

Separation of organic mixtures by pervaporation using crosslinked and filled rubber membranes

S. Ray, S.K. Ray*

Department of Polymer Science & Technology, University of Calcutta, 92 A.P.C. Road, Kolkata 700009, India

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Abstract

Natural rubber (NR) and poly(styrene-co-butadiene) rubber (SBR) were crosslinked chemically with sulfur and accelerator by efficient vulcanization. These were then compounded for physical crosslinking with high abrasion carbon black filler (grade N330) with three different doses, i.e. 5, 10 and 20 phr to obtain three filled membranes from each of these two rubbers (NR-5, NR-10 and NR-20 and SBR-5, SBR-10 and SBR-20). These six filled rubber membranes were used for pervaporative separation of toluene–methanol mixtures up to 11 wt% of toluene in feed. It has been found that with increase in filler doses from membrane-5 to membrane-20, the selectivities and mechanical properties of the membranes increase. All of these membranes showed reasonably good range of flux (20.814 g/m² h for SBR-5 to 10.26 g/m² h for NR-20) and separation factor (286.4 for NR-5 to 183.7 for SBR-5) for 0.55 wt% of toluene in feed. Among these membranes NR-20 and SBR-20 with highest crosslink density showed maximum separation factor for toluene along with good flux. It has also been found that for comparable crosslink density NR membranes showed better separation factor than SBR membranes.

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Keywords: Filled rubber membranes; Chemical/physical crosslinking; Efficient vulcanization system; Pervaporation; Separation factor

1. Introduction

Various rubber membranes have been reported for pervaporative separations especially for organic–organic separations as well as separation of traces of organics from its aqueous mixtures [1–4]. In spite of higher flux in comparison to other non-rubber polymers, the poor selectivity of these rubber membranes limits its applications. In most of the cases the poor selectivity of these rubber membranes are associated with its poor crosslinking.

Most of the rubber membranes are crosslinked (cured) by using sulfur and accelerator. During sulfur crosslinking it forms mono, poly and cyclic sulfur bonded structures in the rubber matrix [1]. Among these three types of bondings, the mono sulfur bondings contribute to effective selectivity of the membranes. Hence, for getting effectively cured rubber membranes monosulfide linkages have to be increased at the expense of poly or cyclic sulfur linkages which contribute little to effective crosslinking as required for restricted permeation.

It has been reported earlier that the ratio of accelerator to sulfur is important to influence the nature of crosslinking and efficient vulcanization with sulfur to accelerator ratio of 1.5:6.0 results in maximum extent of monosulfide linkages as required for effective curing and hence selectivity of the rubber membranes [1]. Above this ratio there is little change in amount of monosulfide linkages. However, the selectivity as well as strength of the rubber membranes can further be improved by incorporating reinforcing fillers in the rubber matrix to produce filled rubber membranes.

The effect of fillers on transport properties of the filled membranes have been reported by various authors [5–9]. In most of these cases silicon rubber membranes have been filled with zeolite for selective organic permeation from its aqueous mixtures [5–7]. In the present work efficiently crosslinked SBR and NR have been compounded with different doses of reinforcing carbon black fillers of high surface area to obtain filled rubber membranes of improved selectivity achieved through chemical crosslinking by efficient vulcanization and physical crosslinking through filler incorporation. The incorporation of fillers not only better the aromatic selectivity of the membranes but also improves the mechanical strength of the otherwise soft rubber

* Corresponding author. Tel.: +91 33 350 8386; fax: +91 33 351 9755.

E-mail address: samitcu2@yahoo.co.in (S.K. Ray).

Table 1
Membranes specifications

Membranes	Carbon black dose (phr)	Chemical crosslink density (by chemical method)	Physical crosslink density (by chemical method)	Chemical crosslink density (by kinetic method)	Physical crosslink density (by kinetic method)
NR-0	0.0	1.14×10^{-4}	0.0	1.19×10^{-4}	0.0
SBR-0	0.0	1.36×10^{-4}	0.0	1.42×10^{-4}	0.0
NR-5	5.0	2.06×10^{-4}	0.92×10^{-4}	2.3×10^{-4}	1.11×10^{-4}
SBR-5	5.0	1.91×10^{-4}	0.55×10^{-4}	2.12×10^{-4}	0.70×10^{-4}
NR-10	10.0	3.11×10^{-4}	1.97×10^{-4}	3.47×10^{-4}	2.28×10^{-4}
SBR-10	10.0	2.73×10^{-4}	1.37×10^{-4}	2.95×10^{-4}	1.53×10^{-4}
NR-20	20.0	4.13×10^{-4}	2.99×10^{-4}	4.8×10^{-4}	3.61×10^{-4}
SBR-20	20.0	3.79×10^{-4}	2.43×10^{-4}	4.01×10^{-4}	3.59×10^{-4}

membranes. These filled membranes have been used for pervaporative separation of aromatic-alcohol, i.e. toluene–methanol mixtures over the concentration range of 0–11 wt% toluene in feed.

2. Experimental

2.1. Preparation of PV membranes

Natural rubber of grade RSS-4 and SBR of grade 1702 as obtained from Tyre Corporation of India, West Bengal were used for preparation of membranes. Carbon black of N330 grade used for compounding the rubber was obtained from the same company. The rubbers were masticated, swelled in toluene for 24 h followed by addition of required amounts (5, 10 and 20 phr) of carbon black in portions with mechanical stirring of the dispersion for 24 h. Sulfur (crosslinker, 1.5 phr) and accelerator (6 phr) was then added and the mixer was stirred for another 8 h. From this rubber dispersion membrane was cast on a smooth and clean glass plate and it was air dried overnight at ambient condition. The membrane was then cured in a hot air oven at 110 °C (40 min for NR and 60 min for SBR membranes).

2.2. Characterization of the membranes

PV membranes are characterized in a similar way as the membrane making polymer itself, i.e. spectroscopic (FTIR), mechanical (tensile properties), thermal (DSC, TGA) [10], etc. However, in the present study instead of synthesizing new polymer from its monomer crosslinked and filled NR and SBR have been directly used as the membrane material. In this case the rubber membranes have been filled with different doses of fillers and crosslinked with efficient vulcanization to better its selectivity. Hence, these membranes were characterized by verifying the compatibility of the fillers with the rubber and the extent and nature of crosslinking in the membrane matrix with the following testings.

2.2.1. Surface morphology of the filled membranes by scanning electron microscopy (SEM)

The rubber membrane samples were coated with gold (Au). The surface morphology of the membranes were observed by using SEM (Scanning Microscope, model no. JSM-5200, made by JEOL, Japan) with the accelerating voltage set to 15 kV.

2.2.2. Mechanical strength

The tensile strength (TS) and elongation at break (EAB) of the polymer film was determined by an Instron-Tensile tester (Instron 4301, Instron Limited, England). The experiment was performed according to ASTM D 882-97. In this work, length of the specimens was 250 mm, the thickness of the specimen was around 0.1 mm and the thickness was uniform to within 5% of the thickness between the grips. The width of the specimens was 20 mm and edges were parallel to within 5% of the width over the length of the specimen between the grips.

2.2.3. Measurement of chemical crosslink density by chemical and mechanical method

Chemical crosslink density of the filled rubber membranes were measured by both chemical and mechanical method by similar experiments as used for unfilled rubber [1].

2.2.4. Measurement of 'physical' crosslink density

The crosslink density as measured by the above method corresponds to both crosslinking due to sulfur–rubber bonding as well as crosslinking due to filler loading. The crosslink density due to only filler loading was thus calculated by subtracting crosslink density of the unfilled (membrane without any filler cured with same accelerator–sulfur ratio as the filled rubber) rubber from the same of the filled rubber. The crosslink densities of all the rubbers due to sulfur crosslinking as well as filler loading are given in Table 1. Physical crosslinking of both NR and SBR by varied doses of filler loading were also evaluated in terms of measurement of V_{f0}/V_{rf} , i.e. the ratio of volume fraction of unfilled rubber (V_{f0}) to the same of filled rubber (V_{rf}) in the swollen gel. The volume fraction of the filled and unfilled rubber was measured from ratio of volume of dry crosslinked filled/unfilled rubber to that of the sorbed and swollen rubber.

2.3. Sorption studies

2.3.1. Sorption isotherm

Thick (1–1.5 mm) membranes of known weights were immersed and equilibrated for 96 h in different known concentrations of methanol–toluene mixtures at 32, 42 and 52 °C. These membranes were then taken out from the solutions and weighed after the superfluous liquid was wiped out with tissue paper. The increment in weight is equal to the total weight of methanol and toluene mixtures sorbed by the membrane.

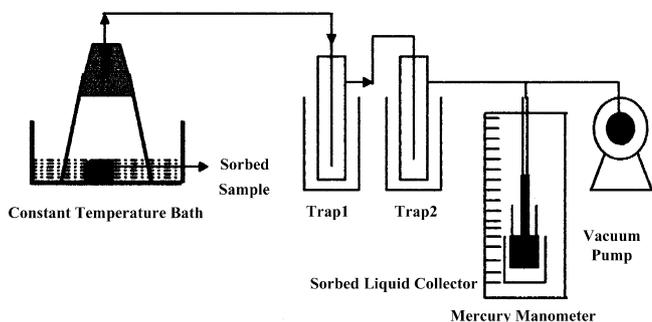


Fig. 1. Schematic diagram for measurement of sorption selectivity.

2.3.2. Sorption selectivity

After measuring the total weight of the sorped membranes from the above experiment, these thick samples were taken in a 250 ml conical flask kept in a constant temperature bath and connected to a cold trap and vacuum pump in series (Fig. 1). The cold trap was immersed in liquid nitrogen flask. The sorped sample was heated under vacuum and the vapour coming out of the thick sorped membranes were frozen and collected in the cold trap immersed in liquid nitrogen. The amount of toluene sorped by the membranes were obtained by analyzing the composition of the liquefied vapour from the cold trap by an Abbe type refractometer. From the total sorption weight and corresponding toluene content (weight) of the membrane, sorption selectivity of the membrane for toluene was calculated from the following equation:

$$\alpha_s = \frac{y_{m,\text{toluene}}/y_{m,\text{methanol}}}{x_{f,\text{toluene}}/x_{f,\text{methanol}}} \quad (1)$$

Here y_{mi} and x_{fi} denotes membrane phase and feed concentration of i th component.

2.4. Permeation studies

PV experiments were carried out at a constant temperature in a batch stirred and jacketed cell [10] with adjustable downstream pressure that was maintained at 1 mmHg. The composition of the permeant was analyzed by an Abbe type refractometer (model no. AR600, MISCO, USA) at 25 °C temperatures for all the samples. The permeation selectivity of toluene was calculated from a similar type of equation as sorption selectivity.

3. Results and discussion

3.1. Preparation of PV membranes

3.1.1. Grades of rubber

Among various grades of natural rubber, RSS-4 grade was selected as it contains minimum amount of non-rubber impurities. Similarly for SBR, SBR-1600 grade was selected because of its easy processibility and uniform properties. The rubbers were masticated to reduce its molecular weight so that it may easily go to its solution in toluene.

3.1.2. Choice of filler

The physical crosslinking of filled rubber depends on compatibility of filler to the rubber matrix. Carbon black filler is known to provide maximum degree of reinforcement (betterment of physical properties) and hence physical crosslinking [11]. Among the various available black fillers, furnace grade carbon black is most widely used because of its high structure and small particle size. Accordingly, in the present work high abrasion furnace (HAF) grade N330 carbon black was used as it shows good balance of structure and surface area as required for good reinforcement and physical crosslinking. Furnace black with particle size smaller than N330 would give better reinforcement and crosslinking. However, these were not chosen because of its difficult processing characteristic [11,12]. Thus, in the present work HAF grade N330 black filler was used for getting optimum physical crosslinking of the rubber-matrix.

3.1.3. Making rubber dispersion

Unlike the conventional way of rubber compounding the carbon black was mixed with the rubber in the solution phase in toluene instead of dry mixing in two roll mill. The mechanical dry mixing of black filler with rubber in roll mill results in better mixing. However, it also results in good amount of gelled mix [13] which is insoluble in any solvent. Thus, carbon black was mixed with rubber in solution phase by mechanical stirring for 24 h to obtain a stable dispersion where from membrane was cast.

3.1.4. Chemical and physical crosslinking

It has been reported [1,13] that efficient vulcanization gives maximum of monosulfide linkage. Hence, varying sulfur accelerator doses in the efficient vulcanization range would give membranes with maximum selectivity. However, conventional compression molding curing at a definite pressure and temperature could not be carried out for these PV membranes as these were too thin (50–60 μm) to be cured in compression molding. Thus, the cured membranes were made by open cure of the cast rubber film in hot-air-oven at the cure temperature without any pressure. Open cure of rubber in absence of any pressure demands higher doses of sulfur and accelerator. In this work thus, sulfur and accelerator dose was fixed at 1.5 and 6 phr, respectively, for 'efficient vulcanization' which produces maximum extent of monosulfide linkage and thus, offer high level of toluene selectivity [1]. However, apart from highest level of chemical crosslinking by efficient vulcanization, crosslinking of the rubber membrane may still be increased physically by filler incorporation. In this present work, thus, the efficiently vulcanized rubber membranes were loaded with three different doses of fine carbon black of high surface area, i.e. 5, 10 and 20 phr of N330, HAF grade carbon black. Although in conventional rubber compounding rubber can be compounded with more than 50 phr of carbon black, in the present work filler loading was limited to 20 phr as the mixing was done in solution phase (to avoid formation of insoluble gel as encountered in conventional two roll mill dry mixing) which could not produce a stable dispersion above 20 phr filler loading. This apart, selectivity was very high (~ 285 compared to ~ 94 of unfilled NR rubber for 0.55 wt% feed concentration of toluene) with reasonable flux

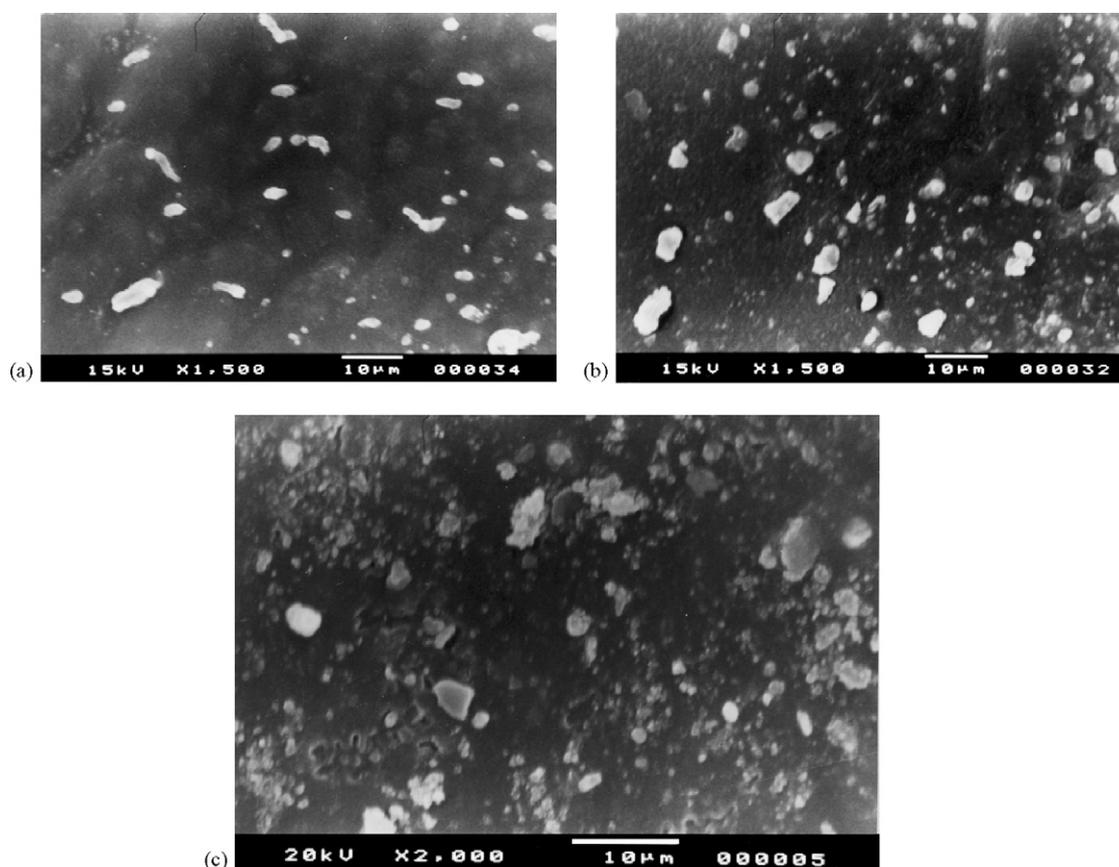


Fig. 2. (a) SEM of filled SBR-5 membrane, (b) SEM of filled SBR-10 membrane and (c) SEM of filled SBR-20 membrane.

at this filler loading. Membranes with filler loading more than 20 phr would give membranes yielding very low flux.

3.1.4.1. Choice of accelerator: Zinc dithio carbamate (ZDC), an ultra fast low temperature curing accelerator was used. This accelerator was chosen as it has been reported to produce less of polysulfide bridges [1,13]. This accelerator also causes rapid curing at low temperature. However, in this present system of open cure in absence of any pressure, around 40 min curing time for NR at 110 °C was sufficient for getting optimum crosslinking density. For NR reversion was found when curing time was given more than 40 min while for SBR more than 60 min of curing time gave the same degree of swelling as that for 60 min.

3.2. Characterization of the membranes

3.2.1. Morphology of the blend membranes by scanning electron microscopy (SEM)

SEM was carried out to characterize the filled rubber membranes in terms of its morphology. SEM was used for these filled membranes to observe its surfaces as well as bulk morphology with micrographs obtained by collecting secondary electrons emitted upon bombarding the filled membrane with high energy electrons. For getting bulk morphology, the polymer samples were annealed in liquid nitrogen and then fractured. The SEMS of the three filled SBR rubber, i.e. SBR-5, SBR-10 and SBR-20 is shown in Fig. 2a–c, respectively. From these figures it is

observed that with increase in filler loading, the surface morphology of SBR becomes gradually more coarser from SBR-5 to SBR-20 signifying poorer compatibility at higher doses of fillers. The clustering of the fillers as shown in the micrographs are due to ‘high structure’ of HAF type N330 fillers used for this study [12]. Similar type of micrographs were also obtained with filled NR membranes where also the morphology becomes ‘coarser’ with increasing filler loading. The micrograph of NR-20 and SBR-20 (cross-section) is shown in Fig. 3 to compare the morphology of these two rubbers with same filler loading. The better filler-rubber compatibility of NR than SBR is quite clear in terms of comparatively finer morphology of NR-20 as shown in the figure.

3.2.2. Mechanical strength

The TS and EAB of the filled and unfilled rubber membranes are given in Table 2. From these values it is observed that with increase in doses of filler from NR-5/SBR-5 to NR-20/SBR-20, TS increases at the expense of EAB signifying increasing extent of reinforcement with increasing filler loading from membrane-5 to membrane-20. The reinforcement of the membranes by incorporating filler is also confirmed in terms of betterment of TS of the filled rubber than the unfilled ones as shown in Table 2.

3.2.3. Physical crosslinking by filler loading

From Fig. 4 it is observed that the ratio of V_{r0}/V_{rf} decreases with a polynomial trend (degree of freedom 2 with regression

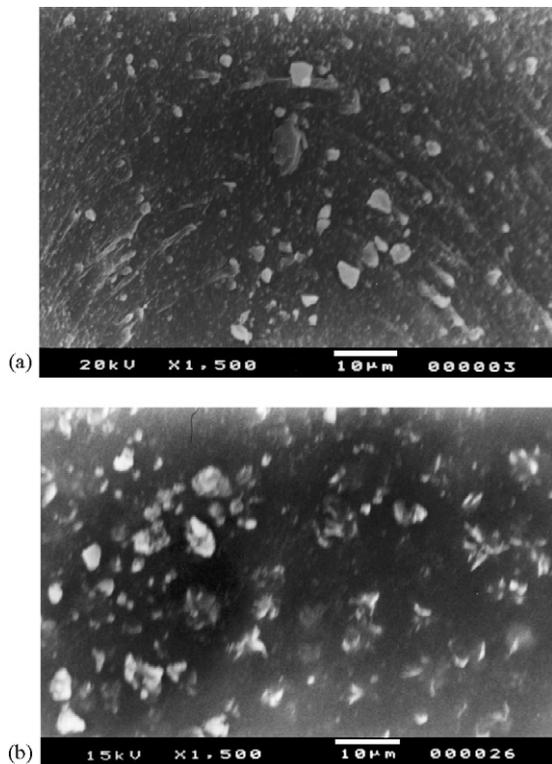


Fig. 3. (a) SEM of filled NR-20 (cross-section) membrane and (b) SEM of filled SBR-20 (cross-section) membrane.

Table 2
Physical properties of membranes

Membranes	Modulus at 100% elongation (MPa)	Tensile strength (MPa)	Elongation at break (%)
NR-0	0.53	7.87	530
SBR-0	0.63	2.77	370
NR-5	1.02	19.74	510
SBR-5	0.94	7.75	350
NR-10	1.54	28.77	495
SBR-10	1.31	12.8	325
NR-20	2.13	32.25	460
SBR-20	1.73	15.65	305

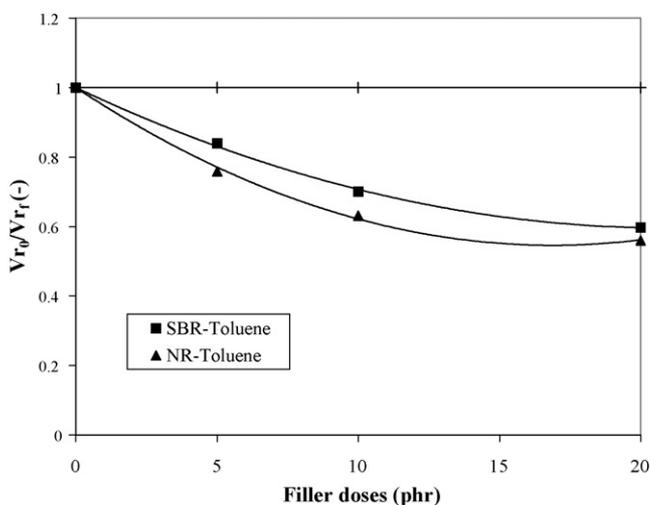


Fig. 4. Variation of V_{t0}/V_{tf} with filler doses for different solvents and fillers.

coefficient close to unity) with increase in filler loading from rubber-5 to rubber-20 for both NR and SBR membranes. The steep deviation of V_{t0}/V_{tf} from unity clearly shows the presence of increasing physical crosslinking from membrane-5 to membrane-20 [13]. From this figure it is also observed that NR shows much steeper decrease of V_{t0}/V_{tf} signifying higher extent of physical crosslinking in filled NR membranes. This may be ascribed to the higher ‘gum strength’ and ‘elasticity’ of NR which retains incorporated fillers and hence crosslinking in a much better way than SBR [13].

3.3. Sorption studies

3.3.1. Effect of feed concentration on sorption isotherm

Fig. 5a shows the variation of total sorption of methanol and toluene of NR-0, NR-5, NR-10 and NR-20 membranes with feed concentration of toluene at 32 °C. In this case NR-0, i.e. the cured membrane without any filler has been considered [1] for comparison of relative performance of filled and unfilled membranes. It is observed from the figure that these sorption isotherms initially follows a linear trend up to around 30 wt% toluene in feed where total sorption of all the membranes are very close to one another. However, above this concentration, the total sorption increases exponentially where they also differ from one another significantly. Similar type of trend line was also observed for SBR membranes.

3.3.2. Effect of crosslink density on sorption isotherm

From the above figure it is also observed that for the same feed concentration, total sorption decreases from NR-0 to NR-20 with increasing filler loading. Initially at low concentration of toluene in feed, the aromatic selective membranes with optimum physical and chemical crosslinking show low sorption but at high toluene concentration in feed, all the membranes are plasticized showing exponential increment of sorption. The NR/SBR-5 membrane with minimum physical crosslinking are plasticized much more than the other two membranes showing large difference in their total sorption.

3.3.3. Effect of type of rubber membrane on sorption isotherm

It is also interesting to note that for the same filler loading, SBR membranes show higher sorption than NR membranes for any feed concentration of toluene as compared between NR-20 and SBR-20 membrane in Fig. 5b. This may be ascribed to more close solubility parameter [13] of SBR than NR with respect to toluene. Further, better compatibility of filler-NR than filler-SBR results in higher extent of free volume and hence higher sorption in SBR membranes. The lower compatibility factor of SBR-carbon black is also confirmed by poorer tensile properties (Table 2) and coarser morphology (Fig. 3) of filled SBR than filled NR membranes.

3.3.4. Effect of temperature on sorption isotherm

Fig. 5c shows the effect of temperature on total sorption. From the figure, it is clear that with increase in temperature total

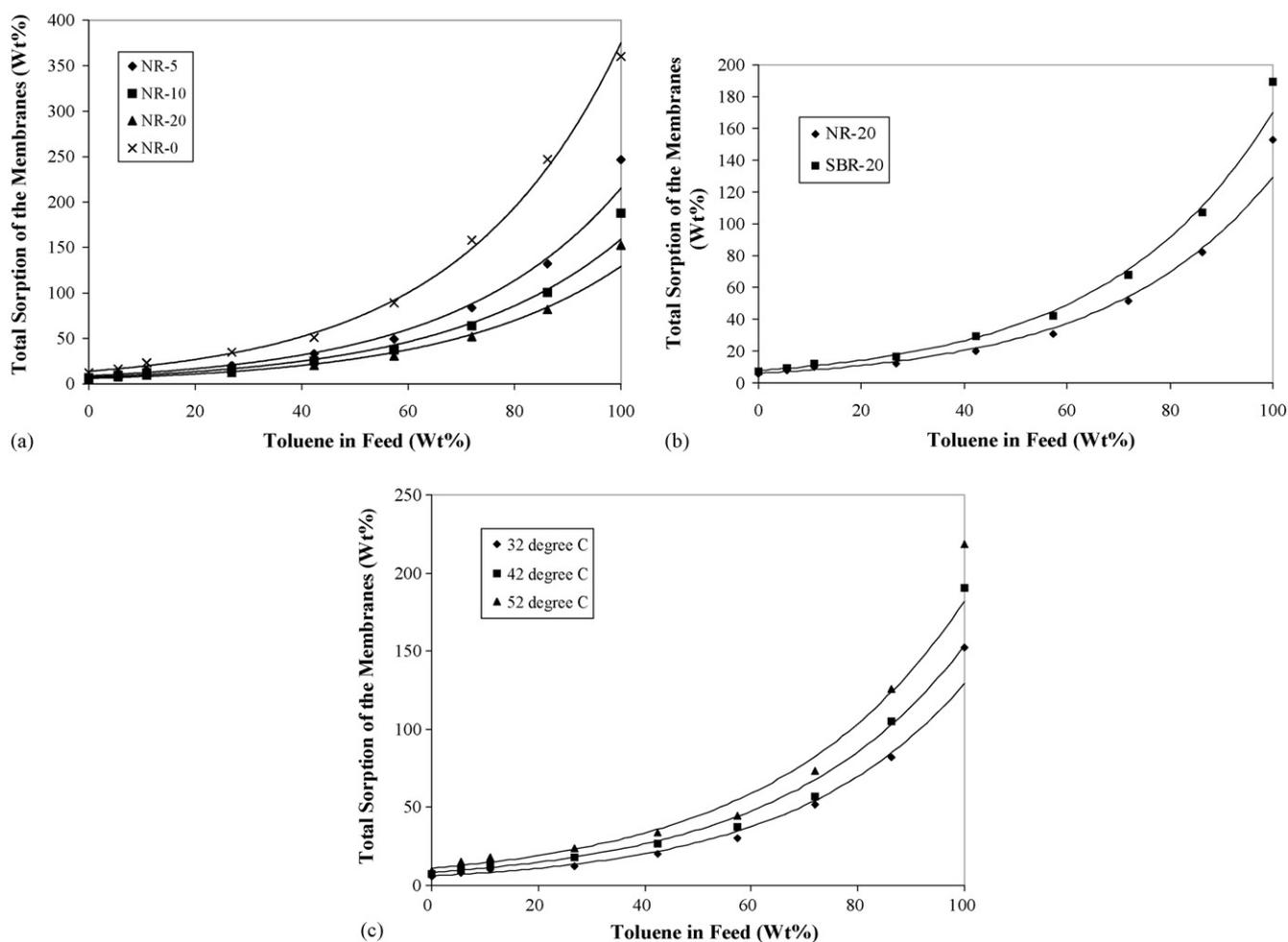


Fig. 5. (a) Sorption isotherm of NR membranes at 32 °C, (b) sorption isotherm of NR-20 and SBR-20 membranes at 32 °C and (c) Sorption isotherm of NR-20 membrane at different temperatures.

sorption increases for NR-20 membrane. Similar kind of trend line is also observed for other membranes.

3.3.5. Sorption selectivity

Fig. 6a shows the variation of toluene content and sorption selectivity for toluene of NR-5, NR-10 and NR-20 membranes with feed concentration of toluene at 32 °C. Similar kind of trend lines were also obtained for filled SBR membranes. From this figure it is observed that toluene sorption of the membranes increases with a polynomial trend with increase in feed concentration of toluene. However, higher feed concentration of toluene in feed highly plasticizes the aromatic selective rubber membranes allowing permeation of both methanol and toluene at higher feed concentration of toluene. Thus, from Fig. 6a it is also observed that at very low feed concentration of toluene, its selectivity is very high (100–140) but it decreases exponentially with increasing feed concentration of toluene. Further, for the same feed concentration of toluene its selectivity follows the reverse trend of total sorption, i.e.

$$\text{NR-5} < \text{NR-10} < \text{NR-20}$$

This may be attributed to increasing extent of physical crosslinking from NR-5 to NR-20 membrane. Between SBR and NR

membranes, for the same filler loading, SBR shows higher toluene sorption but lower toluene selectivity as shown in Fig. 6b for NR-20 and SBR-20 membranes.

3.4. Permeation studies

3.4.1. Effect of feed concentration on toluene separation

Fig. 7a shows the variation of wt% of toluene in the permeate against wt% of toluene in the feed for separation of toluene with NR-0, NR-5, NR-10 and NR-20 membranes. It appears from these McCabe-Thiele type xy diagrams that these filled NR membranes show high toluene separation over the used concentration range (0–11 wt% toluene in feed) without any per-vaporative azeotrope.

3.4.2. Effect of crosslink density on toluene separation

It is also interesting to note that for the same feed concentration the separation characteristic of the NR membranes increases in the following order:

$$\text{NR-20} > \text{NR-10} > \text{NR-5} > \text{NR-0}$$

All of the above membranes are made by efficient crosslinking with same doses of accelerator and sulfur and hence the degree

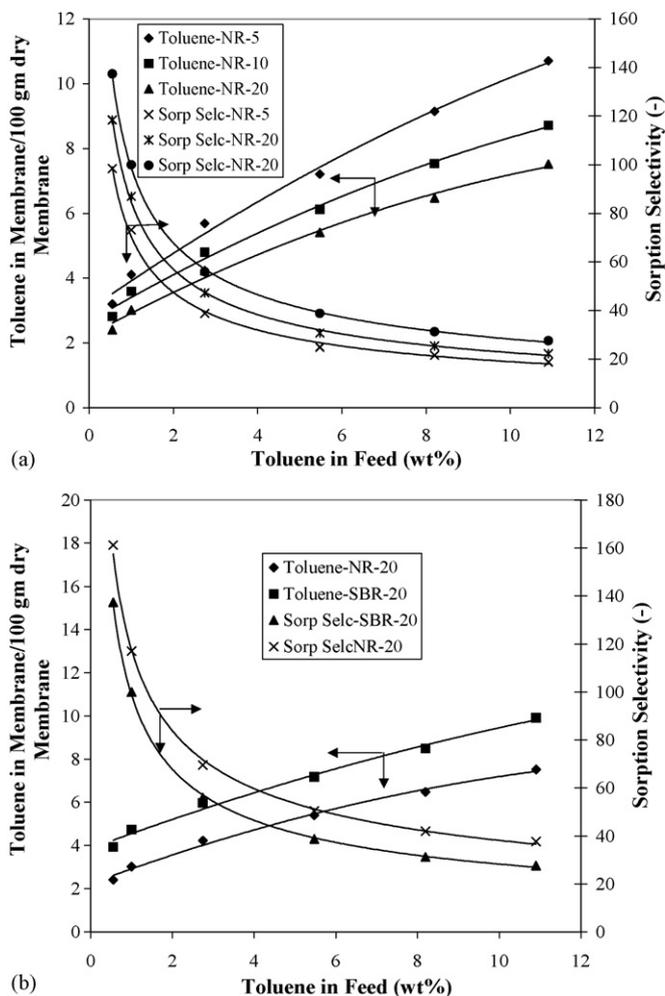


Fig. 6. (a) Variation of toluene content and sorption selectivity for toluene in sorbed membrane for NR membranes at 32 °C and (b) variation of toluene content and sorption selectivity for toluene in sorbed membrane for NR-20 and SBR-20 membranes at 32 °C.

of chemical crosslinking of all these membranes is same. However, they differ in the extent of physical crosslinking which also increases in the above order resulting in that order of separation characteristic. Similar type of trend is also observed for all the SBR membranes.

3.4.3. Effect of type of rubber membrane on toluene separation

Fig. 7b shows the similar type *xy* diagram for NR-20 and SBR-20 membranes. From this diagram it is observed that for the same feed concentration NR-20 shows better toluene separation which may be due to its better physical crosslinking. It imposes more restriction than SBR membrane in permeation.

3.4.4. Effect of feed concentration on flux and separation factor

Fig. 8a shows the effect of feed concentration of toluene on its flux and separation factor for NR membranes. Similar type of trend is also observed for SBR membranes. It appears from this figure that with increase in toluene concentration in feed toluene flux increase at the cost of its separation factor. The decrease in

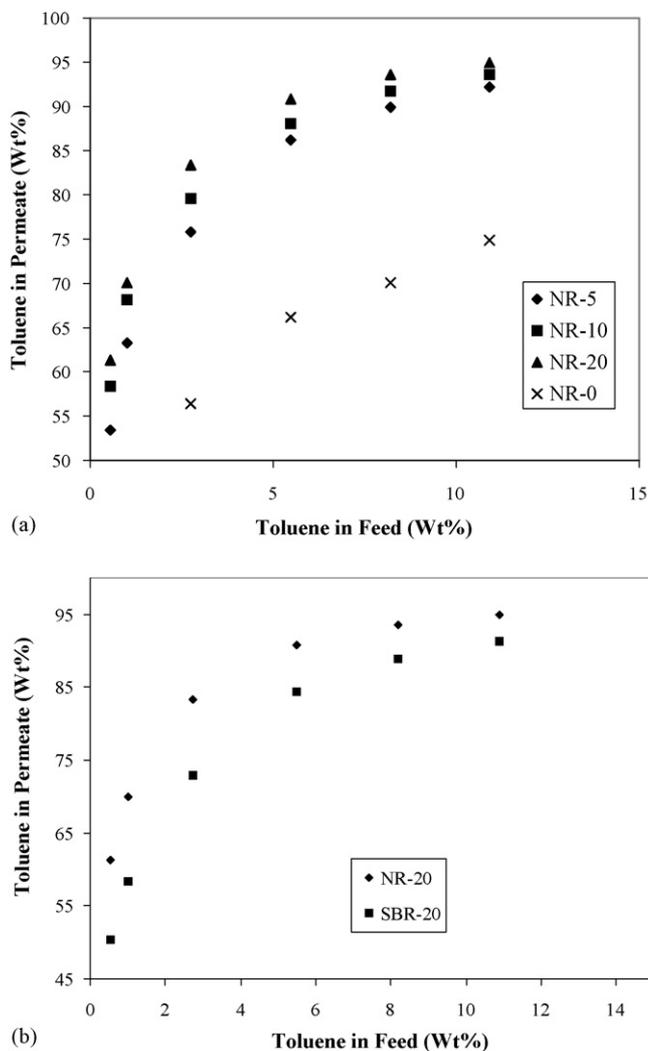


Fig. 7. (a) Variation of permeate concentration of toluene with its feed concentration at 32 °C and (b) variation of permeate concentration of toluene with its feed concentration for NR-20 and SBR-20 membranes at 32 °C.

separation factor with increase in toluene concentration in the feed for the toluene–methanol binary mixture may be attributed to the plasticization of the membrane at high toluene content in the feed.

3.4.5. Effect of filler loading and type of rubber membrane on flux and separation factor

From the above figure it is also observed that for the same feed concentration, separation factor for toluene increases at the cost of its flux increase in filler loading from NR-0/SBR-0 to NR-20/SBR-20 membrane due to increasing degree of crosslinking. As shown in Fig. 8b, for the same feed concentration of toluene, NR-20 membrane shows better separation factor but lower flux than SBR-20 membrane. Higher extent of free volumes of SBR membranes due to its poorer compatibility with filler is responsible for its higher flux but lower separation factor. This aside, more close solubility parameter of SBR than NR with respect to toluene causes more plasticization of the membranes and hence decrease of separation factor with increase in feed concentration of toluene.

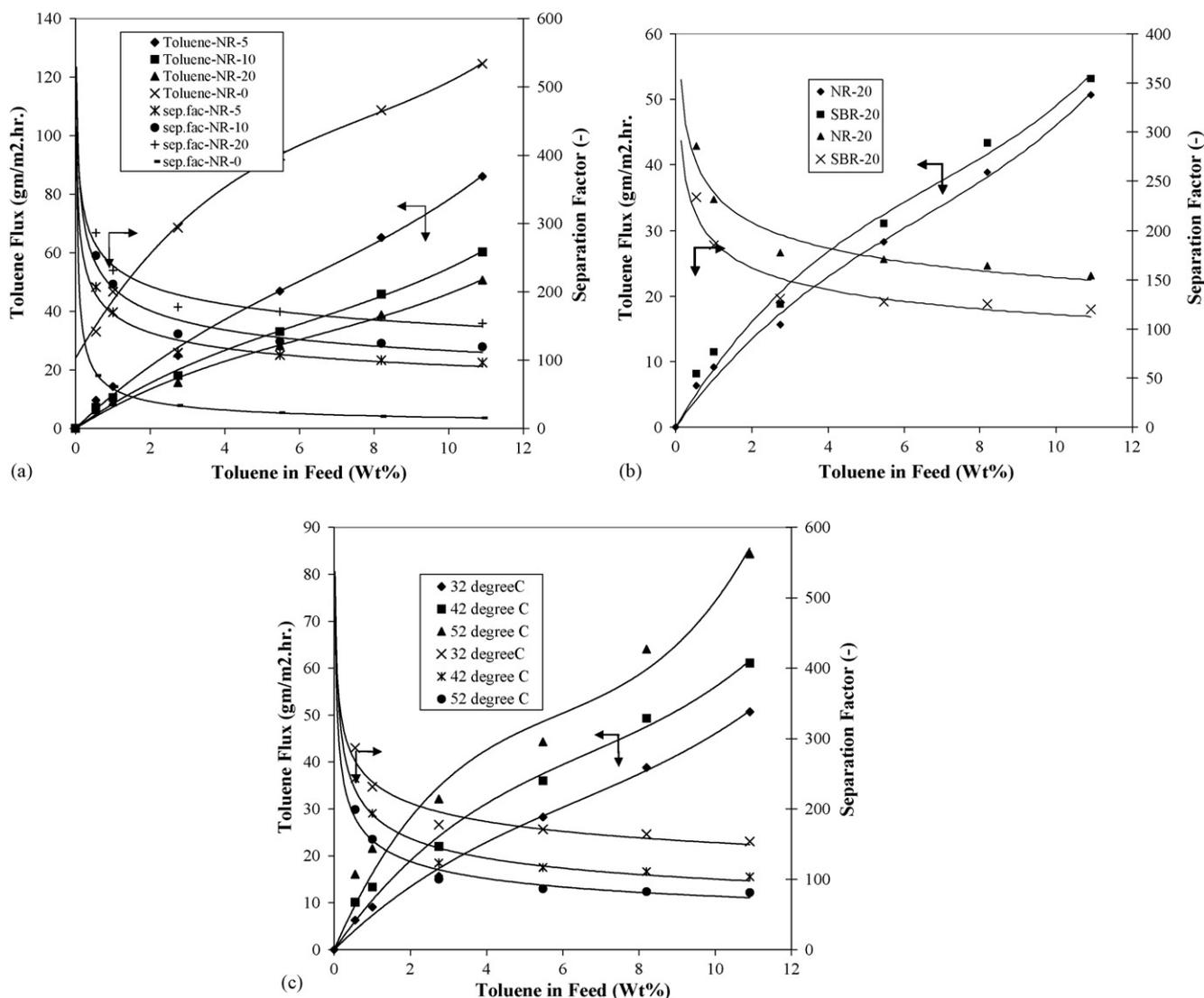


Fig. 8. (a) Variation of flux and separation factor of toluene with its feed concentration for NR membranes at 32 °C, (b) variation of flux and selectivity of toluene with its feed concentration for NR-20 and SBR-20 at 32 °C and (c) variation of flux and separation factor of toluene with its feed concentration for NR-20 at different temperatures.

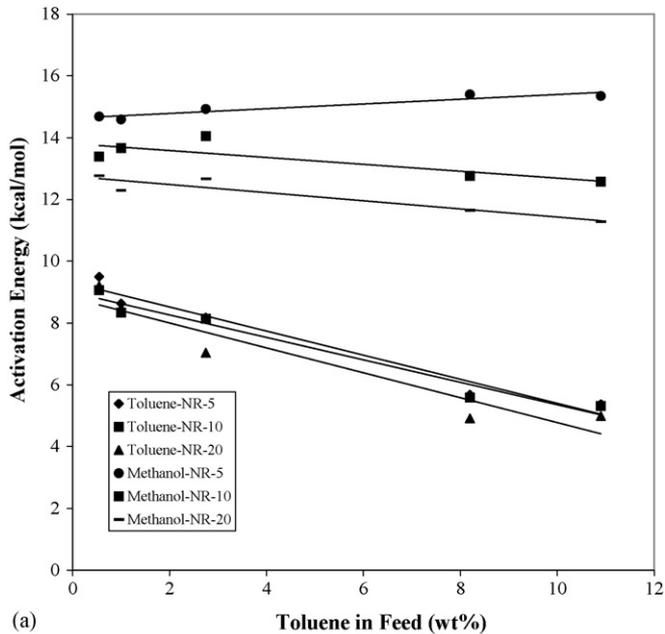
3.4.6. Effect of feed temperature on flux and separation factor

It is evident from Fig. 8c that total flux increases with increase in temperature at the cost of separation factor for NR membranes. Similar kind of results were also obtained for SBR membranes. This may be due to increase in both the total sorption and diffusion of the permeates at higher temperature. The decrease in separation factor for toluene at higher temperature may be ascribed to the increase in flux of methanol at higher temperature. At higher temperature the movement of rubber chains allows permeation of more methanol through the membranes. Higher flux of methanol with temperature is also evidenced by its higher activation energy for permeation as discussed below.

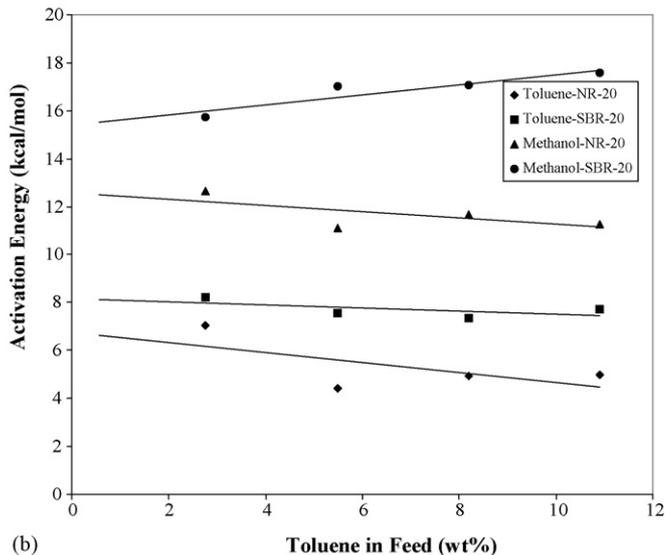
3.4.7. Effect of feed concentration on activation energy

The effect of temperature on permeation can be described by Arrhenius type relationship. Accordingly, activation energy for

permeation of all the membranes at different feed concentrations of toluene were obtained from the Arrhenius type plot of logarithmic of flux against inverse of absolute temperature. For each of these linear plots by best fit method the values of regression coefficient were also found to be close to unity. Activation energy for permeation of both methanol and toluene through filled NR membranes at different feed concentrations of toluene are shown in Fig. 9a. These activation energies (5–8 kcal/mol for toluene and 11–17.5 kcal/mol for methanol) were comparable to those reported for similar system [14]. From this figure it is observed that activation energies of methanol remains marginally constant over the feed concentration of toluene while activation energy for toluene permeation decreases linearly with feed concentration of toluene signifying plasticization of the aromatic selective membrane by toluene which makes easier permeation of toluene at higher feed concentration. The aromatic selective membranes also show lower activation energy of toluene than methanol as shown in the figure.



(a)

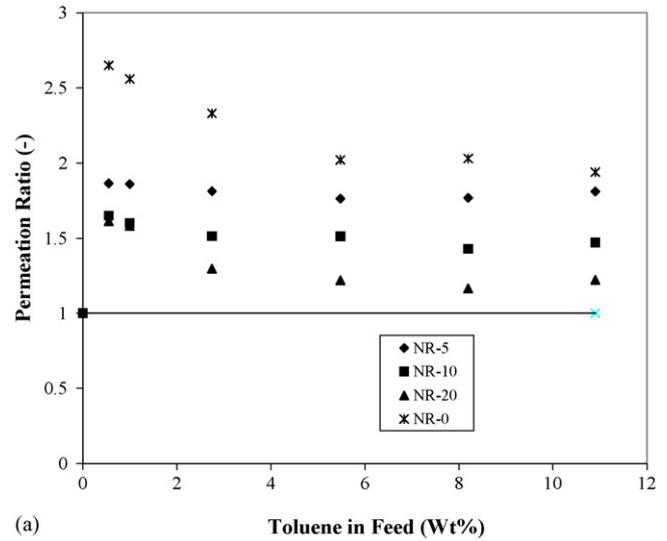


(b)

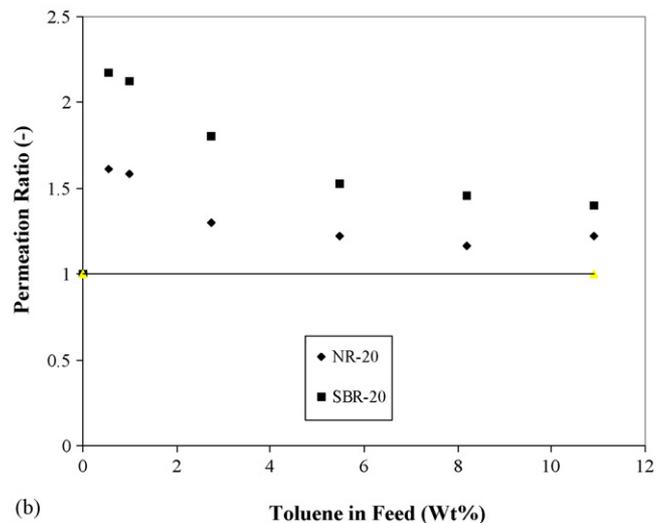
Fig. 9. (a) Variation of activation energy for permeation of NR membranes with feed concentration of toluene and (b) variation of activation energy for permeation of NR-20 and SBR-20 membranes with feed concentration of toluene.

3.4.8. Effect of filler loading on activation energy

From Fig. 9a it is observed that for the same feed concentration activation energy of both toluene and methanol decreases with increasing filler loading. Activation energy is calculated from the slope, i.e. the rate of change of flux with temperature. The change of flux with temperature is less for a membrane loaded with filler due to restriction of movement of the otherwise mobile rubber chain with increasing temperature. This may be the reason for highest activation energy of the unfilled rubber where in absence of any filler, the rubber chains show extensive mobility at higher temperature and hence an increased rate of flux with temperature. Similar kind of trend lines were also obtained with SBR membranes.



(a)



(b)

Fig. 10. (a) Variation of permeation ratio of methanol with feed concentration of toluene for NR membranes at 32 °C and (b) variation of permeation ratio of methanol with feed concentration of toluene for NR-20 and SBR-20 membranes at 32 °C.

3.4.9. Effect of type of rubber membrane on activation energy

Fig. 9b shows the comparison of activation energies for toluene of filled NR and SBR membranes in terms of the same of NR-20 and SBR-20 membranes. From this figure it is observed that NR-20 shows lower activation energy. The better filler-rubber compatibility and hence higher degree of physical crosslinking is expected to cause lower rubber chain mobility at higher temperature with lowering of activation energy for NR-20 in comparison to SBR-20.

3.4.10. Effect of feed concentration on permeation ratio

Permeation factor of a component (here methanol) is a quantitative estimation of the influence of the other component on its permeation through the membrane. From Fig. 10a it is observed that for NR membranes with increase in feed concentration of toluene permeation factor for methanol drastically decreases up to around 2% for toluene in feed and

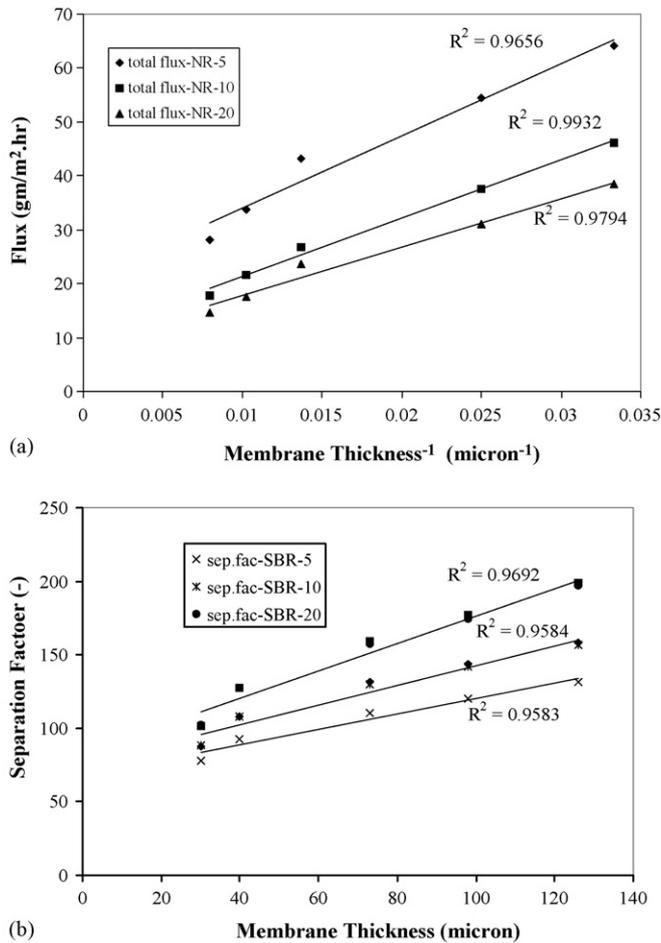


Fig. 11. (a) The effect of membrane thickness on flux at 5.47 wt% toluene in feed at 32 °C for NR membranes and (b) variation of separation factor of toluene with membrane thickness for NR and SBR membranes at 32 °C.

then gradually decreases. From this figure it is also observed that the effect of toluene on methanol flux decreases with increase in filler loading from NR-0 to NR-20 membrane. Similar trends are also observed for SBR membranes. It is interesting to note that for the entire concentration range of feed (0–10 wt% toluene) of the PV experiments for both of these membranes permeation factor for methanol is greater than unity signifying positive coupling effect of toluene on methanol flux. Between NR-20 and SBR-20 membranes, for the same feed concentration of toluene higher permeation factor for methanol is obtained for SBR-20 membrane as shown in Fig. 10b.

3.4.11. Effect of membrane thickness on flux and separation factor

For any homogeneous membrane used for pervaporative studies thickness of the membrane maintains a linear relationship with flux in that flux decreases linearly with thickness of the membrane. Thus, measuring flux at two different thicknesses, it can be normalized at any thickness. However, in the present study the homogeneity of the filled membranes depends on both distributive and dispersive mixing of filler in the rubber matrix [15]. From Fig. 11a it is observed that flux through the NR membranes increases linearly (with regression coefficient >0.9 for all

the membranes as shown in the figure) with decreases in membrane thickness. Separation factor for toluene also follows the same linear trend as shown in Fig. 11b for SBR membranes. These results clearly reveal uniform distribution of fillers within the rubber matrix.

3.4.12. Model calculation of theoretical flux and diffusion coefficient

In a binary system with a non-porous dense membrane pervaporative flux for *i*th component can be described by Fick's first law as,

$$J_i = - \left(\frac{\rho_m D_i}{1 - W_{im}} \right) \frac{dW_{im}}{dl} \quad (2)$$

For very small W_{im} , the above equation reduces to,

$$J_i = -\rho_m D_i \frac{dW_{im}}{dl} \quad (3)$$

However, diffusion coefficient depends on the concentration of the permeating components in the membrane and their mutual coupling effect. For components *i* and *j* the diffusion coefficient can be expressed as [16],

$$D_i = D_{i0} \exp(W_{im} + \beta W_{jm}) \quad (4)$$

$$D_j = D_{j0} \exp(W_{jm} + \gamma W_{im}) \quad (5)$$

Substituting Eqs. (4) and (2) results in:

$$J_i = -\rho_m D_{i0} \exp(W_{im} + \beta W_{jm}) \frac{dW_{im}}{dl} \quad (6)$$

Integrating Eq. (6) over the membrane thickness results in total flux of *i*th component (say toluene) through the membrane:

$$\int_0^L J_i dl = -\rho_m D_{i0} \int_{w_{imf}}^{w_{imp}} \exp(W_{im} + \beta W_{jm}) dW_{im} \quad (7)$$

In the present study the used rubber membranes are found to be highly toluene selective. Hence, plasticization of the membranes are likely to be for toluene only. Thus if toluene is the *i*th component, the coupling parameter β for methanol can be considered to be low or zero. Ignoring the very low concentration of the permeating component on the downstream side (because of very low pressure on this side), Eq. (7) for *i*th (toluene) and *j*th component reduces to:

$$J_i = \frac{D_{i0} \rho_m}{L} [\exp(W_{im}) - 1] \quad (8)$$

and

$$J_j = \frac{D_{j0} \rho_m}{L} [\exp(W_{jm} + \gamma W_{im}) - 1] \quad (9)$$

The density and thickness of the membranes were found experimentally. From the sorption experiments W_{im} and W_{jm} and from permeation data J_i and J_j were obtained. By a linear regression of these permeation and sorption data and comparing these regressed equations with Eqs. (9) and (10), diffusion coefficients at infinite dilution were calculated. The values of coupling parameter γ was adjusted so as to make the predicted flux as close as possible to experimental flux maintaining

Table 3
Diffusion coefficients of toluene ($D_{0,\text{toluene}}$) and methanol ($D_{0,\text{methanol}}$) through all the membranes at infinite dilution

	Name of the membranes					
	NR-5	NR-10	NR-20	SBR-5	SBR-10	SBR-20
Diffusion coefficients at 32 °C						
$D_{0,\text{toluene}}$ ($\times 10^{12}$ m ² /s)	1.43	0.83	0.50	1.11	0.74	0.45
$D_{0,\text{methanol}}$ ($\times 10^{13}$ m ² /s)	0.50	0.357	0.286	0.87	0.714	0.585
γ	0.8	0.795	0.79	0.35	0.75	0.85
Diffusion coefficients at 42 °C						
$D_{0,\text{toluene}}$ ($\times 10^{12}$ m ² /s)	2.00	1.25	0.83	2.5	1.43	0.89
$D_{0,\text{methanol}}$ ($\times 10^{13}$ m ² /s)	1.13	0.847	0.633	1.587	1.176	0.781
γ	0.6	0.43	0.34	0.39	0.65	0.79
Diffusion coefficients at 52 °C						
$D_{0,\text{toluene}}$ ($\times 10^{12}$ m ² /s)	3.33	2.15	1.43	4.65	2.5	1.67
$D_{0,\text{methanol}}$ ($\times 10^{13}$ m ² /s)	2.08	1.667	1.342	3.226	2.212	1.779
γ	0.5	0.32	0.12	0.31	0.6	0.81

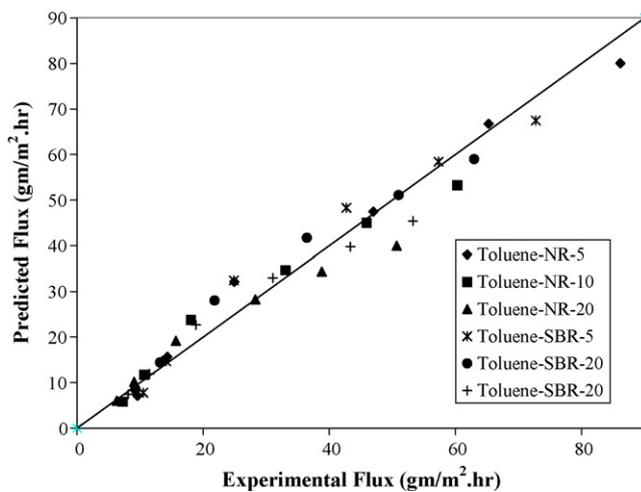


Fig. 12. Parity plot of experimental and predicted toluene flux for NR and SBR membranes at 32 °C.

regression coefficient close to unity. The values of diffusion coefficients at infinite dilutions for both toluene and methanol at various feed temperatures along with the corresponding values of γ are given in Table 3. A representative parity plot of experimental and theoretical flux of toluene for all the used filled NR and SBR membranes at 32 °C is shown in Fig. 12. The validity of the generalized model [17] for the present system is quite satisfactory from the closeness of the theoretical and experimental flux data as shown in the above figure. Sim-

ilar types of parity plots were also obtained for other membranes.

4. Conclusion

Efficiently crosslinked NR and SBR rubbers with maximum of monosulfide linkages as required for maximum aromatic selectivities achievable by chemical crosslinking have been compounded with three increasing doses of reinforcing carbon black fillers. These crosslinked filled rubber membranes have been studied for pervaporative separation of organic–organic toluene–methanol mixtures at different compositions and temperatures. It has been observed that with increasing filler loading from membrane-5 to membrane-20, physical crosslinking increased manifold resulting in increasing tensile strength and toluene selectivities of the membranes. For similar doses of filler loading NR membranes have been found to show better toluene selectivities in contrast to unfilled membranes because of better reinforcement of NR membrane. These rubber membranes will be extremely effective for separation of any organic–organic mixtures where the component to be separated is close in solubility parameter with these rubbers while the other component (not to be separated) is completely insoluble in these rubbers. The relative performances of different membranes used for separation of toluene from its mixtures with other components are given in Table 4. From these results it transpires that the performance of the filled rubber membranes used for the studies show much high separation factor

Table 4
Comparison of performance of toluene separation by various pervaporation membranes

Separation system A/B (wt%)	Membrane used	Flux (kg/m ² h)	$\alpha_{B/A}$	Ref.
Water/toluene (20 ppm toluene in feed)	PEBA (polyether block amide)	–	276	[18]
Methanol/toluene (0.55 wt% toluene in feed)	SBR-1	0.012	162	[1]
Methanol/toluene (0.55 wt% toluene in feed)	NR-20	0.01 (50 μ m thickness)	286	Present work
Water/toluene (0.1–1.0 wt% toluene in feed)	PVA (crosslinked polyvinyl alcohol)	–	0.2	[19]
<i>i</i> -Octane/toluene	Substituted polyimide	2.8 (1 μ m thickness)	113	[20]

for toluene with reasonable flux to those reported for similar systems.

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