where, P is the pressure (KPa), ℓ the membrane thickness (m), z membrane abscissa, the superscript m is the film membrane, the subscripts 1 e 2 correspond to the feed side and permeate side, respectively.

The permeate flux is a function of the chemical potential gradient, according to the expression (Lonsdale et al., 1965; Kataoka et al., 1991):

$$J_i = -\frac{DC_i^m x_i^m}{RT} \frac{d\mu_i}{d\ell} \quad (2)$$

where, J is the permeate flux (mol/m²h), D is the diffusion coefficient (m²/h), C the concentration (mol/m³), x the molar composition, μ the chemical potential (J/mol), R the gas constant (kPa m³/mol K), T the temperature (K) and the subscript i represents the permeate component (methyl acetate, i , water, j).

Assuming that the membrane is in contact with a liquid phase on the feed side and with a vapor phase on the permeate side, the chemical potentials in the membrane interface and in the adjacent phases must be equal. Substituting the definition of the chemical potential at the boundary membrane in Eq. (2) and solving it, the permeate flux equation becomes (Kataoka et al., 1991):

$$J_i = \frac{DC^m}{\ell\gamma^m} \left(\left(\gamma_{1,i} x_{1,i} - \frac{P_2 x_{2,i}}{P_{v,i}} \exp \left\{ \frac{v_i (P_{v,i} - P_1)}{RT} \right\} \right) \right) \quad (3)$$

and, for a binary system, the total permeate flux is:

$$J = J_i + J_j \quad (4)$$

For a binary mixture, the separation factor can be defined through the following expression (Brun et al., 1985; Lee, 1975):

$$\alpha_{i/j} = \frac{J_i \cdot x_{1,j}}{J_j \cdot x_{1,i}} \quad (5)$$

In this work, an expression from Eq. 3 and 4 and using the software Maple 7.0 was developed, which expresses the permeate composition as a function of the feed concentration:

$$x_{2,i} = \frac{1}{2} \left[\frac{\left[x_{1,i} U_1 + U_2 + U_3 - U_4 + \left[x_{1,i} U_1 (x_{1,i} U_1 - 2U_2 + 2U_3 + 2U_4) + U_2 (U_2 + 2U_3 - 2U_4) + U_3 (U_3 - 2U_4) + U_4^2 \right]^{1/2} \right]}{U_4 - U_2} \right] \quad (6)$$

where:

$$U_1 = \frac{DC^m}{\ell\gamma^m} \Big|_i P_{v,j} \gamma_{1,i} x_{1,i} P_{v,i} ; U_2 = \frac{DC^m}{\ell\gamma^m} \Big|_i P_{v,j} P_2 \exp \left(-\frac{v_i (P_1 - P_{v,i})}{RT} \right)$$

$$U_3 = \frac{DC^m}{\ell\gamma^m} \Big|_j P_{v,i} \gamma_{1,j} x_{1,j} P_{v,j} ; U_4 = \frac{DC^m}{\ell\gamma^m} \Big|_j P_{v,i} P_2 \exp \left(-\frac{v_j (P_1 - P_{v,j})}{RT} \right)$$

Feed pressure, P_1 , the permeate pressure, P_2 , the vapor pressure, P_v , the molar volume, v , the mole fraction, x , and the temperature, T are entrance data. The activity coefficient of the feed, γ , was determined by NRTL model.

The permeate fluxes J_i and J_j are then calculated from Eq. (3), where the term $DC^m/\ell\gamma^m$, called transport parameter, must be calculated from regression of the experimental data of the permeate flux and of the concentration. Since $DC^m/\ell\gamma^m$ is known, the separation factor, Eq.(5), and the permeate composition, Eq. (6), can be evaluated.

Simulation Results

Simulation studies were carried out in order to: evaluate the model presented by Kataoka et al. (1991) for the new system studied in this work (methyl acetate-water), validate the equation relating the permeate to the feed compositions developed in this work, and build up a methodology and, consequently, a platform to optimise the process in a large scale focus.

The software used here was developed by Torres-Alvarez et al. (2001), which is based on the model presented by Kataoka et al. (1991) as shown above and with the permeation composition equation developed in this work. It makes use of a user-friendly platform to help

the user interaction with the process. The software is written in Visual Fortran 6 language. The experimental data of the permeate flux versus feed methyl acetate composition were presented in the form of graphs by Kujawski (2000) for the separation of the organic mixture methyl acetate (i) – water (j) using a PERVAP-1070 membrane. In the present work, these experimental data were used to regress the transport parameters $DC^m/l\gamma^m$, for components i and j . The resulting values were 43.488 and 1.353 ($\text{mol}/\text{m}^2\text{h}$), respectively. It is important to mention that the experimental data used in this work were never tested with the presented model and, also, that originally the model was developed for other kinds of membrane and system. The influence of the downstream pressure on the permeation rate, considering the transport parameters constant, were also analyzed.

Both, the experimental data and the calculated values of the permeate component fluxes versus the feed methyl acetate composition are presented in Figure 1. The square and the sphere points represent Kujawski (2000) experimental data, whereas the continuous lines represent the data calculated in this work. It can be observed that the model represents quite well the experimental data for water and the representation of methyl acetate is also suitable. As the membrane is methyl acetate-selective, the permeate flux of methyl acetate is greater than of the water flux and the permeate flux of water remains constant in relation to the feed composition. The total flux (water + methyl acetate) tends to increase.

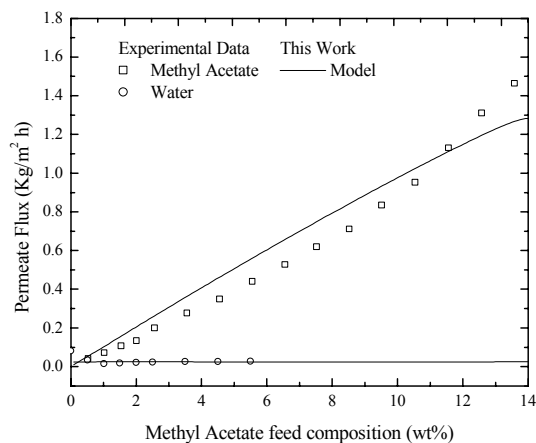


Figure 1. Variation of the permeate flux with feed methyl acetate concentration

In Figure 2, it can be observed that according to the derived equation for the permeate composition, the curve presents a good agreement with the experimental data. Moreover, for high concentrations in the feed (higher than

3% wt), the permeate concentration remains practically constant.

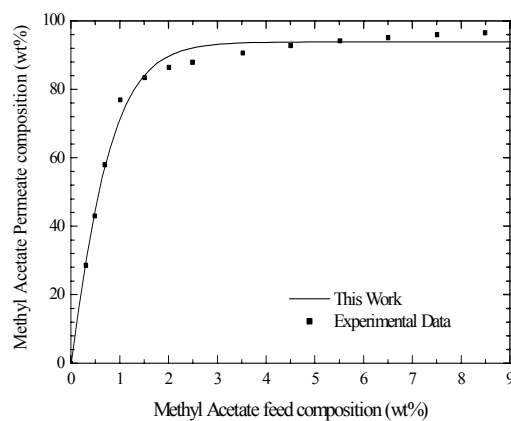


Figure 2. Selectivity Diagram for Methyl Acetate-Water mixture

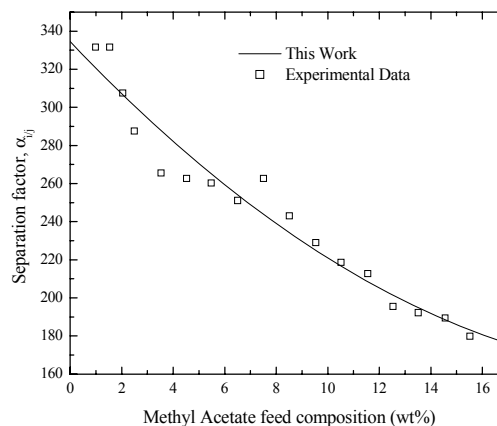


Figure 3. Separation Factor versus feed Methyl Acetate composition $P_2 = 0.1 \text{ KPa}$

The separation factor for the mixture methyl acetate-water with variations in the feed compositions was studied by Kujawski (2000). Considering that the membrane is selective for methyl acetate, the permeation of the most selective component reaches a larger separation when the concentration in the feed is low, while for high concentrations of methyl acetate in the feed, the permeation of the selective component decreases. The

calculated data agree quite well with the experimental data, as can be observed in Figure 3.

The permeate flux behaviours can be seen in relation to the pressure on the permeate side for a fixed feed composition in Figure 4. The profiles show that the total and the methyl acetate fluxes decrease, increasing the permeate pressure, while the water permeation remains almost constant.

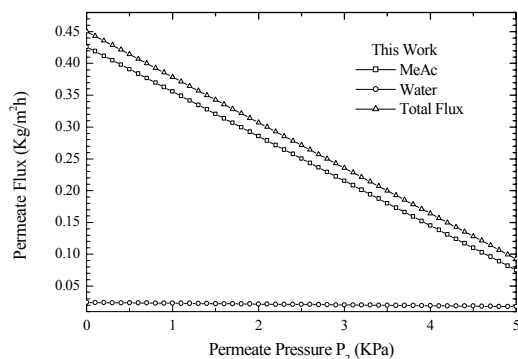


Figure 4. Effect of permeate pressure on the permeate flux ($x_{MeAc} = 5.0\%wt$)

Conclusions

According to the results, it can be concluded that the model represents very well the separation of the mixture methyl acetate-water, using a selective membrane for methyl acetate, mainly considering that, originally, it was developed for other kinds of membrane and system. Also, it is important to consider the analysis related to the feed composition. It was observed that the proposed equation for the methyl acetate composition in the permeate side fits quite well and this depends on the model transport parameter calculation. The influence of the pressure (P_2) on the rate of permeation was analyzed and it was observed that increasing the pressure, the permeation rate decreases. Therefore, for low values of P_2 and low feed methyl acetate concentration, higher will be the permeation rate and the separation factor for methyl acetate.

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