Relationship between mixed and pure gas self-diffusion for ethane and ethene in ZIF-8/6FDA-DAM mixed-matrix membrane by pulsed field gradient NMR

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Abstract

Pulsed field gradient (PFG) NMR was applied to study self-diffusion of an ethane/ethene mixture and the corresponding pure gases in a mixed-matrix membrane (MMM) formed by dispersing ZIF-8 particles in 6FDA-DAM polymer. In addition to the MMM, diffusion measurements of the pure gases were also carried out for the membrane constituents, i.e. ZIF-8 particle bed and the pure polymer film. PFG NMR studies were performed at a high magnetic field of 17.6 T using large magnetic field gradients up to 30 T/m. The former allowed achieving sufficiently large signal-to-noise ratios, while the latter enabled diffusivity measurements to be performed for molecular displacements smaller than the size of ZIF-8 particles. As a result, the gas self-diffusivities for the diffusion inside the ZIF-8 particles dispersed in the MMM and for the diffusion inside the surrounding polymer matrix could be obtained separately. For each gas, the diffusivities inside the ZIF-8 and polymer phases of the MMM were found to be smaller than the corresponding diffusivities in the neat ZIF-8 particle bed and pure polymer film. This observation is explained by the reduced framework flexibility of ZIF-8 and the polymer chain rigidification in the MMM. The ethane and ethene diffusivities in the MMM loaded with the ethane/ethene mixture were compared with the corresponding diffusivities in the MMM loaded with a single gas. It was found that the presence of another gas component in the ZIF-8 particles dispersed in the MMM does not change the self-diffusivity inside the particles for both gases. At the same time, the self-diffusivity of the faster-diffusing sorbate (ethene) in the polymer phase of the MMM was reduced by co-adsorption of the slower-diffusing sorbate (ethane) in the MMM. The analytical expression proposed in our previous work for the long-range diffusivity in MMMs was validated for gas mixtures and pure gases based on the experimental data reported in this work.

Keywords: diffusion, olefin/paraffin separations, mixed-matrix membranes, PFG NMR

1. Introduction

Mixed-matrix membranes (MMMs) are advanced membranes formed by dispersing fillers such as metal organic frameworks (MOFs) and zeolites in polymeric matrices. MOF-containing MMMs often exhibit enhanced permeability and/or permselectivity in comparison to the corresponding pure polymeric films [1-11]. In particular, MMMs formed by dispersing ZIF-8 particles in polymer matrices showed a promising performance in separations of olefin/paraffin mixtures including ethane/ethene and propane/propene mixtures [12, 13]. Recently, fabrication of mixed matrix hollow fiber membranes containing ZIF-8 fillers was demonstrated [14, 15]. For hollow fibers based on 6FDA-DAM polyimide polymer matrix with dispersed ZIF-8 particles it was found that the selectivity of olefin/paraffin separations is similar to that of the corresponding ZIF-8 /6FDA-DAM mixed-matrix membrane [13, 15]. Based on the promising performance in olefin/paraffin separations and the feasibility of fabrication of hollow fibers, ZIF-8 / 6FDA-DAM mixed-matrix films were selected in the present work for detailed microscopic studies of ethane/ethene diffusion.

Until very recently, transport properties of MMMs were measured exclusively by macroscopic techniques such as permeation methods [2-10]. Although such measurements yield application-relevant information on macroscopic transport properties, these measurements cannot be used to resolve different types of sorbate transport on microscopic length scales inside MMMs. Obtaining a detailed understanding of sorbate transport in MMMs on different length scales is desirable, owing to the intrinsic heterogeneity of microscopic transport properties of MMMs where diffusion inside the filler particles or through the external surface of these

particles can be expected to be quite different from the diffusion in the polymer phase. In our recent paper we have reported measurements of a one component sorbate (ethene) in a ZIF-8 /6FDA-DAM MMM using pulsed field gradient (PFG) NMR [16]. In these measurements, a combination of a high magnetic field of 17.6 T and high magnetic field gradients of up to 30 T/m allowed resolving different modes of ethene diffusion in the MMM, including diffusion inside ZIF-8 particles and diffusion in the polymer phase between the particles. In the current work we have expanded our microscopic PFG NMR studies of the one component sorbate to the ethane/ethene mixture in the ZIF-8 /6FDA-DAM MMM. For each of the sorbates, microscopic diffusion data obtained in the MMM loaded with the ethane/ethene mixture is compared with the corresponding data for the MMM loaded with one sorbate only. The microscopic diffusion data reported in this paper includes diffusivities inside the ZIF-8 and polymer phases of the MMM. To our knowledge, this is the first study of microscopic diffusion of sorbate mixtures in an MMM of any type.

In our previous work we have proposed an analytical expression that connects microscopic diffusion data directly accessible by PFG NMR in MMMs and the overall, long range self-diffusion coefficient that can also be measured by PFG NMR in the same MMMs [16]. In this previous work we have also discussed a relationship between the long range self-diffusion coefficient and a macroscopic transport diffusivity which can be obtained from permeation measurements. The PFG NMR diffusion data reported in this paper for the ethane/ethene mixture and pure gases in ZIF-8 / 6FDA-DAM MMM is used to verify and validate the expression for the long-range diffusivity. This provides a new contribution to the development of a comprehensive theoretical description of sorbate transport in MMMs [3, 10, 17].

2. Experimental

2.1 Materials

The self-diffusion of ethane, ethene and an ethane/ethene mixture was investigated in the following three samples: a MMM dense film formed by dispersing 21.8 wt% (30.6 vol%) of ZIF-8 particles in a 6FDA-DAM polyimide matrix, a powder bed containing ZIF-8 particles used in the synthesis of the MMM and a 6FDA-DAM polyimide dense film. Details of synthesis and characterization for the MMM [13, 16], ZIF-8 [18] and 6FDA-DAM polyimide dense film [13] can be found elsewhere. The ZIF-8 particles used in the work have an equivalent spherical crystal radius of around 3.8 μm as determined using SEM [16]. The experimental uncertainty of this value is ~15-20%.

The membrane samples for PFG NMR studies were prepared in the same manner as described in ref. [16]. About 60 mg of the MMM strips and 30 mg of 6FDA-DAM polymer strips (about 2-3 mm wide and 25 ± 5 mm long) were formed into oriented, tightly packed stacks. The stacks of membrane strips were then inserted into 5 mm O.D. NMR sample tubes (Wilma Labglass, Inc.). To prepare the ZIF-8 powder bed samples, around 30 mg of ZIF-8 powder was placed into 5 mm NMR sample tubes.

The NMR tubes containing the porous samples were connected to a custom-made vacuum system and the samples were degassed (*i.e.* made sorbate-free) by application of high vacuum at an elevated temperature (around 413 K) for at least 24 hours. Sorbate loading was performed after sample degassing by cryogenically condensing the desired mass of sorbate(s) into the sample tubes using liquid nitrogen. Mixtures of sorbate were obtained by successively condensing a desired mass of each component to achieve the desired partial pressure when

thermally equilibrated at 298 K. Upon sorbate loading, the NMR tubes were flame sealed and separated from the vacuum system.

The sorbates used in this study were: fully ^{13}C -enriched ethane ($^{13}\text{CH}_3^{13}\text{CH}_3$), single ^{13}C -enriched ethene ($^{13}\text{CH}_2^{12}\text{CH}_2$) and a 1:1 ethane/ethene mixture. All sorbates used in this work had >99% isotopic purity (Sigma-Aldrich). The single-enriched ethene was chosen to avoid any potential relaxation effects caused by magnetic dipolar couplings of the adjacent double-bonded ^{13}C nuclei.

The sorption loadings of samples were determined by comparing the NMR signal of adsorbed sorbate(s) in these samples with the NMR signal in an NMR tube containing only pure ethane or ethene gas at a known pressure, in the same way as discussed in our previous work [16]. The estimated sorbate loadings for all samples are indicated in Table 1. Within our experimental uncertainty, the loading of the MMM is consistent with the assumption that the sorption properties of 6FDA-DAM and ZIF-8 are not changed significantly upon formation of MMM using these materials.

The density of each gas in the gas volume surrounding the porous samples in the NMR tubes was also measured using this method, which gives an estimated loading pressure of sorbate of 3.0 ± 0.6 bar for all samples. For ethane and ethene samples, comparable sorbate loading pressures were confirmed by the observation that the measured self-diffusivities of sorbate(s) in the gas phase of the sealed NMR samples after sufficiently long equilibration times varied by less than 25%. For samples loaded with the ethane/ethene mixture, the equilibrium composition of the gas phase was found to be about 53 ± 5 mol% ethane and 47 ± 5 mol% ethene based on the NMR signal analysis.

Table 1: Sorbate loadings (in mmol g⁻¹) obtained for the porous samples used in this work using NMR signal analysis.

Sorbate	6FDA-DAM	ZIF-8 Powder Bed	MMM
Ethane	0.9 ± 0.2	3.7 ± 0.7	1.2 ± 0.2
Ethene	1.2 ± 0.2	2.7 ± 0.5	1.5 ± 0.3
Ethane (Mixture)	-	-	0.5 ± 0.1
Ethene (Mixture)	-	-	0.5 ± 0.1

2.2 Details of PFG NMR Measurements

Studies of self-diffusion in the MMM membranes and constituent components were performed using a wide-bore 17.6 T Avance III HD (Bruker Biospin) spectrometer at a carbon-13 resonance frequency of 188.6 MHz. Magnetic field gradients with the amplitude up to 30 T/m were generated using a *Diff60* diffusion probe and a *Great60* gradient amplifier (Bruker BioSpin). This combined application of a high-field spectrometer and ability to produce large gradient amplitudes enables the measurement of sorbate self-diffusion coefficients in microporous membranes on small (*i.e.*, micrometer and smaller) length scales of molecular displacements.

Diffusion measurements were carried out using the 13-interval PFG NMR pulse sequence with bipolar gradients, modified by the addition of a longitudinal eddy current delay [19, 20]. This pulse sequence allows the reduction or even complete elimination of disturbing magnetic susceptibility effects. Such susceptibility effects can be expected for heterogeneous porous materials such as the stack of membrane pieces or the porous powders studied in this work. Sinusoidal shaped gradient pulses with an effective duration of about 1.0 ms with gradient amplitudes that varied between about 0.03 and 30 T/m were used. The effective diffusion time

was varied in the range between about 10 ms and 1 s for ethylene diffusion and between about 30 ms and 4 s for ethane diffusion. A longitudinal eddy current delay between ~5 and ~10 ms was used to decrease the time intervals of the sequence during which the PFG NMR signal is reduced by T_2 NMR relaxation down to around 12 ms or less which corresponds to a τ of 3 ms or less in the notation described in ref. [19].

The diffusion data were acquired by measuring PFG NMR attenuation curves, i.e. dependencies of the PFG NMR signal intensity on the effective magnetic field gradient strength (g) with all other pulse sequence parameters held fixed. PFG NMR signal intensities were obtained by integration of the NMR spectra of sorbate molecules. It was verified that the PFG NMR spectra did not have any significant variations in phase or chemical shift for all applied gradient amplitudes. In the case of normal self-diffusion with a single diffusion coefficient (D) PFG NMR attenuation curves can be described using the following relation [19, 21]

$$\Psi = \frac{S(g)}{S(g \approx 0)} = \exp(-Dq^2t) \quad (1)$$

where Ψ is the PFG NMR signal attenuation, S is the PFG NMR signal intensity (i.e. area under the NMR lines of ethane or ethene), t is the time of observation of diffusion process (i.e. diffusion time) as described in ref. [19] and q is defined to be $2\gamma g\delta$ where γ is the gyromagnetic ratio and δ is the effective gradient pulse length. In the case of normal self-diffusion in three dimensions, the mean square displacement (MSD) is related to D and t by the Einstein relation [21]

$$\langle r^2 \rangle = 6Dt \quad (2)$$

The square root of Eq. 2 yields the root mean squared displacement (RMSD), a characteristic

displacement of a diffusion process. For a diffusion process involving two molecular ensembles diffusing with different diffusivities Eq. 1 can re-written as [21]

$$\Psi = \frac{S(g)}{S(g \approx 0)} = \sum_i^{n=2} p_i \exp(-D_i q^2 t) \quad (3)$$

where p_i and D_i are, respectively, the population fraction and self-diffusivity of ensemble i . The diffusivities and population fractions were obtained by fitting the measured PFG NMR attenuation curves using least-squares regression to Eq. 3 and the constraint that $\sum p_i = 1$. This is a well-established analysis of PFG NMR attenuation curves of sorbate diffusion in many nanoporous systems including zeolite beds [21]. The reported experimental uncertainty in self-diffusivities was estimated by taking into account the following contributions: (i) signal-to-noise ratio of the measured PFG NMR signal, (ii) measurement reproducibility for the same PFG NMR sample, and (iii) the influence of sample preparation reproducibility on the diffusion data. For bi-exponential PFG NMR attenuation curves, the uncertainty of the least-squares regression made a significant contribution to the total experimental uncertainty reported in this work.

The ^{13}C NMR spectra of pure ethane and ethene in the gas bulk phase contain only one peak with quadruplet and triplet splittings, respectively. The observed chemical shift for ethane was around 6 ppm and around 123 ppm for ethene, in agreement with chemical shifts reported in literature [22]. The large chemical shift separation of ethane and ethene enable the resolution of the NMR signal contributions of the individual components in an ethane/ethene mixture. The recorded ^{13}C NMR spectra of ethane, ethene and their mixture in the MMM and the MMM constituents have complex splitting patterns – a result of a superposition of triplet/quadruplet peaks with slightly different chemical shifts (100s of Hz) with contributions from the bulk gas phase, the ZIF-8 phase and/or the 6FDA-DAM polymer phase. Examples of the measured ethane

^{13}C NMR spectra are shown in Figure 1S (see supplementary material). The spectra of ethene are qualitatively similar to those shown in Figure 1S.

Longitudinal (T_1) and transverse (T_2) NMR relaxation times were measured using the inversion-recovery and Carr-Purcell-Meiboom-Gill (CPMG) pulse sequences, respectively. In all studied samples the measured NMR relaxation data were consistent with the absence of any distribution over relaxation times of adsorbed sorbate for both T_1 and T_2 relaxation. For the MMM and 6FDA-DAM samples, the T_1 ^{13}C NMR relaxation times were observed to be between about 7 to 10 s for the ethane spectrum and 2 to 3 s for the ethene spectrum. For the ZIF-8 powder bed, the T_1 ^{13}C NMR relaxation time was observed to be about 2 s for the ethane spectrum and 0.2 s for the ethene spectrum. T_2 ^{13}C NMR relaxation times measured by the CPMG pulse sequence were in the range between about 40 to 100 ms for ethane, and about 10 to 20 ms for ethene in all studied porous samples. All NMR measurements were performed at 298 K.

3. Results and Discussion

Fig. 1 shows examples of ^{13}C PFG NMR attenuation curves for ethane diffusion in: a bed of ZIF-8 particles (Fig. 1a), in a pure 6FDA-DAM polymer (Fig 1b), and in the MMM formed by dispersing ZIF-8 particles in 6FDA-DAM (Fig. 1c). The PFG NMR data were obtained for a broad range of diffusion times between 7 ms and 4.1 s.

Fig. 1. Examples of ^{13}C PFG NMR attenuation curves measured for ethane self-diffusion for different diffusion times at 298 K in the following samples: (a) bed of ZIF-8 particles, (b) 6FDA-DAM polymer and (c) mixed-matrix membrane. The solid lines indicate the best fit of the attenuation curves to Eq. 1 in figure (b) and to Eq. 3 in figures (a) and (c). In (c) the dotted and dashed lines represent the attenuation behavior of diffusion inside the ZIF-8 particles and inside the polymer, respectively.

The attenuation curves in Fig. 1a for the diffusion in the bed of ZIF-8 particles show the behavior typical for an exchange of sorbate molecules between the particles and the gas phase surrounding the particles: (i) the initial fast attenuation is followed by a slower decay, and (ii) the fraction of this fast attenuation increases with diffusion time. The fast-decaying component of the attenuation curves corresponds to the molecules that diffuse a fraction of the time inside the particles and the remaining fraction in the gas phase. The slowly decaying component can be attributed to intraparticle diffusion. The effective intraparticle diffusivities (i.e. the diffusivities of the ensemble of molecules in the ZIF-8 particles) and the corresponding population fractions were determined by fitting the attenuation curves in Fig. 1a by Eq. 3. The fitting results are presented in Figs 2 and 3a, respectively, for the population fractions and diffusivities. In these figures and later in the paper, the new data for ethane are presented together with the diffusion

data for ethene which was the focus of our previous work [16]. The ethene data were obtained in the same materials and under the same or comparable conditions as that for ethane. The population fractions in Fig. 2 are shown as a function of $6D_0t$, where D_0 is the intraparticle diffusivity of ethane or ethene measured at the smallest RMSD value (see Fig. 3a) when any effects at the particle boundary can be neglected. These intraparticle diffusivities are equal to $1.5 \times 10^{-11} \text{ m}^2\text{s}^{-1}$ and $8 \times 10^{-11} \text{ m}^2\text{s}^{-1}$ for ethane and ethene, respectively. The data in Fig. 2 allows the estimation of the average size of ZIF-8 particles in the bed. It can be done using the analytical expression for the diffusion-limited tracer desorption from porous particles of radius R [21, 23]

$$p_{\text{intra}} = \sum_{n=1}^{\infty} \frac{6}{n^2 \pi^2} \exp\left(-\frac{\pi^2 n^2 D_0 t}{R^2}\right). \quad (4)$$

The fitting of the measured dependence of p_{intra} on $6D_0t$ in Fig. 2 to Eq. 4 resulted in the value of R equal to $4.1 \text{ } \mu\text{m}$. This value is in good agreement with the average radius of particles estimated from the SEM images ($3.8 \text{ } \mu\text{m}$) [16].

Fig. 2. Dependence of the fraction of the intraparticle ensemble, i.e. the ensemble of molecules that diffuse in the ZIF-8 particles during the time t of the diffusion measurement, on $6D_0t$, where D_0 is the diffusivity of the

intraparticle ensembles measured at the smallest RMSD values. The solid line shows the best fit of the data in the figure using Eq. 4.

It is important to note that Eq. 4 is derived for the case when there are no transport barriers at the external particle surface [21, 23]. Hence, a good agreement between the value of R obtained by using this equation and the average particle radius obtained from the SEM images suggests that there are no noticeable transport barriers at the external surface of the ZIF-8 particles in the bed.

Fig. 3a shows that with increasing RMSD the effective intraparticle diffusivity initially remains constant and then decreases when the RMSD approaches the particle size. This observed diffusivity decrease is consistent with the expectation that the “fastest” ethane molecules with the largest displacements stop contributing to the intraparticle ensemble, i.e. the ensemble of molecules that diffuse in the ZIF-8 particles during the time t of the diffusion measurement, as they desorb to the gas phase surrounding the particles. The results in Fig. 3a show that the dependence of the diffusivity of the intraparticle ensemble on the RMSD for ethene is qualitatively similar to that for ethane.

Fig. 3. Ethane and ethene self-diffusivities as a function of RMSD for: (a) diffusion of the ZIF-8 ensemble, i.e. of the molecules that mostly diffuse inside ZIF-8 particles in the MMM (closed symbols) and diffusion of the intraparticle ensemble in the powder bed (open symbols), and (b) diffusion of the polymer ensemble, i.e. of the molecules that mostly diffuse inside the polymer phase of the MMM (closed symbols) and diffusion in the pure polymer film (open symbols). The dashed line indicates the average particle radius obtained by fitting the data in Fig. 2 to Eq. 4.

Fig. 1b shows the PFG NMR attenuation curves for ethane diffusion in the 6FDA-DAM polymer. It is seen in Fig. 1b that Eq. 1 provides a good description for the attenuation curves in the polymer (see solid line in the figure). A small deviation from this description in the initial parts of the attenuation curves can be attributed to the existence of some insignificant distribution over the diffusion coefficients. The intrapolymer diffusivities obtained from fitting individual attenuation curves in Fig. 1b by Eq. 1 are presented in Fig. 3b as a function of the RMSD. It is seen that this diffusivity remains the same for all the values of RMSD within the experimental uncertainty of the measurement. Fig. 3b shows that the ethene diffusivity in the polymer is also independent of the values of RMSD in the measured range. Based on these observations, we

conclude that in the range of the measured displacements the transport properties of the polymer can be considered to be uniform.

Fig. 1c shows ^{13}C PFG NMR attenuation curves measured for ethane diffusion in the MMM which was prepared using the same ZIF-8 and polymer as those discussed above. In contrast to the attenuation curves measured in the pure polymer film, the attenuation curves in the MMM are not mono-exponential and depend on diffusion time. This behavior can be explained by the existence of the following two ensembles of ethane molecules having different diffusivities during the diffusion time of the measurement: the molecules that mostly diffuse inside ZIF-8 particles (i.e. the ZIF-8 ensemble) and molecules that mostly diffuse in the polymer phase between the ZIF-8 particles (i.e. the polymer ensemble). The diffusivities and fractions of both ensembles were obtained by fitting of the attenuation curves in Fig. 1c by Eq. 3. The fitting results are presented in Fig. 3 and Table S1. It is seen in Fig. 3a that the diffusivity of the ZIF-8 ensemble of ethane rapidly decreases with increasing RMSD values when RMSD becomes comparable with and even larger than the average particle size. The observed diffusivity decrease is related to the ethane molecules leaving the original ZIF-8 particles during the diffusion time. After leaving the particles, such molecules diffuse a fraction of the diffusion time in the polymer phase between the particles where the diffusivity is lower than that in ZIF-8. This results in a decrease of the overall diffusivity of this ensemble. It is seen in Fig. 3a that qualitatively similar dependence of the diffusivity on the RMSD was also observed for the ZIF-8 ensemble of ethene in the MMM. Comparison of the diffusivities obtained at the smallest values of the RMSD for the ZIF-8 ensemble in the MMM with the corresponding diffusivities in the ZIF-8 bed indicates that the diffusivities in the MMM are somewhat smaller than those in the bed for both sorbates. The observed differences can be a manifestation of the reduced flexibility of the ZIF-8

framework due to the confinement in the polymer [11, 16, 24]. The data in Fig. 3a show that for each sorbate there is a good agreement between the dependence of the ZIF-8 ensemble diffusivity on the RMSD in the MMM and that in the particle bed. This agreement indicates that the particle surface permeability in the MMM is essentially the same as in the particle bed. Hence, we can conclude that no transport barriers were formed at the ZIF-8 particle surface in the process of the MMM formation. Such barriers can appear due to blocking the pore entrances of ZIF-8 particles by polymer chains in the MMM.

The data on the intrapolymer diffusivities in Fig. 3b show that the diffusivity in the MMM for both sorbates is somewhat smaller than the corresponding diffusivity in the pure polymer for the RMSDs comparable with the ZIF-8 particle size. At the same time, there is a better agreement (especially for ethane) between the diffusivities of the polymer ensemble in the MMM and in the pure polymer when the RMSDs are smaller than the size of ZIF-8 particles. This observation can be explained by polymer chain rigidification near the external surface of the ZIF-8 particles caused by the incorporation of these particles into the polymer [7]. It can be expected that the presence of such rigidified polymer shells around the particles will influence the diffusion of the majority of gas molecules in the polymer phase of the MMM when displacements become comparable with the distances between the particles. The SEM images of the studied MMM, which were reported in ref. [16], suggest that the spacing between the particles is similar to the particle size. Hence, in agreement with the data in Fig. 3b, the particle size can be used as an estimate of the RMSDs for which the diffusion of the polymer ensemble is expected to be decreased by the presence of the polymer shells.

Fig. 4 shows ^{13}C PFG NMR attenuation curves for diffusion of ethane and ethene in the MMM loaded with the ethane/ethene mixture.

Fig. 4. Examples of ^{13}C PFG NMR attenuation curves for the MMM loaded with the ethane/ethane mixture for different diffusion times at 298 K: (a) attenuation curves for ethene diffusion and (b) attenuation curves for ethane diffusion. The solid lines show the best fit of all attenuation curves to Eq. 3.

The dependence of the attenuation curves on diffusion time for both sorbates shows qualitatively similar behavior as that observed for the diffusion of the single component sorbate in the MMM (Fig. 1c). Since the relationship between the diffusion properties of the MMM and the MMM constituents (i.e. pure polymer film and the ZIF-8 particle bed) was already investigated for the one-component sorbates, the diffusion studies of mixtures were limited only to the MMM.

The diffusivities of the ZIF-8 and polymer ensembles in this mixture sample were obtained for both sorbates as a function of diffusion time by fitting the attenuation curves in Fig. 4 by Eq. 3 (Table S1). These data are compared in Fig. 5 with the corresponding diffusivities in the MMM loaded only with ethane or ethene. Fig. 5 presents the values of $D_{\text{mix}}/D_{\text{pure}}$ for each sorbate and ensemble type, where D_{mix} and D_{pure} are the sorbate (ethane or ethene) diffusivities in the mixture and single-component samples, respectively. The data in Fig. 5a demonstrate that for the smallest diffusion time the diffusivity of the ZIF-8 ensemble in the mixture sample is the same, within the experimental uncertainty, as the corresponding diffusivity in the single-component sample. At

this smallest diffusion time, the molecular exchange between the ZIF-8 particles and the polymer does not influence the diffusivity of the ZIF-8 ensemble. Hence, these diffusivities reflect intraparticle transport properties unperturbed by any boundary effects. The coincidence of diffusivities at small diffusion times was observed for both ethane and ethene diffusion. This observation is in qualitative agreement with the previously reported results for a ZIF-8 crystal bed showing that the intracrystalline diffusivity of ethane and ethene is not changed when the pure gas (ethane or ethene) is replaced by the ethane/ethene mixture inside large ZIF-8 crystals [25].

It is seen in Fig. 5a that at intermediate and large diffusion times the values of D_{mix}/D_{pure} for ethene are significantly smaller than 1 for the ZIF-8 and polymer ensembles. For the latter ensemble these values are significantly smaller than 1 also at small diffusion times. This observation indicates that the ethene diffusivity in the polymer phase of the MMM loaded with the mixture is smaller than the corresponding diffusivity in the MMM loaded only with ethene.

Fig. 5. The ratio of the sorbate (ethane or ethene) diffusivities in the MMM sample loaded with the gas mixture and with the pure gas plotted as a function of diffusion time for: (a) diffusion of the ZIF-8 ensemble in the mixed-matrix membrane and (b) diffusion of the polymer ensemble in the mixed-matrix membrane.

For the ZIF-8 ensemble of ethene the value of D_{mix}/D_{pure} continuously decreases with increasing diffusion time (Fig. 5a). Such reduction of D_{mix}/D_{pure} with diffusion time can be explained by the dependence of the diffusivity of the ZIF-8 ensemble on the diffusion inside the surrounding polymer phase. Due to molecular exchange with the polymer phase the ZIF-8 ensemble diffusivity is reduced with increasing diffusion time (Fig. 3a). This reduction is expected to be stronger for the mixture sample because the diffusivity of the polymer ensemble in this sample is smaller than the corresponding diffusivity in the pure ethene sample (Fig. 5b). As a result, D_{mix}/D_{pure} decreases with time due to molecular exchange with the polymer phase

In contrast to the data for ethene, the values of D_{mix}/D_{pure} for ethane were found to be around 1 for both ensembles and all diffusion times (Fig. 5a,b). This result shows that, within the experimental uncertainty, there is no difference between the diffusivities of ethane in the mixture and single-component samples. It is important to note that the data for the polymer ensemble in Fig. 5b are consistent with the behavior observed in many types of porous materials. The data in this figure show that when the slower-diffusing component (ethane) is added to the faster diffusing component (ethene) in the polymer phase of the MMM, the ethene diffusivity decreases. At the same time, the addition of the faster-diffusing ethene to ethane does not influence the diffusivity of the slower-diffusing ethane in the polymer phase. Qualitatively similar behavior was observed for diffusion of mixtures in zeolites and other types of porous materials [21].

Fig. 6 shows ratios of the effective diffusivity (D_{eff}) obtained from the PFG NMR data for all the molecules of the same type (ethene or ethane) diffusing in the whole MMM and the corresponding diffusivity (D_{model}) estimated for the limit of large diffusion times in MMMs as discussed in the next paragraph. The values of D_{eff}/D_{model} are presented in Fig. 6 as a function of

the RMSDs, which were calculated using Eq. 2 with $D = D_{eff}$. The effective diffusivities were obtained by following a well-established procedure of processing the PFG NMR data, i.e. from mono-exponential regression of the initial part of the PFG NMR attenuation curves that represent the first 25-30% of the signal attenuation using Eq. 1 [21].

Using a series resistance model, we have recently suggested the following relation for the sorbate self-diffusivity (D_{model}) in MMMs in the limit of large diffusion times corresponding to the conditions of fast exchange between the filler and polymer phases [16]

$$\frac{1}{D_{model}} = \frac{1}{D_{ZIF8}^*} \frac{\langle r_{ZIF8}^2 \rangle}{\langle r^2 \rangle} + \frac{1}{D_{Poly}^*} \left(1 - \frac{\langle r_{ZIF8}^2 \rangle}{\langle r^2 \rangle} \right) \quad (5)$$

where D_{ZIF8}^* and D_{Poly}^* denote, respectively, the effective diffusivities in the filler particles and in the polymer phase in the limit of small diffusion times when these diffusivities are not affected by the exchange process. $\langle r^2 \rangle$ and $\langle r_{ZIF8}^2 \rangle$ are, respectively, the values of MSD in an MMM and in the all visited filler particles inside the MMM during a time t , which has to be sufficiently large to ensure the conditions of fast exchange between the filler and polymer phases of the MMM. The ratio $\frac{\langle r_{ZIF8}^2 \rangle}{\langle r^2 \rangle}$ in Eq. 5 can be estimated as the volume fraction of all filler particles

in the MMM, $\frac{v_{ZIF8}}{v}$, raised to the 2/3 power, which is needed to compensate for the

dimensionality difference between the MSD and volume [16]. For the studied MMM, $\frac{v_{ZIF8}}{v} =$

0.306 which yields a value of 0.45 for $\frac{\langle r_{ZIF8}^2 \rangle}{\langle r^2 \rangle}$. Table 2 shows the values of D_{model} calculated

using Eq. 5. These values were used to determine the ratios D_{eff}/D_{model} in Fig. 6.

Table 2: Predicted effective self-diffusivities in the MMM (D_{model}) as calculated using the proposed series resistance model (Eq. 5) for the sorbates used in this work.

Sorbate	$D_{model}, \text{m}^2\text{s}^{-1}$
C_2H_6	2.4×10^{-12}
C_2H_4	1.0×10^{-11}
C_2H_6 (Mixture)	2.4×10^{-12}
C_2H_4 (Mixture)	5.7×10^{-12}

Fig. 6. Normalized effective self-diffusivity in mixed-matrix membrane as a function of RMSD, which is equal to $(6D_{eff})^{1/2}$. In the presentation of the figure, a value of unity (i.e. the dashed horizontal line) represents agreement with Eq. 5. The vertical dotted line indicates the average ZIF-8 particle radius obtained by fitting the data in Fig. 2 to Eq. 4.

Fig. 6 shows that the values of D_{eff}/D_{model} decrease with increasing RMSD for the RMSDs smaller than the ZIF-8 particle size and approach a constant value close to one as the RMSDs become larger than the particle size. The initial decrease of D_{eff}/D_{model} is related to a growth of the number of the sorbate molecules that leave the original ZIF-8 particles and enter the polymer phase, where the diffusion is slower than that in the ZIF-8. At larger RMSDs, the conditions of

the fast exchange between the ZIF-8 particles and polymer are approached. In this case D_{eff}/D_{model} is expected to approach the value of one, which is in agreement with the results in Fig. 6. This observation strongly supports the validity of Eq. 5 for diffusion of mixtures and one-component sorbates in MMMs.

With respect to the ethane/ethene separation using the studied MMM this work provides the following main insights. It was observed that no transport barriers were formed at the external surface of the ZIF-8 particles due to the MMM formation, Experimental evidence was obtained for a reduction of the framework flexibility of the ZIF-8 particles due to the MMM formation. This effect, however, did not lead to any appreciable decrease of the ethane and ethene long-range diffusivities relevant for the mixture separation. Experimental evidence was also obtained for the polymer chain rigidification induced by the MMM formation. This polymer chain rigidification resulted in a small decrease of the long-range diffusivities for both ethane and ethene. It is demonstrated that the diffusivity of ethene in the polymer phase of the membrane loaded only with ethene is larger in comparison to that in the membrane loaded with the ethane/ethene mixture at the same total loading. All other diffusivities measured in the MMM for the pure gases were essentially the same as the corresponding diffusivities in the MMM loaded with the mixture at the same total loading.

4. Conclusions

Self-diffusion of ethane, ethene and ethane/ethene mixture in the MMM formed by dispersing ZIF-8 particles in 6FDA-DAM polymer was investigated by ^{13}C PFG NMR. Complementary ^{13}C PFG NMR diffusion studies were also performed for diffusion of the pure gases in a bed of ZIF-8 particles and in a pure 6FDA-DAM polymer film. The diffusion measurements were carried out for a broad range of the root MSDs which allowed resolving diffusion inside ZIF-8 particles and in the polymer phase of the MMM between the particles. These measurements indicate a small decrease of the gas diffusivities inside the ZIF-8 and polymer phases of the MMM in comparison to the corresponding diffusivities in the ZIF-8 particle bed and pure polymer film. These diffusivity differences can be attributed to a reduced framework flexibility of the ZIF-8 particles and the polymer chain rigidification induced by the MMM formation. A comparison of the ethane and ethene diffusivities for diffusion of the pure gases in the MMM with the corresponding diffusivities for diffusion of the ethane/ethene mixture in the same MMM sample allowed making the following conclusions: (i) for each gas the presence of another gas in the ZIF-8 particles does not change its diffusivity, and (ii) the presence of the slower diffusing ethane slows down the diffusion of faster diffusing ethene in the polymer phase of the MMM. The latter observation is in a qualitative agreement with the behavior reported for many other types of microporous solids. It was demonstrated that the long range self-diffusion in the MMM loaded with the single gases and gas mixture used in this work can be described by a series resistance model presented by Eq. 5.

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