ELSEVIER

Chemical Engineering Journal 138 (2008) 10–19

Chemical Engineering Journal

www.elsevier.com/locate/cej

Characterization of blended polymeric membranes for pervaporation of hydrazine hydrate

Mrinal Kanti Mandal, Sukalyan Dutta, P.K. Bhattacharya*

Department of Chemical Engineering, Indian Institute of Technology Kanpur, Kanpur 208016, India

Received 10 January 2007; received in revised form 14 May 2007; accepted 17 May 2007

Abstract

Pervaporation of commercial hydrazine hydrate (at 64 wt.% hydrazine) was carried out to obtain hydrazine, which in anhydrous form is an important inorganic fuel. Experimental studies were made using various laboratory prepared polymeric membranes, primarily through blending of polymers and the results are analyzed through the measurements of flux and selectivity.

Acrylonitrile–butadiene–styrene (ABS) and ethyl cellulose (EC) polymers, in different ratios, were blended to prepare membranes in order to vary the ratios of hydrophilic-hydrophobic characteristics. The objective was to characterize blended membranes in terms of measurement of contact angle, X-ray diffraction (XRD), positron annihilation techniques (PAL), thermo-gravimetric analysis (TGA) and tensile strength. Sorption studies helped in estimating equilibrium sorption, which further enhanced understanding towards pervaporation selectivity.

It was evident from the results that blended polymers could be useful to develop newer membranes with improved perm-selectivity. Further, adjusting blend composition pervaporation properties could be varied. Analysis of results is based on normalizing the values of flux with respect to thickness, in order to develop better understanding of blended properties of membranes. Values of sorption and diffusion selectivity were also obtained from thermodynamic treatment which is based on Flory–Huggins theory.

Keywords: Hydrazine hydrate; Blended polymer membranes; Acrylonitrile–butadiene–styrene; Ethyl cellulose; Membrane chracterization

1. Introduction

Hydrazine is an important inorganic chemical that upon combustion produces nitrogen and water, unlike hydrocarbon fuels producing carbon dioxide and water. Hydrazine is less flammable and less volatile than hydrocarbon fuels and hence it is used as a component in jet fuels because it produces a large amount of heat when burned. Hydrazine is relatively environment friendly because of its quick degradation. It is used as an oxygen scavenger for water boiler feed and in heating systems to prevent corrosion damage. Further, it is also utilized as a reducing agent for the recovery of precious metals. Because of its versatility, it finds active applications in organic synthesis for agrochemicals and pharmaceuticals; apart from photographic and other uses, such as, heat stabilizers, polymerization catalysts, and flame-retardants, blowing agents for plastics, explosives, and dyes. Recently, hydrazine is applied to LCD (liquid crystal displays) as the fuel to make faster thin-film transistors. For rocket propulsion, anhydrous hydrazine is required; however, by ordinary distillation, 64 wt.% of hydrazine is produced. Therefore, removal of water from hydrate state to produce anhydrous hydrazine is essential. Conventional separation technique, like distillation forms an azeotrope with water at 71.5 wt.% of hydrazine [1]. Further, hydrazine and water, being highly polar substances (surface tension values very close) impart strong hydrogen bonding between them. Therefore, hybrid processes are recommended to seek dehydration. Hydrazine also poses a dangerous fire and explosion risk and can explode during distillation if traces of air are present, apart from other limitations like high-energy consumption and cost. Hence, it is required to search alternative technologies to produce anhydrous hydrazine. Application of membrane technology is one such attempt to address the stated problems [2–4] and the process of pervaporation, in particular, may be interesting to

---

Abbreviations: ABS, acrylonitrile–butadiene–styrene; BM, blended membrane; EC, ethyl cellulose; MEC4, modified ethyl cellulose; PAL, positron annihilation lifetime; PSI, pervaporation separation index; PV, pervaporation; TGA, thermogravimetric analysis; WAXRD, wide angle X-ray diffraction; XRD, X-ray diffraction

* Corresponding author. Tel.: +91 512 259 7093/7127; fax: +91 512 259 0104.
E-mail address: pkbhatta@iitk.ac.in (P.K. Bhattacharya).

1385-8947/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2007.05.023

Nomenclature

b	constant in Eq. (2)
f	free volume fraction
I_3	*ortho*-positrionium intensity
r	spherical free volume radius (nm)
Δr	electron layer thickness (nm)
V_F	free volume of the sphere
w	weight fraction

Greek symbols

α	selectivity
χ	interaction parameter
δ	solubility parameter ($J^{1/2}/cm^{3/2}$)
Φ	volume fraction
γ	activity coefficient
θ	contact angle
ρ	density (g/cm^3)
τ_3	life time of *ortho*-positrionium

Subscripts

H	hydrazine
W	water

Superscripts

D	diffusivity
P	pervaporation
S	sorption

examine because of its potential to separate azeotropic mixtures.

Pervaporation is an energy efficient combination of membrane permeation and evaporation. The process is used for separation of liquid mixture through a nonporous perm-selective membrane. The feed liquid mixture, placed in contact on one side of the membrane, permeates through the membrane and the permeating liquid is removed as vapor from the downstream side. This is a passive process and the driving force for molecular transport is the chemical potential gradient. Permeate vapor is continuously removed to maintain the gradient using a vacuum pump or sweeping gas (normally air or steam) in the downstream side. Vaporization of permeating components extract latent heat from feed liquid; accordingly, external heating of feed liquid may become necessary to make up the loss of enthalpy for maintaining isothermal condition. Pervaporation is potentially applicable to mixtures that are difficult to separate by more conventional techniques, such as azeotropic mixtures or mixtures of close-boiling components.

The selection of polymer for hydrazine hydrate separation plays an important role due to highly alkaline nature of hydrazine (pH >12.5) and only few polymers are available that may withstand such high alkalinity. Further, hydrazine has strong reducing and hydrolyzing effects. Ravindra et al. [5] had used ethyl cellulose (EC) membrane to carry out this separation. Even though, ethyl cellulose is highly selective for water at low concentrations of hydrazine, they obtained low selectivity for 64 wt.% aqueous hydrazine solutions. In an earlier attempt in our laboratory [6] different varieties of hydrophilic and hydrophobic membranes were utilized for hydrazine hydrate separation with all the chosen polymers revealing high selectivity for water; however, with moderate flux. Modified ethyl cellulose polymer, prepared by introducing carbamate groups (reacting ethyl cellulose with phenyl *iso*-cyanate) could increase hydrophobicity, which could provide enhanced flux and selectivity.

Selection of membrane with high water-perm-selectivity may be achieved by increasing the sorption selectivity (water to hydrazine) or diffusion selectivity. For a better sorption ratio, hydrophilic moiety may be introduced into the polymer chain to enhance water sorption; but hydrazine sorption may also increase because of high polarity of the compound. In addition to this, excessive swelling may decrease diffusion selectivity because of increase in free volume, which in turn may further decrease overall selectivity [7]. Various hydrophilic chitoson and modified chitoson membranes were also previously used [8] but were found to provide low values of selectivity. Again, for better diffusion ratio, the hydrophobic moiety may be introduced into the polymer chain. This may, however, decrease permeation rate. Thus, with the introduction of balanced quantities of hydrophilic and hydrophobic moieties, better flux and better selectivity may be obtained. Accordingly, one may combine the properties of hydrophilic and hydrophobic polymers while casting a membrane and may thus achieve higher values of flux and selectivity.

In this regard, a new polymer, acrylonitrile–butadiene–styrene (ABS) was utilized for its both hydrophilic and hydrophobic properties. The present work, therefore, is an attempt to combine ethyl cellulose (hydrophilic) and ABS polymers in different proportions by blending. This is to examine separation of hydrazine hydrate by pervaporation process at fixed operating conditions (temperature: 50 °C, downstream pressure: 0.1 mmHg, static feed condition) using laboratory prepared membranes (ABS blended with ethyl cellulose). Experimental investigations were planned to observe flux and selectivity utilizing these modified membranes. Furthermore, results of this study have been analyzed by calculating interaction parameters between liquid component and polymer.

2. Experimental

2.1. Materials

Hydrazine hydrate (Qualigens, India), ethyl cellulose (ethoxy content 48–49.5%: Loba-Chemie, India), poly-acrylonitrile-co–butadiene–co-styrene (Aldrich Chemical Company Inc.), toluene (Ranbaxy, India) were used. Double distilled water was used throughout the experiments.

2.2. Preparation of membrane

2.2.1. Polymer solution

Ethyl cellulose (EC) polymer (15 g) was dissolved in toluene (85 g). The solution was centrifuged (REMI model-R 24, India) at 10,000 rpm for 15 min for the removal of un-dissolved polymer. The supernatant homogeneous solution was transferred to a conical flask (air tight) and kept for overnight for the removal of entrapped air bubbles. Similar procedures were followed for preparing solutions of acrylonitrile–butadiene–styrene (ABS-15 wt.% in toluene) polymers.

2.2.2. *Blending*

Ethyl cellulose and ABS polymers were mixed on a definite weight ratio. The prepared solution (polymers in solvent) was continuously stirred for 24 h in order obtain homogeneous polymer solution. It was further kept in a vacuum oven for 24 h for removal of any traces of entrapped air bubbles.

2.2.3. *Casting*

The casting of membrane was carried out on a glass plate using a modified thin film applicator (ACME, India) as well as automatic film applicator (BYK Gardener). After around 24 h of solvent evaporation, the membrane was placed in the vacuum oven for another 4 h for the removal of residual traces of solvent. Varying proportions of blended membranes (ABS and EC polymers) are given new names and are reported in Table 1.

Table 1
Composition along with notations of blended membranes

Blending[a]	Membrane
100:0	EC
80:20	BM20
70:30	BM30
60:40	BM40
30:70	BM70
20:80	BM80
0:100	ABS

[a] (in g) of EC:ABS in 100 g of polymer solution.

2.3. *Characterization of membrane*

2.3.1. *XRD*

The molecular packing of the original and blended ABS membranes was investigated with wide angle X-ray diffraction (WAXRD) method. WAXRD curves of the membranes were obtained using an Iso-Debyeflex X-ray powder diffractometer having monochromatic radiation of α-rays emitted by Cu at a wave length of 1.54 Å. Scanning was performed with an angle ranging from 6 to 50 at a rate of 3 °/min with the accelerating voltage of 30 kV and tube current of 20 mA.

2.3.2. *Positron annihilation lifetime (PAL) spectroscopy*

The PAL measurements were carried out using a fast-fast system having a resolution of 300 ps (FWHM for the ^{60}Co prompt γ-rays, under ^{22}Na window settings). The positron source was prepared by depositing around aqueous 2 micro-Curie solution of ^{22}NaCl on a thin aluminium foil (thickness ∼12 μm) which was covered with an identical foil. Approximately, one million counts were collected in each spectrum and four spectra were measured for each sample. The lifetime data were analyzed using PATFIT-88 programs [9]. Source correction was done for all the spectra. The following expression was used to relate *o*-Ps pick-off lifetime (τ_3) and special free volume radius (r) [10,11]:

$$\tau_3 = \frac{1}{2}\left[1 - \frac{r}{(r+\Delta r)} + \left(\frac{1}{2\pi}\right)\sin\left(\frac{2r\pi}{r+\Delta r}\right)\right]^{-1} \qquad (1)$$

where Δr is the electron layer thickness. Further, the fractional free volume f may be estimated from the following empirical relation:

$$f = bV_F I_3 \qquad (2)$$

where V_F is the free volume of the membrane and I_3 is the intensity corresponding to τ_3. The scaling factor b is obtained from variation of free volume with temperature. However, in the absence such data, it may be typically assigned a value of 1.0 nm^{-3} [12].

2.3.3. *Contact angle analysis*

Equilibrium contact angles of water with membranes were measured in saturated environment through sessile drop method using Goniometer (Rame-Hart Inc. Imaging System, USA). Flat sheets were mounted using stainless steel holder and placed in environmental chamber. A glass syringe with a stainless steel needle was used to put the liquid drop on membrane. The angles were measured with RHI software by capturing the image with video camera. Around 5 min stabilization time was allowed to capture the image. Around 50 readings were then recorded in a time span of 1 s and from the average of these readings, an estimation of angle was made. Further, four or five such measurements were made for each liquid on the same membrane and the average value was noted.

2.3.4. *Sorption measurements*

Pre-weighed dry membranes were taken in a conical flask containing water or hydrazine hydrate for estimation of sorption. The flask was kept on shaker bath (model SW-23, Julabo, Germany) under 200 rpm at 50 °C. The membranes in conical flasks were taken out at regular intervals and were wiped with tissue paper for the removal of adhered liquid and subsequently the wet weight of the membrane was measured. The procedure was repeated until consecutive readings of weight of sorbed membranes were found equal. The difference of weights with respect to dry weight of membranes is presented as percentage of sorption.

2.3.5. *Thermo-gravimetric analysis (TGA)*

Thermal stability of the polymer films were examined using the Pyris diamond TG/DTA analyzer (*Perkin-Elmer*). Temperature conditions used were from 30 to 500 °C, and heating rate employed was at 10 °C/min. Nitrogen gas, at the rate of 20 ml/min, was utilized for flushing purpose.

2.3.6. *Mechanical properties*

The tensile strength and elongation (at the break) of the membranes were evaluated by the Tensile Testing Machine (DLC 10 kNG, LLOYD Instruments Ltd., England) as per the procedure, outlined in ASTM D-421A test method.

2.4. Analysis

Hydrazine is a hygroscopic substance which is prone to air oxidation. Further, under exposure to atmosphere it absorbs carbon dioxide and, therefore, analysis of hydrazine sample requires proper precautions. The tedious procedure involved in *Penneman method* [13] of employing potassium iodate as titrant is prone to errors. Therefore, gas chromatograph method [14] was employed for analysis of hydrazine. Concentrations in both the feed and the permeate samples were measured. Gas chromatograph (Nucon, India equipped with TCD) with *Puropack-Q* as reference column and Chromosorb-103 as main column was employed for the purpose. The injector, detector and oven temperatures were set at 210, 220 and 170 °C, respectively. Helium was used as a carrier gas at 20 ml/min. Observed retention time for water was 1.0 and that for hydrazine was 2.46 min for above stated conditions.

2.5. Pervaporation: set-up and procedure

Fig. 1 shows a schematic version of the experimental set-up which was designed, developed and fabricated at I.I.T.-Kanpur (India) for the pervaporation investigations. Pervaporation test cell, made of glass, was having specially designed flanges to lodge the membrane with an effective membrane area of 50.4 cm^2. The membrane was kept on a highly porous stainless steel support with the shiny dense polymeric layer facing the feed solution. Initially, fixed volume of feed solution (hydrazine hydrate of 64 wt.% of hydrazine) was taken on the upper side (feed side) of the cell. Both upstream and downstream sides of the cell were heated (in order to maintain isothermal conditions around the cell [15]) and hence cell surface was covered by heating mantels. The temperatures of both the sides were controlled at 50 °C, using PID controller device (Fuji, Japan).

The membrane upstream side was kept at atmospheric pressure and the downstream side was maintained under vacuum, using a vacuum pump (Vacuum Techniques, Bangalore, India). For collecting permeated pervoporate samples, the condenser line was split into two in which sample traps were placed that could, alternately, allow the collection of sample continuously without interrupting the operation. The permeated vapors are condensed in the trap, which was kept in Dewar flask, filled with liquid nitrogen. The frozen permeate was collected within a specified time interval. The cold traps were brought to room temperature for measuring its weight, using a five decimal balance, to determine mass flux. Subsequently, permeate was analyzed to determine its hydrazine content. To minimize in measurement errors, an average of two separate consecutive readings were taken after the system reached to a pseudo-steady state (negligible removal of permeate volume in comparison to feed volume). All steady-state values of flux and selectivity were taken for analysis purpose. Experiments were repeated until the data recorded came within ±10% error.

3. Results and discussion

3.1. Characterization

Ethyl cellulose and ABS polymers were blended with different proportions to form blended ABS membrane (BM). XRD and positron annihilations techniques were employed for the purpose and results are discussed. Contact angles were also measured for the membranes used for the work. Membrane stabilities were also measured employing thermo-gravimetric analyzer and tensile testing machine.

3.1.1. XRD

WAXRD spectra of ABS and BM membranes are shown in Fig. 2. Both ABS and BM spectrum's display two sharp peaks at 28° and 33°. The sharp peaks suggest the semi-crystalline nature of polymers. However, as EC content increases in the polymer, the spectrum shows variation in intensity low angle range

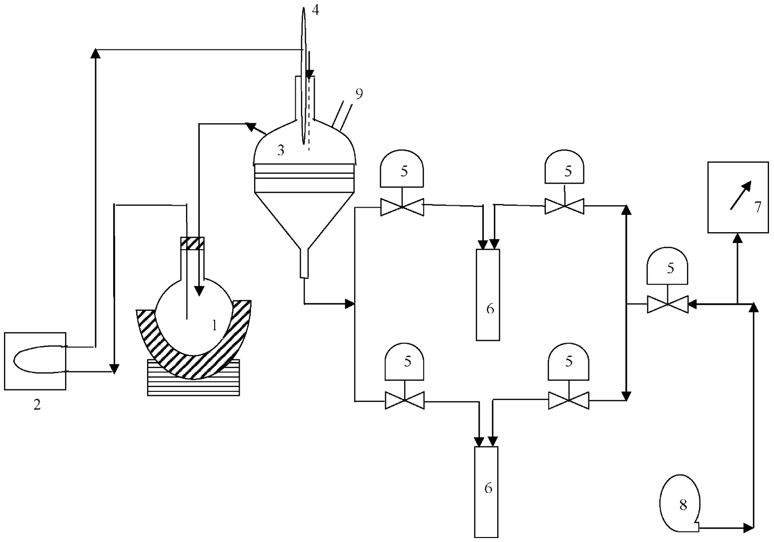

Fig. 1. Experimental set-up for pervaporation: schematic diagram (1, Preheating cell; 2, peristaltic pump; 3, pervaporation cell; 4, thermocouple; 5, needle valves; 6, liquid traps placed in Dewar flask; 7, McLeod gauge, Pirani gauge, capillary column in parallel mode; 8, vacuum pump; 9, condenser).

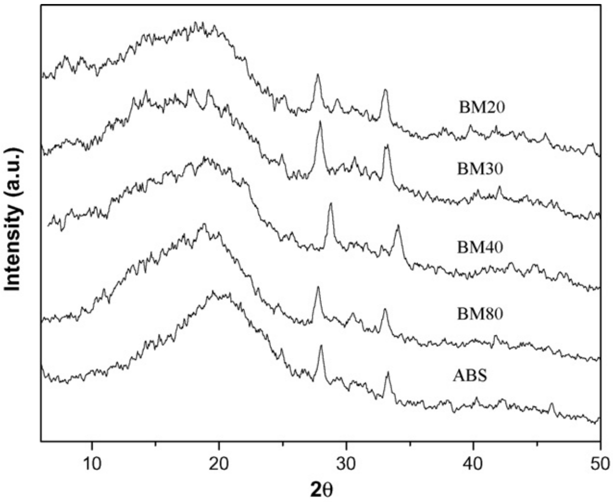

Fig. 2. XRD pattern of blended membranes.

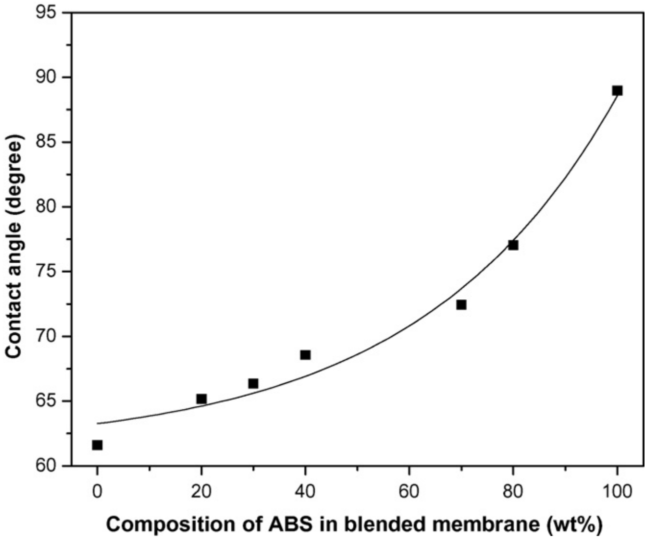

Fig. 3. Variation of contact angle for blended membranes.

(between 6 and 25). Qualitatively, this change suggests that the blended ABS membrane is slightly more amorphous compared to ABS membrane. This amorphous character increases when EC content increases. This may, in a sense, increase the flux.

3.1.2. *Positron annihilation lifetime (PAL) spectroscopy*

A detailed work on positron lifetime spectroscopic analysis was made for varieties of dense membranes in order to obtain, primarily, free volume parameters. In this paper, results pertaining to ABS and modified ABS membranes are presented in Table 2. Ortho positron lifetime (τ_3) values were observed to be smaller for blended membranes, compared to pure EC and ABS membrane. Further, the intensity values steadily decreases from BM20 to BM80. It also shows the calculated values of free volume fraction which was also found to be slightly smaller for blended membranes as compared to EC and ABS. These obtained free volume parameters are, in general, in the same range as given for semi crystalline polymers [16]. Therefore, during blending of EC with ABS, free volume shrinks which, in effect, may reduce diffusivities of species within membranes, eventually reducing flux for BM70 and BM80 membranes than that for ABS membrane.

3.1.3. *Contact angle analysis*

The contact angles of water on blended membranes as well as on pure polymeric EC and ABS membranes were studied and are shown in Fig. 3. It may be observed that with increase in ABS composition the contact angle is increasing exponentially. This suggests that when ABS content in a polymer increases, the hydrophobicity of the polymer also increases. Thus, expectedly, EC membrane on blending with ABS changes its characteristics from hydrophilic to hydrophobic, as evidenced from increase of contact angle.

3.1.4. *Sorption*

Sorption experiments, under equilibrium conditions, were conducted on different blended membranes for both water and hydrazine hydrate system at 50°C. The equilibrium sorption values for both water and hydrazine hydrate system are reported in Table 3. Interestingly, equilibrium sorption values for hydrazine hydrate is higher than that for water for all membranes. Similar attribution was made for EC membrane by Ravindra et al. [5].

3.1.5. *Thermo-gravimetric analysis (TGA)*

Apart from separation characteristics required, membrane stability is one of the major aspects on which commercial viability of PV process may depend based on the membrane proposed. Temperature stability is one of them as the process may be carried out at higher temperatures. This may be because the feed may in itself be available at higher temperatures. Accordingly, testing characterization with regard to temperature stability was carried out, as per Section 2.3.5.

Table 2
Free volume parameters of blended membranes

Membrane	State	τ_3 (ns)	I_3 (%)	r (nm) (sphere)	V_f (nm^3)	f
EC	Dry	2.63	22.5	0.33	0.150593	0.034
BM20	Dry	2.26	23.9	0.30	0.113143	0.027
BM30	Dry	2.26	23.1	0.30	0.113143	0.026
BM40	Dry	2.26	–	0.30	0.113143	–
BM70	Dry	2.28	20.2	0.294	0.106489	0.022
BM80	Dry	2.23	21.2	0.29	0.102202	0.022
ABS	Dry	2.54	21.1	0.32	0.137314	0.029

Table 3
Sorption characteristics of water and hydrazine hydrate ($T = 50\,^{\circ}$C)

Membrane	% Sorption of water (g/g of dry polymer)	% Sorption of hydrazine hydrate (g/g of dry polymer)
EC	4.12	5.23
BM20	2.67	4.81
BM30	2.20	4.56
BM40	1.31	3.53
BM70	1.12	2.21
BM80	0.59	1.27
ABS	0.31	0.50

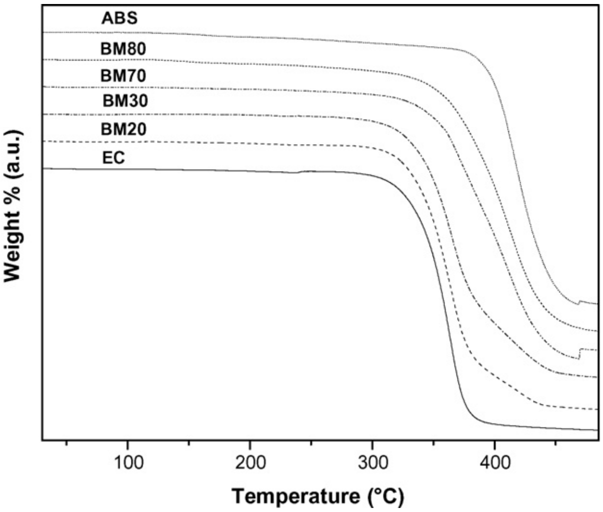

Fig. 4. TGA curves of pure and blended membranes.

Fig. 4 depicts thermal degradation of EC, ABS and blend of EC/ABS membranes. Thermo-grams shows mass loss of a membrane subjected to an increasing temperature environment. Further, all curves start at 100% mass and end at almost thermally decomposed form of the membrane (nearing 0%). Accordingly, it may be clearly inferred that up to around +300 °C all the membranes tested were found to be thermally stable. Beyond which, there is sharp loss of mass of the membranes. Further, one may observe that decomposition temperatures increase with increasing ABS content in blended membranes (ABS observed to be the most thermally stable).

3.1.6. Mechanical properties

In the present work, dense films were prepared and obviously such films were cast at a thickness which should provide mechanical stability to carry out repeated experiments. However, industrially such property can be obtained by producing thin film composite membranes. This further enhances flux by reducing the thickness of the membrane. Still, it was thought to measure tensile strength of dense films in order to verify their stability for prolonged experimentations. Accordingly, tensile strength was measured, as per Section 2.3.6, as well as the membrane's elongation at break point was noted down. Results are reported in Table 4. It is clear from results that EC provides highest tensile strength and as blending is carried out, strength decreases with increasing content of ABS. However, there is marginal differences' being observed for elongation at break point between all the membranes.

Table 4
Tensile strength and percent elongation of pure and blend membranes

Membrane	Tensile strength (MPa)	Elongation at break (%)
EC	44.27	3.81
BM20	34.49	3.09
BM30	31.52	2.92
BM70	17.20	2.90
BM80	13.12	2.85
ABS	20.50	3.08

3.2. Pervaporation: analysis

In the PV process, the feed mixture is contacted with a non-porous perm-selective membrane and separation can be explained by the solution-diffusion mechanism which involves steps of sorption (into), diffusion (through) and desorption (from) [17]. The first and the last steps are usually considered to be fast and to take place at equilibrium; whereas, diffusion is a slower process.

The effects of blending on permeation rate and product concentration were studied by keeping other parameters constant (temperature: 50 °C, downstream pressure: 0.1 mmHg, static feed condition). The permeate flux was calculated using Eq. (3):

$$J = \frac{m}{At} \tag{3}$$

where J is the permeate flux, m the weight of the permeate, A the membrane area and t is the time of operation. Membranes were produced of varying thickness; therefore, the flux was normalized to a membrane thickness of 100 μm and denoted as (J) using Eq. (4):

$$(J) = \frac{Jl}{100} \tag{4}$$

where l is the membrane thickness. Such normalization was based on Fickian behavior during mass transport through the membrane.

The values of normalized flux and thickness are tabulated in Table 5. The flux (J) values for different blended polymeric membrane (EC + ABS) are also plotted in Fig. 5. It may be observed that the experimental values of flux observed with different membranes (EC, BM20 to 80, ABS) do not show any trend with continuous addition of ABS in EC to produce different membranes. As mentioned earlier, this may be due to varying thickness of membranes. Thus, the values of flux were normalized by using Eq. (4). Accordingly, the calculated value of (J) was plotted in Fig. 5 with varying composition of ABS and a trend of the form of sigmoidal decay was obtained. Obviously, such a trend visualizes an initially slow decline with significant decline at later stages. Therefore, between BM40 to BM70 and BM80, there is significant decline of flux with higher dosages of ABS in EC polymer. Further, the results are compared (refer Table 5) to our earlier prepared membrane which was denoted as MEC4 (ethyl cellulose reacted with 4 ml phenyl *iso*-cyanate in 100 g of polymer solution corresponding to 24.2 number of carbamate groups per 100 units of ethyl cellulose). It is evident through comparison that BM70 and BM80 produced better results in terms of selectivity and flux. Thus, blending of EC with ABS, instead of reacting EC with phenyl *iso*-cyanate, may be considered to be an option for hydrazine hydrate separation.

The polymer ABS is a mixture of three polymers; namely acrylonitrile, butadiene and styrene. Butadiene and styrene are hydrophobic in nature whereas acrylonitrile has hydrophilic property. Thus, the compound ABS has both hydrophilic as well as hydrophobic characteristics; though the hydrophobic part is generally dominant. EC is a strong hydrophilic polymer. So, it

Table 5

Flux, selectivity and PSI index ($T = 50\,^{\circ}\mathrm{C}$; downstream pressure = 0.1 mmHg)

Membrane	Thickness, l (μm)	Density (g/cm^3)	Normalized flux (g/m^2 h for 100 μm)	Selectivity ($\alpha^{\mathrm{P}}_{\mathrm{WH}}$)	PSI (g/m^2 h)
EC	60	1.004	4.825	1.710	3.426
BM20	80	0.941	7.657	2.049	8.032
BM30	40	1.017	6.771	2.350	9.141
BM40	70	0.978	6.692	2.500	10.038
BM70	110	1.007	2.717	5.947	13.442
BM80	60	1.089	1.622	10.647	15.648
ABS	75	0.95	4.322	4.587	15.504
MEC4[a]	75	–	4.090	3.230	9.121

[a] Data taken from Ref. [6].

is clear that apart from BM20, the flux decreases as the ABS quantity in the blended membrane (BM20 to 80) increases. This is due to increase in hydrophobic (ABS) character. Similar attributions were made, in an earlier work, on hydrazine hydrate system by Satyanarayana et al. [6].

The measure of selectivity in the pervaporation experiments is the separation factor defined as

$$\alpha_{\mathrm{AB}} = \frac{w''_{\mathrm{A}}/w''_{\mathrm{B}}}{w'_{\mathrm{A}}/w'_{\mathrm{B}}} \tag{5}$$

where w'_{A}, w'_{B}, w''_{A}, w''_{B} denotes the weight fractions of component A and B in the feed solution and in the pervaporate, respectively. The subscript A is the species that is preferentially pervaporated.

According to solution diffusion model [18], the overall selectivity of pervaporation process $\alpha^{\mathrm{P}}_{\mathrm{WH}}$ is the product of sorption $\alpha^{\mathrm{S}}_{\mathrm{WH}}$ and diffusion $\alpha^{\mathrm{D}}_{\mathrm{WH}}$ selectivity's:

$$\alpha^{\mathrm{P}}_{\mathrm{WH}} = \alpha^{\mathrm{S}}_{\mathrm{WH}} \times \alpha^{\mathrm{D}}_{\mathrm{WH}} \tag{6}$$

A thermodynamic approach (as discussed in Section 3.4) was adopted for the estimation of $\alpha^{\mathrm{S}}_{\mathrm{WH}}$. Table 5 shows the values of selectivity's for different membranes. Further, in Fig. 5, such selectivity's are plotted against percent ABS in the blended membranes. It is clear that selectivity increases exponentially with increase in ABS percentage in the blended membrane. However, there is little variation of selectivity up to 40–50 wt.% ABS beyond which selectivity rises significantly (exponentially). Although, not shown in Fig. 5, it is evident from Table 5 that pure polymers (EC and ABS) show much lower values of selectivity with their nearest blended compositions. Thus, one may conclude for proposition of blending of EC with ABS (a mixture of polymers having properties of both hydrophilicity and hydrophobicity) for the facilitation of separation of hydrazine hydrate in a manner that depicts a trend of performance during pervaporation.

In an attempt to analyze the process of Pervaporation, another useful term, namely PSI index, was utilized to assess membrane performance. The PSI index was defined as the product of normalized flux and selectivity in excess of 1 [15]:

$$\mathrm{PSI} = (J) \times (\alpha^{\mathrm{P}}_{\mathrm{WH}} - 1) \tag{7}$$

PSI indexes were plotted against various membranes and are shown in Fig. 6. The figure depicts a simple trend of slightly non-linear form which in itself reflects the usefulness of the definition and estimation of PSI index. Further, it may be observed that the values of PSI increase from around 8–16 g/m^2 h for 100 μm membrane thickness as against blending of ABS in EC from 20 to 80 wt.%, respectively. With such a simple and definite trend, one may conclude that higher weight percent blending of ABS in EC may be favourable for hydrazine hydrate separation through PV. In other words, a blended membrane with higher character-

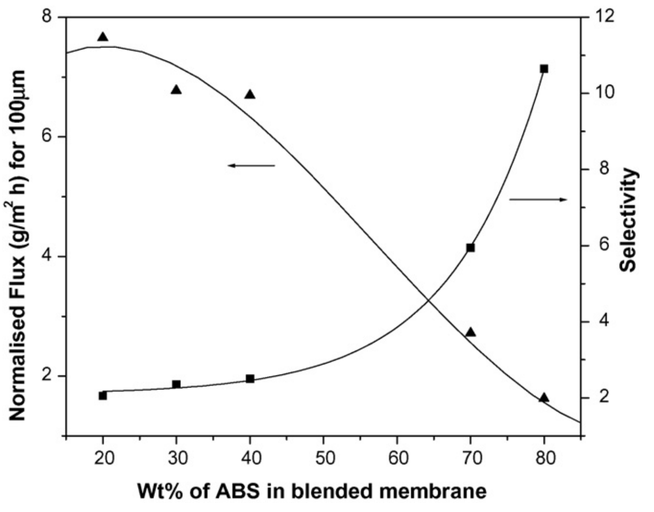

Fig. 5. Flux and selectivity variation for blended membrane.

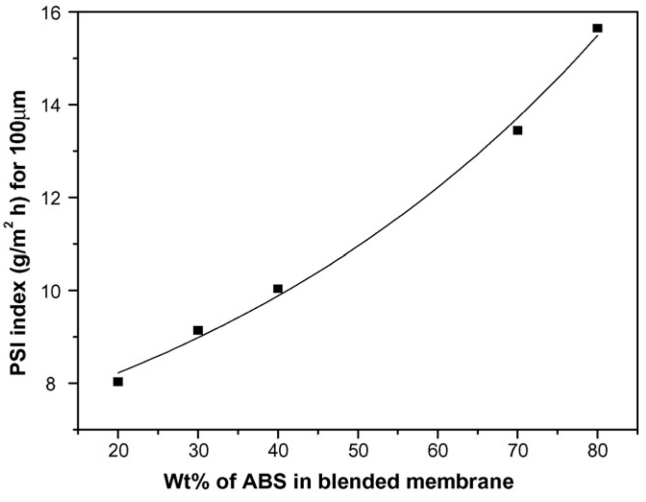

Fig. 6. PSI index for blended membranes.

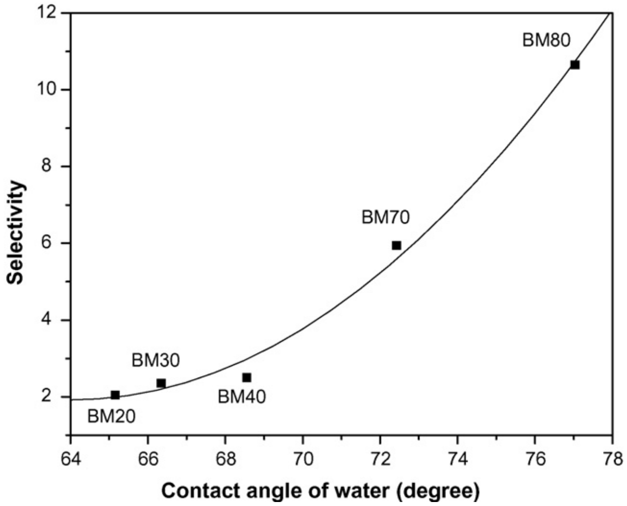

Fig. 7. Variation of selectivity for varying contact angles (water).

istics of hydrophobicity, but not absolute (refer Table 5), may be suitable.

3.3. Contact angle versus PV selectivity

Contact angle which is the interaction between membrane material and feed components is described in details by van Oss [19]. Fig. 7 depicts relationship between process selectivity for blended membranes and contact angles of water in membranes. It is clear that increase in ABS percentage in the blended membrane exponentially increases the selectivity value of dehydration of hydrazine hydrate. This may prove useful to estimate selectivity for blended polymers of unknown pervaporation performance but with known contact angles.

3.4. Thermodynamic treatment: preferential sorption

Pervaporative separation is governed by the chemical nature of the membrane (macromolecular network) and to understand it at the molecular level is complicated; but phenomenologically, one can study the preferential interaction parameter of a liquid with the membrane. Several approaches for selecting membranes have been proposed, but the ideal situation to describe mass transfer can be studied by a solution-diffusion model. However, for choosing an efficient membrane for a specific separation problem, it is desirable to achieve good membrane permeability and selectivity, but the thermodynamic conditions of feed flow and permeate cannot be overlooked. To incorporate these effects, one may employ Eq. (6) in order to utilize the concept of pervaporation selectivity (α^{P}) as being the product of sorption selectivity (α^{S}) and diffusion selectivity (α^{D}). Further, from thermodynamic theory, it is clear that the sorption selectivity may be estimated for a mixed solvent in a polymeric membrane (a three component system: membrane and binary component solution). Accordingly, one may compute preferential interaction parameters for binary component mixture in polymers using Flory–Huggins free energy mixing term (ΔG_{mix}). Further, from the well-known Flory–Huggins theory [20], we have

$$\ln \alpha^{\mathrm{S}} = \ln\left(\frac{\Phi_1}{\Phi_2}\right) - \ln\left(\frac{v_1}{v_2}\right) = \left(\frac{V_1}{V_2} - 1\right)\ln\left(\frac{\Phi_2}{v_2}\right) - \chi_{12}(\Phi_2 - \Phi_1) - \chi_{12}(v_1 - v_2) - \Phi_{\mathrm{p}}\left(\chi_{1\mathrm{p}} - \frac{V_1}{V_2}\chi_{2\mathrm{p}}\right) \quad (8)$$

Here Φ_i is the volume fraction of the ith component in the swollen polymer membrane, v_i the volume fraction of the ith component in the external liquid phase, and V_i is the respective molar volume. Subscripts 1, 2, and p refer to hydrazine, water, and the membrane polymer, respectively. The volume fraction, Φ_{p} of the polymer in the swollen state was calculated from:

$$\Phi_{\mathrm{P}} = \left[1 + \frac{\rho_{\mathrm{p}}}{\rho_{\mathrm{s}}}\left(\frac{M_{\mathrm{a}}}{M_{\mathrm{b}}}\right) - \left(\frac{\rho_{\mathrm{p}}}{\rho_{\mathrm{s}}}\right)\right]^{-1} \quad (9)$$

where ρ_{p} and ρ_{s} are the densities of polymer and solvent, respectively; M_{b} and M_{a} are the mass of the membrane, before and after swelling.

The interaction parameter, χ_{12}, between hydrazine-water was then calculated from the following equation:

$$\chi_{12} = \frac{[x_1 \ln(x_1/v_1) + x_2 \ln(x_2/v_2) + (\Delta G^{\mathrm{E}}/RT)]}{x_1 v_2} \quad (10)$$

where ΔG^{E} is the excess Gibbs free energy of mixing, R the molar gas constant, and T is the temperature. Values of ΔG^{E} were calculated from the values of activity coefficients, γ, of the mixtures (thermodynamic data) as

$$\Delta G^{\mathrm{E}} = RT(x_1 \ln \gamma_1 + x_2 \ln \gamma_2) \quad (11)$$

In the absence of direct experimental data on γ_1 and γ_2, the modified UNIFAC equation was used (at 50 °C) to compute the activity coefficient, γ_i, of component i in the mixture.

Further, polymer–solvent interaction parameter $\chi_{i\mathrm{p}}$ was calculated from Flory–Huggins theory, as per following:

$$\chi_{i\mathrm{p}} = \frac{V_i(\delta_{\mathrm{p}} - \delta_i)^2}{RT} \quad (12)$$

where δ_i is the solubility parameter of the ith component. Solubility parameters δ_{p} of EC and ABS polymers were estimated to be 20.0 and 19.94, respectively. Solubility parameters for hydrazine and water were taken from the literature [21] and the solubility parameters of the blend polymers were calculated from the following additive relationship [20]:

$$\delta = w_1\delta_1 + w_2\delta_2 \quad (13)$$

Here w_1 and w_2 are weight fractions and δ_1 and δ_2 are solubility parameters of EC and ABS, respectively. Interaction parameters calculated from Eqs. (10) and (12) along with the calculated sorption selectivity data are presented in Table 6. Further, Table 7 presents sorption and diffusion selectivity's. The values (diffusion selectivity) are in the increasing order with increasing content of ABS. Explanations of the obtained values of interaction parameters are of standard understandings from

Table 6
Interaction parameters and estimated sorption selectivity for blended membranes with hydrazine/water mixture (64 wt.%) at 50 °C

Membrane	Interaction parameter (χ)		Sorption selectivity (α^{D}_{WH})
	Hydrazine/polymer (χ_{1p})	Water/polymer (χ_{2p})	
EC	3.590	5.406	0.090
BM20	3.595	5.411	0.092
BM30	3.597	5.413	0.091
BM40	3.600	5.416	0.098
BM70	3.607	5.423	0.113
BM80	3.610	5.425	0.133
ABS	3.615	5.430	0.208
Interaction parameter for hydrazine/water (χ_{12})			−2.58

Table 7
Pervaporation, sorption and diffusion selectivity's of blended membranes with hydrazine/water mixture (64 wt.%) at 50 °C

Membrane	Selectivity (α) (water/hydrazine)		
	Pervaporation selectivity	Sorption selectivity	Diffusion selectivity
EC	1.710	0.090	19.00
BM20	2.049	0.092	22.27
BM30	2.350	0.091	25.82
BM40	2.500	0.098	25.51
BM70	5.947	0.113	52.63
BM80	10.647	0.133	80.05
ABS	4.587	0.208	22.05

thermodynamic theory. Accordingly, as the value of interaction parameter decreases, the sorption increases. Further, a negative value of interaction parameter between hydrazine–water suggests towards maximum boiling azeotrope, as per Raoult's law. Table 6 also corroborates with earlier reported experimental results of sorption. It was observed (refer Section 3.1) that sorption of hydrazine–water mixture was higher than with only water for all the membranes. This fact is also realized through Table 6 values; interaction parameters of hydrazine were lower than with water for all the membranes. The diffusion selectivity value calculated in this way reflects only qualitative significance for contributing towards separation through diffusion; perhaps, no quantitative significance may be extracted from these values. From Table 7, it is clear that calculated diffusion selectivity values are large compared to sorption selectivity values. Accordingly, it may be concluded that the separation of hydrazine hydrate may be governed by diffusion; whereas, sorption may be considered of minor importance.

4. Conclusion

Separation of hydrazine–water was carried out through various blended membranes (utilizing EC and ABS polymers) as well as pure EC and ABS polymeric membranes. The membranes thus obtained were characterized with the help of XRD, PAL, contact angle, sorption measurements, TGA and tensile testing.

Through XRD analysis, it was evident that higher ABS content lowers the amorphous character of blended membranes. This may, in a sense, decrease the flux. Results of PV show that normalized flux decreases and selectivity increases with increasing ABS in the blended membrane. Further, it also shows higher values of PSI indexes with increasing ABS. Results are quite promising with highest selectivity and increased order of PSI indexes. Through contact angle measurements, it is verified increasing content of ABS increases hydrophobic characteristic. Positron annihilation technique successfully estimated free volume fraction; the significant reduction of free volume fraction reflected the affect of blending. Although, sorption studies suggested hydrazine showing greater affinity towards membranes but PV results depict, in contrast, membranes to be more water perm-selective. This is only possible if diffusion of water through membranes is much larger. With regard to thermal stability of blended membranes, it was found that decomposition temperatures increase with increasing ABS content. Calculation of permeate-membrane interactions, using Flory–Huggins theory, supported such results (to corroborate, sorption and diffusion selectivity values are reported).

References

[1] R.Q. Wilson, H.P. Munger, J.W. Clegg, Vapour–liquid equilibrium in the binary system hydrazine/water, Chem. Eng. Progr., Symp. Ser. 3 (1952) 115–117.

[2] F. Wolf, P. Pollandt, R. Helmer, Diffusion behaviour of hydrazine through molecular sieve membranes, Z. Chem. 15 (1975) 160–161 (in German) (chemical abstracts, 83,183856).

[3] J.I. Dytnerskij, Membranprozesse Zur Trennung flussiger Gemische, VEB; Deutscher Verlag fur Grundstoffindustrie, Leipzig, 1977 (cited in R. Rautenbach, R. Albrecht, Membrane Process, John Wiely & Sons, Chichester, UK, 1989, p. 368).

[4] R. Ravindra, S. Sridhar, A.A. Khan, Separation studies of hydrazine from aqueous solutions by pervaporation, J. Polym. Sci., Part B: Polym. Phys. 37 (1999) 1969–1980.

[5] R. Ravindra, S. Sridhar, A.A. Khan, A.K. Rao, Pervaporation of water, hydrazine and monomethylhydarzine using ethylcellulose membranes, Polymer 41 (2000) 2795–2806.

[6] S.V. Satyanarayana, P.K. Bhattacharya, Pervaporation of hydrazine hydrate: separation characteristics of membranes with hydrophilic to hydrophobic behaviour, J. Membr. Sci. 238 (2004) 103–115.

[7] R. Agrawal, Separations: perspective of a process developer/designer, AIChE 47 (2001) 967–971.

[8] S.V. Satyanarayana, A.K. Rao, R. Ravindra, P.R. Shah, A.A. Khan, Studies on the separation of ethanol–water and hydrazine–water mixtures by pervaporation, in: Presented in IICT, Golden Jubilee Symposium on Advances in Chemical Engineering, IICT, Hyderabad, August 9–11, 1994.

[9] P. Kirkegaard, N.J. Pedersen, M. Eldrup, PATFIT-88: A Data Processing System for Positron Annihilation Spectra on Mainframe and Personal Computers, Riso National Laboratory, Denmark, 1989.

[10] S.J. Tao, Positronium annihilation in molecular substances, J. Chem. Phys. 56 (1972) 5499–5510.

[11] S.V. Satyanarayana, V.S. Subrahmanyam, H.C. Verma, A. Sharma, P.K. Bhattacharya, Application of positron annihilation: study of pervaporation dense membranes, Polymer 47 (2006) 1300–1307.

[12] A.J. Hill, S. Weinhold, G.M. Stack, M.R. Tant, Effect of copolymer composition on free volume and gas permeability in poly(ethylene terephthalate)-poly(1,4-cyclohexylene dimethylene terephthalate) copolyesters, Eur. Polym. J. 32 (1996) 843–849.

[13] R.A. Penneman, L.F. Audrieth, Quantitative determination of hydrazine, Anal. Chem. 20 (1948) 1058–1061.

[14] L.A. Dee, A.K. Webb, Gas chromatographic separation of hydrazine mixtures and water using a stationary phase that is chemically similar to hydrazine, Anal. Chem. 39 (1967) 1165–1167.

[15] M.K. Mandal, P.K. Bhattacharya, Poly(ether-block-amide) membrane for pervaporative separation of pyridine present in low concentration in aqueous solution, J. Membr. Sci. 286 (2006) 115–124.

[16] L.H. Sperling, Introduction to Physical Polymer Science, John Wiley Publishers, New York, 1986.

[17] C.H. Lee, Theory of reverse osmosis and some other membrane permeation operations, J. Appl. Polym. Sci. 19 (1975) 83–95.

[18] J.G. Wijmans, R.W. Baker, The solution–diffusion model: a review, J. Membr. Sci. 107 (1995) 1–21.

[19] C.J. van Oss, Interfacial Forces in Aqueous Media, Marcel Dekkar, New York, 1994.

[20] B.V.K. Naidu, T.M. Aminabhavi, Pervaporation separation of water/2-propanol mixtures by use of the blend membranes of sodium alginate and (hydroxyethyl) cellulose: roles of permeate-membrane interactions, zeolite filling, and membrane swelling, Ind. Eng. Chem. Res. 44 (2005) 7481–7489.

[21] A.F.M. Barton, CRC Handbook of Solubility Parameters and Other Cohesive Parameters, CRC Press, 1983.