Effect of Feed Concentration on Membrane's Diffusivity in Pervaporation Dehydration Ethylene Glycol and Water Binary Mixture

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Abstract: Diffusion coefficient of a component provides insightful information on the mobility of a component in the membrane. In this study, the diffusion coefficient of water and ethylene glycol in the pervaporation dehydration of ethylene glycol and water binary mixture using a buckypaper supported ionic liquid membrane (BP-SILM-70) was estimated using the modified Maxwell-Stefan equation. The effect of variation in feed concentration on the diffusion coefficient was studied. It is noticed that the diffusion coefficients for water and ethylene glycol were increased with increasing feed concentration of water. Also, it is interesting to note that the relation between the diffusion coefficient of water and ethylene glycol obtained using the modified Maxwell-Stefan equation can be correlated with the feed concentration using an exponential factor relation.

Key words: Pervaporation, modified Mawell-Stefan equation, diffusion coefficient, supported ionic liquid membrane, buckypaper, concentration

INTRODUCTION

As one of the membrane separation processes, pervaporation has been recognized for its effectiveness in separation of liquid mixtures attributed to its unique separation characteristic based on the chemical interactions between components and membrane. The driving force for permeation is supplied by a chemical activity difference between upstream and downstream sides of the membrane. It has been well established that the permeation of components across the membrane in the pervaporation process consist of three fundamental steps (Lonsdale, 1982) selective sorption of component from feed system into the membrane, diffusion of component through the membrane and desorption of the component to the vapour phase on the downstream side of the membrane.

Feed concentration is one of the operating parameters that have prominent effect on pervaporation performance. Most of the researchers observed that variation in feed concentration significantly influence the membrane's pervaporation performance (Cascon and Choudhari, 2013; Hu *et al.*, 2012). This can be due to the fact that the concentration gradient incurred by the various feed concentration would alter the solubility and diffusivity of a component in the membrane. The

alteration of the solubility in correspond to the variation of feed concentration can be experimentally analysed via. a liquid sorption study while the diffusivity can be analysed with a diffusion coefficient. The diffusion coefficient is usually determined through either experimental work based on second Fick's law of diffusion (Ghosh *et al.*, 2006) or calculation using well-established mathematical models (Mafi *et al.*, 2012; Imbrogno and Belfort, 2016; Nigiz and Hilmioglu, 2016). Nonetheless, calculation of diffusion coefficient using mathematical models is more preferable since it does not involve tedious and complicated experimental work. Maxwell-Stefan equation is one of the commonly used mathematical model for pervaporation process (Leppajarvi *et al.*, 2013; Zhang *et al.*, 2008; Izak *et al.*, 2003). The Maxwell-Stefan theory combined the solution-diffusion model and the influence of coupled diffusion. It regards the transport of components through a membrane is affected by collisions among molecules which forms a friction force to initiate the movement of the component in the membrane (Izak *et al.*, 2003).

In our previous study (Ong and Tan, 2015), a buckypaper supported ionic liquid (BP-SILM-70) was successfully applied in the pervaporation dehydration of ethylene glycol aqueous solutions at different operating parameters condition. In this study, it is aimed to elucidate

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the diffusivity in the BP-SILM-70 at different feed concentration using modified Maxwell-Stefan equation. The obtained diffusion coefficient would explain the mass transport behaviour of each component at various feed concentration which alter the pervaporation performance of BP-SILM-70.

Theory: The mathematical model that describes the transport phenomenon in the pervaporation process using BP-SILM was used according to the following assumptions:

- The mass transport that takes place in the membrane obeys the solution-diffusion mechanism
- The pervaporation process is under an isothermal condition
- The solvent sorption in the membrane is at equilibrium with the feed mixture
- The diffusion only occurs in the trans-membrane direction

Estimation of the sorption concentration in membrane: The concentration of each component in the membrane at equilibrium is assumed proportional to its activity in the outer surface adjacent to the membrane interface and the weight fraction of the component sorbed in BP-SILM-70, w'_F was calculated using:

$$w'_F = K_i \times a_{iF} \tag{1}$$

where, K_i is a solubility coefficient that dependent on the activity of the component a_i. The K_i was estimated based on the empirical equation proposed by Rautenbach and Albretch:

$$K_i = s_1 \times \left[1 + \left(\frac{s_1}{s_2} - 1 \right) a_i^m \right] \tag{2}$$

where, s_1, s_2 and m are adjustable parameters which have to be fitted to the experimental sorption data. Meanwhile, the activity a_i is calculated using the following Eq. 3:

$$a_i = \gamma x_i \tag{3}$$

Where:
x_i = The mole fraction of component i
γ = The activity coefficient of the component

The γ value for each component was estimated using an xlUNIFAC Version 1.0 excel file.

Modified Maxwell-Stefan equation: The modified Maxwell-Stefan equation was proposed by Heintz and Stephan to adapt the Maxwell-Stefan approach in pervaporation process as follow:

$$J_i = D_{iM} \left(\frac{w'_i D_{jM} + D_{ij}}{D_{ij} + w'_i D_{jM} + w'_j D_{iM}} \right) \bar{\rho}_M \frac{\Delta w'_i}{\delta} + D_{iM} \left(\frac{w'_i D_{jM}}{D_{ij} + w'_i D_{jM} + w'_j D_{iM}} \right) \bar{\rho}_M \frac{\Delta w'_j}{\delta} \tag{4}$$

$$J_j = D_{jM} \left(\frac{w'_j D_{iM} + D_{ij}}{D_{ij} + w'_i D_{jM} + w'_j D_{iM}} \right) \bar{\rho}_M \frac{\Delta w'_j}{\delta} + D_{jM} \left(\frac{w'_j D_{jM}}{D_{ij} + w'_i D_{jM} + w'_j D_{iM}} \right) \bar{\rho}_M \frac{\Delta w'_i}{\delta} \tag{5}$$

With:

$$w'_i = \frac{w'_{iF} + w'_{iP}}{2} \text{ and } \Delta w'_i = w'_{iF} - w'_{iP}$$

Where:
w'_i and w'_j = The weight fraction of component i and j in the membrane, respectively
w'_{iF} and w'_{iP} = The weight fraction at feed and permeate side for component i and j, respectively
D_{iM} = The average diffusion coefficient of pure component i in the active layer of the membrane
$\bar{\rho}_M$ = The average density of the membrane while
D_{ij} = The couple Diffusiosn coefficient and it was assumed to be an average of D_{iM} and D_{jM}

In order to obtained the diffusion coefficient, D_{iM} and D_{jM} value; the non-linear modified Maxwell-Stefan equation as in Eq. 4 and 5 were resolved by iterative method using the solver function supplied in Microsoft Excel Version 2007.

MATERIALS AND METHODS

Experimental: MWCNTs manufactured via. the chemical vapour deposition technique were supplied by Chengdu Organic Chemical Co., Ltd. These had an outer diameter in the range of 8-15 nm an inner diameter in the range of 3-5 nm and a length of approximately, 50 μm. PVA 95% hydrolysed) with an average molecular weight of 95,000 and [Bmim] [BF$_4$] 98% were purchased from Acros. Sulphuric acid 95-97%, hydrogen peroxide 30%, glutaraldehyde 25% aqueous solution and ethylene glycol were procured from Merck. Absolute ethanol 96% and acetone were supplied from HmbG and fine chemicals, respectively. Distilled water was used throughout the experiments.

Membrane preparation: The BP-SILM-70 was prepared as described elsewhere (Ong and Tan, 2015). In brief, the membrane was synthesized using a vacuum filtration technique. First, the MWCNTs were dispersed in ethanol

and filtered through a 0.45 µm nylon membrane filter. Subsequently, the retained MWCNTs on nylon membrane filter was filtered by a solution consist of a blending of [Bmim] [BF₄] with PVA ([Bmim] [BF₄]-PVA) at a weight ratio of 70/30 to immobilize the [Bmim] [BF₄]-PVA solution into the BP sheets. The resultant BP-SILM-70 was dried at room temperature and cross-linked with glutaraldehyde.

Liquid sorption study: Six set of ethylene glycol-water mixtures with different concentration of ethylene glycol ranging from 0, 20, 40, 60, 80 and 100 wt.% were prepared. The dry weights of the BP-SILM-70 were measured before immersed into these solution mixtures and kept at room temperature for 72 h until the equilibrium state was achieved. The swollen BP-SILM-70 were rapidly removed from the vessel and weighed immediately after blotting the excess adhered liquid with tissue papers. The swollen membrane was then subjected to a vacuum suction to desorb the liquid and collected in a cold trap that immersed in liquid nitrogen. The composition of the collected liquid was determined using KEM Karl Fischer moisture titrator MKS-500.

Pervaporation experiments: The pervaporation of ethylene glycol and water mixtures were carried out as reported in our previous work (Ong and Tan, 2015). BP-SILM-70 was mounted onto a stainless-steel permeation cell with an effective surface area of 8.6 cm². Feed solutions containing five different concentrations of ethylene glycol ranging from 50-90 wt.% were circulated between the feed tank and the permeation cell at a constant flow rate. The operating temperatures of the feed solutions were fixed at 30°C and the downstream pressure was maintained at 0.667 kPa using a vacuum pump. The pervaporation process was operated for 4 h and the permeate vapour was condensed and collected in cold traps immersed in liquid nitrogen. The collected permeate sample was weighed and its composition was analysed using a Karl Fisher moisture titrator. The pervaporation performance was evaluated.

RESULTS AND DISCUSSION

Estimation of the sorption in membrane: The sorption behaviours of the BP-SILM-70 may have strong dependency on the feed concentration. In this case, the concentration of each component in the membrane at equilibrium is assumed proportional to its activity in the outer surface adjacent to the membrane interface (Trong, 1987) and the weight fraction of the component sorbed in BP-SILM-70, w'_F was calculated using Eq. 1.

The adjustable parameters s_1, s_2 and m for the calculation of solubility coefficient, K_i as shown in Eq. 2 was then estimated by means of the experimental data from the liquid sorption study. The estimated adjustable parameter is shown in Table 1.

Table 1: Estimated adjustable parameters, s_1, s_1 and m for water

Variable	Adjustable paramater		
	s_1	s_2	m
Water	1.3382	1.1538	3.9999
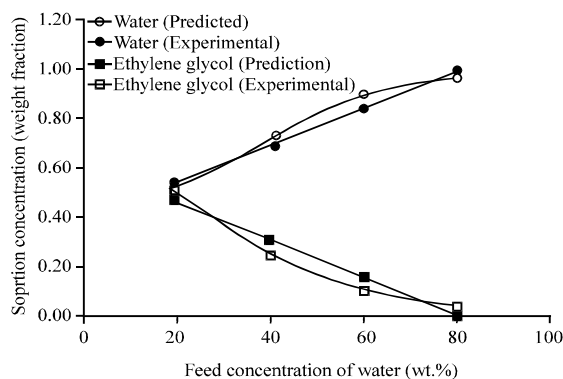
Fig. 1: Experimental and predicted sorption concentration as a function of feed concentration of water

Based on the estimated parameter values in Table 1, the K_i and the composition of the sorption of water and ethylene glycol in BP-SILM-70 were calculated. The sorption concentrations obtained from experimental works and predicted from Eq. 1 were plotted as a function of feed concentration of water as shown in Fig. 1. Both the experimental and predicted sorption concentration of water and ethylene glycol exhibit similar trend with increasing feed concentration of water in the binary mixture. In other words, the increase of water concentration would broaden the difference between the water activity in the solution mixture and the membrane; thereby enable higher water uptake in order to achieve an equilibrium condition. Similar increasing sorption behaviour as a result of increase in activity was also observed in ethylene glycol with increasing feed concentration of ethylene glycol (decreasing feed concentration of water).

However, it is noticed that the sorption concentration of ethylene glycol was relatively low (<55 wt.%) even in the presence of higher feed concentration of ethylene glycol. This can be associated with the larger molecule size of ethylene glycol which cause steric hindrance effect and limit the sorption of ethylene glycol (Du *et al.*, 2008).

The reliability and accuracy of the predicted sorption concentration calculated from Eq. 1 was further investigated by plotting the predicted sorption concentration in a parity plot with the sorption concentration obtained from experimental work. As shown in the parity plot in Fig. 2, the data for the sorption concentration of water and ethylene glycol were found to
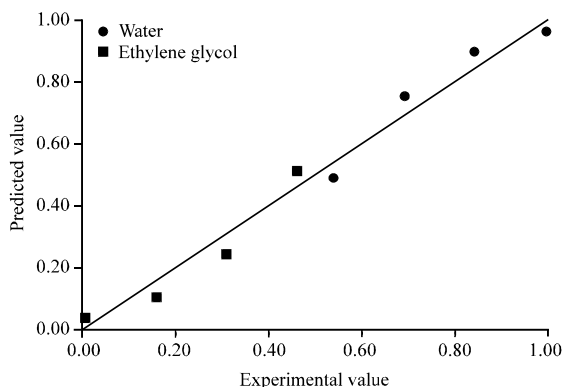
Fig. 2: Parity plot of the predicted and experimental value for the sorption concentration of water and ethylene glycol in BP-SILM-70
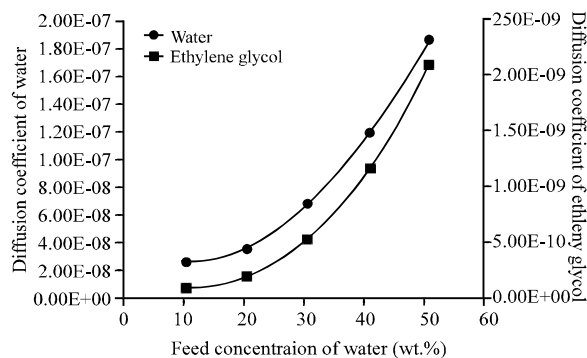

Fig. 3: Diffusion coefficient of water and ethylene glycol at different feed concentration of water

Fig. 4: Diffusion selectivity of BP-SILM-70 as a function of feed concentration of water

be distributed closely to the y = x line. This implies a good reliability of the estimated parameters which enable a good agreement between the predicted and experimental value for the sorption concentration of water and ethylene glycol.

Estimation of diffusion coefficient at different feed concentration of water: By using the experimental data obtained from pervaporation experiment as input parameter to the modified Maxwell-Stefan equation, the diffusion coefficient, D_{iM} of water and ethylene glycol at different feed concentration of water were calculated and plotted as a function of feed concentration of water in Fig. 3.

The affinity of the BP-SILM-70 can also be traced from the diffusion coefficient. As shown in Fig. 3, the diffusion coefficient of water is significantly higher than the diffusion coefficient of ethylene glycol. This indicates a high preferential of BP-SILM-70 to interact with water molecules and render their fast permeation across the membrane.
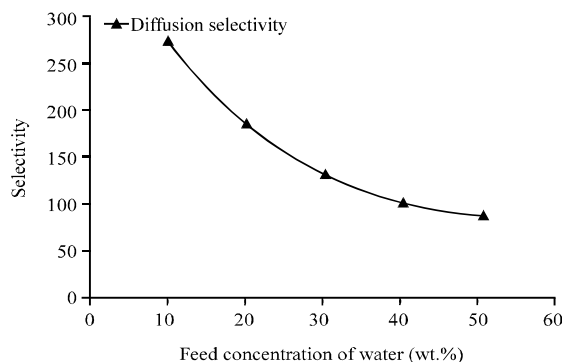
In addition, it is also noticed that the diffusion coefficient of both water and ethylene glycol were concentration dependence. The diffusion coefficient of water was increased with increasing feed concentration of water. This can be attributed to the expansion of membrane's volume due to swelling and decrease the resistance for mass transfer across the membrane, hence render a higher diffusivity of water molecules. However, note that the diffusion coefficient of ethylene glycol was also increased with increasing water feed concentration. This can be due to the synergistic effect from the sorption of water in BP-SILM-70 which caused the occurrence of membrane swelling and increase the solubility of ethylene glycol in the membrane, thereby increase the diffusivity of ethylene glycol.

The diffusion selectivity which was calculated by dividing the diffusion coefficient of water with diffusion coefficient of ethylene glycol was employed to evaluate the selectivity of BP-SILM-70 for water diffusion. As seen in Fig. 4, the diffusion selectivity was decreasing with increasing feed concentration of water. The finding shows that the increase in feed concentration of water has a pronounced effect in increasing the diffusivity of ethylene glycol as compared to water. This can be explained by the coupling effect according to the modified Maxwell-Stefan theory. The increased permeation of water with increasing feed concentration of water would increase the possibility of the collision between water and ethylene glycol molecule; thereby the collision create friction force that speed up the movement of ethylene glycol molecule inside the membrane while the water molecule is slowed down by the frictional interaction (Heintz and Stephan, 1994). Thus, the phenomenon causes a significant increase in ethylene glycol diffusivity as compared to water.

Apart from that, it is interesting to note that the diffusion coefficient of water and ethylene glycol that obtained from Maxwell-Stefan equation formed an
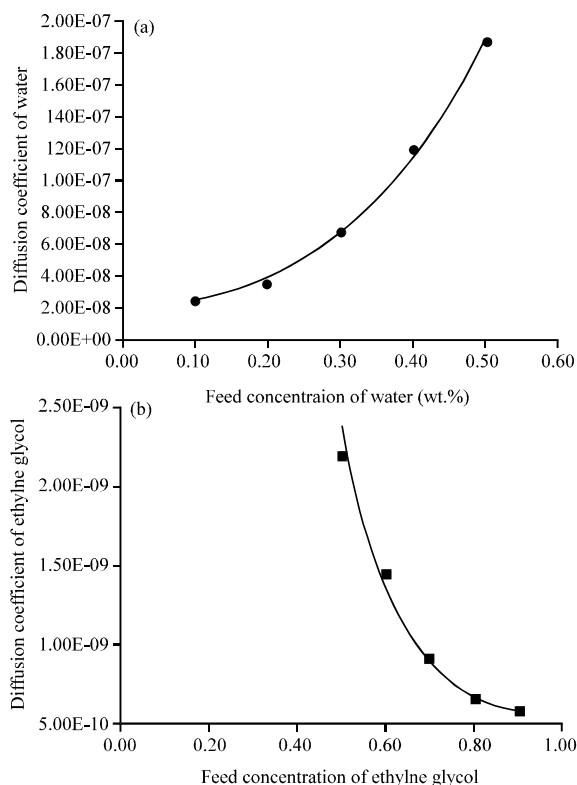
Fig. 5: Exponential plot of the; a) Diffusion coefficient of water versus feed concentration of water and b) Diffusion coefficient of ethylene glycol versus feed concentration of ethylene glycol

exponential factor relation with their own concentration in the feed solution. Figure 5 the diffusion coefficient of water demonstrated a positive exponential relation with the feed concentration of water whereas a negative exponential relation was demonstrated in the diffusion coefficient of ethylene glycol. The R^2 values for the exponential factor relation for water and ethylene glycol were 0.992 and 0.993, respectively which suggest a good reliability of the exponential equation to describe the concentration dependency of the diffusion coefficient of water and ethylene glycol in terms of feed concentration.

CONCLUSION

The diffusion coefficients of water and ethylene glycol in BP-SILM-70 at various feed concentration of water were successfully estimated using the modified Maxwell-Stefan equation. Both the diffusion coefficient of water and ethylene glycol were increased with increasing feed concentration of water, however, the diffusion selectivity was decreased. Interestingly, it is found that the diffusion coefficient of water and ethylene glycol that obtained from the modified Maxwell-Stefan equation can

be described by an exponential factor relation with feed concentration. The estimated diffusion coefficients using the exponential relation were in good agreement with the one obtained from the modified Maxwell-Stefan equation.

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