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Transport of water and methanol vapors in alkyl substituted poly(norbornene)

Stacye R. Thrasher[a], Mary E. Rezac[b,*]

[a]School of Chemical Engineering, Georgia Institute of Technology, Atlanta, GA 30332-0100, USA
[b]Department of Chemical Engineering, Kansas State University, 118 Durland Hall, Manhattan, KS 66506-5102, USA

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Abstract

This report examines the ability of aliphatic-substituted polynorbornenes to separate methanol vapor from water-wet air streams. Single component transport properties of water and methanol were measured for each candidate polymer at 30 °C. The diffusion coefficient, sorption coefficient, and permeability were determined by measuring the rate of mass gain or loss of a sample due to sorption or desorption. The ratio of the permeabilities of the pure components yielded the ideal selectivity. The materials studied in this were methyl-, *n*butyl-, *n*hexyl-, and *n*decyl-polynorbornene. These polymers were glassy, with T_gs of 150–380 °C, and have relatively high fractional free volumes (16–19%). The results of the study showed polynorbornenes were methanol selectivity with ideal selectivities of 1.2–9. This permeation selectivity is due primarily to the solubility selectivity of the materials.

Keywords: Sorption; Diffusion coefficient; Permeability

1. Introduction

Polymeric membranes have been employed to recover vapors from gas streams and to separate gases and vapors based on differences in their permeation rates [1–8]. Commercial success has been realized in the recovery of organic vapors and water from air streams [2,9]. The selective recovery of a single vapor from a gas stream containing multiple condensable components is more challenging. Here, we examine the ability of a series of aliphatic polymers to selectively transport methanol in the presence of water. If high selectivities can be achieved, the membranes may find use in the selective recovery of methanol from gas vents in pulp and paper manufacturing [10,11] or for use in direct methanol fuel cells.

A series of alkyl-substituted polynorbornenes with relatively high fractional free volumes (FFV) were evaluated in this work. As the polymers are hydrophobic, the total sorption of water is expected to be low. Additionally, the high free volume of the polymers should provide for high alcohol sorption. The combination of these properties may be valuable for achieving fast methanol transport relative to the water present. The materials examined and their properties are detailed in the following sections. Finally, the performance of the subject polymers is compared with the performance of other polymers as reported in the literature.

2. Background

2.1. Membrane transport phenomena

Two major transport phenomena are observed from the experimental results of this work: plasticization and clustering. These competing mechanisms are introduced here in order to facilitate the understanding of the experimental results.

2.1.1. Plasticization

Plasticization or swelling increases polymer chain mobility and, in so doing, increases the rate of penetrant transport in the material. Plasticization occurs when the polymer/penetrant interactions are strong. Plasticization is common for 'organic vapors and even for small polar or

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* Corresponding author. Tel.: +1-785-532-4317; fax: +1-785-532-7372.
E-mail address: rezac@ksu.edu (M.E. Rezac).

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quadrupolar molecules such as CO_2, H_2S, and SO_2.' [12]. Typically, this phenomenon is undesirable in separation applications, as the selectivity is diminished due to increased diffusivity of slower penetrant molecules. As the pressure of the plasticizing component approaches its saturation pressure at system temperature, solubility increases and plasticization is induced, thereupon increasing permeability. Plasticization can also be observed by comparing the rate of transport in equilibrium sorption experiments for sorption and desorption. When a material has been plasticized during sorption, the polymer chains become more mobile. This enhanced mobility allows for faster rates of penetrant desorption and thus, larger diffusion coefficients [12].

2.1.2. Clustering

Clustering occurs when penetrant molecules travel as a group of molecules instead of as a single molecule and therefore the diffusion coefficient decreases. This occurs with molecules that can self-associate, like water and methanol [12]. In very hydrophobic environments, these molecules will self-associate, forming a 'cluster' of two or three molecules and will transport as a single large unit. Since the molecules travel as dimers or trimers, the rate of diffusion is greatly reduced. The probability of clustering increases as the total number of penetrant molecules in the condensed phase increases. This phenomenon can be observed from a plot of D_{avg} versus activity. If the molecules cluster, the diffusion coefficient will decrease with increasing penetrant concentration (activity).

Clustering is most commonly found in water/polymer systems. Sun and Chen [13] report that clustering of water molecules occur in a number of polymers, including poly(alkyl methacrylate), ethyl cellulose and poly(dimethyl siloxane) (PDMS). Favre et al. [14] also report the clustering of water molecules in PDMS. Although clustering is predominantly reported in water/polymer systems, other penetrant molecules are reported to cluster as well. Koros and Hellums [12] report both water and methanol clustering in a rubber material (Cariflex IR305) and Sun and Chen [13] report clustering behavior for toluene, xylene, and ethanol in PDMS. In the sorption of xylene and ethanol in PDMS, both clustering and swelling were simultaneously observed.

2.2. Equilibrium sorption

2.2.1. Sorption into glassy polymers

Equilibrium sorption behavior can be classified 'on the basis of the relative strengths of the interactions between the [penetrant] molecules and the polymer or between the [penetrant] molecules themselves within the polymer' [15]. Glassy polymers, such as those studied here, exhibit dual-mode sorption. The dual-mode sorption model considers the glassy solid to consist primarily of an equilibrium densified matrix with a small volume fraction uniformly distributed molecular-scale gaps, or holes, throughout the matrix [12]. During dual-model sorption, some of the gas molecules become immobilized within the microvoids of the glassy materials, filling the 'holes', while the remaining gas molecules retain mobility and dissolve in the bulk of the polymer, following Henry's law.

2.2.2. Sorption into glassy materials with swelling

Vieth et al. [16] extended the dual sorption theory to polymer/penetrant pairs that swell. When the polymer network swells, more binding sites are exposed and sorption levels increase. An example of this behavior has been reported by Vieth et al. [16] for the sorption of water in a polyurethane membrane containing poly(ethylene oxide). Since the concentration of available sites for sorption changes with the degree of sorption, a single, unvarying Langmuir model cannot be used to describe the case of positive deviations from Henry's law.

3. Experimental methods

3.1. Materials

The polynorbornenes investigated in this study were kindly supplied by the BF Goodrich Company. The structure of the repeat unit is shown in Fig. 1 Methyl-, butyl-, hexyl-, and decyl-substituted polynorbornenes were evaluated. The unsubstituted polynorbornene synthesized had a limited elongation-to-break. Therefore, the material was too brittle to form polymeric films for our evaluation. The materials studied here were synthesized via addition polymerization using an organometallic complex as a catalyst [17]. Physical properties of the addition-polymerized materials are given in Table 1 [18]. The FFV reported was calculated using the Bondi [18] method. The specific volume, v_{sp}, is defined as $1/\rho$, where ρ, the density, was experimentally measured. The van der Waal's volume, v_w, was estimated by using van Krevelen's [19] data. Thus, the free volume is given by

$$v_f = v_{sp} - 1.3 v_w \tag{1}$$

and the FFV can be calculated as

$$\mathrm{FFV} = v_f / v_{sp} \tag{2}$$

The greatest challenge for this calculation is the van der Waal's volume of the norbornene ring structure. We approximated this volume by building up the ring in a step-wise fashion from known components. While this may

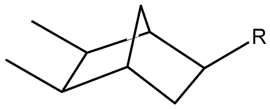

Fig. 1. Chemical structure of addition polymerized polynorbornenes. R represents the alkyl side groups investigated. In this study, methyl-, *n*butyl-, *n*hexyl-, and *n*decyl-side groups were evaluated.

Table 1
Physical properties of addition polymerized polynorbornenes evaluated in this study [18]

R Group	T_g (°C)	Young's modulus (GPa)	Density (g/cm^3)	FFV
Methyl-	>380	1.4	0.986	0.192
Butyl-	>350	0.9	0.970	0.170
Hexyl-	280	0.6	0.965	0.161
Decyl-	150	0.2	0.946	0.159

introduce error in the exact FFV values calculated, errors in this calculation should not seriously influence the comparison between the different pendant groups, because the same ring is present in all polymers investigated here. Ahmed et al. [19] suggest that the Pd catalyzed PNB evaluate here is erythro di-isotactic in structure, when the chain is in the extended, or all *cis*-conformation, the bridgehead carbon is pointing in alternating directions. Ahmed et al. modeled various stereochemistries of PNB and found that both the Pd catalyzed sample and the erythrodi-isotactic model had a scaling of intrinsic viscosity with the molecular weight to a power of approximately 2, resulting in a rigid-rod like behavior.

The polynorbornenes synthesized via ring-opening polymerization (ROMP) and the addition-polymerized polynorbornenes possess very different physical properties even though they are formed from the same monomer. Differences are evident in their thermal properties: the addition-polymerized materials have high glass transition temperatures (up to 370 °C), while the ROMP polymer has a T_g about 35 °C and has poor thermal stability at temperatures above 200 °C. [17] Due to the more attractive characteristics of the addition-polymerized polynorbornenes, these were the materials that were investigated in this study.

The solvent used to cast the films was chloroform (99.9% purity) and supplied by J.T. Baker Company. The methanol (99.9% purity) was supplied by Fisher. The water used in these experiments was tap water. Experiments performed using tap water and deionized water gave very similar results, therefore use of the less pure water was justified. Any dissolved air was removed from the methanol and the water by cycling the liquids through freeze/thaw cycles with liquid nitrogen under vacuum. A minimum of three cycles was performed.

3.2. Film preparation

The films were cast from a chloroform/polymer solution of approximately 3–4 wt% polymer. The solutions were filtered through a 1.2 μm Teflon filter and were cast directly onto a glass plate into a stainless steel casting ring. A second glass plate was placed over the ring in order to reduce the rate of evaporation of the solvent. The casting plates and ring were placed in a solvent-rich environment (glovebag), which limited the evaporation of the solvent from the solution. After approximately 24 h, the films were removed from the glass plate by immersion in water. The films were then dried in under vacuum at about 100 °C to a constant weight. The films were stored in a dessicator until use.

3.3. Sorption experiments

The sorption of vapors into the study polymers was measured at 30 °C using a Cahn D-200 microbalance and an associated vapor handling system [20]. At the start of each experiment, the liquid penetrant was placed into the liquid supply flask. Any dissolved air in the liquid was removed by cycling the liquid through freeze/thaw cycles using externally applied liquid nitrogen to induce freezing. After the liquids were frozen, the vapor phase was removed via a vacuum pump. The liquids were allowed to thaw, refrozen, and the gas phase subsequently removed. A minimum of three cycles was performed. For each material, sorption and desorption experiments were performed at various vapor pressures. During the methanol sorption experiments, the vapor pressure was not adjusted during the run, as there was a minimal drop in the gas phase pressure associated with the methanol sorption. On the other hand, because water has a high affinity for the glass apparatus [21] a large drop in the gas phase pressure would occur if the pressure were not manually controlled during the course of the experiment.

Desorption runs immediately followed the sorption runs. For two of the highest sorbing materials (methyl- and butyl-PNB), desorption experiments were performed manually at an activity (P/P^{sat}) of 1. The transport data at an activity of 1 was obtained by placing the film in a liquid bath for at least 6 h and then measuring the mass loss over time using a Mettler AE260 balance. Transport parameters at unit activity are calculated using this desorption data only.

4. Treatment of experimental data

4.1. Solubility

The equilibrium sorption for each penetrant was calculated using:

$$c = \frac{22414|M_f - M_i|}{\mathrm{MW} V_P} \tag{3}$$

where c is the equilibrium concentration of the penetrant in cm^3(STP)/cm^3 polymer; 22414 is the volume, in cm^3, of one mole of penetrant at standard temperature and pressure; M_i and M_f are the initial and final masses, respectively, both in grams. MW is the molecular weight of the penetrant, in g/mol; and V_p is the polymer volume, in cm^3. Standard conditions were taken as 0 °C and 1 atm.

The solubility coefficient, S, is defined as:

$$S = \frac{c}{p} \tag{4}$$

where p is the vapor pressure.

4.2. Diffusion coefficients

The diffusion coefficient can be determined from the transient portion of the sorption process. The necessary relationships were obtained from the solution of Fick's second law by Crank [22] obeying boundary conditions equivalent to the ones in this study. At short times, the diffusion coefficient can be estimated from a plot of M_t/M_∞ versus the square root of time:

$$\frac{M_t}{M_\infty} = \frac{4}{\sqrt{\pi}}\left(\frac{Dt}{\delta^2}\right)^{1/2} \tag{5}$$

where M_t and M_∞ are the weight gain by the sample at time t and at equilibrium, respectively, δ is the thickness of the sample, and D is the mutual diffusion coefficient. This equation is only valid for applications with a constant diffusion coefficient. However, Crank and Park [23] showed that for cases of non-constant D, the average diffusion coefficient over the entire experimental range is calculated. This method can be applied up to a normalized mass uptake M_t/M_∞ of 0.6 with negligible deviations from the exact solution of Fick's second law. The short term method was used in this study to analyze the data.

Crank and Park [23] also introduced the long-term method to calculate the diffusion coefficient from experimental data. The long-term method proposes a linear relationship in a plot of $\ln(1 - M_t/M_\infty)$ versus time t:

$$\ln\left(1 - \frac{M_t}{M_\infty}\right) = \ln\left(\frac{8}{\pi^2}\right) - \left(\frac{\pi^2 D}{\delta^2}\right)t \tag{6}$$

This method was used for a normalized mass uptake between 0.5 and 0.85. Agreement between the diffusion coefficients from the short and long term methods was very good.

The reported diffusion coefficients were calculated by first averaging the results of the short term and the long term method for each sorption and desorption experiment. Then, the final value is obtained by averaging the results of the corresponding sorption–desorption runs.

4.3. Permeation coefficients

The permeation coefficient of each penetrant has been calculated as the product of the diffusion and sorption coefficients according to

$$P = DS \tag{7}$$

4.4. Buoyancy

All measurements were adjusted to account for buoyancy effects using the method previously described for this system [20].

4.5. Uptake experiments

To determine the maximum degree of penetrant uptake of the films in both water and methanol, swelling experiments were performed. Film samples were dried under vacuum at 100 °C for at least 24 h to ensure that the films were dry. The dry films were placed in a liquid bath for 6 h and the initial and final masses were measured. The maximum penetrant uptake of the materials was calculated as:

$$\text{maximum uptake} = \left(\frac{\text{mass of swollen film}}{\text{mass of dry film}} - 1\right) \times 100\% \tag{8}$$

5. Results and discussion

The results and discussion are presented by discussing each of the transport parameters separately: solubility coefficients, diffusion coefficients, followed by permeability and selectivity. Finally, the discussion of experimental results is followed by a more in-depth analysis of the impact of this research.

5.1. Methanol sorption in polynorbornenes

Fig. 2 displays the sorption isotherms of methanol vapor in methyl-, butyl-, hexyl-, and decyl-PNB. It is evident from the concave upward sorption isotherms of methyl-, butyl-, and hexyl-PNB materials that some degree of swelling is

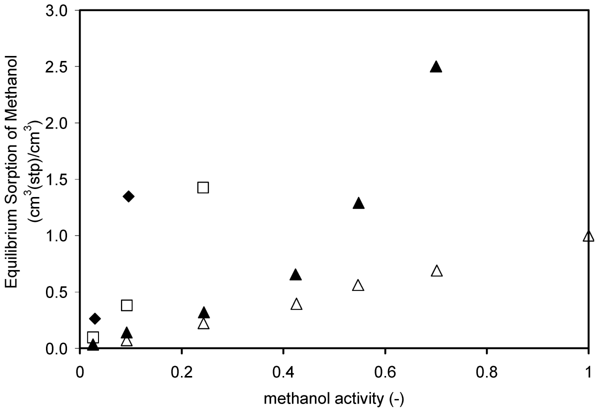

Fig. 2. Comparison of sorption isotherms of methanol in PNB series at 30 °C. Filled diamond (◆)—methyl polynorbornene; open square (□)—*n*butyl polynorbornene; filled triangle (▲)—*n*hexyl polynorbornene; open triangle (△)—*n*decyl polynorbornene.

occurring for these polymer/penetrant pairs. These isotherms appear similar to Flory–Huggins type sorption found in rubbery polymers, where sorption increases almost exponentially with pressure. The methanol sorption isotherm for decyl-PNB does not show the same sorption behavior as the methyl-, butyl-, and hexyl-PNB. Swelling is not apparent for decyl-PNB, as its sorption isotherm is relatively linear, following the Henry's law sorption typical of dual-mode sorption at high activities.

In addition to the *type* of sorption behavior of methanol in the polynorbornenes, the *degree* of sorption is also significant. It is evident that methyl-PNB has the greatest degree of methanol sorption of the four materials. This is probably due to the larger FFV of methyl-PNB.

Free volume, V_f, is the difference between the occupied volume of the polymer molecules, V_o, and the specific volume of the polymer, V. This concept of free volume is typically quantified in terms of FFV, which is simply V_f/V. Glassy materials generally have a much lower free volume than rubbery materials. Pinnau and Toy [24] report that conventional glassy polymers have FFVs of only 2–6%. Methyl-PNB has a relatively high FFV at 19%. The free volume pockets in this material serve as microvoids for methanol molecules to congregate, allowing for higher sorption. A good correlation exists between FFV and methanol sorption in this series of PNB materials (see Fig. 3). As the free volume of the polymer is increased, the sorption of methanol in the matrix is also increased.

5.2. Water sorption in polynorbornenes

Fig. 4 shows the sorption isotherms of water vapor in the PNB materials. Sorption experiments were carried out in an activity range of 0.13 to 0.75, but sorption at $a = 0.13$ was too low to be accurately measured and is therefore not reported. The sorption isotherms for water are quite different from those of methanol. For hexyl-PNB and butyl-PNB, the isotherms are essentially linear. For methyl-PNB and decyl-PNB, the first three data points appear linear and at the highest activity some swelling is apparent, yielding an upward curve.

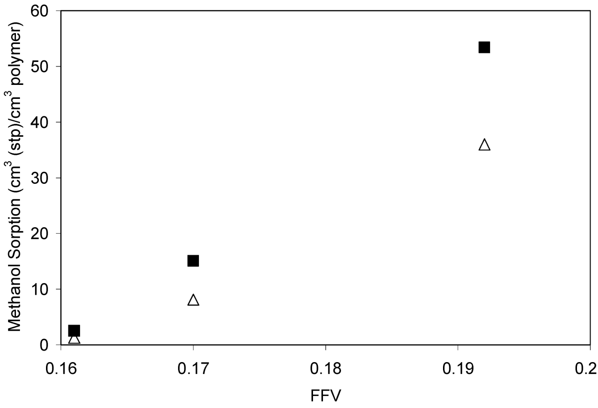

Fig. 3. Correlation of FFV and methanol sorption in PNB materials for methanol vapor activity of 0.55 (open triangles) and 0.70 (filled squares).

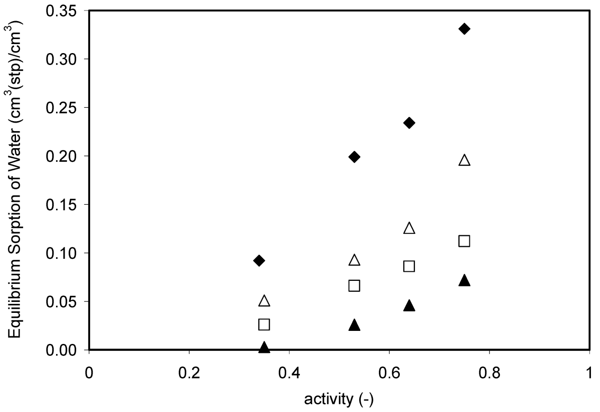

Fig. 4. Sorption isotherms of water vapor in methyl-, butyl-, hexyl-, and decyl-PNB at 30 °C. Filled diamond (◆)—methyl polynorbornene; open square (□)—*n*butyl polynorbornene; filled triangle (▲)—*n*hexyl polynorbornene; open triangle (△)—*n*decyl polynorbornene.

Table 2 displays the sorption values for methyl-, butyl-, hexyl-, and decyl-PNB at high and low activities for both water and methanol. One can see from this data that the sorption of methanol is much greater than the sorption of water in these polymers. The water sorption in this series of polynorbornenes is also roughly correlated with the available free volume. As the free volume increases, the sorption increases. The data for the decyl-PNB does not follow this general trend. The decyl-PNB has higher levels of equilibrium sorption than either the hexyl- or butyl-substituted polymers. Comparison of the series of polymers is complicated by the fact that modification to the alkyl side chain changes not only the FFV, but also the glass transition temperature of the polymers (see Table 1). While the methyl-, butyl-, and hexyl-PNB have T_gs of 280 °C or greater, the T_g of the dry decyl-PNB is only 150 °C. The general trend of increased Henry's law sorption with decreased glass transition temperature has been shown [25].

The depression of the glass transition temperature upon sorption was examined for both solvents in all materials. The T_g in the sorbed state was predicted from additive mixing rules. Upon water sorption, the predicted T_g of the polymer/penetrant mixture remained within 1 °C of the dry polymer T_g. For methanol sorption, the sample T_g was depressed by as much as 160 °C, but all materials remained glassy at the sorption temperature of 30 °C.

5.3. Diffusion coefficients

5.3.1. Methanol transport in polynorbornenes

The diffusion coefficients of methanol vapor in methyl-, butyl-, hexyl-, and decyl-PNB are presented in Fig. 5. One can see that the diffusion coefficients are approximately the same for all four materials, ranging from $\sim 0.8 \times 10^{-12}$ to

Table 2
Equilibrium sorption of methanol and water vapor in PNBs at high and low activities

	Methanol		Water	
	Activity (–)	Sorption (cm^3(STP)/cm^3 polymer)	Activity (–)	Sorption (cm^3(STP)/cm^3 polymer)
Methyl-PNB	0.03	0.26	0.35	0.092
	0.70	53.39	0.75	0.331
Butyl-PNB	0.03	0.10	0.35	0.026
	0.70	15.08	0.75	0.112
Hexyl-PNB	0.03	0.03	0.35	0.003
	0.70	2.50	0.75	0.072
Decyl-PNB	0.03	0.03	0.35	0.051
	0.70	0.69	0.75	0.196

$\sim 7 \times 10^{-12}$ m^2/sec. Although the diffusion coefficients for the four materials are the same order of magnitude, the trends of the transport data vary.

It is apparent from Fig. 5 that clustering of methanol molecules is occurring in methyl- and butyl-PNB. Here, one can clearly see the decreasing diffusion coefficients with increasing penetrant activity. The data for methyl-PNB is especially interesting. The diffusion coefficient at unit activity was measured through liquid uptake experiments to be 3.9×10^{-12} m^2/sec. When included in the plot of D_{avg} versus activity, it is apparent that the diffusion coefficient continues to increase at activities higher than 0.70 and up to unit activity. From this diffusion data, one can observe the competing mechanisms of swelling and clustering. At lower activities (0.03–0.43), the clustering mechanism dominates, as D_{avg} decreases with increasing activity. At intermediate activity levels (0.4–0.7), plasticization and clustering are balanced and the diffusivity is independent of activity. At higher activities (0.7–1), the swelling dominates as D_{avg} increases with increasing activity. For butyl-PNB, it appears as if clustering is dominating diffusion over the entire activity range, as a trend of decreasing diffusion coefficients with increasing activity is consistent over the entire range of activities tested (see Fig. 5). Unlike methyl-PNB, butyl-PNB does not show an increase in diffusion coefficient at higher activities where the diffusivity of methanol at unit activity is 9.5×10^{-13} m^2/sec.

Fig. 5 also displays the diffusion coefficients of methanol in hexyl- and decyl-PNB. D_{avg} is approximately constant with activity for these polymers.

5.4. Water transport in polynorbornenes

The average diffusion coefficients of water vapor in the polynorbornene series are also relatively the same for all four materials over the activity range tested, ranging from $\sim 1 \times 10^{-12}$ to 10×10^{-12} m^2/sec. This is shown in Fig. 6. It should be noted that the diffusion coefficients of water vapor and methanol vapor are approximately the same, therefore any separation of methanol and water by these materials will be due to sorption selectivities.

Although the transport rates are the same order of magnitude for water and methanol, the trends in the D_{avg} versus activity plots are not. As previously mentioned, clustering is most widely reported for water molecules; however, clustering of water molecules is *not* apparent from D_{avg} versus activity plots for the polynorbornene materials. Rather, the four polymers have diffusivities that are essentially independent of concentration within the experimental accuracy available.

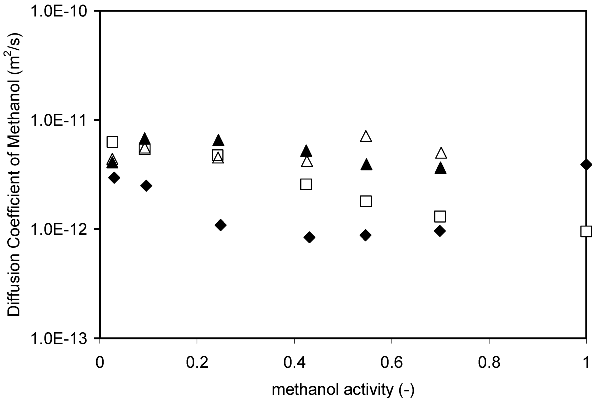

Fig. 5. Diffusion coefficients of methanol vapor in methyl-, butyl-, hexyl-, and decyl-PNB at 30 °C. Filled diamond (◆)—methyl polynorbornene; open square (□)—*n*butyl polynorbornene; filled triangle (▲)—*n*hexyl polynorbornene; open triangle (△)—*n*decyl polynorbornene.

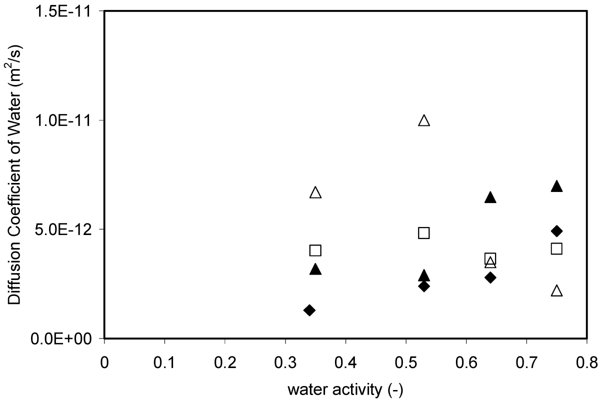

Fig. 6. Diffusion coefficients of water vapor in methyl-, butyl-, hexyl-, and decyl-PNB at 30 °C. Filled diamond (◆)—methyl polynorbornene; open square (□)—*n*butyl polynorbornene; filled triangle (▲)—*n*hexyl polynorbornene; open triangle (△)—*n*decyl polynorbornene.

Table 3
Permeability of methanol and water through alkyl-substituted polynorbornenes

Material	Methanol[a]	Activity dependent?	Water[b]	Activity dependent?
Methyl-PNB	215	Y: increases from 150 to 460	32	Y: increases from 11 to 68
Butyl-PNB	135	N	15	N
Hexyl-PNB	63	N	15	Y: increases from 1 to 21
Decyl-PNB	27	N	22	N

All data at 30 °C.

[a] Reported at activity = 0.09, measured at $a = 0.03$–0.70.

[b] Reported at activity = 0.65, measured at $a = 0.34$–0.75.

5.5. Permeability coefficients and selectivity

The permeability coefficients for methanol and water through alkyl-substituted polynorbornenes were calculated from the product of the independently measured diffusion coefficients and the equilibrium sorption. The results are presented in Table 3. For the most part, the permeabilities were nearly independent on the activity of penetrant applied. Permeabilities of water and methanol in the highly swelling methyl-PNB were dependent upon the applied penetrant activity increasing over the entire range of activities measured. The rate of increase in the permeability also increased with penetrant activity, consistent with the sorption data presented in Figs. 2 and 4.

The ideal selectivity of the materials for the separation of methanol from water was calculated as a ratio of the individual permeability coefficients. For the calculation, the activity of water was set to 0.65 and the activity of methanol to 0.09. These values represent an approximate composition of the water-wet air stream under consideration. The influence of the individual sorption and diffusion selectivities on the pemeability selectivity values is presented in Table 4. Clearly, the permeability selectivity of the materials result from the favorable methanol sorption.

The butyl-PNB and methyl-PNB polymers both show high methanol/water selectivity and high methanol permeability. Either of these materials would be reasonable choices for the current application. As the length of the alkyl side-chain is increased, both the methanol permeability and the methanol/water selectivity are decreased.

Table 4
Selectivities of PNB materials for diffusion, sorption, and permeation of methanol and water

Material	$D_{\mathrm{MeOH}}/D_{\mathrm{water}}$	$S_{\mathrm{MeOH}}/S_{\mathrm{water}}$	$P_{\mathrm{MeOH}}/P_{\mathrm{water}}$
Methyl-PNB	0.9	7.5	6.7
Butyl-PNB	1.5	6.0	9.0
Hexyl-PNB	1.0	4.2	4.2
Decyl-PNB	1.6	0.8	1.2

*Transport parameters used at activity = 0.09 for methanol and activity = 0.65 for water. All data at 30 °C.

5.6. Comparison to other materials

Methanol/water vapor separations have only been studied with a handful of other materials. Namely, PEBAX™, PDMS, a porous silica–alumina materials, a PVA/PAN composite, PTMSP, and PVTMS. Table 5 compares the performance of these materials versus the polynorbornenes. Out of the ten materials shown, it is evident that methyl-, butyl-, and hexyl-PNB show the best methanol/water selectivity, although the permeability coefficients of methanol are low. PTMSP and PVTMS prove to be methanol selective as well, although their selectivities are significantly lower than methyl-, butyl-, and hexyl-PNB.

The only other materials found in the literature to be methanol-selective are polytrimethylsiloxane, PTMSP, and polyvinyltrimethylsilane, PVTMS [26]. These glassy materials both show very high permeabilities [27]. PTMSP has a FFV of 20–27% and PVTMS has a FFV of

Table 5
Comparison of PNBs to other materials for methanol/water vapor separation

Material	P_{methanol} (Barrer)	Selectivity (methanol/water)
Methyl-PNB	215	6.7
Butyl-PNB	135	9.0
Hexyl-PNB	63	4.2
Decyl-PNB	27	1.2
PEBAX™2533[a]	8090	0.32
PDMS[a]	12383	0.70
Silica-alumina ceramic[b]	20480	0.10
PVA/PAN composite[c]	–	0.05
PTMSP[d]	500	1.6
PVTMS[d]	11	1.2

This work and reference a: ideal selectivity based on independently measured permeabilities determined at methanol activity = 0.09 and water activity = 0.64; reference b: permeability calculation based on 1 μm membrane at feed concentration of ~5% MeOH, actual selectivity from mixed-vapor studies for feed composition: 68%MEOH, 32%H_2O; reference c: actual selectivity from mixed-vapor studies for feed composition: 73% MeOH, 27% H_2O; reference d: ideal selectivity based on independently measured permeabilities determined at unreported activities.

[a] Ref. [20].

[b] Ref. [28].

[c] Ref. [29].

[d] Ref. [26].

Table 6
Uptake of methanol and water in liquid phase at 25 °C

Material	Penetrant	c (cm^3(STP)/cm^3)	Degree of penetrant uptake (%)
Methyl-PNB	Methanol	165	23.8
Butyl-PNB	Methanol	48	7.1
Hexyl-PNB	Methanol	6.1	0.9
Decyl-PNB	Methanol	<0.15	*
Methyl-PNB	Water	13.4	1.1
Butyl-PNB	Water	7.4	0.6
Hexyl-PNB	Water	2.2	0.2
Decyl-PNB	Water	2.4	0.2

* Below detection limit.

8–10% [26]. These glassy materials have low methanol permeabilities (500 and 11 Barrer for PTMSP and PVTMS, respectively) and methanol/water selectivities (1.6 and 1.2). It is interesting to note that the common thread of the methanol selective materials reported in the literature and in this work are glassy polymers with high FFV.

5.6.1. Use of polynorbornenes for liquid methanol/water separation

Liquid penetrant uptake experiments were performed on all of the polynorbornene materials to examine the penetrant/polymer interactions and the maximum degree of penetrant uptake that was calculated via Eq. (8). The results of these studies are given in Table 6.

As indicated in Table 6, the methyl-PNB and butyl-PNB materials swell significantly in liquid methanol—24 and 7%, respectively. Due to this strong interaction between the polymer and the methanol, the methanol plasticizes the polymer chains, which probably reduces the selective capabilities of the material for liquid feed separations. Although methyl-PNB has proven to be a methanol-selective material for vapor phase separation at 30 °C, it is anticipated that this selectivity will be diminished for liquid phase separations.

6. Conclusions

A series of alkyl-substituted polynorbornenes were evaluated for their ability to transport methanol and water vapor. The materials had significant differences in their ability to sorb methanol and water. For a given polymer, the diffusion coefficients of methanol and water were not significantly different. Each of the four polynorbornenes had an ideal methanol to water permeability selectivity that was greater than one. The butyl-PNB had the largest ideal permeability selectivity for methanol over water with a value of 9.0. For this series of polymers, the extent of methanol sorption was positively correlated with the FFV of the polymer. The same general trend was observed for water sorption, but the correlation was not as good. Differences in the glass transition temperature of the polymers may also contribute to differences in the extent of sorption, complicating the correlation with free volume. In comparison to other polymers reported in the literature, the study polynorbornenes have higher ideal methanol to water permeability selectivities with somewhat lower methanol permeabilities.

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