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Short communication

Application of Stefan–Maxwell approach to azeotropic separation by membrane distillation

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Abstract

A multicomponent mass transfer model based on the Stefan–Maxwell formalism is developed to predict membrane distillation performance in separating azeotropic mixtures. The developed model accounts for all coupling interactions between the diffusing species as well as for temperature and concentration polarization effects. The model is validated with previously published experimental data of propionic acid/water azeotropic mixture. The model predicts the effect of the process relevant parameters very well. © 1999 Published by Elsevier Science S.A. All rights reserved.

Keywords: Azeotropic separation; Diffusing species; Membrane distillation; Polarization effects

1. Introduction

The ease of components separation from a liquid mixture via distillation depends on the vapor–liquid equilibrium characteristics of the liquid mixture. Solutions with maximum or minimum azeotropic point reach a state in which boiling does not change the liquid composition. Therefore, azeotropic solutions cannot be separated by conventional distillation. Commercially, vacuum distillation and solvent addition are used to shift the azeotropic point position. Capillary distillation [1], diffusion distillation [2], adsorptive distillation [3], membrane distillation [4], pervaporation [5] and reactive distillation [6] are relatively new proposed techniques to overcome the limitations associated with an azeotrope.

Diffusion distillation and membrane distillation shares the same principles except that, in membrane distillation, a hydrophobic porous membrane is used to separate the feed solution from the condensate. Membrane distillation is a thermally driven process in which the feed solution is warmed to a temperature below its normal boiling point and allowed to pass over one of the membrane surfaces, while the other membrane surface is either directly contacted with a cooling liquid or separated by an air-gap from a cooling plate. Because of the temperature difference, a vapor pressure gradient is created resulting in vapor migration from the high to the low partial pressure side (see Fig. 1). The membrane is not directly involved in the separation but it acts as a physical support for the liquid–vapor interface. The presence of membrane makes the air-gap width more controllable in membrane distillation than it in diffusion distillation. The selectivity of membrane distillation process as well as of diffusion distillation process is not only dependent on vapor–liquid equilibria of the components concerned but also on the differences in their diffusion rates across the membrane and air-gap.

Recently, Udriot et al. [4] reported that by the use of membrane distillation process the azeotropic point of the propionic acid/water system disappeared. A simplified theory based on the Fick's first law was presented to calculate the process selectivity. Temperature and concentration polarization phenomena were not considered in their model. In the authors work, no comparison between experimental and theoretical predictions was made.

This work has aimed at developing a mathematical model to predict the role of membrane distillation in separating azeotropic mixtures. Since the Fickian binary approach, used in the Udriot et al. [4] analysis, does not account for all diffusional interactions between the diffusing species, Stefan–Maxwell formalism is used. Temperature and concentration polarization are considered in the model.

2. Theory

For steady state transfer the molar flux into the liquid condensate phase must equal the flux N_i in the vapor phase.

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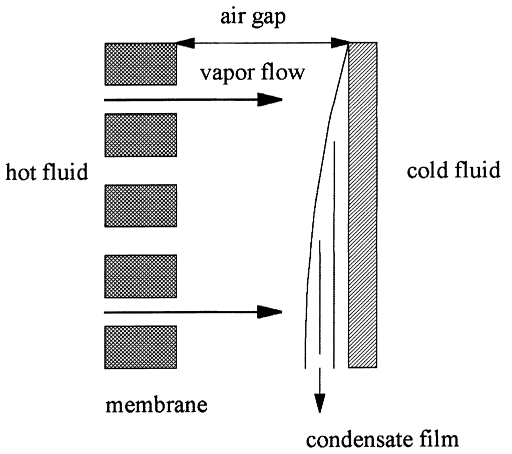

Fig. 1. Schematic drawing of air-gap membrane distillation process.

Therefore, the composition of species i in the permeate is determined by the ratio of the component flux rates:

$$x_i = \frac{N_i}{\sum_{j=1}^{n-1} N_j}, \quad i = 1, n-1. \tag{1}$$

If equilibrium is assumed to prevail at the interfaces, the vapor composition on the evaporation and on the condensation sides may be obtained from

$$y_i = \frac{\gamma_i x_i P_i^0(T)}{P}, \quad i = 1, 2, \ldots, n-1, \tag{2}$$

and the stagnant gas content follows from

$$y_n = 1 - \sum_{i=1}^{n-1} y_i. \tag{3}$$

The activity coefficient γ_i is calculated using Wilson's model and the vapor pressure is calculated using Antoine equation [7].

Since the separation in membrane distillation relies on the difference in volatility and diffusion rates of the concerned components, concentration polarization phenomenon is encountered. Concentration polarization means that the concentration of the slow permeating component at the membrane interface is higher than in the bulk phase, while the opposite is true for the fast permeating component. According to Banat and Simandl [8] the significance of concentration polarization becomes more when the target component that preferentially permeates through the membrane is present in the feed at low concentrations. At steady state the concentration at the membrane interface is

$$x_{im} = x_{ip} - (x_{ip} - x_{ib}) \exp\left[\frac{N_t}{c_t k_{in}}\right], \quad i = 1, \ldots, n-1. \tag{4}$$

The correct description of molecular diffusion in a multicomponent system is given by the Stefan–Maxwell equations, which allow for the diffusional interactions. For one-dimensional steady state transfer in an n-component ideal gas mixture these equations can be written as

$$\frac{dy_i}{d\eta} = RT \sum_{j=1, j\neq i}^{n} \frac{y_i N_j - y_j N_i}{P k_{ij}} = RT \sum_{j=1, j\neq i}^{n} \frac{y_i J_j - y_j J_i}{P k_{ij}},$$
$$i = 1, \cdots, n, \tag{5}$$

where P is the total pressure, R the ideal gas constant, T the average temperature and η is a dimensionless distance given by

$$\eta = \frac{z}{s}, \quad s = \delta\tau + b, \tag{5a}$$

and the binary zero flux mass transfer coefficients by

$$k_{ij} = \frac{D_{ij}}{s}, \quad i \neq j = 1, \ldots, n, \tag{5b}$$

where s is the film thickness, δ the membrane thickness, τ the membrane tortuosity and b is the air-gap width. The vapor phase diffusivity can be estimated using the empirical correlation developed by Fuller et al. [9].

Under steady state conditions, a differential component mass balance along the diffusion path yields

$$\frac{dN_i}{dz} = 0. \tag{6}$$

Thus the molar flux of component i is constant throughout the gas phase from the membrane interface to the cooling surface. The molar fluxes N_i, are made up of diffusive and convective contribution:

$$N_i = J_i + y_i N_t. \tag{7}$$

The matrix-form solution of the Stefan–Maxwell equations, developed by Krishna and Standart [10], gives the following representation of diffusion fluxes:

$$(N) = \frac{P}{RT}[\beta][E_\mathrm{m}][k_{y\mathrm{m}}](y_\mathrm{m} - y_\mathrm{p}), \tag{8}$$

where

$$[k_y] = [R]^{-1}, \tag{8a}$$

and the coefficients R_{ii} and R_{ij} are defined by

$$R_{ii} = \frac{y_i}{k_{in}} + \sum_{k=1, k\neq i}^{n} \frac{y_k}{k_{ik}}, \tag{8b}$$

$$R_{ij} = -y_i\left(\frac{1}{k_{ij}} - \frac{1}{k_{in}}\right). \tag{8c}$$

The correction matrix elements are given by

$$[E_m] = [\Phi][\exp[\Phi] - [I]]^{-1}. \tag{8d}$$

The coefficients Φ_{ij} are defined by

$$\Phi_{ii} = \frac{RT}{P}\left(\frac{N_i}{k_{in}} + \sum_{k=1, k\neq i}^{n} \frac{N_k}{k_{ik}}\right), \tag{8e}$$

$$\Phi_{ij} = -\frac{N_i RT}{P}\left(\frac{1}{k_{ij}} - \frac{1}{k_{in}}\right). \tag{8f}$$

The bootstrap coefficients, β_{ik}, in our case represent the Stefan diffusion coefficients and are given by

$$\beta_{ik} = \delta_{ik} + \frac{y_i}{y_n} \quad (N_n = 0), \tag{8g}$$

where δ_{ik} is the Kronecker delta.

The tortuosity and the membrane thickness were taken into account in the calculation of the diffusion path length. To account for the membrane porosity, the effective flux is

$$(N)_{\mathrm{e}} = \varepsilon(N). \tag{9}$$

For the calculations of the permeate composition by means of the VLE equations, it is essential that the interfacial temperatures of the feed and the condensation surface be known, specifically, at the membrane and condensation surface interfaces. These temperatures can be determined by energy flux calculations. The stages of heat transfer in membrane distillation include heat flux from the feed bulk to the membrane surface, from the membrane surface to the condensation interface and from the condensate interface to the coolant bulk temperature. Performing energy balances on these stages gives that the temperature at the membrane interface is [11]:

$$T_{\mathrm{m}} = T_{\mathrm{b}} - \frac{U_T}{h_{\mathrm{h}}}\left((T_{\mathrm{b}} - T_{\mathrm{c}}) + \frac{\sum N_{i\mathrm{e}}\lambda_i}{h^{\bullet}}\right), \tag{10}$$

and the temperature at the condensation surface interface is

$$T_{\mathrm{p}} = T_{\mathrm{c}} + \frac{U_T}{h_{\mathrm{c}}}\left((T_{\mathrm{b}} - T_{\mathrm{c}}) + \frac{\sum N_{i\mathrm{e}}\lambda_i}{h^{\bullet}}\right), \tag{11}$$

where

$$U_T = \frac{1}{\frac{1}{h_{\mathrm{h}}} + \frac{1}{h^{\bullet}} + \frac{1}{h_{\mathrm{c}}}}. \tag{12}$$

Expressions for h_{c}, h_{h}, and $h^{\bullet}$ can be found elsewhere [11].

The exact solution of Krishna and Standart [10] requires a computer solution for the component molar fluxes. Therefore, an iterative solution procedure, adopting the Newton–Raphson iteration technique, is used to solve the coupled mass and energy equations presented above.

3. Results and discussion

Experimental data reported by Udriot et al. [4] for the azeotropic mixture of propionic acid/water is used to test the model presented in this work. The model predictions are compared to the available experimental data for the effect of feed composition, feed temperature and air-gap width.

3.1. Effect of feed composition

Experimental data, model predictions and vapor–liquid equilibrium data, in the form of an *x–y* diagram are shown in Fig. 2. As demonstrated in the figure the presence of an air-gap eliminates the azeotropic point that exists if the system is only governed by the VLE relationship. This is because the separation effect in membrane distillation is not only based on the VLE of the components concerned but also on the difference in their relative rates of diffusion. As the diffusivity of water in air is higher than the propionic acid diffusivity, water will be enriched in the distillate more than what is expected by the VLE. Accordingly, the azeotropic point is completely eliminated.

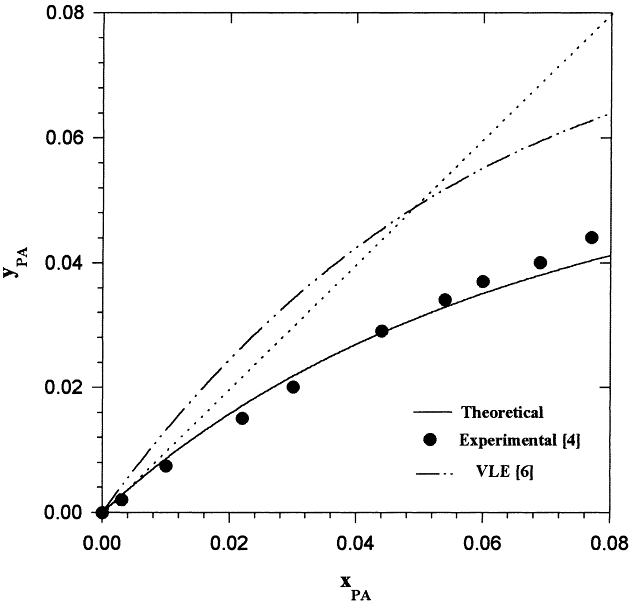

Fig. 2. Effect of propionic acid composition on the permeate composition (T_{h} =60°C, T_{c} =30°C, air-gap=4 mm).

Fig. 2 clearly shows that the model developed in this work closely follows the experimental data. The good fit between the experimental data and the theoretical results is partly due to the account for all coupling interactions between the diffusing species in the model and partly due to the consideration of both temperature and concentration polarization phenomena.

3.2. Effect of feed temperature

Fig. 3 compares the experimental values with those from the model for the effect of feed temperature on propionic acid selectivity. The selectivity as defined by Udriot et al. [4] is

$$\alpha = \frac{x_P}{x_{\mathrm{b}}}. \tag{13}$$

As noticed in the figure, the selectivity of propionic acid is slightly sensitive to the change in the feed temperature. Udriot et al. [4] attributed this to the offset effect of temperature polarization which becomes more pronounced at higher feed temperatures. This predicted behavior agrees well with the experimental data.

3.3. Effect of air-gap width

In Fig. 4, the experimental and calculated azeotropic selectivities are plotted against the air-gap width. The model

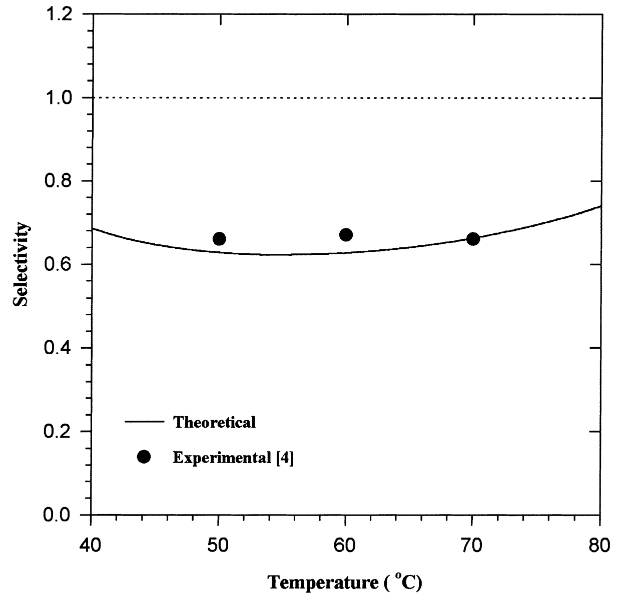

Fig. 3. Effect of feed temperature on propionic acid selectivity (T_c=30°C, air-gap=4 mm, W_{PA}=17.7 wt%).

fairly agrees with the available experimental data. As illustrated in Fig. 4, increasing the air-gap width from 1 to 10 mm does not significantly affect the propionic acid selectivity. On the contrary, the permeate flux is inversely proportional to the gap width as reported by Udriot et al. [4].

4. Conclusions

A multicomponent Stefan–Maxwell-based mathematical model has been developed and validated by comparison with the available literature experimental data for separating propionic acid/water azeotropic mixture by membrane distillation. The model is fully predictive in the sense that no tuning parameters are used. Temperature and concentration polarization effects are included in the model. The model predictions are validated with experimental data for the effect of feed composition, feed temperature, and air-gap width. The model agrees well with the experimental data. In conclusion, the model can be used for further investigation and improvement of the membrane distillation process.

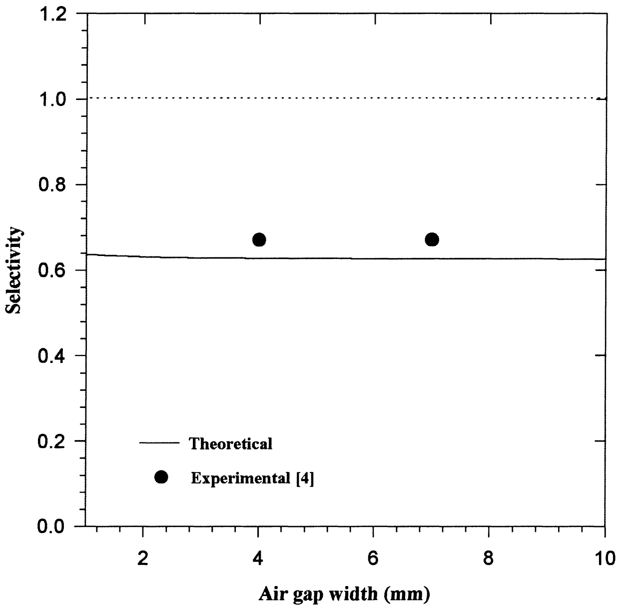

Fig. 4. Effect of air-gap width on propionic acid selectivity (T_h=60°C, T_c=30°C, W_{PA}=17.7 wt%).

5. Nomenclature

b	air-gap thickness (m)
c	molar concentration (mol/m^3)
D	vapor phase diffusivity (m^2/s)
h	heat transfer coefficient (W/m^2 s)
$[I]$	identity matrix (dimensionless)
J	molar diffusion flux (mol/m^2 s)
k	mass transfer coefficient (m/s)
$[k_y]$	matrix of zero flux mass transfer coefficients (m/s)
N	molar flux (mol/m^2 s)
P	total pressure (Pa)
P^0	vapor pressure (Pa)
R	universal gas constant (J/mol K)
$[R]$	matrix defined by Eqs. (8b) and (8c) (m/s)
s	film thickness (m)
T	absolute temperature (K)
U	overall heat transfer coefficient (W/m^2 s)
x	mole fraction in the liquid phase (dimensionless)
y	mole fraction in the vapor phase (dimensionless)
z	distance (m)

Greek Letters

α	selectivity (dimensionless)
$[\beta]$	matrix of bootstrap coefficients (dimensionless)
γ	activity coefficient (dimensionless)
δ	membrane thickness (m)
δ_{ik}	Kronecker delta, 1 if i=k, 0 if $i \neq k$ (dimensionless)
ε	porosity (dimensionless)
η	dimensionless distance (dimensionless)
λ	latent heat of vaporization (J/mol)
$[E]$	matrix of high flux correction factors (dimensionless)
τ	tortuosity (dimensionless)
$[\Phi]$	matrix of mass transfer rate factors (dimensionless)

Subscripts and superscripts

b	bulk
c	cooling plate
e	effective
h	hot region
i,j,k,n	indices denoting component number

m	membrane
p	cooling plate side
T	total
*	air-gap region

Matrix notation

( )	column matrix
[ ]	square matrix
$[\ ]^{-1}$	inverse of a square matrix

References

[1] F. Abu Al-Rub, J. Akili, R. Datta, Distillation of binary mixtures with capillary porous plates, Sep. Sci. Technol. 33 (1998) 10–15.

[2] D. Fullarton, E.U. Schlunder, Diffusion distillation: a new separation process for azeotropic mixtures, Chem. Eng. Fundam. 2 (1983) 53.

[3] F. Abu Al-Rub, Distillation in capillary porous media for separation of biomass ethanol–water mixture, Ph.D. Thesis, The University of Iowa, 1994.

[4] H. Udriot, A. Araque, U. von Stockar, Azeotropic mixtures may be broken by membrane distillation, Chem. Eng. J. 54 (1994) 87.

[5] C.H. Gooding, F.J. Bahouth, Membrane-aided distillation of azeotropic solutions, Chem. Eng. Commun. 35 (1985) 267.

[6] Daniel L. Terrill, Lauren F. Sylvestre, Michael F. Doherty, Separation of closely boiling mixtures by reactive distillation. 1. Theory, Ind. Eng. Process Des. Dev. 24 (1985) 1062.

[7] J. Gmehling, U. Onken, Vapor–Liquid Equilibrium Data Collection (Aqueous-Organic Systems), vol. 1, Dechema, Frankfurt, 1977.

[8] F. Banat, J. Simandl, Removal of benzene traces from contaminated water by vacuum membrane distillation, Chem. Eng. Sci. 51 (1996) 1257.

[9] E.N. Fuller, P.D. Schettler, J.C. Giddings, A new method for prediction of binary phase diffusion coefficients, Ind. Eng. Chem. 58 (1966) 19.

[10] R. Krishna, G.L. Standart, A multicomponent film model incorporating a general matrix method of solution to the Maxwell–Stefan equations, AIChE J. 22 (1976) 283.

[11] F. Banat, J. Simandl, Desalination by membrane distillation: a parametric study, Sep. Sci. Technol. 33 (1998) 201.