

Contents lists available at ScienceDirect

Journal of Membrane Science



journal homepage: www.elsevier.com/locate/memsci

Porous hydrophobic-hydrophilic Janus membranes for nondispersive membrane solvent extraction

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ARTICLE INFO

Keywords: Membrane solvent extraction Hydrophobic-hydrophilic Janus membrane Phase pressures Phenol extraction Acetone extraction

ABSTRACT

Porous membranes having a particular wetting characteristic, hydrophobic or hydrophilic, are used for nondispersive membrane solvent extraction (MSX) where two immiscible phases flow on two sides of the membrane. The aqueous-organic phase interface across which solvent extraction/back extraction occurs remains immobilized on one surface of the membrane. This process requires the pressure of the phase not present in membrane pores to be either equal to or higher than that of the phase present in membrane pores; the excess phase pressure should not exceed a breakthrough pressure. In countercurrent MSX with significant flow pressure drop in each phase, this often poses a problem. To overcome this problem, flat porous Janus membranes were developed using either a base polypropylene (PP) or polyvinylidene fluoride (PVDF) or polyamide (Nylon) membrane, one side of which is hydrophobic and the other being hydrophilic. Such membranes were characterized using the contact angle, liquid entry pressure (LEP) and the droplet breakthrough pressure from each side of the membrane along with characterizations via scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR). Nondispersive solvent extractions were carried out successfully for two systems, octanol-phenol (solute)-water, toluene-acetone (solute)-water, with either flowing phase at a pressure higher than that of the other phase. The phenol extraction system had a high solute distribution coefficient whereas acetone prefers both phases almost identically. The potential practical utility of the MSX technique will be substantially enhanced via Janus MSX membranes.

1. Introduction

Solvent extraction is usually carried out in small or large scale by dispersing one phase as drops in the other phase; after extraction, the phases are separated in a separating funnel in laboratories or in mixersettlers/tall columns in industrial operations. Dispersive industrial extraction operations dependent on phase density difference are problematic due to flooding, loading and low values of allowable phase flow rate ratios. Further, dispersion requires energy; coalescence is problematic especially if emulsion formation takes place. To bypass such problems, nondispersive solvent extraction via a porous hydrophobic membrane was developed [1] wherein the organic phase flowing on one side of the membrane wetted the membrane pores whereas the aqueous phase flowing on the other side and not wetting the pores was maintained at the same or a higher pressure. The aqueous-organic phase interface was immobilized at the membrane pore mouth on the aqueous side; unless the excess aqueous phase pressure exceeds that of the organic by a critical value, ΔP_{crit} , the aqueous-organic interface is stable. Solute/s can be extracted from one phase to the other through this interface without any phase dispersion. This process has been studied and well characterized for flat membranes and especially porous hydrophobic hollow fiber membranes [2–5]. There are numerous applications in many 2-phase systems, large-scale devices, commercial applications [6–12] as well as in analytical chemistry [13]. Recent reviews of membrane solvent extraction (MSX) technique are available [14,15].

Such a concept works with a porous hydrophilic membrane as well: aqueous phase flowing on one side preferentially wets the hydrophilic membrane pores and organic phase flowing on the other side is maintained at a higher pressure [16] below a critical value, ΔP_{crit} .

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https://doi.org/10.1016/j.memsci.2021.119633

Received 31 May 2021; Received in revised form 12 July 2021; Accepted 13 July 2021 Available online 16 July 2021 0376-7388/© 2021 Elsevier B.V. All rights reserved. Nondispersive hydrophilic membrane solvent extraction (MSX) devices have also been scaled up [10,17]. Use of a porous hydrophobic or porous hydrophilic membrane for MSX encounters, however, an operational problem. Countercurrent flow is used for high solute recovery in solvent extraction. Inevitably there is significant pressure drop in the liquid phase flowing on each side of the membrane which may lead to or exceed maximum allowable phase pressure difference at both ends of the narrow flow channels. This leads to possible phase breakthrough if ΔP between the two liquid phases exceeds ΔP_{crit} for the system. It is known that ΔP_{crit} is $\propto (\gamma/d_p)$ where γ is the interfacial tension and d_p is the membrane pore diameter [18]. Lowering d_p leads to a higher ΔP_{crit} but, it can also lead to a higher diffusional resistance through the membrane. Systems with low γ pose operational problems.

A concept was demonstrated [16] wherein a porous hydrophobic membrane was placed on top of a porous hydrophilic membrane; further, the organic phase flowing on the hydrophobic membrane side wetted its pores while the aqueous phase flowing on the hydrophilic membrane side wetted its pores. This configuration allows either liquid-phase to flow at a pressure higher than that of the other phase pressure, allowing considerable flexibility of operation compared to that with a membrane having a single wetting property. This concept has two shortcomings. First, two membranes increase the diffusion distance and reduces mass flux compared to a single membrane. In cases where the solute partition coefficient highly favors a particular phase, addition of a second membrane whose pores are wetted by that phase will not unduly increase the mass transport resistance. Second, both liquids can flow into any space between the stacked membranes. If the membranes are not adhered together or supported on a short enough scale, fluid can collect between the membranes and further increase the solute diffusion distance during solvent extraction.

Therefore, it is highly desirable to have a single membrane which exhibits hydrophobic characteristics on one side and hydrophilic characteristics on the other side. Such a membrane having a hydrophobichydrophilic characteristic is a Janus membrane with asymmetric wettability. The immobilized aqueous-organic phase interface here will be inside the membrane where the physical boundary of the hydrophobic-hydrophilic characteristics of the polymers is located.

Janus membranes have been studied for a few applications, e.g., direct contact membrane distillation (DCMD), emulsion breaking, liquid/fog collection. Studies in DCMD include: composite membranes prepared with fluorinated hydrophobic surface modifying macromolecules during hydrophilic membrane casting [19–21]; dual layer hollow fiber spinning with an outer hydrophobic PVDF layer and an inner PAN-PVDF filled with high thermal conductivity additives [22]; plasma surface modification of hydrophilic flat and hollow fiber membranes of polyethersulfone (PES) [23–25] and flat PVDF membranes [26]; a



Traditional membranes (no coating)

dual-layer membrane [27] with a thin hydrophobic PVDF top-layer and a thick hydrophilic PVDF-polyvinyl alcohol sub-layer prepared by non-solvent thermally induced phase separation. The requirements for good DCMD membranes are: high liquid entry pressure (LEP); high water vapor permeability; low thermal conductivity [19]. Successful MSX requirements are quite different: high phase breakthrough pressure, high solute mass transfer rate in extraction, and high chemical, solvent, and pH resistances, among others. Further, the membrane should be capable of carrying out nondispersive MSX from either side of the membrane unlike that in DCMD.

Janus membranes have also been studied for breaking oil-in-water and water-in-oil emulsions with cotton fabric filter [28], flat membranes [29,30] and hollow fibers [31]. The function of such membranes, the mechanism of separation, the demands on the membrane by the specific systems under consideration and their use configurations are very different from those in membrane solvent extraction. Here we focus on Janus membranes with asymmetric wettability and studying their properties of relevance to MSX as well as their non-dispersive solvent extraction capability (Fig. 1 and Fig. 2). Although Fig. 1 shows a hydrophobic membrane for traditional nondispersive solvent extraction, it may be replaced by a hydrophilic membrane also with aqueous phase in the pores and organic phase outside at a higher pressure. The Janus



Fig. 2. Concentration profile of solute being transferred from one phase to the other in MSX for a composite hydrophobic-hydrophilic membrane, a Janus membrane.

Janus membranes (with coating)



Fig. 1. Comparison between nondispersive solvent extraction pressure constraints in traditional hydrophobic membranes and new Janus membranes.

membranes studied here include: hydrophobic-hydrophilic PVDF obtained by two separate methods; polypropylene with a plasma polymerized and functionalized hydrophilic coating; polyamide (Nylon 6,6) with a plasma polymerized hydrophobic coating.

These membranes have been characterized on both sides by LEP, contact angle, droplet breakthrough pressure, scanning electron microscopy (SEM), and Fourier transform infrared spectroscopy (FTIR). Solvent extraction performances of selected membranes have been studied using two extraction systems: octanol/phenol/water with a high distribution coefficient for solute species phenol into octanol; toluene/acetone/water with a distribution coefficient of around 1 for extraction of acetone from water into toluene. Nondispersive solvent extraction operation with either phase at a higher pressure has been investigated.

2. Experimental

2.1. Materials and chemicals

Porous hydrophilic PVDF and hydrophobic PVDF membranes were obtained from MilliporeSigma (Burlington, MA). Porous hydrophobic PP membrane was obtained from Celgard (Charlotte, NC). Porous polyamide (Nylon 6,6) membrane was obtained from 3M (Saint Paul, MN). Details of the original membranes before modification are provided in Table S.1. These membranes were treated later by a number of methods.

Hydrophobic PVDF membranes from MilliporeSigma (Burlington, MA) with nominal pore size of 0.1 μ m were used to make Janus membranes in-house by functionalizing one side of the membrane. For this method, potassium hydroxide (KOH), acrylic acid (AA, anhydrous), and ammonium persulfate (APS) were obtained from Sigma-Aldrich (St. Louis, MO).

Organic solvents, used for membrane solvent extraction runs and analysis, include acetone (certified ACS grade), toluene (certified ACS grade), ethanol (absolute-200 Proof, molecular biology grade), and octanol (Alfa-Aeser, 99%); all were purchased from Fisher Scientific (Hampton, NH). Phenol (loose crystals, ACS reagent) was purchased from Sigma-Aldrich (St. Louis, MO). Ultra-high purity (UHP) N₂ gas, also used in membrane solvent extraction, was purchased from Airgas, an Air Liquide Company. Deionized (DI) water, used for MSX experiments and membrane characterization, is obtained from the Barnstead water filtration system in-house.

2.2. Membrane surface modifications

In general, a very thin layer of the opposite wetting characteristic is developed on one side of the membrane. Surface modification of porous hydrophobic PVDF membranes was done using KOH and acrylic acid. PVDF membranes were cut and placed in a beaker, floating on top of an aqueous 5 M KOH solution. The beaker was then corked with a rubber stopper, to avoid evaporation, and placed in an oven at 70 °C for either 3,4, or 5 days. After being taken out of the oven, membranes were removed from the solution and washed with deionized (DI) water. Following this, the newly treated side of the membrane was floated on top of another aqueous solution of 11.1 wt% acrylic acid (AA) and 0.4 wt % APS for 5 min. The membrane was then sandwiched between two glass plates and put back into the oven for 2 h at 90 °C. The final membrane was rinsed again with DI water.

For base hydrophilic PVDF membrane samples AKS 6942 A-2, AKS 6942-B-2, AKS-6943 A-4, and AKS-6943 B-4, a thin and highly porous hydrophobic polyfluorosiloxane coating was developed by vacuumbased plasma polymerization on one surface. The ratio of Si/F monomers in these coatings was intentionally kept low at 0.50 to limit the thickness and enhance the hydrophobicity of the surface. Suffix A and B refer to the position of the membrane in the batch reactor. Coatings AKS 6942 A-2 and 6942-B-2 were prepared by keeping the treatment time at 2 min while coating AKS 6943-A-4 and AKS 6943-B-4 were prepared via a treatment time of 4 min. 1,1,3,3 Tetramethyldisiloxane and Perfluorooctane were used as monomers.

More details of such surface modification and the process used can be found in a recent publication by Sharma et al. (2021) [25] especially for porous polyethersulfone hollow fibers; lesser details for flat hydrophilic porous PVDF films are in Ref. [26]. These modifications were implemented by Applied Membrane Technology Inc. (AMT) (Minnetonka, MN). One surface of a porous hydrophilic Nylon BLA020 film was modified also into a hydrophobic surface in the sample AKS-7050 in a similar fashion.

When modifying one surface of a hydrophobic PP membrane sample AKS-7048-PP by plasma polymerization, a two-step process was followed. The preparation involved a combination of a Parylene N vacuum deposition process followed by a plasma polymerization vacuum process. Here the first step involves deposition of Parylene N coatings into the pores of the PP substrate on one side without pore filling followed by creation of functionalized molecular layers via plasma polymerization. Plasma polymerization was also implemented by AMT Inc. (Minnetonka, MN).

2.3. Membrane characterizations

2.3.1. Membrane morphology study

The cross sections and surfaces of the Janus and original (hydrophobic or hydrophilic) membranes were studied using scanning electron microscopy (SEM) (SEM - JSM 7900F Field Emission SEM (JEOL USA, Peabody, MA)). Fourier-transform infrared spectroscopy (FTIR) was performed with an Agilent Cary 670 FTIR spectrometer (Santa Clara, CA) for FTIR spectra of membrane samples. 16 scans were taken for each sample over 4000–400 cm⁻¹ with a resolution of 4 cm⁻¹. Porosity measurement details for PVDF membranes are provided prior to Table S.2.

2.3.2. Wetting properties

Contact angle is the angle at which the liquid-vapor interface meets a solid surface and therefore quantifies the wettability of the surface. An angle between 0° and 90° signifies that the aqueous droplet wets the surface to some degree and thus the surface is hydrophilic. An angle from 90° to 180° indicates a hydrophobic surface. The higher the value of the contact angle, the greater the hydrophobicity. The contact angles were determined using optical tensiometry (Model No. A 100, Rame-Hart Inc., Succasunna, NJ). An approximately 10 µL drop of distilled water is placed on each side of the membrane and the angle is measured through the optical lens.

The LEP is the minimum pressure at which a liquid will break through the largest pore of the membrane. The experimental set up for obtaining such a pressure is available [32] and shown in Figure S.1. The membrane is placed in a cell and a water-filled reservoir is connected to the top of it. Nitrogen gas is slowly pressurized and pushes the liquid out of the reservoir and into the membrane. The pressure at which the liquid (water) is observed coming out of the cell continuously is determined as the LEP.

Studies in the droplet breakthrough pressure (ΔP_B) test is an experiment designed to determine the maximum phase pressure difference that can be used in a solvent extraction system before one phase breaks through into the other phase. Before performing MSX experiments, membranes are tested with the droplet breakthrough test to see whether dual wettability works. The test set up is shown in Figure S.2. A test liquid A (e.g., DI water) is pressurized on one side of the membrane while test liquid B (e.g., toluene) is held at a constant pressure on the other side of the membrane. The pressure of liquid A is increased by 6.86 kPa (1 psi) every 2 min until a drop of the test liquid A can be seen breaking through into test liquid B. Clear PTFE tubing is used in the set-up and is important to be able to see the droplet breaking through. Since either phase can be run at a pressure higher than the other, there are two breakthrough pressures: ΔP_{org} is the breakthrough pressure difference

required for the organic phase to break into the aqueous phase; ΔP_{aq} is the breakthrough pressure difference required for aqueous phase to break into the organic phase. An interfacial tensiometer (model 70545; CSC Scientific Company, Inc., Fairfax, VA) was used to measure the surface and interfacial tensions of the various liquids and systems using the Du Nouy ring method.

2.4. Membrane solvent extraction

Membrane solvent extraction was carried out in a small PTFE cell made in-house with an active membrane area of 9.55 cm^2 (Figure S.3). A PTFE support (ET8200, Industrial Netting) is used above and below the membrane to fill in the excess space in the cell and support the membrane on both sides so that the membrane is not damaged with the excess pressure (be it on either side) during MSX. The cell also uses a PTFE gasket, placed above the membrane, to help seal the cell. A schematic of the system can be seen in Figure S.4. Experiments were made using an organic-solute-aqueous system of either octanol-phenolwater (system 1) or toluene-acetone-water (system 2). The aqueous feed for system 1 consists of 0.1 g/L phenol in water while that of system 2 contains approximately 15% acetone in water.

At the start of any MSX experiment, the aqueous solution is run through the top half of the cell for a couple of minutes before the organic reservoir is pressurized by N_2 and allowed to flow out. Once the system is stabilized (maintains the same flow rate and pressures) for approximately 5 min, a sample is taken. After the sample is taken, either the flow rate or the pressure is changed and stabilized before taking another sample. Each sample is collected for approximately 5–7 min.

For system 1, organic samples are collected and analyzed via UV–Vis with a temperature controller (Varian, Cary 50, Agilent, Santa Clara, CA). The concentration of each sample is measured at a wavelength of 273 nm. See Figure S.5. For system 2, aqueous and organic samples are both collected and analyzed via gas chromatography (GC, HP 6890 Series with flame ionization detector) with a DB 5 ms column (Agilent, Santa Clara, CA). The aqueous samples are first diluted with ethanol before being analyzed. See Figure S.6 and Figure S.7.

The distribution coefficient m_i of solute species i, the overall organic phase-based species i mass transfer coefficient, $\overline{K_o}$, and $\Delta C|_{LM}$ indicating the logarithmic mean concentration driving force for species i are indicated next by equations (1)–(3) respectively. In equations (1) to

$$m_i = \frac{C_{io}}{C_{iw}} \tag{1}$$

$$\overline{K_o} = \frac{\left(Q_{or} \left. C_{io}^b \right|_{exit} \right)}{\Delta C \big|_{LM} A_m} \tag{2}$$

$$\Delta C|_{LM} = \frac{(\Delta C_1 - \Delta C_2)}{\ln\left(\frac{\Delta C_1}{\Delta C_2}\right)}$$
(3)

$$\Delta C_1 = m_i C^b_{iw} \Big|_{in} - C^b_{io} \Big|_{exit}$$
⁽⁴⁾

$$\Delta C_2 = m_i C_{iw}^b \Big|_{\text{exit}} \tag{5}$$

(5), Q_{or} is organic phase flow rate, A_m is the membrane surface area, and C_{io}^b and C_{iw}^b are respectively the bulk solute concentration of species i in organic phase and aqueous phase respectively. The m_i value of system 1 was estimated experimentally by stirring together 50 mL of a water-phenol solution with a concentration of 0.1g phenol/L with 50 mL of octanol for 4 h. The resulting organic phase concentration was then measured via UV–Vis and the m_i value calculated using equation (1). The m_i for system 2 was obtained from literature [33].

3. Results and discussion

3.1. Membrane characterization

In this study, a few commercial flat membranes were obtained and treated on one side either via a plasma polymerization-based coating or by a KOH and acrylic acid treatment as described earlier. The list of original membranes as well as their details can be seen in Table S.1.

Table 1 provides the characterization results of the surface-treated Janus membranes with respect to contact angle, LEP value and breakthrough pressure for the aqueous-organic interface. Contact angle measurements show clearly that dual wettability was achieved for each membrane by both treatment methods. As was seen in a previous publication [26], in plasma polymerization-based treatment of hydrophilic membranes, a thin hydrophobic coating is deposited on one side of a membrane and therefore decreases the pore sizes of the treated side of the membrane. For this reason, the LEP values are always higher when pressurizing water from the hydrophobic coating side on a hydrophilic substrate (see Figure S.8). However, for alkali-treated hydrophobic PVDF membranes, surface hydrophilization/modification takes place; the pore size hardly changes. As a result, the LEP values are changed very little.

Breakthrough pressures were obtained by testing pure solvent (either toluene or octanol) with pure water. No solutes were involved to minimize inconsistencies. Addition of solutes in the system will decrease the interfacial tension of the system and therefore decrease the breakthrough pressure. In a traditional hydrophobic or hydrophilic membrane, either the organic or the aqueous phase will fill the pores, respectively. (Note: with a hydrophilic membrane, one can fill up the pores with the organic phase as well under appropriate conditions if we are not dealing with a hydrogel). To create an immobilized aqueousorganic interface, the pressure of the non-wetting phase needs to be maintained at a higher pressure. The pressure of the wetting phase can never exceed that of the non-wetting phase or else it will get dispersed into the non-wetting phase as droplets. The Janus membranes, having one side hydrophobic, filled with organic phase and one side hydrophilic, filled with aqueous phase, can withstand an excess phase pressure on either side. From Table 1, it is observed that the non-wetting phase of the base membrane (e.g., organic phase in the PVDF AKS 6942 A-2) has a higher breakthrough pressure than that of the wetting phase of the base membrane. This is due to the modification of the pore radius/structure via plasma polymerization as described earlier. The treatments are, however, quite successful, as the aqueous-organic interface can withstand significant pressures before breakthrough occurs. We should add that the hydrophilized side of the PP membrane was stable in 1 N HCl solution for seven days (experiment terminated on 8th day) for potential use in solvent extraction of actinides.

Table 2 is focused on developing simple estimates of the breakthrough pressure of the aqueous-organic phase interface using Young-LaPlace equation and comparing the calculated value with the observed value for a given modified membrane. Using measured LEP values with water and Young-LaPlace equation (Eqn.(6)) without any ~ corrections/modifications, an estimate is first developed for the value of $r_{\text{p,max}},$ the maximum pore radius in the membrane, on both sides. The contact angles (θ) of the hydrophilic sides are assumed to be 0 as water will enter the pores. This estimate is then used in Young-LaPlace equation, along with the interfacial tension for the aqueous-organic system, to predict the breakthrough pressure ΔP_B for the membrane under consideration. Before discussing the results of such calculations, we need to point out that the values of $r_{p,max}$ calculated for PVDF-VVHP membranes are quite close to the corresponding estimates from bubble-point pressure measurements for the same base membrane in an earlier study [34] where the value estimated was $0.23 \,\mu m$.

$$LEP = -\gamma_L cos\theta \frac{2}{r_{max}}$$
(6)

Table 1

Characterization results of various Janus membranes.

Designation #	Contact Angle [°] (water)		LEP [kPa (psi)] (water)		ΔP_{B} [kPa (psi)] (water-toluene)		ΔP_{B} [kPa (psi)] (water-octanol)					
	Treated	Non-treated	Treated	Non-treated	ΔP_{org}	ΔP_{aq}	ΔP_{org}	ΔP_{aq}				
Hydrophilic coated with hydrophobic												
PVDF- VVPP-original hydrophilic membrane												
AKS- 6942 A-2	126	66	255.1 (37)	172.4 (25)	186.2 (27)	68.9 (10)	NT	NT				
AKS- 6942 B-2	114	39	344.7 (50)	220.6 (32)	213.7 (31)	62.1 (9)	NT	NT				
AKS-6943 A- 4	134	70	310.3 (45)	227.5 (33)	206.8 (30)	82.7 (12)	NT	NT				
AKS- 6943 B-4	126	73	296.5 (43)	220.6 (32)	193.1 (28)	103.4 (15)	NT	NT				
Nylon- BLA020-original hydrophilic membrane												
AKS- 7050	126	43	89.6 (13)	75.8 (11)	NT	NT	>13.8 (>2)	20.7 (3)				
Original	NA	40	NA	0	NT	NA	20.7 (3)	NA				
Hydrophobic coated with hydrophilic												
PP- Celgard 2500												
AKS 7048	59	104	>413.7 (>60)	>413.7 (>60)	124.1 (18)	NT	234.4 (34)	>413.7 (>60)				
Original	NA	105	NA	>413.7 (>60)	NA	>413.7 (>60)	NA	372.3 (54)				
KOH and AA treated (hydrophobic membrane hydrophilized on one side)												
PVDF- VVHP-original hydrophobic membrane												
Sample 1 (5-day)	24	121	317.2 (46)	310.3 (45)	165.5 (24)	296.5 (43)	NT	NT				
Sample 2 (4-day)	30	114	320.6 (46.5)	313.7 (45.5)	199.9 (29)	296.5 (43)	NT	NT				
Sample 3 (3-day)	35	118	330.9 (48)	318.5 (46.2)	165.5 (24)	NT	NT	NT				
Original	NA	116	NA	337.8 (49)	NA	289.6 (42)	NT	NT				

NA: Not applicable; NT: Not tested.

Table 2

Breakthrough pressure estimates for a few Janus membranes for toluene-water system.

Designation #	Experimental LEP kPa (psi) (water)		$r_{p,max}$ (µm) calculated		$\Delta P_{\rm B}$ kPa (psi) (treated surface)		$\Delta P_{\rm B}$ kPa (psi) (non-treated surface)				
	Treated	Non-treated	Treated	Non-treated	Measured	Calculated	Measured	Calculated			
Hydrophilic coated with hydrophobic											
PVDF- VVPP											
AKS- 6942 A-2	255.1 (37)	172.4 (25)	0.40	0.84	186.2 (27)	188.6 (27.4)	68.9 (10)	90.1 (13.1)			
AKS- 6942 B-2	344.7 (50)	220.6 (32)	0.17	0.66	213.7 (31)	443.1 (64.3)	62.1 (9)	115.4 (16.7)			
AKS-6943 A- 4	310.3 (45)	227.5 (33)	0.32	0.64	206.8 (30)	233.5 (33.9)	82.7 (12)	119.0 (17.3)			
AKS- 6943 B-4	296.5 (43)	220.6 (32)	0.29	0.66	193.1 (28)	260.6 (37.8)	103.4 (15)	115.4 (16.7)			
KOH and AA treated (hydrophobic membrane hydrophilized on one side)											
PVDF- VVHP											
Sample 1 (5-day)	317.2 (46)	310.3 (45)	0.46	0.24	296.5 (43)	165.8 (24.0)	165.5 (24)	315.0 (45.7)			
Sample 2 (4-day)	320.6 (46.5)	313.7 (45.5)	0.45	0.19	296.5 (43)	167.6 (24.3)	199.9 (29)	403.2 (58.5)			
Sample 3 (3-day)	330.9 (48)	318.5 (46.2)	0.44	0.21	NT	173.0 (25.1)	165.5 (24)	354.7 (51.5)			
Original	NA	337.8 (49)	NA	0.19	NA	NA	289.6 (42)	402.9 (58.4)			

NA: Not applicable; NT: Not tested.

In Table 2, ΔP_B of the treated and untreated side correspond to the breakthrough pressures of the non-wetting and wetting phase of the original membrane, respectively. For these calculations, the contact angle in the Young-LaPlace equation is again 0 as the aqueous phase will completely wet the hydrophilic side and the organic phase will completely wet the hydrophobic side. The aqueous-organic system considered is water-toluene with an interfacial tension of 37.8 dyne/cm. One can use Young-LaPlace equation to reasonably predict the breakthrough pressures. For the KOH and AA treated membranes, the calculated values of the treated and non-treated surfaces seem to be switched when compared to the measured values. This is a limitation of the current method which estimates that the largest pore is on the hydrophobic side, due to the larger contact angle in the Young-LaPlace equation. Due to this, the estimated breakthrough pressure is higher on the hydrophobic side, which is not always the case based on the results of Table 1. Differences between the measured and calculated values may also be due to poor representation of pore shape [35] as well as defects within the coatings and the membrane themselves. It would have been useful also to characterize the underwater oil contact angle and underoil water contact angles of the virgin membrane and the modified membrane surface [31]. It is not entirely clear, however, how this value would be related to the contact angle existing just prior to breakthrough.

3.2. Membrane solvent extraction

Nondispersive solvent extraction runs were performed using membranes listed in Table S.1 and Table 1. Traditionally, fully hydrophobic membranes used in MSX require the pressure of the aqueous, nonwetting, phase to be higher than or equal to that of the organic, wetting phase, so that the organic phase cannot break through into the aqueous phase. With a Janus membrane, where one side is hydrophobic and the other hydrophilic, this pressure limitation is non-existent. Fig. 1 illustrated it conceptually.

Because each liquid phase ultimately is in contact with a piece of the membrane material that is wetted by the other immiscible phase, which cannot just be displaced, it is physically constrained and therefore the separation of phases throughout the solvent extraction system is maintained. Either phase can now be held at a higher pressure so long as the critical excess pressure difference (the breakthrough pressure difference, ΔP_B) from either side is not achieved. The location of the immobilized interface between the two phases (across which the solute is transferred) has changed from the surface of the porous membrane to now somewhere inside the composite membrane (depending on the depth of the coating/surface modification). Membrane solvent extraction can still be carried out successfully as the interface between the two phases still clearly exists. Fig. 2 illustrates the concentration profile in such an MSX system.

Membrane solvent extraction was carried out using the octanol/ phenol/water system (system 1) with a solute (phenol) distribution coefficient m_i (defined by Eqn. (1)) value of ~25.6. Fig. 3 shows the results of using an original hydrophobic PP membrane (Celgard 2500) as well as a hydrophobic PP membrane of which one surface was modified (AKS 7048) to make it a Janus membrane. Here, the organic phase-based overall mass transfer coefficient (K_o) has been plotted against the aqueous flow rate (Q_{aq}) for a specific organic flow rate (Q_{or}). For an original Celgard 2500 membrane, a ΔP of 48.3 kPa (7 psi), with the excess pressure being on the aqueous side, was maintained throughout the experiment. However, for the PP-based AKS 7048 Janus membrane, a ΔP of 34.5 kPa (5 psi), with excess pressure on the organic side, was maintained. This demonstrates that nondispersive MSX can be successfully carried out with an excess liquid phase pressure on the organic side of a base hydrophobic membrane.

The observed behavior of mass transfer coefficient in Fig. 3, with variation in aqueous flow rate, is reasonable since m_i is $\gg 1$ for which it is known that aqueous phase transport resistance controls in hydrophobic membranes [5]. Hence, as the aqueous phase flow rate increases, the overall transport resistance decreases. On the other hand, with a Janus membrane having an aqueous layer inside the membrane on the other side, the aqueous side resistance is significantly increased. Correspondingly, aqueous flow rate variation effect is significantly muted.

One cannot however conclude that a Janus membrane is not as good for mass transfer. For example, in back extraction of a solute from an organic phase into an aqueous phase with the solute preferring the aqueous phase, a hydrophobic membrane with organic phase inside the pores will have a high mass transfer resistance. A Janus membrane will have significantly reduced resistance since part of the pore length is now occupied by the aqueous phase having a low resistance. A hydrophilic Nylon substrate hydrophobized on one side (AKS 7050) was also used in the octanol/phenol/water system. Fig. 4 plots K_o as a function of Q_{aq} and Q_{org} while maintaining a ΔP of 11.4 kPa (1.6 psi) with excess pressure on the aqueous side. This further proves that regardless of the substrate (whether originally hydrophobic or hydrophilic), nondispersive MSX can be carried out using a Janus membrane.

The behavior of the mass transfer coefficient in Fig. 4 with either phase flow rate variation can also be explained. In the originally hydrophilic Nylon membrane with a $m_i \gg 1$ system, the membrane aqueous phase resistance is high. An increase in aqueous phase flow rate provides little mitigation; therefore, the overall mass transfer coefficient in the surface-modified membrane increases very slowly with Q_{aq} . However, a small increase in Q_{org} increases K_o significantly since now in the modified membrane, organic phase resistance has increased a bit due to a small hydrophobized thickness in the membrane; increased organic flow





Fig. 4. Effect of Q_{aq} and Q_{org} on K_o for octanol/phenol/water system of a hydrophilic Nylon membrane hydrophobized on one side (AKS-7050): For Q_{aq} variation, $Q_{org} = 1.3$ ml/min; for Q_{org} variation, $Q_{aq} = 1.1$ ml/min $\Delta P = 1.6$ psi, excess pressure on the aqueous side.

rate mitigates it.

Experiments were also carried out varying the ΔP in various systems, testing excess pressure in either the organic or the aqueous phase, while maintaining a constant organic and aqueous flow rate. Fig. 5 illustrates the behavior for such conditions for two different Janus membranes, PP-AKS-7048 and Nylon AKS 7050. The overall mass transfer coefficient, K_o , does not change significantly with varying pressure on either side of these membranes which is consistent with the concept of nondispersive MSX.

The SEM micrographs of the surfaces and cross-sections of original Celgard 2500 and treated AKS 7048 are shown in Fig. 6. The plasmapolymerized coating on the Celgard 2500 covers the entire surface of the membranes and decreases the pore size at the surface. The cross section in Fig. 6d shows that the thickness of the coating is ultra-thin. Figure S.9 provides the FTIR spectra of the hydrophilized side of PP membrane vis-à-vis the original PP membrane.

Another chemical system (toluene-acetone-water) was used to study nondispersive MSX with Janus membranes. This system, system 2, has a solute (acetone) distribution coefficient m_i of 0.938, much lower than that of system 1. Since the value of m_i is approximately 1, acetone is almost equally favored by both the aqueous and the organic phase. The membrane PP-AKS 7048 with a base hydrophobic PP membrane hydrophilized at the other end was also used with this system. The aqueous and organic flow rates were varied while the pressure difference was maintained at 34.5 kPa (5 psi) with the organic phase being at



Fig. 5. Effect of phase pressure on overall solute mass transfer coefficient in MSX for octanol/phenol/water system using a hydrophobic PP membrane hydrophilized on one side (AKS 7048) and a hydrophilic Nylon membrane hydrophobized on one side (AKS 7050): $Q_{org} = 1.3 \text{ ml/min}$, $Q_{aq} = 2.1 \text{ ml/min}$. Negative ΔP (in psi) corresponds to an excess pressure on the organic side while positive ΔP (in psi) corresponds to an excess pressure on the aqueous side.



Fig. 6. SEM micrographs of flat PP membranes. (a) PP original surface; (b) PP AKS 7048 coated surface; (c) Part of PP original cross section which is 30 µm thick; (d) PP AKS 7048 cross section showing coated surface at the top (about 200 nm thick).

a higher pressure (Fig. 7). Varying either flow rate achieves approximately the same K_o values (subject to individual side fluid mechanics) indicating that the hydrophilic surface modification does not add a significant resistance to the system.

We now focus on PVDF membranes. The FTIR spectra of PVDF membranes (Fig. 8a) show that the AA treatment functionalizes and stabilizes the hydrophilization of the surface of a hydrophobic membrane. Around 1720 cm⁻¹, there is a hint of a peak for samples B, C, and D (treated PVDF samples). It is the same peak found in the functionalized/hydrophilized PVDF membranes in Ref. [36] wherein the first step involves KOH treatment [37]. Because the membranes studied here received only a slight treatment on one side, the peak around 1720 cm⁻¹ due to –COOH stretching vibration is much less intense than that in Ref. [36] where the whole membrane was hydrophilized. Other peaks due to fluorocarbon (1250-1000 cm⁻¹) and the hydrocarbon (1450–1350 and 900-800 cm⁻¹) were also identified in alkali-modified PVDF [38]. Fig. 8b illustrates the SEMs of the virgin hydrophobic PVDF membrane surface and that surface modified by surface treatment with



Fig. 7. MSX for toluene/acetone/water system using a hydrophobic PP membrane treated on one side via plasma polymerization (AKS-7048): $\Delta P \sim 5$ psi (excess org. pressure). For Q_{aq} variation, $Q_{org}=1.8$ ml/min. For Q_{org} variation, $Q_{aq}=1.1$ ml/min.

KOH for 5 days followed by an AA solution. The brighter surface of modified PVDF membrane clearly identifies a changed surface. However, the pore sizes appear hardly changed. Another source [39] successfully employed KOH-based hydrophilization of the surface of porous flat PVDF membrane to make a Janus membrane and studied direct contact membrane distillation process. The membrane appeared unchanged in mechanical properties except for surface discoloration. We observed a similar color change.

The results of studies with PVDF membranes used in MSX experiments are shown next. Fig. 9 and Fig. 10 compare results of an original hydrophobic PVDF membrane and a membrane treated on one side for 5 days with KOH followed by an AA treatment. The KOH/AA treated membrane was run with a ΔP of about 69 kPa (10 psi), with excess pressure on the organic side, while the original was run at a ΔP of about 10 psi, with excess pressure on the aqueous side.

In Fig. 9, we illustrate the variation of the overall mass transfer coefficient with aqueous phase flow rate variation. With the extraction system of toluene/acetone/water, the effect of aqueous phase flow rate variation is quite similar for both membranes since the membrane section whether it is hydrophobic or hydrophilic will behave in a similar fashion for the KOH-treated membranes. The treated membrane performs almost on par with the original membrane, again proving the success and benefit of Janus membranes for use in MSX. Interestingly, we observe a somewhat similar behavioral pattern in Fig. 10 for these membranes when organic phase flow variation is studied. For the originally hydrophilic PVDF membrane hydrophobized on one side by plasma polymerization process, AKS-6943A-4, the pore size gets reduced leading to an increase in membrane resistance. In Fig. 11, we see that this reduces the overall mass transfer coefficient K_0 a bit. In Fig. 11, our main goal is to show that increased pressure on either side of the membrane does not essentially affect the mass transfer rate for given aqueous and organic phase flow rates.

There are a few general topics of some interest in such a study



Fig. 8a. FTIR spectrum for PVDF membrane samples; Sample A: original PVDF-VVHP (hydrophobic); Sample B, C and D: PVDF treated with KOH for 3, 4, and 5 days respectively followed by an AA solution.



Fig. 8b. SEM micrographs at 10,000X magnification of flat PVDF membrane surfaces: 1) virgin PVDF membrane; 2) PVDF surface treated with KOH for 5 days followed by treatment with an AA solution.



Fig. 9. Effect of Q_{aq} for toluene/acetone/water system for a pristine hydrophobic PVDF membrane and a hydrophobic PVDF membrane treated with KOH and an acrylic acid soln.: $Q_{org} = 1.8 \text{ ml/min } \Delta P = 10 \text{ psi}$ (excess *org.* pressure) and 10 psi (excess *aq.* pressure) for the 5 M KOH treated and original membrane, respectively.



Fig. 10. Effect of Q_{org} for toluene/acetone/water system for a pristine hydrophobic PVDF membrane and a hydrophobic PVDF membrane treated with KOH and an acrylic acid soln.: $Q_{aq} = 1.1 \text{ ml/min } \Delta P = 10 \text{ psi}$ (excess *org.* pressure) and 10 psi (excess *aq.* pressure) for the 5 M KOH treated and original membrane, respectively.



Fig. 11. Effect of phase pressure on overall solute mass transfer coefficient in MSX for toluene/acetone/water system using a hydrophilic PVDF membrane hydrophobized on one side (AKS-6943 A-4): $Q_{org} = 1.8 \text{ ml/min}$, $Q_{aq} = 2.1 \text{ ml/min}$. Negative ΔP (in psi) corresponds to an excess pressure on the organic side while positive ΔP (in psi) corresponds to an excess pressure on the aqueous side.

regarding the various membrane modifications. In plasma polymerization-based surface modification, one would like to know the element distribution due to the coating. In Figures S10 and S11, we illustrate those aspects for the virgin Nylon BLA 020 membrane and the modified Nylon AKS 7050 membrane, respectively. These clearly indicate the presence and surface distribution of the elements F and Si introduced by the coating process. Similar analysis at another site of the same coated membrane indicated an essentially identical distribution of elements F and Si beside C and O.

In the plasma polymerization-based surface modifications, special attention was given to short contact time [26] so that the pore surface decrease via hydrophobic polymer grafting did not go too far as can happen along with complete hydrophobization [23]. This yields higher breakthrough pressure without affecting the mass transfer resistance much.

Hydrophilic membranes having small pore sizes have been used in lithium extraction and back extraction studies [40–42]. These articles deal with small pore hydrophilic membranes created from poly (etheretherketone) (PEEK) based PEEK/SPEEK blend, Poly (ethylene-*co*-vinyl alcohol, EVAL) etc. Due to the small pore size, their breakthrough pressures are considerably higher. However, solvent extraction processes often need a back extraction step and are designed such that in one of them the solute is preferred by the organic phase and in the other it is preferred by the aqueous phase. Thus, porous hydrophilic membranes are useful where the solute is preferred by the aqueous phase and are not useful where the solute is preferred by the organic phase. Using the same hydrophilic membrane for both steps incurs considerable mass transfer penalty in the latter case.

The possibility of carrying out nondispersive MSX with composite membranes having different wetting properties on two sides of the membrane can also be extended to one side having some solute selectivity due to the membrane structure. A graphene oxide laminate based composite membrane [43] would then become useful in such a context. Additional membrane materials and structures where the membrane wetting property modification goes deep into the membrane are also of interest. Tuning of the wetting property changeover across the membrane thickness may be utilized to enhance the mass transfer rate in MSX for systems having high or low values of the solute distribution/partition coefficient. It would be useful also to investigate the performance of such Janus membranes in hollow fiber form especially for metal extractions and back-extractions [8,11,44]. Here we had used a simple solvent such as toluene or octanol for solvent extraction of the solute, acetone or phenol. In metal extraction, invariably a complexing agent will be present in a solvent to react reversibly with the metal ions for enhanced and selective extraction.

4. Concluding Remarks

Janus membranes having hydrophobic and hydrophilic wetting characteristic on two sides of a porous membrane can be used to eliminate the pressure limitation that plagues nondispersive MSX. Using such a membrane, one can now operate non-dispersively with either phase flowing at a pressure higher than that of the other phase. Porous PVDF and PP membranes were treated on one side either through plasmapolymerization or a KOH/AA treatment and a Janus membrane with dual wettability was successfully created. The starting PVDF membrane was either hydrophobic or hydrophilic. A similar strategy was employed with a porous hydrophilic Nylon membrane as well. The membranes were used in two different solvent extraction systems in MSX, having widely different solute distribution coefficients. The developed Janus membranes were able to perform on par with the original membrane while the "wetting" phase for the original membrane was held at a higher pressure over that of the "non-wetting" phase, something that has never been done before. It is important to note that Janus membranes are novel to MSX because directionality of the pressure gradient across the membrane is no longer crucial; further solvent extraction can take place on both sides of the membrane. In DCMD for example, Janus membranes are only capable of utilizing one side. Therefore, use of Janus membranes in nondispersive MSX is very novel.

Declaration of competing interest

The authors declare that they have no conflict of interest.

Acknowledgements

The authors gratefully acknowledge support for this research from NSF Awards IIP1034710, IIP 1822130. This research was carried out in the NSF Industry/University Cooperative Research Center for Membrane Science, Engineering and Technology that has been supported via two NSF Awards IIP1034710 and IIP-1822130. LR and KKS thank Celgard for providing the polypropylene membrane, 3M for making the Nylon membranes available and Millipore Sigma for providing the PVDF membranes. LR thanks CME Department at NJIT for partial support as a TA.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.memsci.2021.119633.

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