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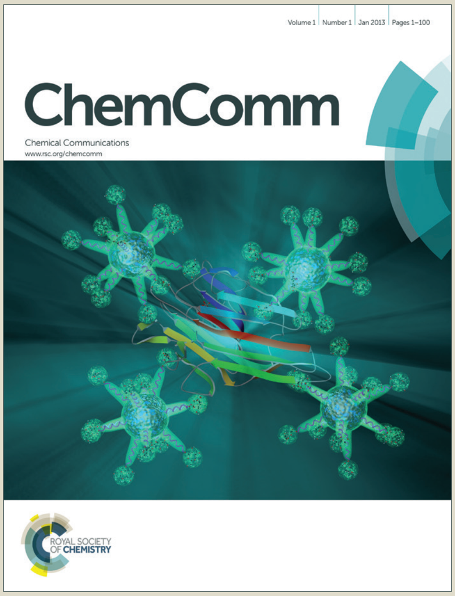

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Relationship between Single-File Diffusion of Mixed and Pure Gases in Dipeptide Nanochannels by High Field Diffusion NMR

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High field NMR diffusometry reveals single-file diffusion of CO/CH$_4$ mixture in dipeptide nanochannles with a coincident mobility for CO and CH$_4$. In contrast to the relationship commonly observed for normal diffusion, this mixture mobility is only slightly smaller than that of pure CO which diffuses much faster than pure CH$_4$.

Molecules restricted to diffuse through unidimensional channels so narrow that they cannot pass each other may exhibit single file diffusion (SFD). For this type of anomalous diffusion, the sequential order of diffusing molecules is preserved, resulting in a deviation from the usual time dependence of the mean square displacement (MSD) observed for normal diffusion. While MSD increases proportionally with time for normal diffusion, for SFD in sufficiently long channels when all boundary effects at the channel margins can be neglected it grows with the square root of time[1]

$$< z^2(t) >= 2Ft^{1/2} \qquad (1)$$

where *F* is the single-file mobility factor and *t* is the diffusion time. Hence, an important consequence of SFD is a significant slowdown in the growth of MSD with time in comparison to that for normal diffusion. This property opens a possibility for highly selective separations if one component in the mixture exhibits normal diffusion and another SFD.[1-7] Inducing single-file diffusion in catalytic systems can also be beneficial since single-file conditions offer better control over catalytic reactions.[1, 8-11] Clearly, for separations and catalysis in single-file systems, more than one sorbate component is expected to be present inside the channels. While diffusion of mixtures of different types of molecules in single-file channels has been the focus of many theoretical and simulation studies,[1-13] until now there have been no reports on experimental investigations of transport of sorbate mixtures under the SFD conditions.

Here we present and discuss observation of SFD of pure CO and CH$_4$ as well as their mixture in L-Ala-L-Val (AV) nanochannels by pulsed field gradient (PFG) NMR, which is also known as pulsed gradient spin-echo (PGSE) NMR. The comparison of the diffusion behavior of the sorbate mixture and that of the pure components reported in this letter expands on previous experimental studies of molecular SFD, which were performed with single-component sorbates.[14-19] Observation of molecular SFD was first published for CH$_4$ and CF$_4$ in one-dimensional channels of AlPO$_4$-5 zeolite using ^{1}H PFG NMR.[14, 15]

AV is a microporous crystalline dipeptide material containing helical channels of mean diameter (*d*) of ~0.51 nm.[20] It was selected for this work because of our recent studies of diffusion and tracer exchange of Xe atoms in AV nanochannels.[21-23] These previous studies were performed using a combined application of ^{129}Xe PFG NMR and hyperpolarized ^{129}Xe spin tracer exchange NMR. These studies revealed that Xe in AV nanochannels is a highly ideal single-file system.

Diffusion of CO and CH$_4$ (Sigma-Aldrich, 99 atom % ^{13}C) in AV nanochannels was investigated by ^{13}C PFG NMR. The kinetic diameters of CO and CH$_4$ molecules are approximately 0.34 and 0.41 nm, respectively,[24] which are larger than the radius of AV nanochannels (~0.255 nm). Hence, SFD is expected for both types of molecules inside the channels. PFG NMR can be used to directly measure the dependence of MSD on diffusion time in porous solids.[1] Therefore, this technique is ideally suited for distinguishing SFD, characterized by the MSD time scaling given by Eq. 1, from normal diffusion. The detection of the relatively weak ^{13}C NMR signal of gas molecules in AV nanochannels was enabled with the aid of a high field (17.6 T) NMR spectrometer located at the National High Magnetic Field Laboratory (AMRIS) facility in Gainesville, FL. High magnetic field gradients up to 23T/m were employed to study diffusion for root MSD as small as 10^{-6} m. The measurements were performed across a broad range of

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diffusion times between 30 ms and 1 s. The 13-interval bipolar PFG NMR sequence[25] with longitudinal eddy current delay was selected for these diffusion studies. The T_1 and T_2 NMR relaxation times were measured by this sequence at small gradient strength by either changing the time interval between the first and second radiofrequency $\pi/2$ pulse (for T_2 measurements) or between the second and third radiofrequency $\pi/2$ pulse (for T_1 measurements) while keeping all other sequence parameters constant. The measured T_1 relaxation times for the CH_4 and CO molecules adsorbed in the channels were around 1.5 and 0.6 s, respectively. The T_2 relaxation times were estimated to be 16 and 22 ms for CH_4 and CO, respectively. All NMR measurements were performed at 298 K.

Three NMR samples were prepared, each containing AV solid with the average channel length of around 50 μm and gas at 10 bar total loading pressure. For sample preparation, approximately 55 mg of AV was added to a 5 mm NMR tube and evacuated overnight under high vacuum at 373 K. The samples were then loaded with CO and CH_4 by cryogenic freezing of the selected gas(es) from a calibrated volume of the vacuum system using liquid nitrogen. After loading with gases, the sample tubes were flame-sealed. For the samples loaded with pure gases the resulting equilibrium gas pressure in the sample tubes at 298 K was 10 ± 0.1 bar. For the mixture sample the partial pressure of each sorbate at 298 K was 5 ± 0.1 bar. These loading pressures correspond to sorbate densities of 0.57 and 0.48 mol/kg for adsorbed CO and CH_4 molecules, respectively, in the single sorbate samples. The corresponding densities of CO and CH_4 in the mixture sample were 0.34 mol/kg and 0.20 mol/kg (total 0.54 mol/kg). These densities were estimated by comparing ^{13}C NMR spectra obtained for the AV samples with those of the samples containing only pure CH_4 or CO gas prepared in the same way as discussed in our previous work.[26, 27] References 26, 27 also provide additional information on the PFG NMR spectrometer used in the work reported in this communication.

Due to the one-dimensional nature of the AV channels, sorbate molecule diffusion is constrained to the channel axis. However, these channels are expected to be more or less randomly oriented in the NMR tube. For random channel orientation the attenuation of the PFG NMR signal (Ψ) of sorbate molecules is expected to obey the following relation:[1, 21, 22]

$$\Psi(q,<z^2(t)>)=\sqrt{\frac{\pi}{2q^2<z^2(t)>}}\,erf\left(\sqrt{\frac{q^2<z^2(t)>}{2}}\right) \qquad (2)$$

where $q=2\gamma g\delta$, γ is the gyromagnetic ratio, g is the gradient amplitude, δ is a duration of a single gradient pulse, $<z^2(t)>$ is the MSD along the direction of the channel and t is the effective diffusion time.[25] However, the helical nature of the AV channels alters the measured MSD. As discussed in our previous work,[22] the actual MSD ($<z^2>_{helix}$) of the molecules is larger than the measured MSD (Eq. 2) by a factor of $(3\cdot d_{mol}/c)^2$, where d_{mol} is the diameter of the molecule and c (~10 Å) is the pitch of the helix in AV channels.

Figure 1 (a) shows the ^{13}C PFG NMR attenuation curves measured in the single sorbate samples for a broad range of diffusion times. In the presentation of Figure 1, the attenuation curves measured in the same sample for different diffusion times will collapse onto a single curve if diffusion occurs by the single-file mechanism. As seen in Figure 1 (a), all of the attenuation curves measured in the same sample for different diffusion times are, within the experimental uncertainty, coincident. Hence, it can be concluded that the MSD is governed by the SFD mechanism for gas diffusion under our experimental conditions. The results of least square fitting of the attenuation curves to Eq. 2 where the time dependence of MSD is given by Eq. 1 are shown in Figure 1 (a) as solid lines. Thus, Eqs. 1 and 2 provide a satisfactory fit for both samples. Some minor deviation between the fitting lines and the experimental data could be a consequence of deviations of the distribution over channel orientations in the NMR samples from the completely random distribution. The fits from Figure 1 were used to calculate the single-file mobility factors (F) along the actual diffusion path in the helical AV channel. The resulting values of

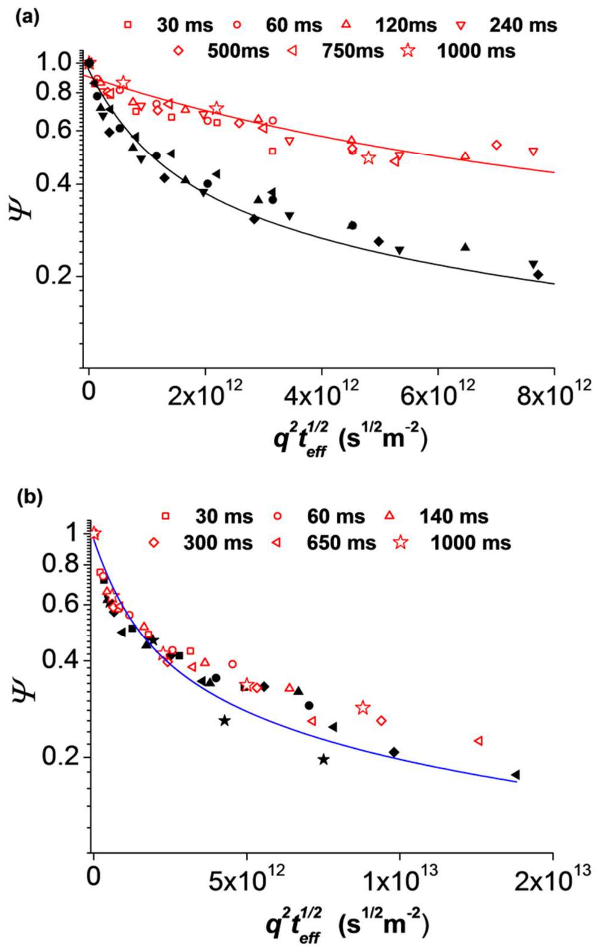

Figure 1. ^{13}C PFG NMR attenuation curves measured for the diffusion of CO (filled symbols) and CH_4 (unfilled symbols) at 298 K in AV samples loaded with (a) a single gas

(CO or CH_4) and (b) a CO/CH_4 gas mixture. Solid lines show the best fits to Eq. 2 where the MSD obeys Eq. 1.

F are shown in Table 1. Consistent with its larger size and molecular mass, CH_4 diffuses more slowly than CO, as captured by its SFD mobility.

Figure 1 (b) presents the ^{13}C PFG NMR attenuation curves for the CO and CH_4 diffusion in the sample containing the mixture of the two gases. As seen in the figure, *there is a strong coincidence between the attenuation curves measured for different diffusion times and different sorbates*. As discussed above, such coincidence indicates SFD as the transport mechanism with the same values of *F* (within the experimental uncertainty) for both types of gas molecules. The solid line in the figure shows the best fit for all the data in the figure using Eqs. 1 and 2. The resulting mobility factor along the helical path is reported in Table 1. Such close agreement between the attenuation curves for CO and CH_4 in Figure 1 (b) indicates that the rate of diffusion in the mixture sample is the same for both species. This is an expected result because under the conditions of SFD molecules cannot pass one another inside the channels. The data in Table 1 shows that the single-file mobility in the mixture sample is intermediate to those obtained in the single-sorbate samples.

Numerous studies of normal diffusion under the conditions of extreme confinement in microporous solids indicate that addition of a slower-diffusing sorbate component to a faster-diffusing component can slow down the diffusion of the faster diffusing sorbate.[1] At the same time, addition of a faster-diffusing component to a slower-diffusing component does not significantly alter the self-diffusivity of the slower-diffusing component.[1] In contrast to these observations for normal diffusion, our SFD data in Table 1 show the opposite trend. It is seen that the mobility factor in the CO/CH_4 mixture sample is much larger than that in the single-component CH_4 sample, which exhibits the slowest diffusion rate (Table 1). The total density of all sorbate molecules is approximately the same in both samples. This relationship between the single-file mobility factors in the mixture and single-component CH_4 sample can be rationalized by noticing that under the conditions of SFD the displacement of any molecule strongly depends on the displacements of its neighbors, resulting in highly correlated transport. In the mixture sample, high local mobility of CO molecules trapped in-between CH_4 molecules affords a high mobility for these CH_4 molecules in comparison to the case when CO molecules in the channels are replaced by CH_4 molecules (i.e., the pure CH_4 sample with the same number density). It is important to note that recent molecular dynamics (MD) simulations[28] revealed qualitatively the same relationship between the single-file mobility factors as those discussed above for CO, CH_4 and CO/CH_4 mixture in AV channels. The MD simulations were performed for SFD of single-component gases and gas mixtures in single-wall carbon nanotubes. In these simulations the authors explored the effect of changing the relative concentration of two types of gases in a mixture on *F* while keeping the overall density of molecules constant. In complete analogy to the systems discussed in this letter, both sorbate components in the simulations exhibit SFD as pure sorbates and in a mixture. It was shown that, in agreement with our experimental data, the single-file mobility for a mixture is intermediate between those for single-components.

Table 1. Single- File mobilities (F) obtained from fitting the attenuation curves in Figure 1 using Eqs 1. And 2.

	Pure Components		Mixture
	CO	CH_4	CO/CH_4
$F \times 10^{13}$ ($m^2 s^{-1/2}$)	28 ± 2	7.0 ± 0.6	20 ± 1

Figure 2 summarizes all the PFG NMR data for CO, CH_4 and CO/CH_4 mixture diffusion in AV. It shows the intra-channel MSD ($\langle z^2 \rangle_{helix}$) as a function of diffusion time on a double log scale for the three studied samples. The MSD values were obtained by fitting individual attenuation curves in Figure 1 using Eq. 2. In order to verify the applicability of Eq. 1 for the PFG NMR data shown in Figure 2, we fitted the data using a modification of Eq. 1 by replacing $t^{1/2}$ with t^{α}, where α is taken to be a fitting parameter. The best fit values of α were found to be in the range between 0.49 and 0.52 with an uncertainty of 0.05. This result confirms the applicability of Eq. 1 for the studied diffusion of CO and CH_4 molecules. The solid lines in Figure 2 show the result of fitting the data for each sample using Eq. 1. It was verified that the values of *F* corresponding to the best fit lines in Figure 2 are in agreement with the data in Table 1.

For ideal single-file systems where diffusion is approximated as a random walk of particles with hard-core interactions a transition from SFD to the center-of-mass (COM) diffusion is predicted to occur at sufficiently large displacements in single-file channels.[29, 30] COM is characterized by a linear dependence of the MSD on diffusion time as in the case of normal diffusion.

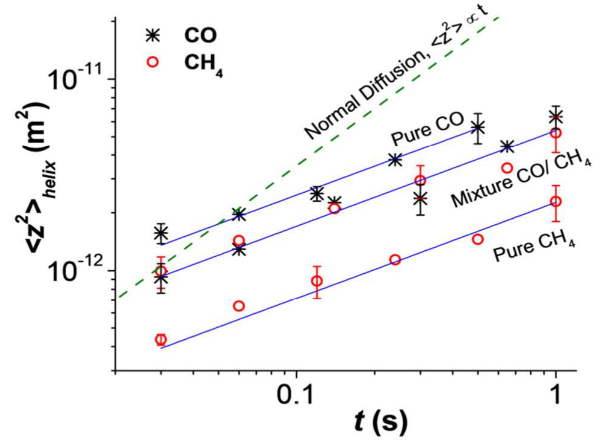

Figure 2. Time dependence of the MSD obtained by fitting the ^{13}C PFG NMR attenuation curves for CO and CH_4 diffusion shown in Fig. 1 to Eq. 2. A correction has been applied to the measured MSD values to account for the helical topology of the AV channels, as discussed in the text. Solid lines are least-squares fits using Eq. 1. The dashed green line represents the time scaling of normal diffusion.

Under our experimental conditions such transition is not observed for the diffusion of CO and CH_4 molecules in AV nanochannels. This result is in qualitative agreement with the previous study of the Xe diffusion in the same AV sample that revealed the MSD time scaling given by Eq. 1 for the whole range of MSDs,[21-23] which are similar to the MSDs reported in this communication for CO and CH_4. As discussed in our previous work,[22] the lack of the expected transition to the COM diffusion can be related to deviations of the diffusion process in AV channels from that in the considered model system due to possible molecular clustering induced by long-range interactions in AV channels.

To our knowledge, this communication represents the first experimental evidence of SFD in a mixture of different types of molecules. While both CO and CH_4 individually have different SFD mobilities in AV nanochannels, it is shown that both species in the mixture start exhibiting the same SFD mobility. This coincident SFD mobility is greater than that of pure CH_4 but smaller than that of pure CO in the same nanochannels. The observed relationship between the SFD mobility for the gas mixture and those for the corresponding pure gases was found to be in a qualitative agreement with the results of recent MD simulations of SFD for similar gas mixtures in single-wall carbon nanotubes.

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Notes and references

The authors declare no competing financial interests.

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