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Separation of Binary Solvent Mixtures with Solvent Resistant Nanofiltration Membranes

Part A: Investigation of Separation Performance

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Abstract

This paper is Part A of a two paper series seeking systematical investigation of the feasibility of separating binary solvent mixtures with solvent resistant nanofiltration (SRNF) membranes. A series of binary solvent mixtures with different physical and chemical properties (dielectric constant, surface tension, Hansen solubility parameter and viscosity) was chosen, and single factor analysis was performed to tap the potential of solvent separation using different commercial SRNF membranes (MPF^{TM} series, StarMem^{TM} series, DuraMem^{TM} Series). It was found that the DuraMem^{TM} 150 allowed the separation of ethanol/1-hexane mixtures with a separation factor of around 6, which is the highest for solvent separation in SRNF so far. The presence of preferential permeation was found to be mainly dependent on the membrane structure and differences in the Hansen solubility parameter and polarity between the solvents and membrane. Some important hypotheses, like that dense SRNF membranes had larger possibility to separate binary solvent mixtures, separation process followed the typical solution-diffusion mechanism, and that the Hansen solubility parameters and polarity of membranes and solvents were main factors affecting the separation, were putting forward for the first time.

Key words: solvent separation; solvent resistant nanofiltration; Hansen solubility parameter; dielectric constant; hexane/ethanol

1. Introduction

1.1 Current developments of solvent separation in SRNF

Solvent resistant nanofiltration has gained much attention since late 1990s. Increasingly more and more researchers have studied the membrane preparation, transport mechanism, process modeling and application of SRNF, and lots of interesting and encouraging discoveries have been disclosed. However, some aspects of SRNF, such as swelling, authentic mass transfer mechanism, membrane fouling, and ability of solvent separation still lack thorough understanding [1-7], during which separating solvent mixtures with SRNF draws less attention and no significant results have been found. Machado et al. [4] investigated the possibility of separating solvent mixtures using the MPF series membranes with a large number of binary solutions and over a wide range of operating conditions. Despite the large permeation differences of the pure solvent components, no separation effect could be discerned. Transport of binary mixtures of heptane/xylene and hexane/cyclohexane through a laboratory made PDMS membrane was studied by Robinson and co-workers [2], no change in the compositions of permeate liquids compared to feed liquids. Geens et al. [3] found almost same results for binary mixtures of water and alcohols. Darvishmanesh et al. [5] selected a series of membranes from reverse osmosis (RO) to ultrafiltration (UF) to separate hexane/ethanol mixtures, and inferred that the separation factors close to one indicated that transport occurred completely by convection or by coupled diffusion. Atsushi et al. [8] investigated the transport of various binary systems through a PDMS-based dense membrane, and suggested that the selectivity of the solvent in these systems seems to depend upon the similarity of the molecular structures of hexane and solvent, corresponding to entropy mixing, and the interaction of the hexane-solvent-membrane polymer, corresponding to enthalpy mixing. Although preferential permeation happened for some binary systems, their separation factors were almost below 2. Patrick et al. [9, 10] developed membrane rejection maps and membrane selectivity maps to choose suitable membrane-solvent-solute systems, and presented a phenomena-based model for multi-component permeation through SRNF membranes based on solution-diffusion, pore-flow and mutual coupling mechanisms. The study was quite inspiring and performed in binary and ternary solvent mixtures, yet it mainly focused on solute-contained systems and separation of solvent mixtures was not investigated. In summary, although some efforts have been made to explore the potential of separating solvent mixtures with SRNF membranes, main factors and separation mechanisms dominating this process still need to be further investigated. Solvent separation is necessary in many industries, such as the bio-ethanol or bio-butanol production industry, the waste reagents recovery industry and so on [11, 12]. Currently most industrially adopted ways of separating solvent mixtures are distillation and pervaporation (PV). SRNF is an environmentally friendly process with no extra heating and phase transition, and the energy demand of it is less than that of the PV process and the distillation process. If SRNF could be extended to the solvent separation process, it would reduce the consumption of energy and resources and as a result the environmental strain on the planet.

1.2 Traditional ways of fluid separation

Will SRNF, as a promising unit operation integrated in food, catalyst recovery, pharmaceutical and petrochemical industry, be able to expand itself into solvent separation process? To explore its possibility in this area, first of all, traditional ways of separating solvent mixtures will be briefly reviewed so that we can better understand the solvent separation process.

Distillation and rectification are mostly industrially used methods for separating fluid mixtures [13]. They depend on the different volatility of the components to achieve separation. First and foremost, the liquid mixture is to be boiled, which is fundamental in distillation. The resulting vapor phase mainly comprises more volatile components which will be condensed afterwards, and the liquid phase contains less volatile components. In practice, multi-stage distillation process is carried out in the form of countercurrent distillation, as we also called rectification, in a column. The liquid mixture to be separated is fed to the bottom of the column, where it is to be boiled. Then the vapor liquid equilibrium will be reached and mass transfer between two coexistent phases takes place. Therefore, with respect to distillation or rectification, it is the heating operation that primarily destroys, or at least weakens the interaction force between solvent molecules, changes some constituents into vapor phase, and thus makes solvent separation feasible. The main disadvantages of distillation/rectification are a risk of thermal degradation of the components, a high energy demand and sometimes costly investment in equipment.

Another kind of technique available for liquid separation is a membrane-based one, PV, which can effectively separate azeotropic, close boiling, isomeric or heat-sensitive liquid mixtures [14, 15]. Usually there exist two phases, the liquid-phase feed and the vapor-phase permeate, and the PV membrane acts as a selective barrier between the two phases. The driving force for the separation, normally provided by keeping the permeate side under vacuum or heating the feed side, is the difference in the partial pressures of the components on the two sides. The transmembrane process is usually described with solution diffusion mechanism [16], about which permeants dissolve in the membrane material at various degrees (expressed in terms of solubility) and then diffuse through the membrane matrix at different speeds (expressed in terms of diffusivity). The separation is achieved between different components whose solubility and/or diffusivity differ. Differences of components in solubility only or/and diffusivity in the PV membrane are not sufficient for effective separation, but the heating operation at the feed side and/or the vacuum operation at the permeate side definitely weaken the interaction between solvent molecules are of great importance for fluid separation in PV process.

1.3 Investigation of solvent separation with SRNF membranes

As stated above, it is fundamental for solvent separation to find a way to destroy, or at least weaken the interaction among solvent molecules. Normally there exist four kinds of basic forces among these molecules, i.e. the dipole-dipole interaction, dipole-induced dipole interaction, London dispersion force and hydrogen bond force, and according to the solvent type, the overall forces may vary from one kind to a combination [17]. Moreover, the Hansen solubility parameter (represented as σ), composed of three partial solubility parameters accounting for dispersion forces, polar forces, and hydrogen bonding, is a single well-accepted parameter evaluating intermolecular energy [18]. The difference between solubility parameters of two components, δ_i, and δ_j, can be a measure for their affinity in terms of thermodynamic similarities as in Equation (1).

$$\Delta\delta_{i,j} = |\delta_i - \delta_j| \tag{1}$$

With respect to SRNF, a pressure-driven membrane-selective process with no additional heating or phase change involved to destroy the intermolecular forces, only the interactions between membrane and solvent will lead to the effective separation. If binary solvent mixtures through a SRNF membrane are to be separated, the following assumptive equations should be established.

$$F_{im} >> F_{jm} \tag{2}$$

$$F_{im} >> F_{ij} \tag{3}$$

In Equation (2) and (3), the subscripts i, j and m mean one solvent component i that preferentially permeates the SRNF membrane, another solvent component j that is mostly retained in the feed solution and the membrane, respectively. $F_{i\text{-}m}$, $F_{i\text{-}m}$ and $F_{i\text{-}j}$ are the interaction forces between the solvent i and the membrane m, the solvent j and the membrane m, the solvent i and j, respectively. However, it is still unsure which solvent or membrane parameter, or a combination of them, is able to appropriately represent the interaction forces for this ternary system. Furthermore, if this parameter is identified, the achieved separation needs to be determined in terms of the differences of this parameter for the binary solvent-membrane. To try to answer this question, the important parameters influencing solvent transport through SRNF membranes will be shortly reviewed according to existing reports.

The solubility parameter is of great importance for the mass transfer process in the SRNF membrane, which has been reported in literature [2, 5, 8-10, 19-21], and it can be calculated by the group contribution method [18]. Similar solubility parameters between the membrane and solvent indicate a good compatibility of the polymer and the solvent, and surely a high flux would be expected. The surface tension, another valuable factor reflecting the mutual affinity, is also adopted by lots of researchers for membrane-based processes [4, 22-25]. Close surface tension values help the solvent to dissolve in the membrane top layer. Besides these two factors, viscosity of the solvent, and polarity of the membrane and solvent are other common parameters thought to affect solvent transport process in many studies [2-4, 22, 25-28]. Viscosity often hinders the mass transfer, especially for the convection part in the membrane, and if the polarity of a solvent is close to that of a membrane, high flux may be usually available. Since much attention has been paid to these parameters and their important influences in previous reports, detailed discussions about them are avoided. However, these four key parameters will be chosen for this research.

To thoroughly understand the feasibility of separating binary solvent mixtures using SRNF membranes, various commercial SRNF membranes of different materials (polyimide and polydimethylsiloxane), hydrophilic- hydrophobic properties and porosity (dense, semi-porous and micro-porous) were selected. With regard to binary solvent mixtures, a wide range of solvent pairs was selected based on their viscosity, surface tension, dielectric constant and solubility parameters differences. What's more, single factor analysis will be performed to identify parameters which are vital to solvent separation.

2. Experimental

2.1 Membranes and solvents

The StarMem^{TM} and DuraMem^{TM} series membranes were purchased from Evonik Membrane Extraction Technology Ltd. (MET), and the MPF-44 membrane from Koch Industries. Before used, the membrane sheet was cut into suitable pieces, and pretreated in relevant solvent systems for several weeks. The relevant solvent fluxes before and after pretreatment showed no much difference, indicating the stability and durability of these membranes. flushed with ethanol to clean up the preservatives at the membrane surface. Additionally, about 50 mL of ethanol would permeate the membrane to wash out the residues during preparation prior to use. All membranes were specified to be stable in a broad range of solvents, the properties of which were shown in Table 1.

Table 1

All the solvents were of analytical grade, purchased from Beijing Chemicals (Beijing, China). According to the four key parameters discussed above influencing solvent transport through SRNF membranes, the 2-butanone/ethyl acetate and 2-butanone/tetrahydrofuran (THF) system were chose mainly based on their dielectric constant differences, and the N, N-dimethylformamide (DMF)/acetonitrile, hexane/tetrachloride (CCl_4) system, the methanol/glycol, dimethyl sulfoxide

(DMSO)/glycol system, and the methanol/acetonitrile, methanol/CCl_4 system on their surface tension, viscosity, solubility parameter differences, respectively. Relevant properties of all the solvents used were listed in Table 2-5 [29, 30].

Table 2-5

2.2 Experimental set-up

A HP 4750 dead-end filtration set-up was used in this work, and the detailed description about this equipment could be found in previous paper [5].

2.3 Methods

2.3.1 The filtration test

200 mL of every binary solvent mixture, the molar ratio of which is 1:1, was loaded in the vessel, and concentration polarization at the membrane surface was minimized by a Teflon-coated magnetic stir bar on top of the membrane. The process was at room temperature, and the solvent permeability (L/hm^{2}bar) was determined by dividing the measured flow (L/h) over the membrane area and the pressure difference. The solvent flux and separation factor of one membrane sample were determined every 1 hour for 2 hours total. To avoid solvent evaporation, the permeates were put in a container filled with ice-water mixture. Each binary solvent series was repeated three times with different samples of the same membrane sheet. The maximum parallel experimental errors were up to 5% in all cases.

2.3.2 Sample composition tests

The composition of each binary solvent system was determined with a Shimadzu GC 2010 gas chromatograph (flame ionization detector), and a polyethylene glycol-coated DB-WAX column from Agilent Technologies (30 m, 0.32 mm I.D, 0.25

μm thickness) was used for analysis. The internal standard method was applied for the analysis of the samples compositions, and the separation effect was given by the separation factor α in Equation (4).

$$\alpha_{ij} = \frac{y_i/y_j}{x_i/x_j} \qquad (4)$$

In this equation, *i* and *j* denote the binary solvent components, and y_i, y_j and x_i, x_j are compositions of the permeate side and the feed/retentate side, respectively, which can be described by means of mole fractions, mass fractions or volume fractions. The component *i* permeates preferentially if the value of α_{ij} is larger than one.

3. Results and discussion

3.1 Solvent permeation through SRNF membranes

The permeabilities of solvent mixtures were shown in Figure 1. It could be seen that permeabilities of most solvent series were relatively larger for loose membranes like DuraMem^{TM} 500, 900 and StarMem^{TM} 240 than those for dense membranes, i.e. MPF-44, DuraMem^{TM} 150, 200, 300 and StarMem^{TM} 122. Except for viscous solvent mixtures like glycol/DMSO and methanol/DMSO, their permeabilities were quite low for all membranes. Considering that the aim of this work was to investigate the separation performance of SRNF membranes, detailed discussion about solvent permeabilities was avoided.

Figure 1

3.2 The separation performance of binary solvent mixtures

Results for binary solvent mixtures are illuminated in Figure 2-5.

Figure 2

Figure 3

From Figure 2 to 3, it is easy to tell that for all the membranes used, the separation factors of 2-butanone/ethyl acetate, 2-butanone/THF, DMF/acetonitrile and hexane/CCl_4 are almost equal to one, which indicates that the difference in surface tension or dielectric constant only is not able to result in effective separation. Surface tension, as an easily measurable parameter for both the membrane and solvent, has been adopted by lots of researchers to represent membrane-solvent affinity [23, 24, 31]. It is a measure of the intermolecular forces at the surface of the polymeric membrane or that of the solvent, and can be used to describe the repulsion/attraction phenomena at the membrane/solvent interface. Hydrophobic membranes, corresponding to low values of surface tension, are expected to have a small flux for solvents with high surface tension values and vice versa. Furthermore, surface tension may also correspond to the affinity between solvents, for solvents with similar surface tension are supposed to be easily miscible [30]. Although surface tension could partially represent the interactions between the membrane and solvent, i.e. F_{i-m}, F_{j-m} and F_{i-j}, clearly differences in this parameter only are not able to allow effective separation. Dielectric constant of the membrane or solvent, an important property reflecting their polarity and polarity difference between the membrane and solvent, is critical for the flux behavior [4, 25, 28, 32]. Similar polarities of the membrane and solvent often expect a higher flux, and also that of solvents is more compatible [30]. This with no doubt tells that dielectric constant is another significant factor could be used to describe the interaction forces in the ternary system. However, again almost no separation was found between 2-butanone and ethyl acetate or 2-butanone and THF in spite of their obviously large differences in polarity while other important properties remain quite similar. Therefore, it is not sufficient describing the interaction forces for the ternary system through only dielectric constant differences, some other parameters are to be fixed.

As far as the viscosity is concerned, it mainly works in micro-porous membranes when convection or viscous flow dominates transport, or strong swelling in dense membranes happens which results in the pore-like structure at the membrane surface and/or so-called "valleys" created in the membrane structure, and it is usually the reciprocal of the solvent flux [2, 4, 25]. As can be seen in Figure 4, despite the huge viscosity difference of methanol/glycol or glycol/DMSO, either for the micro-porous membrane like DuraMem^{TM} 900 or dense membranes like DuraMem^{TM} 150 and StarMem^{TM} 122, no significant separation is observed, which implies that the viscosity may be not an appropriate parameter for measuring interactions of the ternary system and again confirmed that convective or viscous transport may not be suitable for solvent separation in SRNF due to coupled diffusion of solvent mixtures [5].

Figure 4

Figure 5

Figure 5 provides the results of solvent pairs based on solubility parameter differences. No separation was found between methanol and acetonitrile, while for methanol and CCl_4, preferential transport of methanol happened for DuraMem^{TM} 150, 200, 300 and MPF-44. It seems that the difference in solubility parameter might enable solvent separation. The Hansen solubility parameter is expressed in the following form [33].

$$\sigma = \left[\sigma_d{}^2 + \sigma_p{}^2 + \sigma_h{}^2\right]^{1/2} \tag{4}$$

In this equation σ_d, σ_p and σ_h are the dispersion forces, polar forces and hydrogen bonding forces, respectively. This ternary parameter is able to characterize the comprehensive interaction between molecules [29], and thus it should have the ability to reflect the interactions of solvent molecules and solvent-membrane polymer. However, solvent pairs of methanol and acetonitrile, similar in other three properties expect for the solubility parameter, saw no notable preferential transport. Surprisingly, for the methanol-CCl_4 mixture, between which large differences in solubility parameter and dielectric constant exist, methanol permeated by priority for the DuraMem^{TM} 150, 200, 300 and MPF-44. Nevertheless, the flux of this mixture was small (see Fig.1) for the DuraMem^{TM} series, indicating that the different volatile rates of methanol and CCl_4 might greatly influence the selectivity. Additionally, the color of the retentate for these membranes was light yellow, which hinted that the membranes might lose their original properties in contact with CCl_4 since these membranes are stable in alcohols. But the low flux of methanol/CCl_4 in a way proved that the DuraMem^{TM} series membranes maintained their structure stability when exposed to CCl_4. Moreover, MPF-44 made from PDMS also shows a slight possibility for separating methanol and CCl_4. Although the experimental results may not be entirely reliable, they provide a promising clue, i.e. will the combined differences in both solubility parameter and dielectric constant enable solvent separation in SRNF?

3.2 Separation of ethanol/hexane using SRNF membranes

To answer the question of the above paragraph and to confirm our hypothesis, a new solvent pair of ethanol and hexane was selected. The relevant properties of them were shown in Table 6 and the separation factors in Figure 6.

Table 6

Figure 6

As can be seen in Figure 6, expected separation is observed for DuraMem^{TM} 150, 200, 300, StarMem^{TM} 122 and MPF-44, and especially for DuraMem^{TM} 150, the separation factor is approximately 4. This is quite encouraging, for no separation factor as high as 4 has ever been reported for solvent separation in existing literature in the SRNF field. For MPF-44, StarMem^{TM} 122, DuraMem^{TM} 200 and DuraMem^{TM} 300, preferential transfer of ethanol happened, yet all the separation factors were below 1.5. The phenomenon could be explained with the classical solution-diffusion mechanism, according to which the solvent transfer is based on its dissolution in membrane material at the surface and diffusion through the membrane matrix [16]. SRNF is a pressure-driven process with no additional energy involved, and the most possible way to destroy or waken the intermolecular forces between solvent mixtures has to depend on the interaction between the polymer molecules and the solvent molecules. In other words, if one component permeates through the SRNF membrane by priority, its ability of dissolving in the membrane surface and diffusing through the membrane matrix has to be much stronger than the other's; at the same time, the interaction between this component and the membrane also needs be much stronger than between itself and the other component, just like what was illustrated in Equation 2 and 3. Accordingly, to achieve effective solvent separation in SRNF, the membrane should have a highly dense top layer, and simultaneously have a sublayer in which the number of voids are as less as possible; that is to say, if preferential solvent transport happens in SRNF, it matters a lot that solvent molecules ought to dissolve in the membrane surface and then permeate through the free volume between membrane matrix, and that mass transfer through the pores at the membrane surface or channels/voids in the body matrix should be avoided as much as possible. Of all the membranes used, DuraMem^{TM} 150 should be the densest one according to its MWCO value compared with the other membranes', on condition that MWCO has always been adopted as a good indicator of the membrane porosity state [34]. The scanning electron microscope (SEM) picture of DuraMem^{TM} 150 also confirms our judgment [35]. As can be seen in Figure 7, the dense top layer and very few finger-like patterns in its sublayer structure indicate that this membrane has a rigid dense structure. Therefore, the separation factor of ethanol/hexane for DuraMem^{TM} 150 is higher compared to that for other membranes.

Figure 7

3.3 Confirmation of the experimental results

For the transport of ethanol/hexane through DuraMem^{TM} 150, the total flux was 0.04 L/(m^2•h•bar). To validate our judgment, an attempt to improve the total flux was made by setting the applied temperature and pressure at 40 °C and 55.17 bar, respectively, according to the brochure of DuraMem^{TM} 150 provided by the manufacture. The separation factors are listed in Table 7.

Table 7

From table 7, separation factors as high as about 6 were observed for five membrane sheets, and ethanol/hexane flux was 0.073 L/(m^2•h•bar). This relatively small flux indicated that there was little concentration change in the retentate, and that concentration polarization effects had no significant influence on the separation effect of ethanol/hexane. Besides, improved separation factor values implied that the applied temperature might play an important role in solvent separation. Different applied temperature led to different dissolution and diffusion rates for ethanol and hexane. The molecule size of ethanol is smaller than that of hexane, and the affinity between ethanol and DuraMem^{TM} 150 is far larger than that between hexane and DuraMem^{TM} 150. Therefore, the ethanol molecules transport through the membrane at a higher rate. It is worthy of much attention for no such high separation factor has been reported for fluid separation in SRNF till now. What's more, this exciting discovery draws our greater attention to the reason why the differences in both solubility parameter and dielectric constant are able to lead to effective separation. The Hansen solubility parameter itself is often used to characterize intermolecular forces, and why the polarity has to be taken into account?

The Hansen solubility parameter is expressed by Equation (4), during which the polar cohesive energy, σ_p, represents the permanent dipole-permanent dipole interactions. The calculation of this parameter was given by Hansen and Beerbower in Equation (5) [33].

$$\sigma_p = 37.4(DM)V^{\frac{1}{2}} \qquad (5)$$

In this equation DM and V denote the solvent dipole moment and solvent volume, respectively. However, the induced dipole, a potentially important factor particularly for solvents with zero dipole moments, was not treated specifically in this approach. Hansen himself was also aware of this problem and discussed it in his books [33]. For example, the reported dipole moments of carbon disulfide are mostly 0 for gas phase measurements, supplemented by 0.08 in hexane, 0.4 in carbon tetrachloride, 0.49 in chlorobenzene, and 1.21 in nitrobenzene [33]. Likewise, the dipole moment of hexane is 0, but it will change once in contact with ethanol, due to the instantaneous dipole moment caused by it. Besides, the same will happen between hexane and DuraMem^{TM} 150, which is a medium polar polymer membrane made from P84 polyimide and the dielectric constant of it is about 3.3 [25, 36]. Therefore, Hansen solubility parameter may be not able to fully cover the overall important forces between molecules, especially for the mixture of polar and non-polar solvents where induced dipole forces also play a significant role. Additionally, dielectric constant, widely used as a measure for the polarity of membranes or solvents, provides a more comprehensive way of reflecting the interaction due to the polarity effect for the binary solvent-membrane system. Thus, taking differences in the dielectric constant into account is a necessary complement when measuring the interactions between solvents and membranes, due to the defect of Hansen solubility parameter.

4. Conclusion

SRNF membranes have the potential to separate solvent mixtures. Transport of ethanol-hexane through DuraMem^{TM} 150 has confirmed the feasibility of this process.

The most appropriate mechanism that could be applied to explain the preferential permeation remains the solution-diffusion mechanism, which demands that the membrane should have a dense top layer and a void-free sublayer, and convective mass transfer be avoided as much as possible.

The Hansen solubility parameter and dielectric constant, for both solvents and membranes, are thought to be factors of great importance resulting in effective separation. Preferential permeation might happen when differences in these two parameters between one solvent and membrane are sufficiently small, and that between two solvents are large enough. Further investigation is needed to provide accurate values of differences in these two parameters which allow separation.

To further investigate this process, tailor-made SRNF membranes based on the principles stated above ought to be prepared. Membranes with clear physical and chemical characteristics are of great assistance to separate solvent mixtures.

A mathematical model predicting this process is to be developed in the second part of this work.

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Figure Captions

Figure 1 Solvent permeabilities of binary solvent mixtures for SRNF membranes in this work

Figure 2 Separation factors of 2-butanone/Ethyl acetate and 2-butanone/THF

Figure 3 Separation factors of DMF/Acetonitrile and Hexane/CCl_4

(Note: Some data are unavailable due to lack of membrane stability or reliable flux.)

Figure 4 Separation factors of Methanol/Glycol and Glycol/DMSO

(Note: Some data are unavailable due to lack of membrane stability or reliable flux.)

Figure 5 Separation factors of Methanol/Acetonitrile and Methanol/CCl_4

(Note: Some data are unavailable due to lack of membrane stability or reliable flux.)

Figure 6 Separation factors of Ethanol/Hexane

Figure 7 The SEM cross-section image of DuraMem^{TM} 150 used in this study

Figure 1

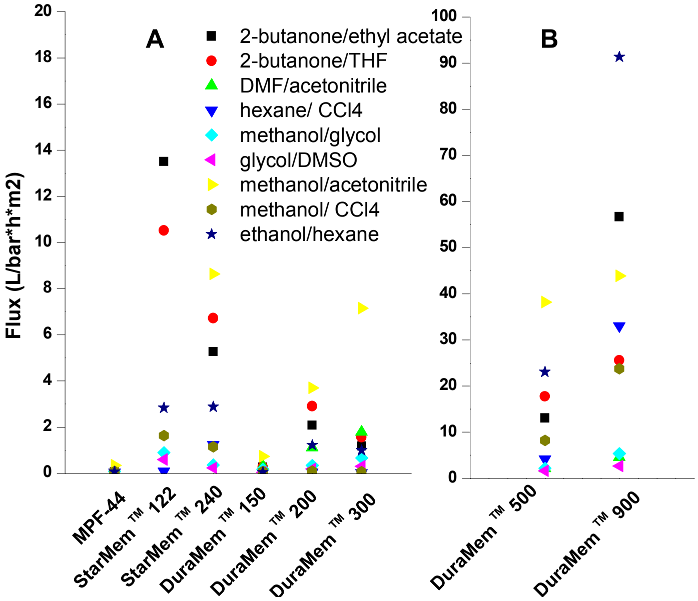
A
B
Flux (L/bar*h*m2)
0
2
4
6
8
10
12
14
16
18
20
0
10
20
30
40
50
60
70
80
90
100
■ 2-butanone/ethyl acetate
● 2-butanone/THF
▲ DMF/acetonitrile
▼ hexane/ CCl4
◆ methanol/glycol
◀ glycol/DMSO
▶ methanol/acetonitrile
⬢ methanol/ CCl4
★ ethanol/hexane
MPF-44
StarMem ™ 122
StarMem ™ 240
DuraMem ™ 150
DuraMem ™ 200
DuraMem ™ 300
DuraMem ™ 500
DuraMem ™ 900

Figure 2

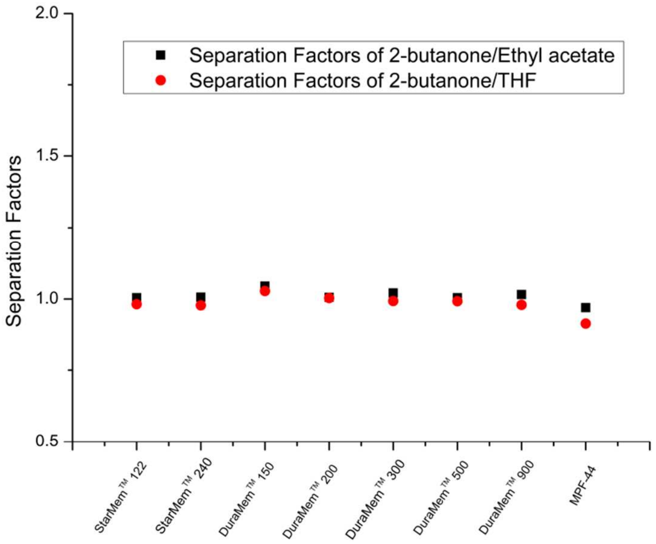
2.0
1.5
1.0
0.5
Separation Factors
■ Separation Factors of 2-butanone/Ethyl acetate
● Separation Factors of 2-butanone/THF
StarMem™ 122
StarMem™ 240
DuraMem™ 150
DuraMem™ 200
DuraMem™ 300
DuraMem™ 500
DuraMem™ 900
MPF-44

Figure 3

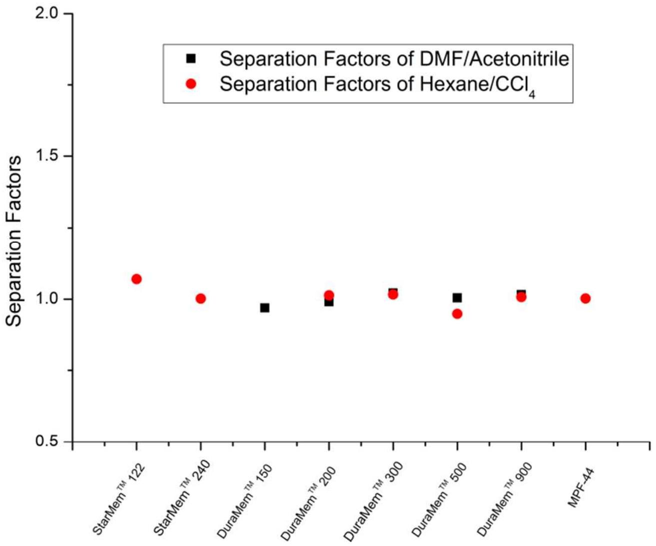
■ Separation Factors of DMF/Acetonitrile
● Separation Factors of Hexane/CCl_4
Separation Factors
2.0
1.5
1.0
0.5
StarMem™ 122
StarMem™ 240
DuraMem™ 150
DuraMem™ 200
DuraMem™ 300
DuraMem™ 500
DuraMem™ 900
MPF-44

Figure 4

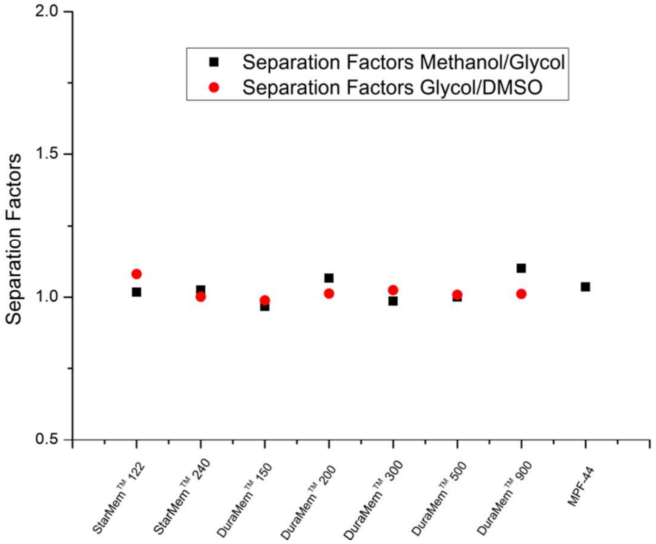
2.0
1.5
1.0
0.5
Separation Factors
■ Separation Factors Methanol/Glycol
● Separation Factors Glycol/DMSO
StarMem™ 122
StarMem™ 240
DuraMem™ 150
DuraMem™ 200
DuraMem™ 300
DuraMem™ 500
DuraMem™ 900
MPF-44

Figure 5

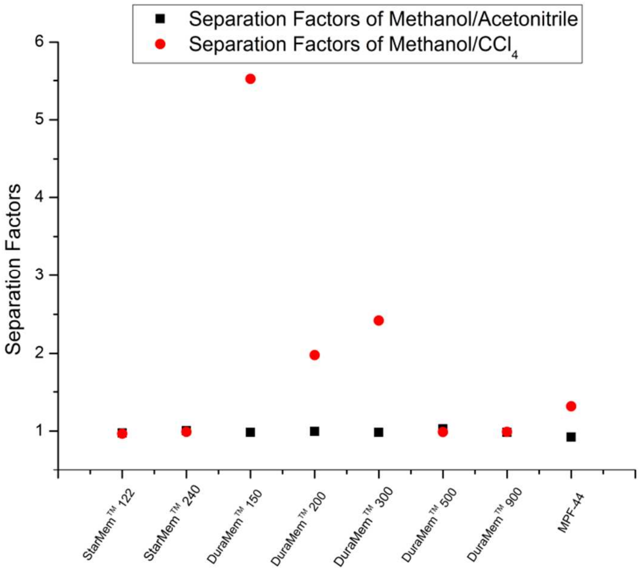
■ Separation Factors of Methanol/Acetonitrile
● Separation Factors of Methanol/CCl$_4$
Separation Factors
6
5
4
3
2
1
StarMem™ 122
StarMem™ 240
DuraMem™ 150
DuraMem™ 200
DuraMem™ 300
DuraMem™ 500
DuraMem™ 900
MPF-44

Figure 6

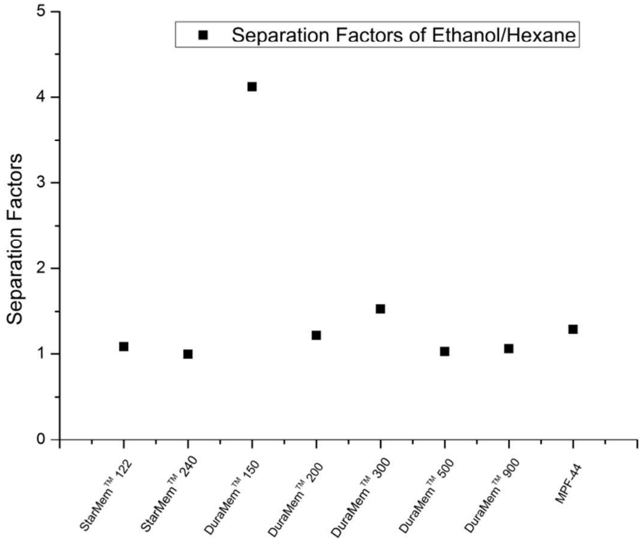
■ Separation Factors of Ethanol/Hexane
Separation Factors
0
1
2
3
4
5
StarMem^{TM} 122
StarMem^{TM} 240
DuraMem^{TM} 150
DuraMem^{TM} 200
DuraMem^{TM} 300
DuraMem^{TM} 500
DuraMem^{TM} 900
MPF-44

Figure 7

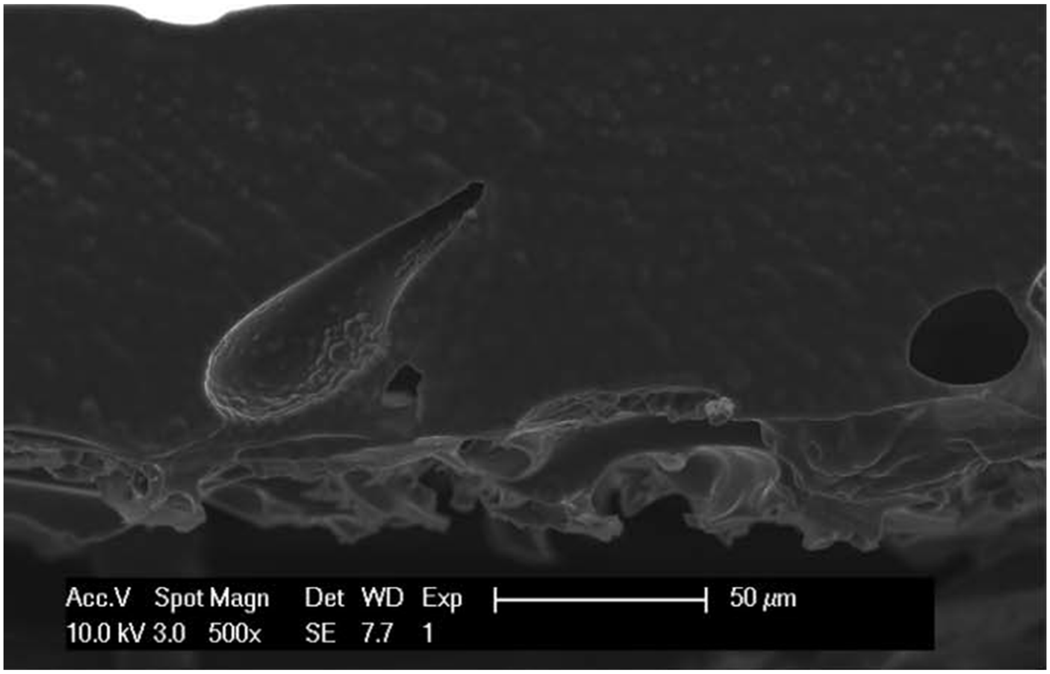

Table captions

Table 1 Properties of SRNF membranes used in this work

Table 2 Properties of 2-butanone/ethyl acetate and 2-butanone/THF

Table 3 Properties of DMF/acetonitrile and hexane/ CCl_4

Table 4 Properties of methanol/glycol and glycol/DMSO

Table 5 Properties of methanol/acetonitrile and methanol/CCl_4

Table 6 Properties of ethanol/hexane [24,25]

Table 7 Separation factors of ethanol/hexane for DuraMem^{TM} 150

Table 1

Manufacture	Type	Material	Nature	MWCO[a] (Dalton)
Evonik MET	StarMem^{TM} 122	Polyimide	Semi- hydrophobic	220
Evonik MET	StarMem^{TM} 240	Polyimide	Semi-hydrophobic	400
Evonik MET	DuraMem^{TM} 150	Modified Polyimide	Semi-hydrophobic	150
Evonik MET	DuraMem^{TM} 200	Modified Polyimide	Semi-hydrophobic	200
Evonik MET	DuraMem^{TM} 300	Modified Polyimide	Semi-hydrophobic	300
Evonik MET	DuraMem^{TM} 500	Modified Polyimide	Semi-hydrophobic	500
Evonik MET	DuraMem^{TM} 900	Modified Polyimide	Semi-hydrophobic	900
Koch	MPF-44	Polydimethylsiloxane	Hydrophilic	250

a: MWCO=molecular weight cut-off, defined as MW for 90% rejection. All the data were from the product brochure.

Table 2

Properties	2-butanone	ethyl acetate	THF
Viscosity/ mPa·s	0.423	0.449	0.46
Solubility parameter/ $MPa^{1/2}$	19.02	18.1	19.43
Surface tension/ $mN \cdot m^{-1}$	23.97	23.75	26.5
Dielectric constant	**18.51**	**6.02**	**7.45**

Table 3

Properties	DMF	Acetonitrile	Hexane	CCl_4
Viscosity/ mPa·s	0.802	0.344	0.307	0.965
Solubility parameter/ $MPa^{1/2}$	24.9	22.5	14.93	17.79
Surface tension/ mN·m^{-1}	**35.2**	**26.64**	**17.9**	**26.77**
Dielectric constant	36.71	36.04	18.51	18.2

Table 4

Properties	Methanol	Glycol	DMSO
Viscosity/ mPa·s	**0.5525**	**20**	**1.996**
Solubility parameter/ $MPa^{1/2}$	29.65	32.9	29.86
Surface tension/ $mN \cdot m^{-1}$	22.07	48	42.86
Dielectric constant	32.46	37.7	48.9

Table 5

Properties	Methanol	Acetonitrile	CCl_4
Viscosity/ mPa·s	0.5525	0.344	0.965
Solubility parameter/ MPa$^{1/2}$	**29.65**	**22.5**	**17.79**
Surface tension/ mN·m^{-1}	22.07	26.64	24.93
Dielectric constant	**32.46**	36.04	**2.328**

Table 6

Properties	Ethanol	Hexane
Viscosity/ mPa·s	1.074	0.307
Solubility parameter/ $MPa^{1/2}$	**26.59**	**14.93**
Surface tension/ $mN \cdot m^{-1}$	22.1	17.89
Dielectric constant	**24.89**	**1.88**

Table 7

Membrane pieces	Separation Factors		
	1	2	3
1	6.1959	5.9214	5.6899
2	6.0158	5.8848	5.9367
3	6.3353	6.4223	6.0650
4	6.8787	6.6927	6.194
5	6.5112	6.2388	6.239