

**SYNTHESIS OF BUCKYPAPER SUPPORTED  
IONIC LIQUID MEMBRANE FOR  
PERVAPORATION PROCESS**

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**SYNTHESIS OF BUCKYPAPER SUPPORTED IONIC LIQUID MEMBRANE  
FOR PERVAPORATION PROCESS**

**by**

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## LIST OF ABBREVIATIONS

$[(C_3H_7)_4N][B(CN)_4]$	Tetrapropylammonium tetracyanoborate
$[BF_4]^-$	Tetrafluoroborate ion
[Bmim]	1-butyl-3-methylimidazolium
[Bmim][ $BF_4$ ]	1-butyl-3-methylimidazolium tetrafluoroborate
$[Cl]^-$	Chloride ion
$[NO_3]^-$	Nitrate ion
[NTf <sub>2</sub> ]	Bis(trifluoromethyl-sulfonyl)imide ion
[Omim]	1-octyl-3-methylimidazolium
$[PF_6]^-$	Hexafluorophosphate ion
ABE	Acetone-butanol-ethanol
BLM	Bulk liquid membrane
BP	Buckypaper
BP-SILM	Buckypaper supported ionic liquid membrane
CNTs	Carbon nanotubes
CVD	Chemical vapour deposition
EDX	Energy dispersive X-ray
ELM	Emulsion liquid membrane
GC	Gas chromatograph
GPU	Gas permeation unit
MMM	Mixed-matrix membrane
MWCNTs	Multi-walled carbon nanotubes
PDMS	Polydimethylsiloxane
POMS	Poly(octylmethylsiloxane)
PVA	Polyvinyl alcohol
PVDF	Polyvinylidene fluoride
PVP	Poly(vinyl pyrrolidone)
SEM	Scanning electron microscopy
SILM	Supported ionic liquid membrane
SLM	Supported liquid membrane
SWCNTs	Single-walled carbon Nanotubes



TCE	Trichloroethylene
TGA	Thermogravimetric analysis
TOA	Trioctylamine
UV-Vis	Ultraviolet visible

## LIST OF SYMBOLS

$A$	Effective membrane surface area
$a_i$	Thermodynamic activity of component $i$
$a_{jk}$	Interaction parameters of group $j$ and $k$
$c$	Concentration of component
$D$	Diffusion coefficient
$D_{ij}$	Coupled diffusion coefficient
$D_{iM}$	Average diffusion coefficient of component $i$ in the the membrane
$D_{i0}$	Infinite diffusion coefficient of component $i$
$D_i^0$	Relative diffusion of component $i$
$\tilde{D}_{ji}$	Effective diffusion coefficient
$E_D$	Activation energy of diffusion
$F$	Reagent factor for Karl Fischer titrator
$J$	Permeation flux
$j$	Molar flux
$K$	Partition/solubility coefficient
$l$	Distance of diffusion
$m_{BP}$	Weight of BP
$m_{BP-SILM}$	Weight of BP-SILM
$m_{BP-SILM}'$	Weight of swollen BP-SILM
$P_i^G$	Permeability of component $i$
$p_{iF}$	Partial pressure of component $i$ in the feed
$p_{iP}$	Partial pressure of component $i$ in the permeate
$p^{sat}$	Saturated vapour pressure of component
$Q$	Quantity of the permeate collected
$Q_k$	Surface parameter of group $k$
$R_k$	Volume parameter of group $k$
$r$	Relative volume parameter
$T$	Absolute temperature
$\Delta t$	Time interval of pervaporation process
$V$	Partial molar volume of component

$V_m$	Volume fraction of the membrane
$v$	Local velocity of component
$v_k^{(i)}$	Number of group $k$ in component $i$ .
$W$	Weight of the permeate sample in titration flask
$w'_i$	Weight fraction of component in the membrane
$X$	Weight fraction of component in the feed
$\chi_{im}$	Binary interaction parameter between component $i$ and membrane
$X'_j$	Fraction of group $j$ in the liquid
$x$	Mole fraction of component
$Y$	Weight fraction of component in the permeate
$\alpha$	Membrane selectivity
$\beta$	Separation factor
$\beta_{Diff}$	Diffusion selectivity
$\beta_{Sorp}$	Sorption selectivity
$\gamma_i$	Activity coefficient of component $i$
$\gamma_i^R$	Residual activity coefficient of component $i$
$\gamma_i^c$	Combinatorial activity coefficient of component $i$
$\delta$	Membrane thickness
$\varepsilon$	Plasticization coefficient
$\emptyset$	Volume fraction of component
$\Gamma_k$	Activity coefficient of group $k$
$\Gamma_k^i$	Activity coefficient of group $k$ in pure component $i$ .
$\theta_i$	Surface fraction of component $i$
$\bar{\rho}_M$	Average density of the membrane

# **SINTESIS MEMBRAN CECAIR IONIK BERPENYOKONG KERTAS- BUCKY UNTUK PROSES PENYEJATTELAPAN**

## **ABSTRAK**

Membran cecair berpenyokong adalah salah satu konfigurasi membran cecair yang menggunakan bahan fasa cecair sebagai membran dan diperangkap ke dalam substrat berliang. Sejak kebelakangan ini, idea tentang penggunaan membran cecair berpenyokong dalam proses penyejattelapan telah menarik tumpuan ramai penyelidik. Tetapi penggunaan membran cecair berpenyokong menghadapi masalah ketidakstabilan yang berpunca daripada kehilangan membran cecair. Kajian ini bertujuan untuk membangunkan membran cecair berpenyokong dengan kestabilan yang tinggi dengan menggunakan kertas-bucky sebagai substrat berliang dan diperangkap dengan cecair ionik 1-butyl-metylimidazolium tetrafluoroborat [Bmim][BF<sub>4</sub>] untuk membentuk membran cecair ionik berpenyokong kertas-bucky. Kertas-bucky terdiri daripada kelompok nano-tiub karbon dinding berlapis mampu memerangkap membran cecair ionik secara berkesan disebabkan oleh saiz liang yang kecil and struktur liang yang berliku-liku. Untuk meningkatkan lagi kestabilan membran, [Bmim][BF<sub>4</sub>] telah dicampur dengan polivinil alkohol sebelum diperangkap dalam kertas-bucky. Struktur membran cecair ionik berpenyokong kertas-bucky yang terhasil didapati berbeza dengan membran asimetrik, di mana fasa membran dan sokongan telah digabungkan dalam satu lapisan. Struktur tersebut membolehkan pembentukan membran simetri yang tipis tanpa menjejaskan sifat mekanikal membran. Prestasi membran cecair ionik berpenyokong kertas-bucky dalam proses penyejattelapan yang melibatkan campuran perduaan yang terdiri

daripada etilena glikol dan air menunjukkan keupayaan membran tersebut dalam penyahhidratan larutan akueus etilena glikol. Kewujudan kertas-bucky dan [Bmim][BF<sub>4</sub>] didapati telah meningkatkan prestasi pemisahan dan kebolehtelapan intrinsik membran. Membran cecair ionik berpenyokong kertas-bucky telah menunjukkan prestasi penyejattelapan yang tinggi dengan fluks penelapan yang bernilai 102 g·m<sup>-2</sup>·j<sup>-1</sup>, faktor pemisahan setinggi 1014, kebolehtelapan air yang bernilai 13106 GPU dan kememilihan membran untuk air yang bernilai 13 dengan berat air dalam kepekatan larutan suapan sebanyak 10% pada suhu 30 °C dan 5 mmHg tekanan hilitan. Di samping itu, membran cecair ionik berpenyokong kertas-bucky juga mampu untuk memisahkan campuran pertigaan; etil asetat, etanol dan air yang membentuk azeotrop. Fluks penelapan sebanyak 385 g·m<sup>-2</sup>·j<sup>-1</sup>, faktor pemisahan yang bernilai 247, kebolehtelapan air 4730 GPU dan kememilihan membran untuk air yang bernilai 39 telah diperolehi pada suhu 30 °C dan 5 mmHg tekanan hilitan. Membran cecair ionik berpenyokong kertas-bucky telah mempamerkan prestasi yang tekal dalam operasi selama 120 jam. Pekali resapan etilena glikol dan air pada operasi parameter yang berlainan telah dianggar dengan menggunakan model matematik semi-empirikal berdasarkan pengubahsuaian persamaan Maxwell-Stefan. Dengan merujuk pada pekali resapan yang dianggar, pemisahan membran cecair ionik berpenyokong kertas-bucky dalam proses penyejattelapan bagi penyahhidratan campuran perduaan etilena glikol/air adalah dikawal oleh proses resapan.

# **SYNTHESIS OF BUCKYPAPER SUPPORTED IONIC LIQUID MEMBRANE FOR PERVAPORATION PROCESS**

## **ABSTRACT**

Supported liquid membrane (SLM) is one of the liquid membrane configurations that employ a liquid phase substances as membrane and immobilized in a porous supporting membrane. Recently, the idea of using SLM in pervaporation process has attracted a great deal of research attention. However the use of SLM in pervaporation has always suffered from instability problem which is mainly due to the displacement of liquid membrane. In the present research work, it is aimed to develop a high stability SLM by employing buckypaper (BP) as supporting membrane and immobilized with an ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate [Bmim][BF<sub>4</sub>] to form a buckypaper supported ionic liquid membrane (BP-SILM). The BP, which is composed of entangled assemblies of multi-walled carbon nanotubes (CNTs), can effectively entrap the infiltrated the ionic liquid membrane due to its smaller pore size and highly tortuous porous structure. In order to further enhance the membrane stability, the [Bmim][BF<sub>4</sub>] was blended with polyvinyl alcohol (PVA) prior to the immobilization in the BP. The resulted BP-SILM structure, in which the membrane and support phase were merged into a single layer, was found to be different from that of conventional asymmetric membranes. The BP-SILM structure allows the formation of a thinner symmetric membrane without compromising its mechanical properties. The pervaporation performances of the BP-SILM in the binary mixture of ethylene glycol and water showed an excellent capability to dehydrate ethylene glycol aqueous solutions. The presence of BP and

[Bmim][BF<sub>4</sub>] was observed to significantly enhance the separation performance and the intrinsic membrane permeability. The BP-SILM exhibited high pervaporation performance with a permeation flux of 102  $\text{g}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ , separation factor as high as 1014, water permeance of 13106 GPU and membrane selectivity of 13 for water with 10 wt.% feed concentration of water at 30 °C and 5 mmHg downstream pressure. On the other hand, the BP-SILM was also capable to break ternary azeotropic mixtures of ethyl acetate, ethanol and water. A permeation flux of 385  $\text{g}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ , separation factor of 247, water permeance of 4730 GPU and membrane selectivity of 39 for water were obtained at 30 °C and 5 mmHg downstream pressure. The BP-SILM also demonstrated a robust pervaporation performance over an operation of 120 hours. The diffusion coefficients of ethylene glycol and water at different operating parameter were estimated using a semi-empirical mathematical model based on modified Maxwell-Stefan equation. Based on the estimated diffusion coefficient obtained, the separation of BP-SILM in pervaporation dehydration of ethylene glycol/water binary mixture is more on diffusion control.

## CHAPTER 1

### INTRODUCTION

#### 1.1. Pervaporation

For the past few decades, pervaporation has been viewed as an effective strategy for liquid separation. The term “pervaporation” was first introduced by Kober (1917) when reporting the selective permeation of water from aqueous solutions of albumin and toluene through a cellulose nitrate film. In general, a pervaporation system is composed of a dense membrane that serves as a separating barrier between two compartments and regulates the mass transport across the membrane. The driving force for the separation in pervaporation process is mediated by chemical activities difference created between the upstream and downstream sides of a membrane, for this reason, a vacuum pump or sweeping gas is usually applied at the downstream side. The component which is preferentially removed from the liquid mixture possesses higher affinity to permeate through the membrane and undergoes a phase change from liquid to vapour. The overview of the molecule transport in pervaporation process is illustrated in **Figure 1.1**.