

Modeling of volatile organic compounds removal from water by pervaporation process

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Abstract

Pervaporation is a membrane technology utilizing a dense non-porous homogeneous polymeric film as a selective separation barrier. In recent years, pervaporation using dense membranes has emerged as a promising remediation method for trace organic removal from dilute aqueous solutions. The mathematical model commonly used to determine liquid and polymer phase resistances is the resistance-in-series model. In most studies the concentration or pressure gradient is considered as the driving force. In the present study a model was developed based on resistance-in-series model considering the chemical potential gradient as the true driving force in which the total resistance to mass transfer is defined as the sum of the liquid, membrane and vapor resistance. The model was validated by the experimental data available in the literature for various organic solutions and different membranes including PDMS and composite membranes. The results obtained show that the liquid phase boundary layer plays a significant role in overall mass transport for all cases under study and ignoring this contribution could lead to a significant error in design and scale-up applications. It was also shown that the flux of permeating component is unaffected by the downstream pressure at low pressures up to 10 mmHg which indicates that for such systems the operating condition can be economically designed based on a moderate vacuum at downstream side instead of using a full expensive vacuum system.

Keywords: VOCs; Membrane; Pervaporation; Mass transfer; PDMS

1. Introduction

Water is a vital substance for human and other living creatures. Shortage of water in major parts of the world makes necessary the investigation on

water treatment and recycling systems. Volatile organic compounds (VOCs) are a category of important contaminants for drinking water sources and industrial wastewater. Presence of these substances in a certain amount in water can jeopardize the life of living creatures. At present, different processes such as biological treatment, adsorption

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by carbon actives, and air stripping in packed columns are used at industrial scale for VOCs removal. However, these methods are subjected to some limitations [1]. Carbon adsorption process is economical only at low VOC concentration and the need for frequent regeneration of carbon bed makes the process unattractive for the water with high VOCs concentration. Deactivation of microorganism due to contact with VOCs contaminants during a biological treatment and the lack of precise knowledge about its mechanism make the process operationally complex. Air stripping has a limited ability for removal of VOCs especially for low Henry's constant compounds. Pervaporation is a membrane technology utilizing a dense non-porous homogeneous polymeric film as a selective separation barrier. In recent years, pervaporation using dense membranes has emerged as a promising treatment method for the removal of trace volatile organic compounds from dilute aqueous solutions.

The majority of researches conducted to date on this process have been focused to characterize the suitable membranes for the purpose of VOCs removal from water as toxicants. In this process, organophilic dense membranes are usually used for the separation of trace concentration VOCs from water. It is well known from previous experimental and theoretical investigation that the overall transport of VOCs from liquid phase at the upstream side to vapor downstream side is not exclusively controlled by the membrane resistance. The mass transport of solutes from bulk solution to the liquid–membrane interface may be the rate controlling step in overall transport in very dilute solutions [2–7]. This phenomenon has been recognized as concentration polarization effect in the literature. This is unlike the separation of concentrated solutions where the liquid boundary layer resistance may have a lesser significance. In these situations, the interaction between different penetrants in the membrane plays a great role, the matter which is not remarkable in removal of trace concentration VOCs.

The mathematical models are commonly used to describe the transport of low concentration solutes in water through the membrane are based on the resistance-in-series types. In these models, the resistance in the liquid phase boundary layer and the membrane phase is considered in series, while the resistance at the downstream vapor phase is ignored due to high vacuum applied. However, in a state-of-the-art article by Ji et al. [1], it was clearly shown that at high downstream pressure between 15 mmHg to solute saturation vapor pressure the resistance in vapor phase may become significant. In most of resistance-in-series models presented to date, the concentration or pressure gradient is considered as the driving force for the transport of solutes through the membrane. In the present study, a new model is developed based on resistance in series considering the chemical potential gradient as the true driving forces in which the overall resistance to mass transport is considered as the sum of individual resistances in liquid, membrane and vapor phases. The advantage of considering the chemical potential gradient as the main driving force in this study, is theoretically rationalized by the fact that the thermodynamic equilibrium at both liquid–membrane and vapor–membrane interfaces is well described by the equality in chemical potential of permeating component (rather than the equality of concentration). The methodology for recovery of the transport model parameters is discussed and the contribution of each individual resistance to the overall resistance against mass transport is quantitatively evaluated using the experimental data available in the literature for several solutes-membrane systems.

2. Model description and simplifying assumption

The model proposed herein, is subjected to the following assumption:

- (1) The permeability (transport coefficient) in membrane phase is considered to be constant due to dilute system.

- (2) Coupling of fluxes between solute and solvent is neglected.
- (3) The process is assumed to be isothermal. It means that the temperature polarization in the liquid boundary layer due to evaporation is negligible.
- (4) As usual in all solution-diffusion models, the pressure across the membrane is assumed to be constant and equal to liquid phase pressure.
- (5) Finally, as usual, it is assumed that at both liquid–membrane and membrane–vapor interfaces, the thermodynamic equilibrium are instantaneously established.

Fig. 1 depicts schematically the transport process in which chemical potentials of diffusing solutes, *i*, at bulk phases and interfaces were clearly shown.

We start with description of molar flux of penetrating component, *i*, at liquid phase:

$$N_i = k_l(\mu_{i,l} - \mu_{i,l}^*) \tag{1}$$

From the above equation, the liquid phase resistance is defined as

$$R_{liq} = \frac{\Delta\mu_{i,l}}{N_i} = \frac{1}{k_l} \tag{2}$$

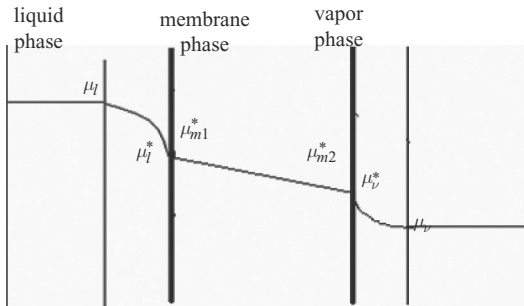


Fig. 1. Schematic diagram of the transport process with presentation of driving force.

The membrane phase molar flux and resistance is written as:

$$N_i = \frac{L_m}{t}(\mu_{i,m1}^* - \mu_{i,m2}^*) \tag{3}$$

$$R_{mem} = \frac{\Delta\mu_{i,m}}{N_i} = \frac{t}{L_m} \tag{4}$$

where *t* denotes membrane thickness.

Similarly, the molar flux and resistance for vapor phase:

$$N_i = k_v(\mu_{i,v}^* - \mu_{i,v}) \tag{5}$$

$$R_{vap} = \frac{\Delta\mu_{i,v}}{N_i} = \frac{1}{k_v} \tag{6}$$

The molar flux also can be defined in terms of overall resistance using an overall driving force:

$$N_i = \frac{\Delta\mu_{i,t}}{R_t} \tag{7}$$

where *R_t* represents the total combined resistance and defined as:

$$R_t = \sum R = \frac{1}{k_l} + \frac{t}{L_m} + \frac{1}{k_v} \tag{8}$$

At very low pressure (high vacuum) applied at the downstream side, the vapor phase resistance can be safely neglected, thus reducing Eq. (8) to

$$R_t = \sum R = \frac{1}{k_l} + \frac{t}{L_m} \tag{9}$$

To calculate the overall driving force in the process (chemical potential gradient), which is the sum of individual driving force in the liquid, membrane and vapor phase, we can use the last assumption made in our modeling:

$$\begin{aligned} \mu_{i,l}^* &= \mu_{i,m1}^* \\ \mu_{i,v}^* &= \mu_{i,m2}^* \end{aligned} \tag{10}$$

This leads to a simple expression for the overall driving force for the whole process:

$$N_i = \frac{\Delta\mu_{i,l}}{R_i} = \frac{\mu_{i,l} - \mu_{i,v}}{R_i} \quad (11)$$

where, $\mu_{i,l}$ and $\mu_{i,v}$, denote the chemical potential of diffusing component i , at the liquid and vapor bulk phases.

According to classical thermodynamic definition, the chemical potential of component i , in a specific phase α , $\mu_{i,\alpha}$, is expressed as [8]:

$$\mu_{i,\alpha} = \mu_{i,\text{ref}} + RT \ln a_{i,\alpha} + \int_{p_{\text{ref}}}^{p_i} \bar{\nu}_i dp - \int_{T_{\text{ref}}}^{T_i} S_i dT \quad (12)$$

where $\mu_{i,\text{ref}}$ is the chemical potential at reference pressure (i.e. saturation pressure). Assuming a constant temperature for whole process, the last term in the above equation can be dropped:

$$\mu_{i,\alpha} = \mu_{i,\text{ref}} + RT \ln a_{i,\alpha} + \bar{\nu}_i(p - p_{\text{ref}})$$

Further simplification can be made in the above equation, considering that the term $\bar{\nu}_i(p - p_{\text{ref}})$ is negligible in comparison to the term $RT \ln a_{i,\alpha}$. Knowing that the activity for the liquid phase is, $a_{i,\alpha} = \gamma_{i,\alpha} \cdot x_i$ and for the vapor phase, $a_i = p_i/p_i^*$, the overall chemical potential difference, $\mu_{i,l} - \mu_{i,v}$, is given by

$$\mu_{i,l} - \mu_{i,v} = RT \ln \left(\frac{\gamma_{i,l} x_i P_i^{\text{sat}}}{y_i P} \right) \quad (13)$$

Combining the relationship (7) and (14) leads to:

$$N_i = K^0 RT \ln \left(\frac{\gamma_{i,l} x_i P_i^{\text{sat}}}{y_i P} \right) \quad (14)$$

or

$$N_i = \frac{\Delta\mu_{i,l}}{R_i} = K^0 RT (\ln(\gamma_{i,l} x_i P_i^{\text{sat}}) - \ln(y_i P)) \quad (15)$$

where K^0 is the inverse of overall resistance and is called the overall mass transfer coefficient.

3. Model parameters estimation

Plotting the molar flux of permeating component against $\ln(\gamma_{i,l} x_i P_i^{\text{sat}})$, the overall mass transport coefficient can be obtained from the slope and vapor phase composition from intercept of the resulting line based on Eq. (15). By reproducing of these results for a membrane with different thickness and plotting the variation of overall resistance vs. membrane thickness, the individual mass transfer coefficient for liquid and membrane phase (k_l and L_m) can be estimated from intercept and slope of the linear plot, respectively (based on Eq. (9)).

Two sets of experimental data are required to estimate the model parameters: (1) variation of permeating component flux with VOCs concentration in liquid feed mixture and (2) variation of permeating component flux with membrane thickness. The data available in the literature for separation of toluene, trichloroethane and methylene chloride by PDMS [1] and separation of toluene by a kind of composite membrane [9] were used to recover the model parameters.

Fig. 2 shows, a linear plot of component flux, N_p , against $\ln(\gamma_{i,l} x_i P_i^{\text{sat}})$ for various VOCs-membrane systems. Since the concentration of solutes is very low in water, the infinite dilution activity coefficients [10–11] were used in calculations. All figures indicate almost a linear relationship between the component flux and the overall driving force. The parameter $K^0 RT$ was obtained from the slope of the resultant line for each case.

Then, the variation of overall resistance $R_i = 1/K^0 RT$ with membrane thickness were plotted for each case to determine the individual liquid and membrane phase mass transfer coefficients. Fig. 3 shows these plots for various VOC-membrane systems. Table 1 also summarizes the values obtained for the liquid and membrane phase mass transfer coefficients.

The values obtained for individual mass transfer coefficients reveal that the variation in liquid phase values is less than those obtained for membrane phase. This can be justified by the

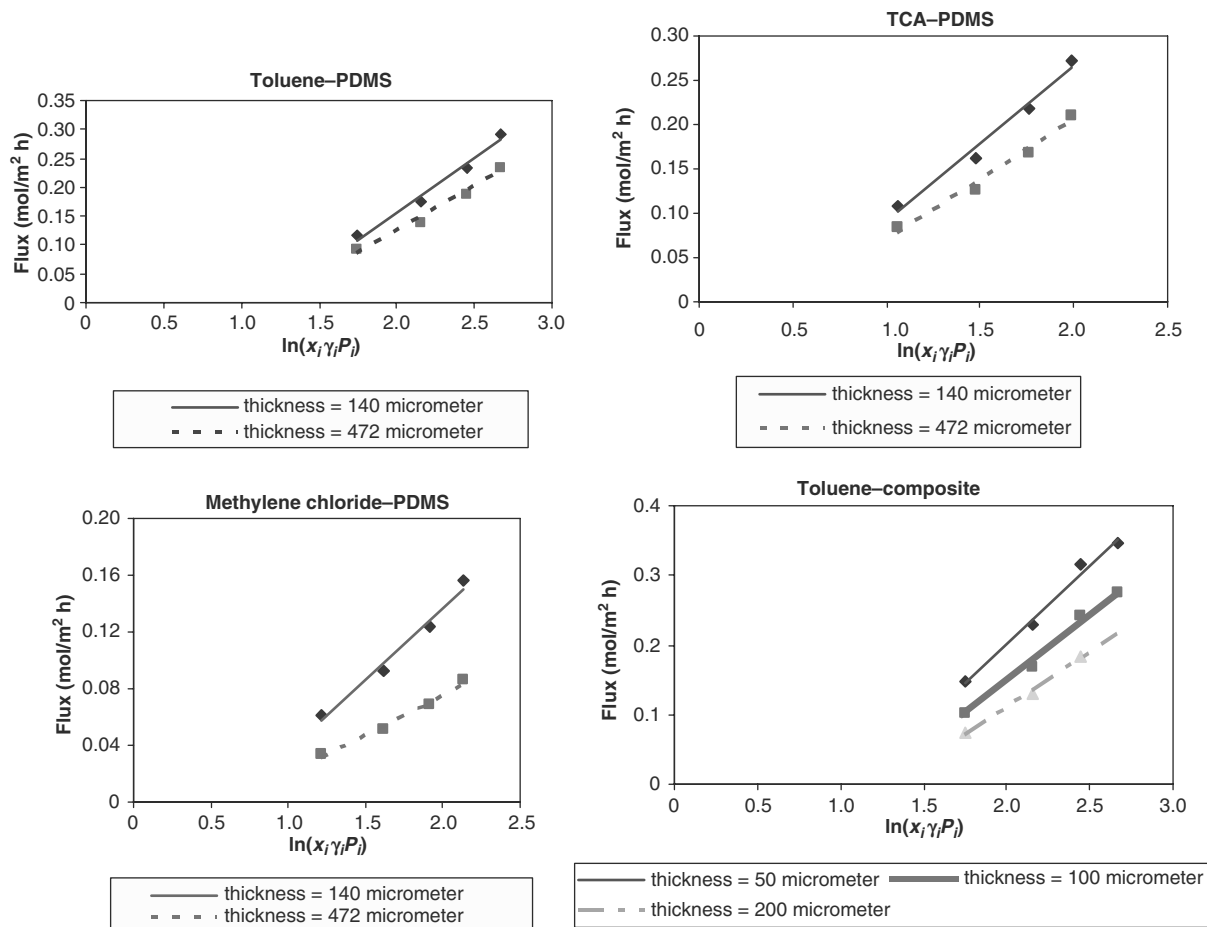


Fig. 2. Plots of component flux for various VOCs-membrane systems.

fact that the liquid phase mass transfer coefficient is independent of membrane thickness and type of solutes and is only a function of hydrodynamic flow in the liquid boundary layer while, membrane phase coefficient depends on the membrane characteristics and the affinity between polymer and solutes.

4. Results and discussion

4.1. Concentration polarization and its role in transport process

Many studies acknowledge that the resistance mass transfer in liquid boundary layer plays a

significant role in overall transport [4–5]. To quantify this contribution, we have used the liquid mass transfer coefficient (k_l) to estimate the liquid concentration in liquid-membrane interface (x_i^*). This can be calculated by considering the relationship between the steady state flux and the driving force in the liquid phase:

$$N_i = k_l(\mu_{i,l} - \mu_{i,l}^*)$$

$$N_i = k_l RT \ln(x_i/x_i^*) \quad (16)$$

The mole fraction of solutes in toluene-PDMS system at liquid bulk phase (x_i) as well as the

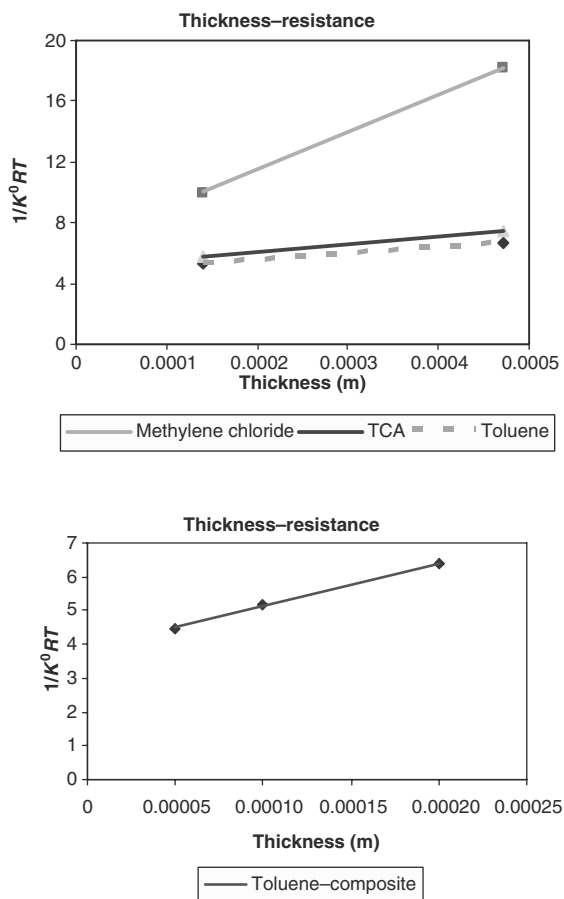


Fig. 3. Plot of the overall resistance vs. membrane thickness for determining liquid and membrane phase mass transfer coefficient.

Table 1
Liquid and membrane phase mass transfer coefficient for various VOC-membrane systems

VOC-membrane	$L_m \times 10^7$ (mol ² /h m J)	$K_1 \times 10^3$ (mol ² /h m ² J)
Toluene–PDMS	4.11	0.35
Methylene chloride–PDMS	0.67	0.255
Trichloroethane–PDMS	3.26	0.333
Toluene–composite	1.32	0.54

Table 2
Concentration of toluene at liquid bulk phase and liquid–membrane interface in a 140 μm PDMS

$x \times 10^{-5}$	J (kg/m ² h)	$x_i^* \times 10^{-5}$
1.93	1.9410	0.995
2.91	2.5304	1.15
3.89	3.4580	1.12
4.87	4.7275	1.03

calculated mole fraction at the liquid–membrane interface using Eq. (16) are included in Table 2.

The values of table clearly shows that interface concentrations are almost between 1/4 to 1/2 of bulk phase concentrations which indicate formation of a strong concentration polarization in liquid phase adjacent to the membrane interface. The role of boundary layer resistance can be alternatively quantified by calculating the contribution of liquid phase resistance to the overall resistance

$$\left(\frac{1/k_l}{1/k_l + t/L_m} \right).$$

This calculation was made for all VOSs–PDMS and toluene–composite systems are shown in Table 3.

The calculated values denote that in all cases under study, mass transfer of solute from liquid bulk phase to membrane interface is the rate controlling step in the overall transport process.

Table 3
Fraction of liquid phase resistance from total resistance

Solute	Thickness of PDMS		
	472 μm	140 μm	
Toluene	0.85	0.95	
Trichloroethane	0.67	0.87	
Methylene chloride	0.35	0.65	
	Thickness of composite membrane		
	200 μm	100 μm	50 μm
Toluene	0.54	0.7	0.83

Ignoring this effect and designing the separation system exclusively based on membrane resistance can lead to erroneous results. However, for design purposes the role of liquid boundary layer should be reduced to improve the permeation rate. This can be achieved by means of a suitable flow pattern, applying a temperature field, or designing a vibrating pervaporation module. In a recent article, Vane and Alvarez [12] reported that a small vibration amplitude yielded remarkable performance gains on their commercial plant.

4.2. Concentration of solute at membrane phase

Calculation of solute concentration in membrane at the liquid–membrane interface allows having an estimation about possible transport mechanism in membrane phase, whether sorption or diffusion is predominant factor. To do this calculation, a thermodynamic model is required to relate the concentration of solute at liquid phase to the concentration of solute in membrane phase at the liquid–membrane phase. The Flory–Huggins model is known to be capable to describe the sorption of VOCs in dense polymer membranes such as PDMS [13]. This model is given for a single solute:

$$\ln a_s = \ln \Phi_s + \Phi_p + \chi \Phi_p \quad (17)$$

where χ is the enthalpy interaction parameter in Flory–Huggins model which was found from literature [14] for some solute-PDMS systems.

However, for a very dilute system, the Henry's law can be used as an alternative for estimation of the concentration in membrane phase from liquid phase activity at the interface. The Henry's equilibrium constant can be recovered from Flory–Huggins model based on the following procedure [15]:

$$H_i = \lim_{\Phi_i \rightarrow 0} \left(\frac{a_i}{\Phi_i} \right) = \exp[(1 - \Phi_i) + \chi(1 - \Phi_i)^2] = \exp(1 + \chi) \quad (18)$$

Table 4 shows the interfacial concentration of toluene and trichloroethane in PDMS membrane at a constant liquid feed concentration of $C = 1$ mol/L. The higher value of Φ_i for toluene in PDMS justifies the higher flux for toluene which is in agreement with the results reported by Peng et al. [16] about a faster permeation of toluene in PDMS compared to other solutes.

4.3. Effect of downstream pressure

Downstream pressure (vacuum) is a key factor in permeation rate in the pervaporation process. With an increase in downstream pressure the flux of permeating component normally decreases due to the reduction of effective driving force across the membrane and approaches to zero at component saturation pressure. However, an increase in permeation rate by employing a high vacuum in downstream side is accomplished

Table 4
Interfacial concentration in membrane phase

Solute	Concentration			
	Interface (liq–mem)		Interface (mem–vap)	
	Φ_i^S	$C_i^S \times 10^4$ (mol/cm ³)	Φ_i^S	$C_i^S \times 10^4$ (mol/cm ³)
Toluene	0.038	3.58	0.022	2.49
Trichloroethane	0.0014	0.141	0.00126	0.127

Table 5
Variation of molar flux with downstream pressure for different VOCs–PDMS systems, membrane thickness = 140 μm

P (mmHg)	Molar flux (mol/m ² h)		
	Toluene	Trichloroethane	Methylene chloride
0.12	0.1369	0.1146	0.0659
1.54	0.1332	0.1138	0.0648
3.42	0.1315	0.1117	0.0644
5.88	0.1182	0.1116	0.0566
9.75	0.1110	0.1058	0.0505

in expense of high operation cost. Therefore, a general tendency exists in industry, for employment of a moderate vacuum. To demonstrate the effect of downstream pressure, the permeation rate of different solutes through PDMS membrane with a thickness of 140 μm and feed concentration of 1 mol/L have been calculated from literature data [1] and are shown in Table 5. The values obtained show that the flux of a permeating component is marginally affected by the downstream pressure up to 10 mmHg. Consequently, it is not necessary to employ full vacuum to increase the flux. However, the level of pressure up to which the flux remains unaffected may vary for other solute-polymer systems. It should be also noted that the insignificance of downstream pressure is limited to level of 10 mmHg and the permeation flux certainly decreases as we approach the solute saturation pressure. Unfortunately, due to lack of data for fluxes in higher pressures, a complete evaluation could not be achieved.

5. Conclusion

In this study a mathematical model was developed based on resistance-in-series using chemical potential as true driving force which takes into account the membrane phase as well as adjacent

liquid boundary layer resistance. A simple expression was derived for overall driving force based on easily accessible bulk phase properties. The method of model parameter estimation was explained. The experimental data available in the literature for various organic solutions and different membranes including PDMS and a kind of composite membrane were used to identify rate controlling step in overall transport. The results obtained reveal that the liquid phase boundary layer plays a significant rule in overall mass transport for all cases under study and ignoring this contribution could lead to a significant error in design and scale-up applications. The interfacial concentrations at both sides of membrane interface were found using a thermodynamic model which justifies a faster permeation of some solutes such as toluene across the membrane is due to their higher solubilities. It was also shown that the flux of permeating component is unaffected by the downstream pressure at low pressures up to 10 mmHg which indicates for such systems the operating condition can be economically designed based on a moderate vacuum at downstream side instead of using a full expensive vacuum system.

Nomenclature

a_i	activity of i in liquid (–)
C_i	molar concentration of i in liquid (mol/m ³)
k_l	liquid phase mass transfer coefficient (mol ² /h m ² J)
k_v	vapor phase mass transfer coefficient (mol ² /h m ² J)
K^o	overall mass transfer coefficient (mol ² /h m ² J)
L_m	phase mass transfer coefficient (mol ² /h m J)
N_i	molar flux of i (mol/m ² h)
R_{liq}	liquid phase resistance (h m ² J/mol ²)
R_{vap}	vapor phase resistance (h m J/mol ²)
R_{mem}	membrane phase resistance (h m J/mol ²)
R_t	overall resistance (h m ² J/mol ²)
P	pressure (mmHg)

P_i^{sat}	saturation pressure (mmHg)
T	temperature (K)
x_i	mole fraction of i in bulk liquid (–)
x_i^*	mole fraction of i in liquid at membrane interface (–)
y_i	mole fraction of i in vapor (–)

Greek symbols

$\mu_{i,l}$	chemical potential of i in liquid phase (J/mol)
$\mu_{i,m}$	chemical potential of i in membrane phase (J/mol)
$\mu_{i,v}$	chemical potential of i in vapor phase (J/mol)
γ_i	activity coefficient in liquid (–)
ϕ_i	volume fraction of i in membrane (–)

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