RELATIONSHIP BETWEEN DIFFUSION AND STRUCTURE IN SELECTED NANOSTRUCTURED SYSTEMS BY NMR

By

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To my Mom and Dad
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LIST OF ABBREVIATIONS

BET BET adsorption isotherm
BSA Bovine serum albumin
CFHP Continuous flow hyperpolarized
D Derivative term of a PID controller
DLS Dynamic Light Scattering
EMT Hexagonal polymorph of faujasite type zeolite
FAU Faujasite type zeolite
FID Free Induction Decay
FRAP Fluorescence Recovery after Photobleaching
I Integral term of a PID controller
IL Ionic Liquid
MC Monte Carlo simulation
MRI Magnetic Resonance Imaging
MSD Mean square displacement
NMR Nuclear Magnetic Resonance
P Proportional term of a PID controller
PADMAC Poly(diallyldimethylammoniumchloride)
PEEK Polyetheretherketone
PFG NMR Pulsed Field Gradient Nuclear Magnetic Resonance
PGSE PFG NMR spin echo pulse sequence
PGSTE PFG NMR stimulated echo pulse sequence
PGSTE-LED PFG NMR stimulated echo longitudinal encode decode pulse sequence
r.f. pulse Radio frequency pulse
RTD Resistive/Resistance Temperature Detector
<table>
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<th>Abbreviation</th>
<th>Description</th>
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<tr>
<td>RTIL</td>
<td>Room Temperature Ionic Liquid</td>
</tr>
<tr>
<td>SBA15</td>
<td>Santa Barbara Amorphous materials type 15; a type of mesporous silica</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
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<tr>
<td>SEOP</td>
<td>Spin exchange optical pumping</td>
</tr>
<tr>
<td>TMS</td>
<td>Tetramethylsilane</td>
</tr>
<tr>
<td>TZLC</td>
<td>Tracer Zero Length Column Technique</td>
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<td>Xe 2D EXSY</td>
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\[ A(g) \] Amplitude of PFG NMR signal as a function of magnetic field gradient \( g \)

\( B_0 \) The amplitude of the applied external static magnetic field

\( B_1 \) The amplitude of the oscillating applied magnetic field due to a radio frequency pulse

\( B_{\text{eff}} \) The amplitude of net effective magnetic field

\( c \) Concentration of molecules or ions

\( c_{\text{crystal}} \) Concentration of random walkers in the domain (crystal) in MC simulation

\( c_{\text{gas}} \) Concentration of random walkers in the interdomain space (gas) in MC simulation

\( C \) A constant in the Stokes-Einstein equation

\( d_{\text{eff}} \) Effective diameter of particle components separated by transport barriers

\( D \) Diffusion coefficient

\( E \) Activation energy for diffusion

\( g \) Amplitude of the magnetic field gradient

\( J \) Flux of molecules or ions
Boltzmann constant

Length of an elementary diffusion step on MC simulation lattice

Amplitude of individual spin magnetization along transverse (X-Y) plane

Amplitude of net transverse magnetization

Amplitude of net magnetization along z axis

Equilibrium value of net magnetization along z axis

Number of random walkers in the domain (crystal) at time $t$ in MC simulation

Number of random walkers in the domain (crystal) at time $t = 0$ in MC simulation

Number of spins in the spin up state

Number of spins in the spin down state

Probability density

Spin polarization factor

Probability of an elementary diffusion step through the domain boundary leading into the domain (crystal) in MC simulation

Probability of an elementary diffusion step through the domain boundary leading into the interdomain space (gas) in MC simulation

Probability of an elementary diffusion step inside the domain or in the interdomain space, in x or y direction in MC simulation

Radial coordinate of position of molecule/ion/nuclear spin in spherical coordinate system

Hydrodynamic radius of a particle (molecule/ ion)

Mean square displacement

Gas constant
\( \hat{S} \)  
Spin angular momentum

\( t \)  
Time

\( t_1 \)  
Duration between the first and the second r.f. pulse in 2D NMR exchange spectroscopy pulse sequence

\( t_2 \)  
The duration of signal acquisition in 2D NMR exchange spectroscopy pulse sequence

\( t_{\text{eff}} \)  
Effective diffusion time

\( T \)  
Absolute temperature

\( T_1 \)  
Longitudinal (Spin-Lattice) NMR relaxation time

\( T_2 \)  
Transverse (Spin-Spin) NMR relaxation time

\( T_{\text{LED}} \)  
Duration between the fourth and fifth r.f. pulse in PGSTE-LED pulse sequence for eddy current dissipation

\( v(t) \)  
Velocity as a function of time

\( z \)  
z coordinate of position of molecule/ion/nuclear spin

\( \gamma \)  
Gyromagnetic ratio

\( \gamma(t) \)  
Ratio of number of random walkers in the domain (crystal) at any time \( t \) to the number of random walkers in the domain at time \( t = 0 \)

\( \delta \)  
Duration of magnetic field gradient pulse

\( \Delta \)  
Diffusion time

\( \eta \)  
Viscosity

\( \hat{\mu} \)  
Magnetic moment of a nuclear spin

\( \tau \)  
Duration between the \( \frac{\pi}{2} \) and \( \pi \) r.f. pulse in PFG NMR spin echo pulse sequence

\( \tau_1 \)  
Duration between the first and second r.f. pulse in PFG NMR stimulated echo pulse sequence
$\tau_2$  
Duration between the second and third r.f. pulse in PFG NMR stimulated echo pulse sequence

$\tau_{\text{crystal}}$  
Time for elementary diffusion step inside the domain (crystal) in MC simulation

$\tau_{\text{gas}}$  
Time for elementary diffusion step in the interdomain space (gas) in the MC simulation

$\tau_m$  
Duration between the second and the third r.f pulse in the 2D NMR exchange spectroscopy pulse sequence also referred to as the mixing time

$\tau_p$  
Duration of the r.f. pulse

$\phi_i$  
The phase angle of individual spin magnetization vectors

$\Phi$  
Flip angle of a r.f. pulse

$\psi$  
Amplitude of signal attenuation in PFG NMR experiment

$\omega$  
Larmor frequency

$\omega_{\text{ref}}$  
Larmor frequency of reference nuclei

$\omega_{\text{sr01}}$  
Operating frequency of NMR spectrometer
This work presents results of studies of transport of molecules and ions in several selected types of nanostructured materials. For the most part, the transport studies were performed using an experimental technique, which is known as pulsed field gradient nuclear magnetic resonance (PFG NMR). The systems under study can be divided into two types: (i) organized soft matter systems, such as ionic liquids and, (ii) porous solids, such as zeolites and mesoporous silicas. All studied systems exhibit well-defined structure on the length scales ranging from one nanometer to several hundreds of nanometers. Study of transport properties over a wide range of length scales, which were in many cases comparable with the sizes of structural inhomogeneities (particles, domains, etc.) of the investigated systems, allowed clarifying structural properties of these systems as well as provided new information on the relationship between these properties and diffusion of molecules and ions in these systems.

Pulsed field gradient NMR allows performing measurements of the mean square displacements (MSD) of molecules and ions as a function of diffusion time. This work presents development and implementation of this technique under conditions of high magnetic field (17.6 T) and ultra high gradient strengths (30 Tm\(^{-1}\)) with precise...
temperature control over a temperature range from 218.2K to 423K. Application of ultra high gradients resulted in a possibility of diffusion measurements on the length scale of displacements as small as 90 nanometers under the conditions of high signal-to-noise ratios resulting from a high magnetic field. In addition to PFG NMR, also another NMR technique was used, viz. continuous flow hyperpolarized $^{129}$Xe 2D exchange spectroscopy (CFHP $^{129}$Xe 2D EXSY). This technique works on the principle of NMR tracer exchange and allows for monitoring time dependence of uptake or release of NMR labeled molecules in regions or domains of interest. This technique was used in “the work in progress” section reported later in the thesis. Simplistic Dynamic Monte Carlo simulations were also performed to complement experimental Xe 2D EXSY studies.
Molecular Transport in Complex Nanostructured Materials

There are many life cycle processes and also many industrial applications that strongly depend on transport of molecules and ions on small, i.e. micrometer and submicrometer, length scales. In many cases transport properties on small length scales control system properties on macroscopic length scales. Study of molecular transport on small length scales is thus required to improve the understanding of system properties in such cases. In this dissertation the term ‘nanostructured materials’ refers to materials exhibiting structural heterogeneity on length scales between one nanometer and several micrometers. Such materials depict unique properties of scientific interest as a consequence of the inherent nanostructural heterogeneity. Understanding transport and structural properties of such materials on small length scales thus hold key to their successful application.

Heterogeneity in molecular/ion transport on small scales is often a direct consequence of the heterogeneity in the corresponding structural properties. Thus, knowledge of one type of property can help understanding the other. Self-diffusion is often the primary mechanism of molecular/ion transport. Transport studies at small length scales thus heavily rely on investigations of self-diffusion under the conditions of interest. The dissertation reports investigation of self-diffusion on various relevant length scales. Such investigation allowed obtaining information about structure and unique transport properties in several materials of scientific and industrial importance. The work reported in this dissertation addresses various questions of interest, pertinent to each of
the materials and thus further the understanding of the relationship between transport and structural properties of nanostructured materials in general.

**Basics of Diffusion**

Diffusion process can be defined as a random, thermal motion of molecules leading to elimination of spatial variations in molecular densities. In the old days, following the experimental studies by Adolf Fick (1885) about the diffusion of matter, it was thought that concentration gradients were the driving force for diffusion. This is expressed mathematically by the Fick's first law\(^1\)\(^2\), which can be written for the case of one-dimensional diffusion as

\[
J = -D \frac{\partial c}{\partial z},
\]

(1.1)

where \(J\) is the flux of diffusing species along the \(z\) direction, \(c(z)\) is their concentration, and \(D\) is the corresponding diffusion coefficient. This diffusion coefficient is often referred to as transport diffusion coefficient. Eq. 1.1 is analogous to the expression for a heat flux in the case of heat transport. Although \(D\) is often independent of concentration at small molecular concentrations, it can be a function of the concentration at large concentrations. Application of equation 1.1 in combination with the mass balance written for an elementary volume element leads to the Fick's second law of diffusion

\[
\frac{\partial c}{\partial t} = \frac{\partial}{\partial z} \left[ D(c) \frac{\partial c}{\partial z} \right].
\]

(1.2)

For the case where \(D\) is independent of concentration, the above equation simplifies to

\[
\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial z^2}.
\]

(1.3)
Contrary to the old days, it is now understood that the real driving force for diffusion is a gradient of chemical potential rather than the concentration gradient. In addition to the above discussed diffusion process leading to the mass transport, there is also self-diffusion that occurs due to random, thermal motion of molecules even under conditions when macroscopic concentration gradients and gradients of chemical potential are absent. Although transport diffusion and self-diffusion occur based on the same microdynamic mechanism, the coefficients of transport and self-diffusion are not necessarily the same. Self-diffusion of molecules in the absence of any induced mass transport plays an important role in different types of processes. Hence, there is a significant interest in knowledge of self diffusion coefficients.

Strictly speaking, the definition of diffusion coefficients under conditions of a macroscopic concentration gradient as given by Fick’s 1st law of diffusion (equation 1.1) refers to transport diffusivity. However similar treatment can also be done for the case of self-diffusion by tagging or labeling a certain fraction of diffusing molecules. Let us assume a situation where these tagged molecules are confined to a certain region of space at time zero under conditions when the overall molecular concentration is the same at any point in the considered system. Thus the formal definition of self-diffusivity can be given by

$$J^* = -D_{\text{self}} \left. \frac{\partial c^*}{\partial z} \right|_{c=\text{const}}, \quad (1.4)$$

where, $c^*$ is the concentration of the labeled/tagged molecules. For the simple case of one-dimensional diffusion with a constant diffusivity and the initial concentration of labeled molecules that can be presented as a delta function, equations 1.1 and 1.4 have the following solution³
\[ c = \frac{A}{\sqrt{4\pi t}} \exp\left(-\frac{z^2}{4Dt}\right), \]  

(1.5)

where \( A \) is the normalizing constant. Fickian flux equations for the case of three-dimensional diffusion written over an elementary volume can be presented as

\[ -J_i = \sum_j D_{ij} \frac{\partial c}{\partial j}, \]  

(1.6)

where \( D_{ij} \) is the diffusion coefficient in \( i \) direction due to concentration gradient in the \( j \) direction (with \( i, j = x, y, z \) for the Cartesian coordinate system). It should be noted that the equation 1.6 can be used to represent flux for the case of transport diffusion as well as self-diffusion. The only difference would be that the quantity \( \frac{\partial c}{\partial j} \) would be replaced by the gradient of labeled molecules in a system where the macroscopic concentration gradients are absent \( \left( \frac{\partial c}{\partial i} \right)_{c=\text{const}} \).

\( D_{ij} \) in the equation 1.6 can be presented in the form of the diffusion tensor as

\[
\overline{D} = \begin{bmatrix}
D_{xx} & D_{xy} & D_{xz} \\
D_{yx} & D_{yy} & D_{yz} \\
D_{zx} & D_{zy} & D_{zz}
\end{bmatrix}
\]

Fick’s second law of diffusion for the case of 3-dimensional diffusion with the concentration-independent diffusivity can be written as

\[
\frac{\partial c}{\partial t} = \sum_i \sum_j D_{ij} \frac{\partial^2 c}{\partial i \partial j}
\]  

(1.7)

When the self-diffusion coefficient of molecules is equal in all the directions, as it happens in the case of diffusion in homogeneous liquids and gases, the system is regarded to be diffusionally isotropic. For systems with such properties of self-diffusion
the diffusive flux at any point is always perpendicular to the surface of constant concentration and only the normal flux \((i = j)\) terms in equation 1.6 can assume non-zero values. Hence the flux equation 1.6 and 1.7 can be simplified to

\[ -J_i = D \frac{\partial c}{\partial t}, \]

where \(D_{xx} = D_{yy} = D_{zz} = D\) and

\[ \frac{\partial c}{\partial t} = D \sum_i \frac{\partial^2 c}{\partial i^2}, \]

where \((i = x, y, z)\). The corresponding diffusion tensor has the following form

\[
\begin{bmatrix}
D & 0 & 0 \\
0 & D & 0 \\
0 & 0 & D
\end{bmatrix}
\]

For a closed system the total mass of diffusing species remains constant. In this case the total mass \(M\) of diffusants at any time can be obtained from the corresponding concentration profiles. For the case of isotropic diffusion starting from a point source within the sample at \(r = 0\), the concentration distribution is given by

\[
\frac{c}{M} = \frac{\exp\left(-r^2/4Dt\right)}{(4\pi Dt)^{3/2}},
\]

where \(M\) is the total mass of the diffusants. \(c/M\) gives the probability of finding a molecule at a certain position \(r\) at time \(t\) if this molecule was located at the origin at time zero. \(c/M\) is equivalent to the Diffusion Propagator or a probability density function \(P(r_2, r_1, t)\). It gives probability of finding a molecule originally located at position \(r_1 (r_1 = 0 \text{ in Eq. 1.10})\) at a new position \(r_2 = r\) after time \(t\). This function is a Gaussian
for isotropic diffusion and the mean square displacement of the molecules is obtained from the variance of the Gaussian as

\[ \langle r^2(t) \rangle = \int r^2 \frac{\exp \left( -\frac{r^2}{4Dt} \right)}{\left( 4\pi Dt \right)^{3/2}} \, dr = 6Dt. \]  

(1.11)

Corresponding expressions for the mean square displacements of molecules for 1 and 2-dimensional isotropic diffusion are

\[ \langle r^2(t) \rangle_{1D} = 2Dt, \]
\[ \langle r^2(t) \rangle_{2D} = 4Dt. \]  

(1.12)

Equations 1.11 and 1.12 are referred to as Einstein Relations. They offer another way of defining self-diffusion coefficients of molecules. Treatment of diffusion propagators for anisotropic diffusion is somewhat more complicated and is normally done for a given system of diffusants/medium on a case-by-case basis.

**Relationship between Diffusion and Viscosity**

In general, self-diffusivity can be related to viscosity (\( \eta \)) or fluidity (\( \frac{1}{\eta} \)) using the Stokes-Einstein relation

\[ D = \frac{kT}{C \pi \eta r_s}, \]  

(1.13)

where \( k \) is the Boltzmann constant, \( T \) is the absolute temperature, \( c \) is a constant and \( r_s \) is the effective hydrodynamic (Stokes) radius. The equation is derived for diffusion of rigid non-interacting spheres diffusing in a continuum solvent at a low Reynolds number. In such a case the constant \( C \) has a value of 6, and the equation assumes its most commonly used form. However, there can be cases when such simple relation is no
Experimental Study of Molecular Diffusion

Different experimental techniques can be used to study diffusion on different length scales of displacements. If the focus of diffusion study is on the elementary steps associated with molecular diffusion, then techniques such as small-angle neutron scattering are used. Such techniques probe length scales that are in the range of 1 nm. Diffusion studies on these length scales can provide a wealth of useful information. Length scales around 1 nm are, however, too small in comparison to displacements important for many types of applications. For the latter the probed root mean squared displacements should be much larger than the size of individual elementary diffusion steps. Pulsed field gradient NMR (PFG NMR) and tracer zero length column (TZLC) techniques are representatives of the methods capable of recording self-diffusion coefficients on the length scale of 1 micrometer (or smaller) and on the length scale of dozens of micrometers, respectively. Self-diffusion coefficients can be measured by monitoring (a) mean square displacements of molecules over a given observation time or (b) by monitoring a flux of labeled molecules or the rate of exchange of such molecules between different molecular environments. The representative of the type (a) techniques is PFG NMR, and the representatives of the type (b) methods are TZLC and NMR tracer exchange method. In contrast to self-diffusion measurements, transport diffusion coefficients are measured under the conditions of macroscopic concentration gradients. The latter measurements can be performed either under conditions of a steady state with a fixed concentration gradient or under transient conditions with a changing uptake or release fluxes as the system evolves towards sorption equilibrium.
Zero length column technique (ZLC) can be used for measurements of transport diffusion coefficients.

The work reported in this dissertation mostly focuses on studies of self-diffusion and on the relationship between self-diffusion and structural properties of several selected systems. PFG NMR was the main experimental technique used in this work. This technique is a powerful tool for measurement of self diffusion. It allows measuring mean square displacement of the molecules over distances much larger that size of individual diffusants, in the range of 10s of nm to 10s of micrometers. While this means that the measured displacements are sufficiently long to see a fully developed diffusion process, thereby sampling many individual elementary steps of the diffusing species, these displacements often remain to be small enough to observe different diffusion behavior in different regions within complex nanostructured materials. PFG NMR has the unique advantage of being non-invasive, a feature shared by all NMR-based methods. The resolution of this technique is mostly limited by the strength of the applied magnetic field gradients.

Most of the experimental studies reported in this work fall with the premise of PFG NMR performed under conditions of high magnetic field (17.6 T) and ultra high magnetic field gradients (up to 30 T/m). The theory of PFG NMR is discussed in Chapter (2) of this dissertation.
Nuclear magnetic resonance (NMR) spectroscopy is a technique that utilizes nuclear magnetism associated with certain atomic nuclei to extract information related to molecular physics such as structure, orientation, and the mean square displacements of molecules. The principles of NMR are also routinely used in magnetic resonance imaging (MRI) for advanced imaging, especially in biological and medical fields.

NMR spectroscopy and related techniques rely on the simple notion that some atomic nuclei possess intrinsic nuclear magnetism that can be exploited in the presence of an external magnetic field (B0) by applying electromagnetic radio frequency (r.f.) pulses. Application of such pulses under the resonance conditions lead to the energy absorption by the nuclei. The frequency of the r.f. pulses is highly dependent on the external magnetic field and the nuclei under study. The energy radiated back by the nuclei contains information about the quantum-mechanical properties of the atomic nuclei, which in turn can help obtaining information about the structure and dynamics of the molecules containing the nuclei.

**Basics of NMR**

All atomic nuclei possess a quantum-mechanical property called spin angular momentum or spin. In contrast to the origins of any angular momentum in classical mechanics, the spin angular momentum does not arise from any rotational motion. Instead, it is an intrinsic property of elementary particles, including protons and neutrons making up atomic nuclei. All atomic nuclei with a non-zero spin angular momentum are magnetically active because they also have a non-zero intrinsic magnetic moment.
\[
\hat{\mu} = \gamma \hat{S},
\]

where \( \hat{\mu} \) is the magnetic moment and \( \hat{S} \) is the spin angular momentum. \( \gamma \) is a constant known as the gyromagnetic ratio, which can be positive or negative. Depending on the sign of \( \gamma \) the magnetic moment may either be aligned parallel or anti-parallel to the direction of the spin, viz. the direction of spin-polarization. In the absence of any external magnetic field the distribution of spin-polarization axes and corresponding magnetic moments of individual nuclei in a macroscopic sample is completely isotropic. Therefore, net nuclear magnetization in the sample is zero.

![Figure 2-1. (a): Schematic representation of spin precession in presence of an external magnetic field \( B_0 \) (b): Angle of precession cone depends on initial spin polarization.](image)

However, when an external magnetic field is applied, it exerts a torque on the nuclear magnetic moment of individual nuclei and causes the spin polarization to move on a cone always keeping the same angle between the directions of magnetic moment and the field (Fig 2-1a). Such type of motion is known as precession. The fixed angle is set by the angle between the field and the direction of the initial spin polarization vector.
The frequency of precession \( (\omega_0) \) which is referred to as the Larmor frequency\(^{11,12} \), depends on the amplitude of the magnetic field \( B_0 \)

\[
\omega_0 = -\gamma B_0.
\] (2.2)

**Longitudinal Magnetization**

The distribution of the spin polarizations in the sample is expected to be isotropic (i.e. uniform) in the absence of the external magnetic field. As a result, there is no net magnetization in the sample before the external field is applied (Fig 2-2a). Each nuclear spin is surrounded by other nuclear spins and electron clouds, all of which are magnetic entities. As a consequence, all these entities contribute to a formation of a local, viz. microscopic magnetic field in the immediate vicinity of each nucleus. This microscopic field is expected to fluctuate in both magnitude and direction due to rapid molecular tumbling and microscopic thermal perturbations. Hence, the net magnetic field seen by each nuclear spin also fluctuates a little in magnitude and direction as a function of time. This causes a gradual breakdown of constant angle spin precession of the nuclear spins. As time progresses, the nuclear spins wander between different precession cones and eventually sample various orientations. The process of such wandering under conditions of applied magnetic field causes a breakdown of isotropy in distribution of spin polarization directions. The resulting steady-state distribution of spin polarizations is anisotropic with a slight bias towards spin orientations that have corresponding magnetic moments along the direction of the applied magnetic field; i.e. an orientation of lower energy. Eventually a stable (yet dynamic) thermal equilibrium is reached, which results in the formation of a net macroscopic nuclear magnetization in the sample along the direction of the applied magnetic field (Fig 2-2b). In the convention
of NMR, the direction of the external magnetic field and resulting nuclear magnetization is assumed to coincide with the +z direction of the static coordinate system. This direction is also referred to as the longitudinal direction.

![Diagram of NMR](image)

Figure 2-2. (a) No magnetization in absence of external magnetic field. (b) Thermal equilibrium and emergence of longitudinal net magnetization in presence of external magnetic field $B_0$. The longitudinal magnetization $M_0$ is the vector sum of individual magnetic moments $m_i$.

**Transverse Magnetization**

Since nuclear magnetism is very small compared to that resulted from other magnetization mechanisms in the sample (electronic magnetization, bulk magnetization etc), detection of nuclear magnetization along the z direction (also called longitudinal direction) is impractical. In NMR a different approach is used, which is based on detecting nuclear magnetization in a plane perpendicular to the longitudinal direction. This is achieved by application of an additional oscillating magnetic field called the $B_1$ field. The direction of this field is normal to the direction of the static magnetic field $B_0$. The $B_1$ field is generated by passing an alternating current through an excitation coil. Typically, the amplitude of this field is many orders of magnitude smaller than that of the static magnetic field. The frequency of the $B_1$ field is chosen to be sufficiently close to
the Larmor frequency resulting in the resonance phenomenon. In this case, the effect of the oscillating field on the net nuclear magnetization builds up with time. As a result, this relatively weak field is able to have a large effect on the net nuclear magnetization. It is important to note that the frequency of the field and the duration of its application are the most important parameters. Since the Larmor frequencies and, hence, the frequency of the $B_i$ field are typically in the range of radio waves, application of such a field is commonly referred to as application of an r.f. pulse in NMR jargon. The duration of the r.f. pulse determines the angle by which the net nuclear magnetization is tilted from the $z$ direction towards the transverse plane. This angle, which is also referred to as the as the flip angle $\Phi$ is given by the following equation

$$\Phi = \frac{1}{2} \gamma B_i \tau_p,$$

(2.3)

where $\tau_p$ is the duration of the r.f. pulse. A flip angle of $90^\circ$ will thus tilt the net nuclear magnetization that was originally along the $z$ axis into the transverse plane (Fig. 2-3). Following the tilting, this magnetization precesses in the X-Y plane with the Larmor frequency (Fig. 2-3). Once the r.f. pulse is turned off, the direction of the net magnetization gradually returns to the equilibrium one, which coincides with the direction of the static external magnetic field $B_0$. This process of relaxation is discussed in more detail in the next section.

The discussion above is based on the classical NMR theory. A better understanding of the effect of an r.f. pulse, and of NMR basics in general, can be achieved using a quantum mechanical treatment. Such quantum mechanical treatment is given in many texts that deal with the theory of NMR.
Figure 2-3. Rotation of net initial magnetization $M_0$ oriented along $+z$ direction, into the transverse plane by $90^0$ r.f. pulse. The transverse magnetization $M_{x-y}$ precesses in the transverse plane with Larmor frequency $\omega_0$.

**NMR Relaxation**

Under the conditions of equilibrium, in the presence of a static magnetic field $B_0$, the net nuclear magnetization is directed along the $+z$ axis, and there is no magnetization in the transverse plane. Any perturbation from this state results in a non-equilibrium situation. In particular, the perturbation can be caused by an application of an r.f. pulse that tilts the magnetization into the transverse plane. The process of returning of the net nuclear magnetization to its equilibrium state is referred to as NMR relaxation. Two types of NMR relaxation can be distinguished: 1) Spin-spin/Transverse, or $T_2$ relaxation and 2) Spin-Lattice/Longitudinal, or $T_1$ relaxation. The following paragraphs aim to provide a brief explanation of the two types of NMR relaxation mentioned above. Complete description of these processes can be found in 11-13.

$T_2$ NMR relaxation is the process that concerns with the gradual decay/extinction of transverse magnetization to zero and, thereby, with the return of the net
magnetization to its equilibrium value in presence of a static external field $B_0$. When a 90 degree r.f. pulse is applied and the net magnetization is turned into the X-Y plane, the individual spins producing this magnetization are in phase coherence. Due to perturbation of the local magnetic field by neighboring nuclear spins and electronic clouds, each nuclear spin experiences a slightly different field and, hence, precesses at a slightly different frequency. As time after the 90 degree r.f. pulse progresses, various spins in the sample de-phase, i.e. loose phase coherence completely. As a consequence, the net transverse magnetization gradually decays to zero. This process is known as secular contribution to $T_2$ NMR relaxation. In addition, fluctuating, microscopic (i.e. local) magnetic field, which can exhibit frequencies in the range of Larmor frequency, can act as tiny r.f. pulses on the transverse magnetization component of individual nuclear spins. Such r.f. pulses turn the magnetic moments of individual nuclei away from the X-Y plane. This process also results in a gradual decay of the transverse magnetization. It is referred to as the non-secular contribution to $T_2$ NMR relaxation. Typically, the net rate of transverse relaxation can be characterized by a time constant $T_2$, as shown in the following equation

$$M_{x-y}(t) = M_{x-y}(0) \times \exp\left(-\frac{t}{T_2}\right),$$

where $M_{x-y}(t)$ is the net transverse magnetization at time $t$ and $T_2$ is the spin-spin/Transverse NMR relaxation time.

$T_1$ NMR relaxation is the process that concerns with the gradual growth of the net nuclear magnetization to its equilibrium value along the +z direction in the presence of a $B_0$ field. Perturbations in the local magnetic field that cause the non-secular part of $T_2$
NMR relaxation are also responsible for the $T_1$ NMR relaxation process. Consider the situation immediately after application of a $90^\circ$ r.f. pulse so that the longitudinal magnetization at that instant is equal to zero. Due to rapid molecular tumbling each nuclear spin is expected to experience perturbations in the local magnetic field. If the transverse component of the local field experienced by a nuclear spin oscillates with a frequency close to the Larmor frequency then it will act as a tiny r.f. pulse for the nuclear spin. Such oscillating local field acts on the nuclear spins and try to turn and reorient the individual nuclear spin magnets. As the orientations with the spin magnetic moment along the direction of the field have lower energy, such orientations are gradually favored and result in a re-growth of the magnetization along the z axis. The same mechanism causes growth of the net nuclear magnetization when the sample is first exposed to a static external magnetic field, as discussed in the previous section of this chapter. The rate of the growth of the net magnetization along the z-direction due to $T_1$ relaxation can be characterized by the longitudinal relaxation time ($T_1$)

$$M_z(t) = M_0 \left(1 - \exp\left(-t/T_1\right)\right)$$

(2.5)

where $M_z(t)$ is the net longitudinal magnetization at time $t$, $M_0$ is the net equilibrium magnetization, which points along $+z$ direction. The equation 2.5 holds for the cases when the net longitudinal magnetization is equal to zero at $t = 0$, in presence of an external magnetic field. In particular this can occur when a) external magnetic field is turned on at $t = 0$, b) a $90^\circ$ r.f. pulse is applied at $t = 0$.

For a case where the external magnetic field is turned off at $t = 0$ and assuming that by that time the longitudinal magnetization has already attained the equilibrium
value $M_0$, the decay of the net magnetization after the external magnetic field is turned off is given by

$$M_Z(t) = M_0 \times \exp(-t / T_1).$$

(2.6)

In yet another case where the net magnetization is tilted to the $-z$ direction by the 180 r.f. pulse such that $M_Z(t) = -M_0$ at $t = 0$, the re-growth of the net magnetization along the $z$ direction is given by

$$M_Z(t) = M_0 \left(1 - 2 \exp(-t / T_1)\right).$$

(2.7)

**Signal Detection**

The signal detection, as mentioned briefly in the section on Transverse Magnetization, is done in the transverse (X-Y) plane. The induced net nuclear magnetization performs precessive motion in the transverse plane. The amplitude of the magnetization decays with time due to $T_2$ NMR relaxation. The detection is performed by a coil of wire placed near the sample. Due to the precessive motion of the transverse magnetization, the coil experiences a changing magnetic field. This in turn, according to Maxwell’s laws induces an electric current in the coil which is detected as a signal. The signal thus detected is referred to as free Induction decay (FID). NMR signals are usually presented as frequency domain data obtained by Fourier transformation of the FID. Such frequency domain data are known as NMR spectra. Though it may be expected that for a given external magnetic field $B_0$ the resonance frequency of all the atomic nuclei of a certain type (e.g. $^1$H) are the same (and equal to Larmor frequency), in reality the frequencies of such nuclei show small deviations for different local environments. This effect is known as chemical shift. It is a consequence of slight
variations in the effective field experienced by a nucleus due to the local atomic environment. For example, the signal from $^1$H in a CH$_3$ group will have a different chemical shift than that of $^1$H in CH$_2$ or $^1$H in water. Chemical shift data allow identifying different atomic environments or presence of different compounds. Chemical shifts are typically documented as the difference in frequency of the measured NMR signal relative to the NMR signal of a reference compound for the same type of nuclei. For example, a common reference compound for $^1$H NMR is Tetramethylsilane (TMS). It is important to note that the frequency of the NMR signal for the reference compound and hence the chemical shifts from the measured compound are magnetic field dependent and can vary from one experimental setup to another, based on different strength of the external magnetic field. To circumvent this problem, and present NMR spectra in a format independent of the magnetic field strength, parts per million (ppm) units are used instead of frequency units. Chemical shift in ppm units is calculated as

$$\delta^* = \frac{\omega - \omega_{\text{ref}}}{\omega_{\text{SF01}}}$$

where $\delta^*$ is the chemical shift in ppm, $\omega$ the measured frequency, $\omega_{\text{ref}}$ is the reference frequency and $\omega_{\text{SF01}}$ is the so called ‘Carrier Frequency’ i.e. the operating frequency of the magnet. The use of ppm scale greatly simplifies the comparison of data acquired at different amplitudes of the constant magnetic field.

Pulsed Field Gradient (PFG) NMR

PFG NMR is a specialized NMR method that allows for measurements of diffusion propagator and of the corresponding mean square displacements of molecules. Since the mean square displacements can be related to the self-diffusion coefficients by the
Einstein relations (equations 1.11 and 1.12), PFG NMR effectively facilitates measurement of diffusivities. PFG NMR exploits the fact the Larmor frequency of the precession of the nuclear spins is field dependent. Application of a gradient of magnetic field along the z direction allows for the labeling of the positions of nuclear spins along this direction based on their Larmor frequency.

If we neglect the effect of microscopic inhomogeneities in the local field discussed earlier, it can be assumed that in the presence of an external constant magnetic field $B_0$, all the nuclear spins in the sample experience the same magnetic field. A total nuclear magnetization is induced in the sample along the z-direction. When the net magnetization is turned into the transverse plane by the 90 degree r.f. pulse, it precesses in the X-Y plane with the Larmor frequency. In PFG NMR, a gradient of magnetic field along the z direction is applied when the net nuclear magnetization is in the transverse plane. The Larmor frequency of precession under the influence of magnetic field gradient is given by

$$\omega = -\gamma (B_0 + g z),$$

(2.9)

where $\omega$ is the Larmor frequency, $\gamma$ is the gyromagnetic ratio, $B_0$ denotes the amplitude of the static external magnetic field along the +z direction; $g$ is the linear gradient of the magnetic field superimposed on the $B_0$ field and $z$ is the spatial coordinate along the z axis. Equation 2.9 shows that application of the magnetic field gradients thus makes the Larmor frequency to be position dependant, effectively labeling the nuclear spins based on their spatial coordinate along the z-direction.
PFG NMR Spin Echo Pulse Sequence

In principle, all PFG NMR pulse sequences use the idea of applying magnetic field gradient during at least two short time intervals when the magnetization is in the transverse plane. The simplest illustration of a PFG NMR self diffusion experiment can be made using the most basic PFG NMR pulse sequence, viz. the PFG NMR spin echo sequence (PGSE), which is also known as the PFG NMR Hann echo sequence or the Stejskal and Tanner Sequence.\textsuperscript{14-19}

Figure 2-4. Schematic of the PFG NMR spin echo pulse sequence.

Figure 2-4 shows a schematic presentation of the PFG NMR spin echo pulse sequence. The sequence consists of two r.f. pulses ($\frac{\pi}{2}$ and $\pi$). Each r.f. pulse is followed by application of a field gradient of identical amplitude $g$ and duration $\delta$. In the simplest approximation, these two gradient pulses can be regarded as rectangular, though use of more complex pulse shapes is possible, as long as the two gradient pulses are identical. The effect of the first r.f. pulse is to bring the longitudinal magnetization to the transverse plane. Up until this point, all the nuclear spins experience the same magnetic field and precess at the same Larmor frequency. As a
consequence, all the spins are in phase coherence and the initial phase of all the spins in the transverse plane can be assumed to be equal to zero immediately after the application of the first $\pi/2$ pulse. Application of the first field gradient pulse makes the Larmor frequency of spins at various positions in the sample to be coordinate dependent. The varying Larmor frequencies cause the spins to precess at different rates. Consequently, some spins begin to lead, while the others lag. The application of the first gradient pulse thus de-phases the individual spin magnetization vectors that contribute to the net transverse magnetization. The time interval between the application of the $\pi/2$ r.f. pulse and the $\pi$ r.f. pulse is consequently called the de-phasing interval. The de-phasing interval leads to a reduction in the amplitude of the net transverse magnetization. The two gradient pulses in the sequence are separated by a fixed observation time $\Delta$. This time interval is added to let the molecules (nuclear spins) have an opportunity to change their positions due to diffusion. The effect of the second $\pi$ r.f. pulse serves to invert the accumulated phase differences in the transverse plane, such that for any pair of spins the positive phase differences becomes negative and vice versa. At this point the magnetic field gradients of the same duration and amplitude are applied again. In the event that the molecules (and hence individual spins in these molecules) did not move during the interval $\Delta$ between the applications of the two gradient pulses, the second pulse is expected to compensate for the de-phasing effect of the first gradient pulse. The application of the second pulse should thus re-phase the individual spin magnetization vectors and restore the transverse magnetization to its initial value. The time interval between the application of the $\pi$ r.f. pulse and the beginning of acquisition is consequently called the rephasin interval.
Such completely refocused magnetization will appear exactly at time $\tau$ after the application of the $\pi$ r.f. pulse\textsuperscript{14,16,18,19}. It is referred to as a spin echo. In the case if the molecules (and hence nuclear spins) have moved during the interval between the applications of the gradient pulses the refocusing of the transverse magnetization will be incomplete. As a result, its intensity will not be restored to its initial value. The extent of the decrease of the intensity of the refocused transverse magnetization (echo) contains information about the mean square displacements of the molecules.

A quantitative treatment of the experiment to relate the signal attenuation to the molecular diffusion can be carried out by determining the net phase accumulated by individual spins and using this phase to calculate the vector sum of individual magnetic moments by the end of the pulse sequence. The net phase accumulated by the spins during the pulse sequence is

$$-\phi^{(i)} = \int_{0}^{\tau} \gamma B_{\text{eff}} dt - \int_{\tau}^{2\tau} \gamma B_{\text{eff}} dt,$$

(2.10)

where $B_{\text{eff}} = B_0$ in the absence of field gradient and $B_{\text{eff}} = B_0 + gz$ in the presence of field gradient pulses. For a change in a position of spin $(i)$ from $z_1^{(i)}$ to $z_2^{(i)}$, the equation will simplify to

$$-\phi^{(i)} = \gamma \delta g \left[ z_1^{(i)} - z_2^{(i)} \right].$$

(2.11)

The tacit assumption here is that the duration of the field gradient $\delta$ is much smaller than the diffusion time interval $\Delta$, i.e. $\delta \ll \Delta$. Therefore the molecular displacements during the time interval $\delta$ are expected to be negligibly small in comparison to those during the time $\Delta$. Hence the molecular positions $z_{1(2)}^{(i)}$ can be expected to remain
unchanged during the application of the field gradient pulses. The projection of the individual magnetization vectors on the direction that coincides with that of the transverse magnetization immediately after the application of first $\pi/2$ r.f. pulse is proportional to the cosine of the phase of nuclear spins. Hence the net transverse magnetization at any time can be presented by the sum of the corresponding projections of individual magnetic moments at that time

$$M_{x-y} = \sum M_{x-y}^i \propto \sum \cos \phi^i.$$  \hspace{1cm} (2.12)

Using the conditional probability $p(z_1)dz_1$ to find a molecule at any position between $z_i$ and $z_i + dz_i$ and the corresponding diffusion propagator $P(z_2, z_1, \Delta)dz_2$, which gives probability that a molecule initially at the position $z_i$ can be found after time $\Delta$ at a position with the coordinates between $z_2$ to $z_2 + dz_2$, the net transverse magnetization at the end of the spin echo pulse sequence can be written as

$$M_{x-y} = M_0 \int \int \cos(\gamma \delta g(z_1 - z_2))p(z_1)P(z_2, z_1, \Delta)dz_1dz_2.$$  \hspace{1cm} (2.13)

This equation was obtained by substituting Eq. 2.11 into Eq. 2.12 and replacing summation in Eq. 2.12 by integration over the initial and final positions of molecules. Eq. 2.13 can be rewritten in the terms of the signal attenuation $\psi$ as

$$\psi = \frac{M_{x-y}}{M_{x-y}^0} = \int \int \cos(\gamma \delta g(z_1 - z_2))p(z_1)P(z_2, z_1, \Delta)dz_1dz_2,$$  \hspace{1cm} (2.14)

where $M_{x-y}^0$ is the transverse magnetization in the case when there is no diffusion. This magnetization coincides with that immediately after application of the first r.f. pulse. The diffusion propagator $P(z_2, z_1, \Delta)$ discussed above is the one-dimensional equivalent of
the more general three dimensional diffusion propagator \( P(r_z, r_{\parallel}, t) \) discussed in chapter 1. The one-dimensional propagator was used because the attenuation in a PFG NMR experiment discussed above is sensitive only to molecular displacements along a single (viz. \( z \)) direction, due to the one-dimensional nature of the field gradients. The quantity \( p(z) = 1 \) is a constant for a homogeneous medium while \( P(z_2, z_1, \Delta) \) is given by

\[
P(z_2, z_1, \Delta) = \frac{1}{\sqrt{4\pi D\Delta}} \exp\left(\frac{-(z_2 - z_1)^2}{4D\Delta}\right).
\]

Using this expression the signal attenuation \( \psi \) in Eq. 2.14 can be simplified to

\[
\psi(\delta g, t_{\text{eff}}) = \exp\left(-\gamma g \delta^2 D t_{\text{eff}}\right),
\]

where the effective diffusion time denoted by \( t_{\text{eff}} \) is given by \( t_{\text{eff}} = \Delta - \frac{\delta^2}{3} \). Substituting Einstein relation (Eq.1.12) into this equation gives

\[
\psi(\delta g, \Delta) = \exp\left(-\gamma g \delta^2 \frac{\langle z^2 \rangle}{2}\right),
\]

where \( \langle z^2 \rangle \) is the mean square displacement in the direction of the field gradients. For isotropic three-dimensional diffusion in a homogeneous medium the diffusion coefficient is expected to be the same in all directions and the equation 2.17 can be rewritten as

\[
\psi(\delta g, \Delta) = \exp\left(-\gamma g \delta^2 \frac{\langle r^2 \rangle}{6}\right),
\]

where \( \langle r^2 \rangle = \langle x^2 \rangle + \langle y^2 \rangle + \langle z^2 \rangle = 3\langle z^2 \rangle \). Equations 2.16-2.18 give the expression for signal attenuation measured by the PFG NMR spin echo pulse sequence. Typically, in a PFG
NMR experiment the signal attenuation $\psi$ is recorded as a function of the square of the field gradient strength $g$ under the conditions when all the other parameters of the pulse sequence are kept constant. Such dependencies of $\psi$ on $g^2$ are referred to as the attenuation curves. The attenuation curves allow for a direct determination of the mean square displacements and the corresponding diffusivities using the equations of the type Eq. 2.16-2.18.

Effects of NMR relaxation were not included in the derivations for the signal attenuation for the PFG NMR spin echo pulse sequence discussed above. This is justified by noting that the attenuation is the ratio of the signal at a particular gradient strength to that in the absence of any field gradient. Contributions of the NMR relaxation to both the signals are identical. Hence, the signal reduction due to NMR relaxation is cancelled in the PFG NMR attenuation. However any measured PFG NMR signal is reduced by NMR relaxation processes. In the case of the PFG NMR spin echo pulse sequence the net magnetization is in the transverse plane for the duration of the entire pulse sequence. Hence, the signal is reduced only due to $T_2$ NMR relaxation. $T_1$ NMR relaxation does not influence the signal intensity in this case. The exponential factor that accounts for the signal attenuation due to $T_2$ NMR relaxation is $\exp\left(-\frac{2\tau}{T_2}\right)$. When working with materials/systems where NMR relaxation times are much larger than the diffusion times, the relaxation effects are not a huge concern. However, there might be instances where loss of signal due to $T_2$ NMR relaxation imposes a restriction on the usability of the PFG NMR spin echo pulse sequence. Such a situation may arise due to small $T_2$ relaxation times sometimes coupled with the need to use large diffusion times.
In such cases somewhat more complex PFG NMR sequences can be used to reduce the effect of short $T_2$ NMR relaxation time.

**PFG NMR Stimulated Echo Pulse Sequence**

Figure 2-5. Schematic of PFG NMR stimulated echo pulse sequence. The sequence splits the $\pi$ r.f. pulse in the standard spin echo pulse sequence into two $\pi/2$ pulses and thus stores the magnetization along the $-z$ axis during time interval $\tau_2$. This sequence is of great advantage for systems in which the $T_2$ NMR relaxation time is much shorter than $T_1$ NMR relaxation time.

Figure 2-5 shows a schematic for the standard PFG NMR stimulated echo pulse sequence$^{21,22}$ (PGSTE) used in PFG NMR. This sequence can be viewed as a modified version of the PFG NMR spin echo pulse sequence. The first r.f. pulse and the subsequent field gradient pulse appear to be identical in both sequences. They serve the same purpose, which was discussed for the case of the PFG NMR spin echo pulse sequence. However the $\pi$ pulse in the PFG NMR spin echo sequence is replaced by two $\pi/2$ pulses. The second $\pi/2$ r.f. pulse in the PFG NMR stimulated echo pulse sequence, serves to reorient the net magnetization from the transverse plane to the $-z$ axis. Third $\pi/2$ r.f. pulse again tilts the magnetization from the $-z$ axis back to the
transverse plane. The combination of the second and third pulses fulfills the same role as that played by the \( \pi \) r.f. pulse in the PFG NMR spin echo sequence, which was discussed above. It is important to note that the first and the second field gradient pulses have to be identical for the sequence to work properly. The time interval between the first and the second r.f. pulses and that between the third r.f. pulse and the beginning of the signal acquisition are known as the de-phasing and the re-phasing intervals, respectively. Both time intervals need to have the same duration, which is denoted as \( \tau_1 \) in Figure 2-5.

The PFG NMR stimulated echo pulse sequence offers a particular advantage for PFG NMR diffusion studies of materials, which exhibit slower decay of magnetization of diffusing species due to longitudinal \( T_1 \) relaxation than that due to transverse \( T_2 \) relaxation, i.e. \((T_1 > T_2)\). For this sequence the signal is reduced due to \( T_2 \) relaxation only during the two time intervals of duration \( \tau_1 \), when the magnetization is in the transverse plane. A factor \( \exp\left(-\frac{2\tau_1}{T_2}\right) \) gives a signal reduction due to this relaxation process. The net magnetization is along the longitudinal direction during the time interval denoted as \( \tau_2 \) in Fig. 2-5. As a result, the signal reduction during this time interval is expected to occur according to the mechanism of the \((T_1)\) NMR relaxation by a factor of \( \exp\left(-\frac{\tau_2}{T_1}\right) \).

If \((T_1 > T_2)\) and \( \tau_1 \ll \tau_2 \), the measured signal is expected to be significantly less reduced by NMR relaxation in the case of the PFG NMR stimulated echo sequence than in the case of the PFG NMR spin echo sequence for the same time \( \Delta \). Moreover, the diffusion time \( \Delta \) can be increased in the PFG NMR stimulated echo pulse sequence in
a broad range by increasing the time interval \( \tau_2 \). In this case, the NMR relaxation related loss of signal due to increased diffusion time would exclusively take place due to \( T_1 \) NMR relaxation. This provides a possibility to perform PFG NMR diffusion measurements on systems/materials using diffusion times much larger than \( T_2 \) NMR relaxation times. Use of such large diffusion times would not be possible with the PFG NMR spin echo pulse sequence. Large diffusion times are typically required in cases where the self diffusion coefficients of molecules are particularly small, and the use of the largest achievable field gradients by itself is not sufficient to produce sufficiently large signal attenuation. In conclusion, the PFG NMR stimulated echo pulse sequence offers clear advantages over the PFG NMR spin echo sequence under the measurement conditions of small \( T_2 \) NMR relaxation times coupled with the requirement of large diffusion times. For the case of an isotropic, normal (i.e. Fickian) diffusion the expression for the signal attenuation measured by the PFG NMR stimulated echo pulse sequence is the same as that for the PFG NMR spin echo sequence

\[
\psi(\delta g, t_{\text{eff}}) = \exp \left( -\frac{\gamma g \delta}{D_{\text{eff}}} \right)
\]

(2.19)

where the effective diffusion time denoted by \( t_{\text{eff}} \) is given by \( t_{\text{eff}} = \Delta - \frac{\delta}{3} \).
PFG NMR Stimulated Echo Longitudinal Encode-Decode Pulse Sequence

Figure 2-6. Schematic of the PFG NMR stimulated echo longitudinal encode decode pulse sequence. The sequence appends an additional delay $T_{LED}$ at the end of the standard PFG NMR stimulated echo pulse sequence. Eddy currents disturbances decay during the delay while the magnetization is stored along the z axis.

Figure 2-6 shows schematic presentation of the PFG NMR stimulated echo longitudinal encode-decode or longitudinal eddy current delay pulse sequence (PGSTE-LED)\textsuperscript{23}. This sequence is a modified version of the PFG NMR stimulated echo pulse sequence. In comparison to the latter sequence, PGSTE-LED contains two additional $\pi/2$ r.f. pulses separated by the time $T_{LED}$ at the end of the sequence. The function of these two pulses is to change the direction of the net magnetization from the transverse plane to the longitudinal plane (along $-z$) for the time interval $T_{LED}$ and then bring it back to the transverse plane for detection. The modification is introduced to shield the acquired signal from disturbing effects of the eddy currents generated due to rapid gradient switching. Any PFG NMR experiment relies on the application of the field gradients to study molecular self diffusion. However, when the field gradient pulses (especially high-amplitude pulses) are switched on or off, the changing magnetic field can introduce eddy currents in the gradient coils which, in turn, cause magnetic field
inhomogeneity. Such field inhomogeneity is undesirable during signal detection and can be avoided by increasing the time delay between the end of second field gradient pulse and the beginning of acquisition, to allow for eddy current dissipation. In the PFG NMR spin echo and stimulated echo pulse sequences increase in the delay between the end of the second gradient pulse and the beginning of acquisition requires introduction of the same delay increase between the end of the first gradient pulse and the next r.f. pulse because of the requirement that $\tau / \tau_1$ times have to be the same for both gradient pulses. Such increases of the delays lead to the increases of the time intervals when the net magnetization is in the transverse plane and, hence susceptible to the (typically) more potent of the two NMR relaxation mechanisms, namely $T_2$. PGSTE-LED sequence addresses this problem by taking the net magnetization from the transverse plane to the longitudinal direction (-z) axis, which is followed by a delay $T_{LED}$ for eddy current dissipation. This delay is known as the LED delay. Signal is reduced only due to $T_1$ NMR relaxation during the LED delay. PGSTE-LED sequence thus offers a clear advantage over the PFG NMR stimulated echo pulse sequence under the measurement conditions characterized by short $T_2$ NMR relaxation times coupled with the need for large field gradients, which are likely to introduce disturbing eddy currents. The expression for the signal attenuation in a PGSTE-LED experiment is given by Eq. 2.19.

**PFG NMR Stimulated Echo with Bipolar Gradients Pulse Sequence**

Figure 2-7 shows a schematic for the PFG NMR stimulated echo pulse sequence with bi-polar gradients,$^{24-27}$ i.e. the 13-interval sequence; all the pulse sequences discussed above have used only unipolar gradients.
Figure 2-7. Schematic of the PFG NMR stimulated echo pulse sequence with bipolar gradients. This pulse sequence uses bipolar gradients to suppress artifacts due to magnetic susceptibility, also referred to as internal gradients.

The PFG NMR stimulated echo pulse sequence discussed earlier offers a good possibility to study molecular self-diffusion in materials characterized by $T_1 \gg T_2$, especially in cases where $T_2$ relaxation times are small and/or there is a need to use large diffusion times. However, in heterogeneous media characterized by different magnetic susceptibilities in different locations within the sample, the presence of background magnetic field gradients (which are caused by such susceptibility variations in the presence of a constant magnetic field) may lead to additional signal attenuation. The latter can introduce systematic artifacts in the measurements of self-diffusion. Such artifacts may also manifest themselves in terms of shifts of the echo position in the time domain and/or frequency shifts in the frequency domain. The PFG NMR stimulated echo pulse sequence with bipolar gradients (Fig. 2-7) addresses this problem. The sequence can be viewed as a modification of the PFG NMR stimulated echo pulse sequence where each of the two positive field gradient pulses of duration $(2\delta)$ and amplitude $(g)$ is replaced by a pair of gradient pulses, each of duration $(\delta)$ and
amplitude \( g \), with opposite polarity separated by a \( \pi \) r.f. pulse. The change in the polarity of the applied gradient pulses is negated by \( \pi \) r.f. pulse between them, such that the bipolar gradient-r.f. pulse sandwich taken as a whole, is equivalent to a gradient pulse of duration \( (2\delta) \). However these r.f. pulses will reduce to zero any influence of the background gradients on the measured signal, for those background gradients that have the same polarity and amplitude over the sequence duration. For the case of an isotropic normal diffusion the expression for the signal attenuation using the 13-interval pulse sequence is given by\(^{25}\)

\[
\psi(\delta g, t_{\text{eff}}) = \exp\left(-\left(2\gamma g \delta\right)^2 D t_{\text{eff}}\right),
\]

(2.20)

where the effective diffusion time denoted by \( t_{\text{eff}} \) is given by \( t_{\text{eff}} = \Delta - \frac{\tau}{2} - \frac{\delta}{6} \).

**Generalized Attenuation Equation**

The general form of attenuation equation for normal isotropic diffusion used for all the pulse sequences discussed above can be simplified to the following form

\[
\psi(\delta g, t_{\text{eff}}) = \exp\left(-\left(k\right)^2 D t_{\text{eff}}\right),
\]

(2.21)

where \( k = \gamma g \delta \) for PGSE, PGSTE/PGSTE-LED pulse sequences and \( k = 2\gamma g \delta \) for the 13-interval pulse sequence. The effective diffusion time \( t_{\text{eff}} \) is \( \left(\Delta - \frac{\delta}{3}\right) \) for PGSE, PGSTE/PGSTE-LED and \( \left(\Delta - \frac{\tau}{2} - \frac{\delta}{6}\right) \) for the 13-interval sequence. In the case where the PFG NMR sample contains several ensembles of molecules, each diffusing with a unique characteristic diffusivity, the attenuation equation can be expressed as a summation of several weighted exponential terms.
\[ \psi \left( \delta g, t_{\text{eff}} \right) = \sum_{i} p_i \exp \left( -\left( k^2 D_{i} t_{\text{eff}} \right) \right) = \sum_{i} p_i \exp \left( -\left( k^2 \frac{r_i^2 (t_{\text{eff}})}{6} \right) \right), \]

(2.22)

where \( p_i \) denotes the fraction of molecules diffusing with the diffusivity \( D_i \). The right hand part of the equation 1.35 was written using the Einstein relation (Eq. 1.11).

**PFG NMR and Anisotropic Diffusion**

Self diffusion in complex systems/materials can be anisotropic due to physical arrangement of the system resulting in different structural properties along different directions. Examples of such systems include liquid crystals, biological cells, and porous materials. For systems with diffusion anisotropy the process of diffusion is characterized by all the elements of the diffusion tensor \( \bar{D} \). In this case the PFG NMR signal attenuation is expected to depend on the orientation of the applied gradients with respect to the system morphology. If PFG NMR measurements of a material consisting of randomly-oriented particles exhibiting diffusion anisotropy are performed along a single direction (i.e. z-direction, as discussed above), the measured PFG NMR attenuation is no longer expected to comply with Eq. 2.21. In this case a powder averaging over all possible orientations can be used to obtain an expression for the signal attenuation. Such powder averaging for anisotropic free (i.e. unrestricted) diffusion results in

\[ \psi = \frac{1}{4\pi} \int_{0}^{2\pi} \int_{0}^{2\pi} \exp \left\{ -\left( \gamma g \delta \right)^2 t_{\text{eff}} \left( D_{xx} \cos^2 \theta + D_{yy} \sin^2 \theta \cos^2 \phi + D_{zz} \sin^2 \theta \sin^2 \phi \right) \right\} \sin \theta d\theta d\phi, \]

(2.23)

where \( D_{ii}, (i = x, y, z) \) represent the principle elements of the diffusion tensor. This equation may be further simplified on a case by case basis using the knowledge of the geometry of the system. A specific case of the signal attenuation for anisotropic
diffusion will be discussed later in this thesis in relation with the PFG NMR self diffusion studies of mesoporous SBA-15 materials. In these materials the diffusion of sorbate molecules through mesoporous channels is studied, where the channels may or may not be connected by micropores located in the channel walls.

**PFG NMR Attenuation Curves**

Diffusion data are obtained from dependencies of the intensity of the PFG NMR signal \( A \) on the amplitude of the magnetic field gradients \( g \). Such plots are referred to as the *Attenuation curves*. The signal intensity is determined by integrating the area under selected line(s) of the frequency-domain NMR spectra recorded by the PFG NMR diffusion pulse sequence. The extent of signal attenuation \( \psi \) can be calculated from the ratio of attenuated signal in presence of field gradients to the unattenuated signal in absence of the gradients as

\[
\psi = \frac{A(g)}{A(g = 0)} = \frac{M_{x-y}}{M_{x-y}^0}.
\]  

(2.24)

The later part of the equation 2.24 shows equivalency in the attenuation as defined by the ratio of \( A(g) / A(0) \) above and that defined in equation 2.14.

**Development of PFG NMR Diffusion Measurements under Conditions of High Magnetic Field and High Magnetic Field Gradients**

**Overview of Technical Challenges**

All the PFG NMR studies reported in this work were conducted on a wide-bore Bruker Biospin Ultrasheilded NMR spectrometer operating at 1H resonance frequency of 750 MHz (17.6T). This spectrometer is located at the McKnight Brain Institute’s ‘Advanced Magnetic Resonance Imaging and Spectroscopy (AMRIS)’ facility, which is a part of the National High Magnetic Field Laboratory, on the University of Florida
High (upto 30 Tm-1) magnetic field gradients were generated using a custom ordered Bruker diff60 diffusion probe and Bruker Great60 current amplifier. Successful deployment of such high magnetic field gradients in a highly reproducible manner as well as overcoming many technical problems related to the gradient application and the signal acquisition required significant development-type work that is briefly discussed in this section. The PFG NMR diffusion studies presented in this dissertation were routinely performed in a broad temperature range between 218K and 423K. This was possible due to development of high-precession temperature control, which is also briefly discussed below.

A significant part of the PFG NMR diffusion studies reported in this thesis involved study of sorbate diffusion under the conditions of very low (between $10^{-12}$ to $10^{-14}$ m²s⁻¹) self diffusion coefficients. In order to produce sufficient signal attenuation for such low diffusion coefficients it was necessary to apply strong gradient pulses viz. pulses that are characterized by large duration ($\delta$), or amplitude ($g$) or the combination of both. In many cases systems with slow diffusion coefficients also exhibit low $T_2$ NMR relaxation times for the diffusing species. Therefore application of gradient pulses with large amplitudes if possible is preferred over pulses with large durations. It is important to note that PFG NMR measurements in cases of anomalous or restricted diffusion, fail to give easily interpretable information about diffusion dynamics if the conditions of narrow pulse approximation are not satisfied.³⁰,³¹ The narrow pulse approximation requires that 1) the effective diffusion time $t_{eff}$ is sufficiently large in comparison to the gradient pulse duration $\delta$, i.e. $t_{eff} \gg \delta$ and 2) the displacements during the application of the gradients are negligibly small. Thus application of gradient pulses with small
duration and large amplitude becomes the condition of choice. Application of high-amplitude field gradient pulses over a small duration of time requires optimization of the shape of the gradient pulses as well as reduction of the disturbing effects of the $B_0$ field inhomogeneity and eddy effects. Each of the tasks mentioned in this subsection was performed successfully, as discussed in more details below.

**Optimization of gradient pulse shapes**

Magnetic field gradients are generated by passing a current through a gradient coil. The current, which is applied in the form of pulses designed to produce gradient pulses of the desired shape, are generated by a high capacity current amplifier. This amplifier will be referred to as the gradient amplifier. This subsection describes the development of the experimental capability to measure very small root mean squared displacements (MSD) of diffusing molecules (or ions) over length scales as small as 90 nm. To measure such small displacements an application of very strong field gradients (ca. 30 T/m) is required. In addition, the gradient durations have to be as small as possible due to limitations imposed by short $T_2$ NMR relaxation times and narrow pulse approximation, as mentioned earlier. To generate strong (around 30 T/m) field gradients, currents as large as 50 A are required in the gradient coils. Applying a step input in current that switches from 0 A to 50 A is virtually impossible even for the state of the art current amplifiers. So, if it is attempted to apply a rectangular gradient pulse, the shape of the actual pulse will be far from rectangular. It will suffer from erratic and uncontrollable distortions due to response from the coil. Such effects become non negligible, especially when large gradient amplitudes and extremely small gradient durations are used. Distortions in field gradient shapes can easily jeopardize the
accuracy and reproducibility of PFG NMR measurements. This problem was addressed by studies of the most appropriate shape and durations of the ramp up and down of the pulses. In particular, linear ramp and a $\pi/2$ sine ramp were used in these studies. As mentioned earlier, though the simplest and most ideal shape of gradient pulses is rectangular, other more complex pulse shapes need to be used in practical applications.\(^{32}\)

Another disadvantage of rapid step-like changes in current is related to possible generation of disturbing eddy currents in the gradient coil. These currents are generated by rapidly changing magnetic field due to rapid switching of gradients. Eddy currents are expected to produce additional, uncontrolled magnetic field gradients that affect the field homogeneity during signal acquisition in an erratic way and are, hence, undesirable. Use of a linear or a $\pi/2$ sine ramp up/down for applied gradients leads to a gradual, well-controlled change in the field and, thereby, minimizes eddy currents.

Gradient pulses with sinusoidal or trapezoidal shapes are commonly used in PFG NMR to slow down the rate of rise and fall of the magnetic field gradient.\(^{28,32}\) With these considerations in mind various possible shapes for gradient pulses were explored. An optimized shape should a) provide an accurate reproduction of the pulse shape, and b) minimize eddy currents and, at the same time, allow for reaching the full gradient amplitude at the shortest possible time. The current output of the gradient amplifier was studied using a digital oscilloscope. The digital oscilloscope allowed observation of differences (if any) between the gradient shape prescribed by the software and the current output of the gradient amplifier connected to the gradient coil. After several iterations, ideal rise and fall times that allowed high fidelity shape reproduction of the
gradient without increasing unnecessarily gradient duration were determined. For the strongest gradient pulses on the order of 25 Tm\(^{-1}\) or more and relatively short (ca. 1 ms) pulse duration, the \(\pi\) sine shapes were found to be the most appropriate. For longer pulse durations the most optimum shape was determined to be a modified trapezoidal shape where the linear ramp up was replaced by a \(\frac{\pi}{2}\) sine shape. The latter shape offers an advantage of smaller effective gradient duration for a given area under the gradient in comparison to that of a pure \(\pi\) sine shape.

Even though the use of gradual rise and fall edges of gradient pulses (due to application of sine-shaped or linear ramps) mitigate the production of eddy currents, the problem with eddy currents still persists. To address this problem a delay called as gradient stabilization time is typically allowed after the application of the gradient pulses. The delay allows for the dissipation of eddy currents. The efforts to find optimized shapes of gradient pulses were also motivated by the need to minimize the gradient stabilization times required after application of each gradient pulse. The presence of gradient stabilization time is especially important after the application of the last gradient pulse in the sequences, which is followed by acquisition, because the eddy currents can introduce random field inhomogeneities and can thereby adversely affect the signal during acquisition, as mentioned earlier in this text. Such field inhomogeneity, if present, compromises the quality of the PFG NMR data. The presence of a gradient stabilization time can also be of importance after application of the first field gradient pulse in the PFG NMR spin echo pulse sequence because if the eddy current tail from the first gradient pulse extends into the time interval of the second gradient pulse the effective gradient during re-phasing interval will not be equal to that during the de-phasing
interval. If the difference is significant, the PFG NMR spin echo sequence will not work properly as desired. With optimized gradient shapes the appropriate gradient stabilization times were determined to be around 750 $\mu$s.

**Preemphasis adjustment and $B_0$ compensation**

Eddy currents are highly undesirable in PFG NMR. In addition to arranging for gradual rise and fall of gradient amplitudes in gradient pulses and using time intervals for gradient stabilization, preemphasis adjustment and $B_0$ compensation offer possibilities to suppress eddy currents. The eddy currents obey the Lenz law of electromagnetism. According to this law field gradients generated by eddy currents are directed to oppose the change in flux that generated them. Preemphasis adjustment exploits this fact and suppresses eddy currents by overdriving the current at the leading and failing edges of the gradients pulses, thereby causing the gradient coils to self-compensate for induced eddy currents.$^{28}$ Preemphasis adjustment was done in collaboration with a Bruker Biospin engineer (Mr. Sergey Bizunok). The adjustment was perfumed to eliminate eddy currents and to decrease further the gradient stabilization time. The correction applied by the preemphasis adjustment software is implemented in the form of three exponential corrections with different amplitudes and time constants. The corrections are applied at the beginning and end of gradient current waveform. These preemphasis exponential corrections were optimized by monitoring a water FID signal that was generated at different time delays after a gradient pulse. Successful implementation of preemphasis adjustment allowed further reduction in gradient stabilization time to values as small as 400 $\mu$s.
An additional option to ensure a highly-homogeneous $B_0$ field after the application of gradients is offered by the $B_0$ compensation software and hardware. It is aimed at eliminating shifts in $B_0$ field and related field inhomogeneities caused by rapid switching of large gradients. Such field shifts can affect the signal acquired after short time intervals following a gradient pulse. $B_0$ compensation works by passing additional currents through the sweep coil of the magnet simultaneously with the gradient pulses. Such additional currents aim to pre-compensate for distortions introduced by gradient switching. These correction currents for $B_0$ compensation, much alike pre-emphasis adjustment, are also controlled by three exponential functions with different amplitudes and time constants. $B_0$ compensation was also done in collaboration with Mr. Sergey Bizunok (Bruker Biospin). The values of these amplitudes and time constants were determined iteratively by observing a water FID signal that was generated at different time delays after a gradient pulse.

Rigorous optimization of gradient shapes and gradient stabilization times coupled with extensive pre-emphasis adjustment and $B_0$ compensation have resulted in an ability to successfully implement PFG NMR with ultra high gradient strengths up to 30 Tm$^{-1}$ in the presence of high magnetic field (17.6 T). This makes our research group at the University of Florida the only one of its kind in the US due to the capability to work with a combination of such strong field gradients and such a strong field.

**Gradient calibration**

For correct calculation of diffusion coefficients based on PFG NMR data, the gradients generated by the gradient coils should be known with high precision. Though
the gradient coils are roughly calibrated to produce a known value of field gradient amplitude per ampere of supplied current \((G^1 cm^{-1} A^{-1})\), small deviations may exist in the actual and the prescribed value of field gradients generated by the coil. As a result, calibration of gradients is necessary. High precision gradient calibration can be carried out by performing PFG NMR diffusion measurements on standard samples with well known diffusivities.\(^{33}\) This approach is very accurate because it allows accounting correctly for effective field gradients experienced by diffusing molecules (ions). The calibration experiments were carried out using a standard water sample containing around 30% of normal (protonated) water in deuterated water. Details of the calibration experiments are provided in\(^ {34}\). The relationship between the applied and the actual gradient experienced by the diffusing molecules (ions) is given by

\[
D_{\text{measured}} \times g_{\text{applied}}^2 = D_{\text{literature}} \times g_{\text{actual}}^2 ,
\]

(2.25)

where \(D_{\text{measured}}\) and \(D_{\text{literature}}\) are the measured and the reported literature values of diffusion coefficient respectively, \(g_{\text{applied}}\) is the gradient amplitude reported by the software and \(g_{\text{actual}}\) is the calibrated gradient value as experienced by the diffusing molecules (ions).

**Temperature Control**

High precision temperature control of PFG NMR samples is of great importance in PFG NMR measurements. Any variations in temperature during the course of each PFG NMR experiment, which can last a couple of hours or even longer, introduce artifacts in the PFG NMR attenuation curves and thus compromise reliability of diffusion data. To study various systems discussed in this dissertation PFG NMR measurements
had to be carried out over a very broad range of temperatures from 218.2K to 423.2K. Thus, ability to control temperature over a large range with a very high precision was required. Such capability did not exist and had to be developed for the purposes of the studies reported in this work.

The sample temperature in the PFG NMR probe is controlled by a flow of a cooling gas (nitrogen gas or air). The temperature of the cooling gas is regulated by a heating element placed very close to the NMR sample tube, and the sample temperature is measured by a resistive temperature detector (RTD), which is also placed very close to the NMR sample tube. In addition, the temperature in the volume of the PFG NMR probe normally occupied by a sample can also be monitored by placing an RTD temperature element into a regular sample tube and introducing this tube into the probe instead of a sample. In addition to an RTD temperature element the tube contained ground silica of roughly the same volume as the sample volumes used in the studies reported in this dissertation. The heat input to the heating element is controlled using a PID controller with feedback control using the sample temperature from the RTD element outside the sample tube. Rigorous tuning of the PID controller was carried out to find exceptionally robust sets of proportional gain (P), integral (I), and derivative (D) rate constants. Air passed through a moisture trap was used as the cooling gas for temperatures in the range between 295.2K and 423.2K. For low temperature measurements, cold nitrogen gas, generated by a coil heater immersed in a liquid nitrogen bath was used as the cooling gas. This enabled controlling the sample temperature in a broad range of temperatures from 218.2K to 298.2K. Successful implementation of nitrogen boil off using a coil heater to control temperature was a
particularly challenging task. Correct configuration of the system had to be conceived to prevent liquid nitrogen from entering into the NMR probe and yet allow for sufficient cooling by the effluent nitrogen gas. As a result of the optimization of the temperature control an ability to regulate and maintain temperature at a desired value between 218K to and 423K with a 0.2 °K maximum drift, around the set point was developed.
Many types of soft matter systems with a well defined nanostructural organization (i.e. organized soft matter systems) that consist of oppositely charged polyatomic ions are of interest for fundamental research as well as for industrial applications. Study of diffusion of molecules/polyatomic ions and its relationship with the nanostructure in these materials on various relevant length scales helps understand various properties of these materials. PFG NMR was used to study diffusion in the following types of materials a) ionic liquids b) protein-polyelectrolyte coacervates c) pure and mixed micellar systems. Results obtained for each of these system types will be discussed separately in the following sections.

**Room Temperature Ionic Liquids**

**Influence of Water on Diffusion in Imidazolium based Ionic Liquids**

**Motivation**

Molten salts, which are liquid at temperatures around room temperature, are referred to as room temperature ionic liquids (RTILs). Many RTILs exhibit a number of interesting properties such as an excellent solubility for polar and non-polar compounds, negligible vapor pressure, large liquidus range (viz. range of temperature between normal melting and boiling point/decomposition temperature), high ionic conductivity, and good thermal stability. All these properties make RTILs a very attractive type of media for chemical reactions and separations.\(^{35}\) In addition, RTILs can be used as heat transfer/storage fluids, lubricants, etc.\(^{35-38}\)

RTILs are usually hygroscopic. As a result, they can absorb significant amounts of water.\(^{35,39-41}\) Even those RTILs which are sometimes considered to be hydrophobic
show an ability to absorb water from the surrounding gas phase.\textsuperscript{42,43} It has been demonstrated that various properties of ionic liquids such as solubility, polarity, viscosity and conductivity depend on the water content.\textsuperscript{35,41,42} An addition of water can also change chemical reactions of solutes in RTILs. For example, the influence of water was observed for oxygenation of toluene in the presence of palladium in the 1-n-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF$_4$]) ionic liquid. For this reaction an addition of water can lead to a change of the main product from benzaldehyde to benzoic acid.\textsuperscript{44}

Nanostructural organization of aqueous solutions of ionic liquids and its changes with increasing water concentration have been a focus of many recent studies.\textsuperscript{8,41,45-58} In particular, investigations using a number of methods, which include IR spectroscopy and density functional calculations, revealed the formation of hydrogen bonds between water and anions in imidazolium-based ionic liquids.\textsuperscript{8,40,52,55} These studies showed that at low water concentrations water exists in a non-self-aggregated state. In this case water molecules form complexes mostly with anions rather than with other water molecules. The data discussed above are in a qualitative agreement with the results of recent molecular dynamics (MD) simulations, which indicate that water molecules in RTILs tend to be isolated from each other at small water concentrations.\textsuperscript{45,53,54} In contrast, a water percolation cluster can be formed at high water concentrations corresponding to molar fractions of water $\geq 75\%$.\textsuperscript{45}

The results of MD simulations reported in Refs. \textsuperscript{45,46,53} show that for sufficiently small water concentrations diffusion coefficients of ions in aqueous solutions of RTILs increase continuously with increasing water content. This observation is supported by
the data provided by electrochemical measurements of ion transport rates in aqueous solutions of ionic liquids.\textsuperscript{59} In this chapter results of direct studies of an influence of water content on diffusion of ionic species and water in two selected RTILs are reported. Both RTILs contain the same cation 1-ethyl-3- methylimidazolium ([emim]\textsuperscript{+}). However, they have different anions, ethylsulfate ([EtSO\textsubscript{4}]\textsuperscript{-}) and triflate ([TfO]\textsuperscript{-}). The diffusion studies were carried out by proton pulsed field gradient (PFG) NMR technique. PFG NMR was previously applied to investigate diffusion in RTILs (see, for example, Refs.\textsuperscript{60-65}). However, until now a systematic study of an influence of water on the collective process of ion diffusion in imidazolium-based RTILs in a large temperature range has not been reported. This gap is filled by the present work. A comparison is also made between experimentally measured self-diffusivities and those obtained from previous MD simulations for [emim][EtSO\textsubscript{4}].\textsuperscript{54}

**Details of PFG NMR Experiments**

**Sample preparations**

RTIL and RTIL/water samples for PFG NMR studies were provided by the research group of Dr. Brennecke from University of Notre Dame. Mixtures of the RTILs and water were prepared by adding weighted amounts of water into the water-free RTILs. The water concentration in the studied samples of the RTILs was varied in the range between 0 and 15% w/w.

The IL [emim][EtSO\textsubscript{4}] and [emim][TfO] were purchased from Solvent Innovation (both > 99% purity). The samples were dried with rotary evaporation and heating under high vacuum (< 67 Pa) for two days. The water mass fraction of the final products was less than 500 ppm, as measured by Karl-Fischer titration with a Metrohm 831 KF Coulometer.
The pure RTILs or aqueous solutions of RTILs were introduced into the standard 5 mm NMR tubes. The mixtures were prepared in glass vials and mixed well before taking the appropriate size sample out for each NMR tube. In all cases the sample height in a vertically-oriented tube was $\leq$ 15 mm. This height was sufficiently small to ensure the absence of disturbing convection effects under our measurement conditions at elevated temperatures. After loading with RTIL samples the NMR tubes were flame sealed to avoid changes in the water content.

It was shown in Ref.66 that [emim][EtSO$_4$] can degrade in the presence of water to form [emim][HSO$_4$]. However, the degradation is a slow process leading to a decomposition of only 28% or less of [emim][EtSO$_4$] over the period of 1.5 or more years. The [emim][EtSO$_4$]/water samples used in this study were made with fresh [emim][EtSO$_4$] and tested within 2 weeks after preparation. Therefore it is believed that the results are for primarily [emim][EtSO$_4$] mixtures.

**PFG NMR studies**

Diffusion measurements of ions and water were performed using the standard PFG NMR stimulated echo pulse sequence $^{10,67}$ in a broad range of temperatures between 288 K and 354 K. In most cases it was sufficient to use gradients with the maximum amplitude of around 10 T/m. Diffusion data were obtained from dependencies of the intensity of the PFG NMR signal ($A$) on the amplitude of the magnetic field gradients ($g$). The signal intensity was determined by integrating the area under selected line(s) of the frequency-domain NMR spectra recorded by the PFG NMR stimulated echo pulse sequence (Fig. 3-1). Different lines in such spectra can correspond to different species. Hence, diffusion data for a chosen type of species in a
sample can be obtained by selecting an appropriate line in the spectrum for data processing. For the NMR lines exhibiting no significant overlap with the lines of other types of ions or molecules in the sample the diffusivity ($D$) was determined from the measured attenuation ($\psi$) of the PFG NMR signal by using Eq. 2.21. When a selected NMR line has a contribution from two or three different types of molecules and/or ions having different diffusivities the attenuation curves were described as a sum of two or three weighted exponential terms and were fit using Eq. 2.22.

The signal attenuation was measured under the conditions when only the value of $g$ was varied and all other parameters in the PFG NMR stimulated echo sequence remained constant. The value of $\delta$ in all cases was much smaller than $\Delta$, thus $t_{\text{eff}} \approx \Delta$. The effective diffusion time was changed by changing the value of $\Delta$. For each temperature the measurements were performed for at least two effective diffusion times equal to 24.78 ms and 49.78 ms.

**Experimental Data and their Interpretation**

Figure 3-1 shows an example of $^1$H NMR spectra of [emim][EtSO$_4$] containing water. The spectrum in Fig. 3-1 was recorded using the free induction decay (FID) sequence.$^{10,67}$ The NMR lines labeled 2,4,6,7,8, and 9 are assigned to the [emim]$^+$ cation,$^{68}$ while lines 1 and 3 are assigned to the [EtSO$_4$]$^-$ anion. The line 5 is attributed to water.$^{69}$ The lines 2 and 6 originate from the protons of the ethyl chain of [emim]$^+$, while the line 4 belongs to the protons of the methyl group attached to the imidazolium ring of the cation. The lines 7, 8 and 9 can be assigned to the protons of the imidazolium ring. The lines 1 and 3 belong to the protons of the ethyl side chain of [EtSO$_4$]$^-$. The chemical shift of the water line (5) was observed to shift downfield with
increasing water concentration. Such changes in the chemical shift can be attributed to a decrease in the extent of hydrogen bonding between water and anions with increasing water concentration.69

The corresponding proton NMR spectra recorded for [emim][TfO] were similar to those presented in Figure 3-1 with the exception of the [EtSO₄]⁻ lines. As expected, the latter lines were absent in the [emim][TfO] spectra. There was no contributions from [TfO]⁻ in these spectra because [TfO]⁻ are proton-free ions.

In all studied samples the NMR line of water showed some overlap with the lines corresponding to either anion, cation or both. An extent of the overlap was different for different water concentrations due to strong dependence of the chemical shift of the water line on the water concentration.

Figure 3-2 shows examples of the PFG NMR attenuation curves measured for [emim][EtSO₄] containing water. It is seen in Fig. 3-2 that the attenuation curves for

![Figure 3-1](image)

Figure 3-1. ¹H NMR spectrum of [emim][EtSO₄] containing 10% (w/w) water. A) For chemical shifts in the range between 0 and 10 ppm to show all lines. B) For chemical shifts in the range between 3.75 and 4.63 ppm to show lines 3 – 6.
[emim]$^+$ and [EtSO4]$^-$ are monoexponential in agreement with Eq.2.21. This is an expected behavior because the cation and anion lines at the chemical shifts of 1.5 ppm (#2) and 1.2 ppm (#1), which were used to measure these attenuation curves, represent the pure lines with no noticeable contribution from other types of molecules or ions. It was verified that for different pure lines originating from the same type of species the measured proton PFG NMR attenuation curves remained the same within the experimental uncertainty. Fig. 3-2 also shows that the attenuation curve for water deviates significantly from the monoexponential behavior predicted by Eq.2.21. This deviation is assigned to the existence of an overlap of the water line at 4.2 ppm with the neighboring [emim]$^+$ lines centered at 4.38 and 4.07 ppm. The analysis of the changes of the line shape with increasing gradient strength confirmed this assignment. The PFG NMR attenuation curve corresponding to this line was fitted by Eq. 2.22 with $n = 2$ and $D_2$ equal to the diffusivity of [emim]$^+$ (Fig. 3-2). This allowed determining the water diffusivity, i.e. $D_1$ in Eq. 2.22. The same type of fitting procedure was employed to determine water diffusivities in all other cases.
Figure 3-2. $^1$H PFG NMR attenuation curves measured for the sample of [emim][EtSO$_4$] containing 7% (w/w) water for $t_{\text{eff}} = 49.33$ ms at $T = 288$ K. The data are shown for the [emim]$^+$ line at 1.5 ppm (○), the [EtSO$_4$]$^-$ line at 1.2 ppm (▲), and the water line at 4.2 ppm (■). The latter line has a contribution from the [emim]$^+$ lines centered at 4.38 and 4.07 ppm. Solid curves show the best fit results using Eq. 2.21 for the cation and anion and using Eq. 2.22 with $n = 2$ for water. Eq.2.22 was used due to the existence of an overlap between the water and [emim]$^+$ lines.
Table 3-1. Diffusivities of \([\text{emim}]^+\) and water recorded by proton PFG NMR in the samples of \([\text{emim}][\text{TfO}]\) with different water concentrations and at different temperatures. The experimental uncertainty reflects deviations between the diffusivities measured at the same water concentration and temperature but for different diffusion times and different delays between the first and the second \((\pi/2)\) r.f. pulses of the PFG NMR stimulated echo sequence. It also reflects deviations between the corresponding data obtained using different NMR lines of the same type of species under the same measurement conditions.

<table>
<thead>
<tr>
<th>Water Concentration (w/w)</th>
<th>([\text{emim}]^+) Diffusivity (\times 10^{10}) (m(^2)s(^{-1}))</th>
<th>288 K</th>
<th>298 K</th>
<th>309 K</th>
<th>321 K</th>
<th>335 K</th>
<th>354 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>[emim](^+)</td>
<td>0.28</td>
<td>0.40</td>
<td>0.66</td>
<td>1.00</td>
<td>1.70</td>
<td>2.90</td>
</tr>
<tr>
<td></td>
<td>water</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>5%</td>
<td>[emim](^+)</td>
<td>0.66</td>
<td>0.90</td>
<td>1.19</td>
<td>1.50</td>
<td>2.00</td>
<td>--------</td>
</tr>
<tr>
<td></td>
<td>water</td>
<td>3.60</td>
<td>4.70</td>
<td>5.80</td>
<td>8.00</td>
<td>1.19</td>
<td>--------</td>
</tr>
<tr>
<td>7%</td>
<td>[emim](^+)</td>
<td>0.80</td>
<td>1.10</td>
<td>1.40</td>
<td>1.58</td>
<td>2.00</td>
<td>11.0</td>
</tr>
<tr>
<td></td>
<td>water</td>
<td>3.70</td>
<td>4.70</td>
<td>6.60</td>
<td>8.00</td>
<td>1.19</td>
<td>1.22</td>
</tr>
<tr>
<td>10%</td>
<td>[emim](^+)</td>
<td>1.09</td>
<td>1.50</td>
<td>1.80</td>
<td>1.80</td>
<td>2.00</td>
<td>2.12</td>
</tr>
<tr>
<td></td>
<td>water</td>
<td>4.40</td>
<td>5.70</td>
<td>8.00</td>
<td>8.00</td>
<td>1.20</td>
<td>2.2</td>
</tr>
<tr>
<td>12%</td>
<td>[emim](^+)</td>
<td>1.16</td>
<td>1.56</td>
<td>1.80</td>
<td>1.80</td>
<td>2.00</td>
<td>2.12</td>
</tr>
<tr>
<td></td>
<td>water</td>
<td>3.97</td>
<td>6.00</td>
<td>6.00</td>
<td>6.00</td>
<td>1.89</td>
<td>2.93</td>
</tr>
<tr>
<td>14%</td>
<td>[emim](^+)</td>
<td>1.33</td>
<td>1.91</td>
<td>1.91</td>
<td>1.91</td>
<td>2.00</td>
<td>2.12</td>
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<tr>
<td></td>
<td>water</td>
<td>4.00</td>
<td>6.00</td>
<td>6.00</td>
<td>6.00</td>
<td>1.89</td>
<td>2.93</td>
</tr>
</tbody>
</table>
Table 3-2. Diffusivities of [emim]$^+$, [EtSO$_4$]$^-$, and water recorded by proton PFG NMR in the samples of [emim][EtSO$_4$] with different water concentrations and at different temperatures. The experimental uncertainty reflects deviations between the diffusivities measured at the same water concentration and temperature but for different diffusion times and different delays between the first and the second ($\pi/2$) r.f. pulses of the PFG NMR stimulated echo sequence. It also reflects deviations between the corresponding data obtained using different NMR lines of the same type of species under the same measurement conditions.

<table>
<thead>
<tr>
<th>Water Concentration (w/w)</th>
<th>Diffusivity × 10$^{11}$ (m$^2$s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>288 K</td>
</tr>
<tr>
<td>0%</td>
<td></td>
</tr>
<tr>
<td>[emim]$^+$</td>
<td>------</td>
</tr>
<tr>
<td>[EtSO$_4$]$^-$</td>
<td>------</td>
</tr>
<tr>
<td>water</td>
<td>------</td>
</tr>
<tr>
<td>5%</td>
<td></td>
</tr>
<tr>
<td>[emim]$^+$</td>
<td>2.80 ±0.14</td>
</tr>
<tr>
<td>[EtSO$_4$]$^-$</td>
<td>2.10 ±0.11</td>
</tr>
<tr>
<td>water</td>
<td>17.9 ±0.9</td>
</tr>
<tr>
<td>7%</td>
<td></td>
</tr>
<tr>
<td>[emim]$^+$</td>
<td>3.60 ±0.18</td>
</tr>
<tr>
<td>[EtSO$_4$]$^-$</td>
<td>2.84 ±0.14</td>
</tr>
<tr>
<td>water</td>
<td>19.00</td>
</tr>
<tr>
<td>10%</td>
<td></td>
</tr>
<tr>
<td>[emim]$^+$</td>
<td>5.00 ±0.25</td>
</tr>
<tr>
<td>[EtSO$_4$]$^-$</td>
<td>3.93 ±0.20</td>
</tr>
<tr>
<td>water</td>
<td>18.0 ±0.92</td>
</tr>
<tr>
<td>12%</td>
<td></td>
</tr>
<tr>
<td>[emim]$^+$</td>
<td>5.80 ±0.29</td>
</tr>
<tr>
<td>[EtSO$_4$]$^-$</td>
<td>4.80 ±0.24</td>
</tr>
<tr>
<td>water</td>
<td>23.0 ±1.1</td>
</tr>
<tr>
<td>14%</td>
<td></td>
</tr>
<tr>
<td>[emim]$^+$</td>
<td>6.56 ±0.33</td>
</tr>
<tr>
<td>[EtSO$_4$]$^-$</td>
<td>5.80 ±0.29</td>
</tr>
<tr>
<td>water</td>
<td>25.0 ±1.3</td>
</tr>
</tbody>
</table>
Tables 3-1 and 3-2 present proton PFG NMR diffusion data for the [emim][TfO] and [emim][EtSO4] samples, respectively. The diffusivities were obtained for at least two effective diffusion times ($t_{eff}$) equal to 24.8 ms and 49.8 ms and for two values of the time interval between the first and the second ($\pi/2$) r.f. pulses of the PFG NMR stimulated echo sequence ($\tau_1$) equal to 1.5 ms and 3.0 ms. For each temperature and water concentration the measured ion diffusivities at different values of ($t_{eff}$) and ($\tau_1$) remained the same within an uncertainty less than ±10%. This uncertainty was used as an experimental uncertainty for ion diffusivities. The experimental uncertainty for water diffusivity was in some cases higher due to the existence of an overlap between the NMR line of water and those of ions. It is important to note that all diffusion data were obtained by proton PFG NMR, which allowed simultaneous and high-precision monitoring of diffusivities of all proton-containing species in the samples. No data are shown for [TfO]$^-$ because these ions are proton-free. The diffusion data are shown only for the temperatures that are smaller than the following two temperatures: (i) the temperature corresponding to an onset of condensation of water in an upper part of the NMR tubes with the RTIL samples and, (ii) the temperature corresponding to the appearance of a noticeable dependence of the measured effective diffusivity on diffusion time due to convection effects. Both condensation and convection effects prevented reliable PFG NMR measurements at temperatures larger than those given in Tables 3-1 and 3-2. These effects occurred due to the existence of a temperature gradient in sealed NMR tubes with the RTIL samples under our measurement conditions at elevated temperatures.
Previous MD simulations\textsuperscript{54} on [emim][EtSO\textsubscript{4}] found self-diffusivities for the cation and anion to be a factor of 2-3 lower than the PFG NMR values. This discrepancy is typical of that observed for other ionic liquid systems, and is likely due to deficiencies in the force fields used to model interactions between the ions. Interestingly, however, the MD simulations are consistent with the PFG NMR findings that the cation has a slightly higher self-diffusivity than the anion.

It was observed that in the temperature range used in this study the temperature dependencies of the measured diffusivities can be described by the Arrhenius law:

\[ D = D_0 \exp\left(\frac{-E}{RT}\right), \tag{3.1} \]

where \( E \) is the activation energy for diffusion, \( R \) is the gas constant, and \( D_0 \) denotes the pre-exponential factor. Figure 3-3 shows some examples of the measured temperature dependencies.

Figure 3-4 shows dependencies of the activation energy for diffusion on water concentration in [emim][TfO] and [emim][EtSO\textsubscript{4}]. It is seen that the change of the water concentration from zero to around 0.7 water molecules per anion-cation pair leads to a noticeable drop in the activation energy. A further increase in the water concentration leaves the activation energy essentially unchanged within the experimental uncertainty. A clear correlation was observed between the concentration dependencies of the activation energy (Fig. 3-4) and the corresponding concentration dependencies for the ion diffusivities. Examples of the latter dependencies are shown in Fig. 3-5 for a selected temperature of 298 K. Qualitatively similar results were obtained for all other temperatures used in this study.
Figure 3-3. Temperature dependencies of the measured diffusivity of [emim]+ (○), [EtSO4]- (▲), and water (■). A) For the aqueous solution of [emim][TfO] with 5% (w/w) water. B) For the aqueous solution of [emim] [EtSO4] with 5% (w/w) water. Solid lines show the best fit results using Eq. 3.1.
Figure 3-4. Dependencies of the activation energy for diffusion on water concentration, which is presented as a number of water molecules per anion-cation pair ($n_{\text{water}} / n_{\text{anion-cation pair}}$), for [emim]$^+$ (○), [EtSO$_4$]$^-$ (▲), and water (■). A) For [emim][TfO]. B) For [emim][EtSO$_4$].
Figure 3-5. Diffusivities of [emim]$^+$ (○), [EtSO$_4$]$^-$ (▲), and water (■) measured by proton PFG NMR as a function of the number of water molecules per anion-cation pair at 298 K. A) For [emim][TfO] B) For [emim][EtSO$_4$]. Also shown for comparison are the values of the reciprocal viscosity (×) for these ionic liquids at the same temperature as reported by Rodriguez H. and Brennecke J.
It is seen in Fig. 3-5 that an increase in the water concentration from zero to ca 0.7 water molecules per anion-cation pair results in a significant increase in the ion diffusivities at 298 K. This correlates with a decrease in the activation energy for diffusion observed for the same change in the water concentration (Fig. 3-4). An addition of more water to the RTIL samples after this initial change of the water concentration leads to a less pronounced increase in the ion diffusivities. The values of the reciprocal viscosity\(^7^0\) show the same general trend as the ion diffusivities (Fig 3-5), \textit{i.e.} they increase with increasing water concentration. In the presentation of Fig. 3-5 the extent of this increase becomes smaller with increasing water concentration.

It is interesting to note that in the water-free sample of [emim][EtSO\(_4\)] the diffusivity of a more bulky cation is approximately a factor of two larger than that of a less bulky anion (Fig. 3-5B). The data in Fig 3-5 show that this anomalous difference in the diffusivities decreases significantly with increasing water concentration. The exact same behavior was observed in the MD simulations.\(^5^4\)

For both types of ionic liquids the diffusivity of water in the ionic liquid was found to increase gradually with increasing water concentration (Fig. 3-5). The diffusivity values of water in the RTIL samples were much larger than those of the ions but, at the same time, much smaller than the corresponding diffusivity of pure water (2.3\times10^{-9} \text{ m}^2\text{s}^{-1} at 298 K).\(^7^1\)

Recent experimental studies and computer simulations have shown that RTILs exhibit the existence of polar and nonpolar regions.\(^4^1,4^6,7^2-7^4\) The imidazolium-based RTILs containing imidazolium cations with small (\(\leq C_1\)) alkyl side chains are known to form many discontinuous nonpolar regions in a sea of a continuous three-dimensional
network of polar domains. The results of previous experimental and computational investigations suggest that an addition of small amounts of water into such ionic liquids leads to a formation of complexes between water and ions. For sufficiently small water concentrations such complexes can be described as symmetric 1:2 H-bonded complexes: \( \text{anion} \cdots \text{HOH} \cdots \text{anion} \). Under these conditions water molecules tend to be isolated from each other. However, at large water concentrations (\( \geq 75\% \) molar) a percolating network of water can be formed.

The results shown in Figures 3-4 and 3-5 may be explained based on the nanostructural organization of RTILs discussed above. When a small amount of water molecules is introduced into the water-free RTILs, these molecules are incorporated into the polar domains, which are formed by the charged head groups of the cation and anion. The water molecules are expected to form \( \text{anion} \cdots \text{HOH} \cdots \text{anion} \) type complexes through hydrogen bonding. This behavior was observed in previous computational and experimental studies. As a result of the formation of such complexes the electrostatic interactions between the cations and anions become partially screened by water. Such screening of the electrostatic interactions could be the reason for the observed decrease in the activation energies for ion diffusion and a corresponding increase in the ion diffusivities (Figures 3-4 and 3-5). The smallest non-zero water concentration used in this study (around 0.7 water molecules per anion-cation pair) was sufficiently large to ensure that all anions in the samples can form H-bonds with water because each water molecule is capable of forming such bonds with two anions. Hence, an increase in the water concentration beyond this initial level would not lead to any increase in the number of the anions which directly interact with water molecules. The
absence of a major qualitative change in the local environment of the anions due to such additional increases in the water concentration explains why the corresponding changes of the ion diffusivities and of the activation energies for diffusion of ions become smaller after the first change in the water concentration from zero to around 0.7 water molecules per anion-cation pair (Figures 3-4 and 3-5). A further increase in the water concentration after this initial change can result in the formation of secondary hydrogen bonds of water with the existing anion⋯HOH⋯anion complexes and/or lead to the formation of small clusters of water molecules.\textsuperscript{45,46} It is important to note that even at the largest water concentration used (around 2.3 water molecules per anion-cation pair) the water concentration remains too small for the formation of the percolation water cluster. As a result, the water diffusivity in the studied samples was in all cases much smaller than the diffusivity of pure water.

The unusual diffusion behavior observed in the experiments and MD simulations (\textit{i.e.} the bulkier cation has a larger self-diffusivity than the anion) has been observed for different types of RTILs\textsuperscript{53,54,60,65,77} and has been explained as being due to anisotropic displacement of the ions; displacement along the ring plane and perpendicular to a vector between the two ring nitrogen atoms is favored over other displacement directions.\textsuperscript{78} The electrostatic interactions that lead to ordering of the liquid on nanometer length scales may result in this motion being favored. It is not universally observed, however. PFG NMR and MD simulations of pyridinium-based ionic liquids with bis(trifluoromethanesulfonyl)amide anions have shown that the larger cations can have smaller self-diffusivities than the anions.\textsuperscript{61}
An addition of water was observed to reduce significantly the magnitude of the anomalous difference between the diffusivities of the cations and anions (Fig. 3-5). This can be attributed to a partial screening of the electrostatic interaction between the cations and anions by water molecules. As a result of such screening the domain structure is expected to become more fluid and the cooperative character of the ion diffusion less pronounced.

For diffusion of hard spheres in a continuum solvent the relationship between viscosity and diffusivity obeys the Stokes-Einstein relation Eq. 1.13. The existence of strong interactions between cations and anions is expected to limit the use of this expression for RTILs.\textsuperscript{6,7,60,79} The results of a recent computational study\textsuperscript{8} show that the non-validity of Eq.1.13 for the case of these ionic liquids can be related to dynamical heterogeneities in RTILs. Nevertheless, a good correlation between the reciprocal viscosity and the diffusivity of the largest species in the studied RTIL samples, \emph{i.e.} the [emim]\textsuperscript{+} cations, was observed in all cases (Fig. 3-5). A somewhat poorer correlation between the reciprocal viscosity and the diffusivity of the [EtSO\textsubscript{4}]\textsuperscript{-} anions measured for different water concentrations (Fig. 3-5B) can be attributed to the fact that an increase in the water concentration transforms the anions from the smallest (at zero water concentration) to the second largest (at non-zero water concentration) species in the studied RTIL samples.

**Summary**

The above discussed results of the PFG NMR diffusion studies of imidazolium-based RTILs with and without water are reported in references\textsuperscript{9,80}. Briefly, it was observed that the presence of water in the RTILs at the concentration slightly larger than one water molecule per two anion-cation pairs leads to a significant change in the
values of diffusivities and activation energies for diffusion of ions in comparison with those in the corresponding water-free samples. A further increase of the water concentration resulted in less pronounced changes in the parameters characterizing ion diffusion. This behavior can be understood by noticing that the initial water concentration of around one water molecule per two anion-cation pairs is already sufficiently high to ensure the formation of hydrogen bonds between each anion and water. Hence, an increase of the water concentration beyond this initial level would not lead to an increase in the number of anions directly interacting with water. In the water-free ionic liquid [emim][EtSO₄] the diffusivity of the bulkier [emim]⁺ cation was found to be larger than that of the less bulky [EtSO₄]⁻ anion. This anomalous relationship between the size and diffusivity of diffusing species can be attributed to the existence of well-defined local structures in RTILs resulting in a cooperative character of ion diffusion and even in an appearance of diffusion anisotropy for the cation diffusion. With increasing water concentration these structures could become progressively less defined leading to a change towards normal relationship between the size and diffusivity of diffusing species.

**Polyelectrolyte-Protein Coacervates**

**Heterogeneity of Polyelectrolyte Diffusion in the Coacervates**

**Motivation**

Polyelectrolyte-protein coacervation is a special case of complex coacervation wherein a macromolecular solution composed of a protein and an oppositely charged polyelectrolyte, forms a metastable biphasic suspension as a result of electrostatic interactions and the entropy gained from small ion release. Upon centrifugation, this suspension separates into two liquid phases: a dense phase (coacervate), which is rich
in protein and polyelectrolyte, and a dilute solution phase, which contains an equilibrium mixture of protein and polyelectrolyte. The latter phase can either be molecularly dispersed or exist in some state of soluble aggregation. Until recently, most studies on protein-polyelectrolyte coacervation focused on various applications such as microencapsulation of active food components,\textsuperscript{81,82} pharmaceutical agents,\textsuperscript{83} or enzymes,\textsuperscript{84} as well as on selective protein separation.\textsuperscript{85} Such investigations have often involved protein mixtures (e.g. whey protein) and polyelectrolytes (e.g. gum Arabic) that are heterogeneous with respect to molecular weight (MW) and/or chemical composition. Due to such polydispersity, experimental observation of true liquid-liquid phase transitions in such systems has been a very challenging task. This polydispersity impedes experimental studies of the effects on coacervate structure of key variables, such as ionic strength, pH, protein charge anisotropy and polymer charge density, charge stability, and chain stiffness, all of which influence protein-polyelectrolyte complexation.\textsuperscript{86} However, even with polydisperse polyelectrolytes, it is possible to observe full retention of activity for enzymes confined in coacervate droplets, confirming not only the preservation of protein structure but also a level of diffusional mobility far in excess of that predicted from coacervate viscosity.\textsuperscript{87}

Recent studies of coacervates formed from a well-characterized, structurally homogeneous globular protein (bovine serum albumin (BSA)) and a narrow molecular weight distribution cationic polyelectrolyte (poly(diallyldimethylammoniumchloride) (PDADMAC)),\textsuperscript{88} have provided new information about the dynamics and structure of protein-polyelectrolyte coacervates. Among these findings are: (i) Multiple diffusion modes of proteins observed by both dynamic light scattering (DLS)\textsuperscript{88} and fluorescence
recovery after photobleaching (FRAP),\textsuperscript{89} (ii) A large fraction of “fast” proteins with diffusivity only six times smaller than the corresponding diffusion coefficient in a dilute protein solution,\textsuperscript{86} (iii) Rheological behavior indicative of a tenuous solid-like network at a low strain, prone to disruption with increasing shear,\textsuperscript{89} and (iv) Dense (protein-rich) domains observed by Cryo-TEM on length scales between tens and hundreds of nanometers.\textsuperscript{89} The existence of such domains was found to be consistent with Guinier analysis of static light scattering.\textsuperscript{88,89} All these observations point to mesophase separation within the coacervate (i.e. phase separation on the length scale in the order of one micron or less), leading to the existence of protein-rich microdomains suspended in a continuous phase with a lower protein concentration.\textsuperscript{89} The hypothesis about such mesophase separation finds additional support from the results of small angle neutron scattering studies.\textsuperscript{90}

While it might be assumed that the electrostatic interactions in coacervates would guarantee that differences in concentration of negatively-charged proteins between different types of domains would be mirrored by those of polycations, no direct data about structural and diffusional heterogeneity of polyelectrolytes in coacervates have been reported, primarily because proteins tend to dominate the signal in most scattering experiments. In this chapter such data for the diffusion of PDADMAC in PDADMAC-BSA coacervates are presented and discussed. The diffusion studies were carried out by pulsed field gradient (PFG) NMR. The PFG NMR technique was previously applied for measurements of diffusivities of polyelectrolytes in coacervates,\textsuperscript{91} but only with gradients of relatively small strength (0.5 T/m), which limits spatial resolution. Hence, no data on diffusion heterogeneity over small length scales were reported. In the present
study, PFG NMR diffusion measurements were carried out with large (up to 30 T/m) gradients, allowing observation of displacement-dependent polyelectrolyte transport properties in coacervates on the sub-micrometer length scale, in a manner similar to recent PFG NMR studies of the diffusion of guest molecules on sub-micrometer length scale in nanoporous materials.  

**Experimental Details**

**Materials and preparation of coacervate samples**

The coacervate samples were provided by the research group of Dr. Dubin, the University of Massachusetts at Amherst. The details of the sample preparation are as follows. Poly(diallyldimethylammoniumchloride) (PDADMAC) of $M_w = 219$ kDa ($M_n = 141$ kDa) and $M_w = 700$ kDa ($M_n = 460$ kDa) samples were prepared by free radical aqueous polymerization of diallyldimethylammoniumchloride$^{93}$ and characterized after dialysis and lyophilization by membrane osmometry and light scattering. Bovine serum albumin (BSA) ($M_w \approx 68$ kDa) with total fatty acid content $\leq 1.2$ mg/g was purchased from Roche Diagnostics (Indianapolis, IN). Deuterium oxide ($D_2O, 99.8\%$) was purchased from Cambridge Isotope Laboratories, Inc (Andover, MA). 0.1 N and 1 N HCl and NaOH solutions were obtained from Fisher Scientific. Milli-Q-Water was used in the preparations of all samples.

BSA and PDADMAC were dissolved separately in 0.05-0.1M NaCl solution to give stock solutions of 6 g/L and 1.2 g/L, respectively. Each stock solution was then filtered individually (0.20 µm Cellulose Acetate, Sartorius Inc.), and the pH of each solution was adjusted to 4.0 (non-interacting conditions) with 0.1 N HCl. Equal volumes of BSA and PDADMAC solutions were mixed to give an initial protein:polymer weight ratio ($r$) of 5, and the pH of the mixture was adjusted to the desired pH by gradual addition of 0.1 N
NaOH and 1 N NaOH. The mixture was centrifuged for 30 min at 4000 rpm at room temperature and the upper clear solution (supernatant) was removed by pipette from the lower optically clear and viscous fluid (coacervate). Centrifugation was repeated several times to ensure full removal of supernatant. Samples for PFG NMR studies were prepared by introducing the coacervate into a 5mm NMR tube using the same procedure as that described earlier for ionic liquids in the previous section.

**NMR measurements**

NMR studies were performed with three BSA-PDADMAC coacervate samples (Table 3-3). In addition, NMR spectra of a sample containing only BSA (i.e. sample A1 in Table 3-3) were recorded to ensure the proper assignment of NMR lines to BSA or PDADMAC. The relative amounts of BSA in the pure protein sample and that in the coacervate samples were essentially the same; i.e. ~ 20 % protein by weight. In order to minimize the proton NMR signal of water, H$_2$O in the coacervates was repeatedly exchanged by D$_2$O to attain a level of 90 % v:v D$_2$O as discussed in Ref.$^{90}$.  

<table>
<thead>
<tr>
<th>Sample</th>
<th>Type</th>
<th>PDADMAC molecular weight</th>
<th>Ionic strength</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$M_w$ (kDa) and ($M_w/M_n$)</td>
<td>(mM)</td>
<td></td>
</tr>
<tr>
<td>A1</td>
<td>BSA</td>
<td>-</td>
<td>~ 7</td>
<td>100</td>
</tr>
<tr>
<td>A2</td>
<td>BSA-PDADMAC</td>
<td>700 (1.55)</td>
<td>7.7</td>
<td>100</td>
</tr>
<tr>
<td>A3</td>
<td>BSA-PDADMAC</td>
<td>219 (1.52)</td>
<td>8.5</td>
<td>100</td>
</tr>
<tr>
<td>A11</td>
<td>BSA-PDADMAC</td>
<td>219 (1.52)</td>
<td>9.0</td>
<td>50</td>
</tr>
</tbody>
</table>

Diffusion measurements were performed for a broad range of diffusion times (between around 30 and 200 ms) using the PFG NMR stimulated echo sequence (PGSTE). Each PFG NMR attenuation curve was obtained by measuring the signal
intensity as a function of the amplitude of the magnetic field gradients \( g \) and keeping all other parameters of the stimulated echo sequence the same. The total measurement time needed to measure one attenuation curve was larger than 1 hour for all samples. The signal intensity \( A(g) \) at different gradient strengths was obtained by calculating the area under the selected lines of frequency-domain NMR spectra. For each attenuation curve the same integration range on the frequency scale was used.

Diffusivities in the studied coacervate samples were obtained by fitting the measured attenuation curves using an equation of the type of Eq.2.22 with several weighted exponential terms corresponding to distinct ensembles of diffusing species with different diffusivities. Under our experimental conditions, \( \delta \) was always much smaller than the effective diffusion time, i.e. \( t_{\text{eff}} \approx \Delta \). The effective diffusion time was varied by changing the separation between the second and third \( \pi/2 \) pulses \( (\tau_2) \) of the PFG NMR stimulated echo sequence (Fig. 2-5) and keeping all other parameters of the sequence constant. In these measurements \( \delta \) was equal to 3.43 ms and the separation between the first and the second \( \pi/2 \) pulses \( (\tau_1) \) was equal to 4.4 ms. In addition, several measurements were performed with \( \tau_1 = 3.9 \) ms and \( \delta = 2.9 \) ms to verify that for a given diffusion time the measured diffusivities are independent of the value of \( \tau_1 \). The experimentally observed lack of such dependence confirmed that our data are not distorted by the magnetic susceptibility effects. All measurements were performed at room temperature (293 K) to avoid occurrence of disturbing convection effects.
Experimental Data and their Interpretation

Figure 3-6. $^1$H NMR frequency-domain spectra of A1, A2, A3 and A11 coacervate samples obtained from the free induction decay (FID) signal.

Figure 3-6 shows the frequency-domain $^1$H NMR spectra recorded by the free induction decay (FID) sequence for the samples listed in Table 3-3. The strong line at about 4.6 ppm is assigned to H$_2$O. The half width of this line is significantly smaller in the pure protein sample (A1) than in the coacervate samples. This can be attributed to a lower mobility of water in the latter samples. The broad feature between 2 and 0 ppm in the spectrum of the pure BSA sample is attributed to the protein since the only non-BSA line that we can expect to see in this sample is the water line at around 4.6 ppm. The lines between 4 and 0 ppm in the spectra of coacervate samples A2, A3 and A11 originate from both polyelectrolyte and protein. Comparison of these lines with the spectrum of A1 indicates that the strongest polyelectrolyte lines, with no or little overlap with the water and/or protein lines, are located in the region between 4 and 2 ppm.
These lines can be assigned to the N-methyl protons, and the CH$_2$ protons of the five-membered rings of PDADMAC.

Figure 3-7. $^1$H NMR spectra of coacervate sample A11 obtained by the PFG NMR stimulated echo pulse sequence for $t_{\text{eff}} = 28.85$ ms and the following two gradient strengths: 0.4 T/m (A), and 13 T/m (B). The relative intensity of B has been significantly increased to facilitate the comparison of the shape of the spectra. Note the disappearance of the water signal at around 4.6 ppm in the spectrum (B) corresponding to large gradient strength.

Comparison of the frequency domain spectra recorded by the PFG NMR stimulated echo pulse sequence for $g \geq 0$ (see, for example, spectra in Fig. 3-7) with those in Fig. 3-6 revealed that the broad feature in the range between 2 and 0 ppm (Fig. 3-6), assigned to the protein, has completely vanished from the coacervate spectra obtained by the PFG NMR sequence. This effect is attributed to the short NMR transverse relaxation time ($T_2 < 1$ ms), which was estimated from the results of the measurements of the protein signal in the coacervate samples using FID and the stimulated echo sequence. Under conditions of the application of the stimulated echo sequence, the duration of the signal decay with time constant $T_2$ cannot be smaller than
the value of $2\delta$, here equal to around 7 ms. As a result, no visible protein lines were recorded by this sequence under the measurement conditions. It was verified that even for values of $\delta$ much smaller than 3.4 ms but still suitable for diffusion measurements, the PFG NMR stimulated echo sequence fails to detect sufficiently strong protein lines. Hence, only diffusion data for PDADMAC are reported.
Figure 3-8. $^1$H PFG NMR attenuation curves for diffusion of PDADMAC in the coacervate samples A2 (a), A11 (b), and A3 (c). The curves were measured for the following effective diffusion times: 28.85 ms (■), 43.85 ms (●), 58.85 ms (▲), 73.85 ms (▼), 98.85 ms (□), and 198.85 ms (○). The attenuation range for small diffusion times could not be expanded beyond that shown in the figure because larger duration and/or amplitude of the gradients, which is required to achieve larger attenuation, would lead to overheating of the gradient coil.

The attenuation curves for PDADMAC were obtained by integrating the frequency-domain spectra in the range between 3.8 and 1.8 ppm and plotting the resulting integral values as a function of $(g^2 \delta)^2 t_{\text{eff}}$, s$^{-1}$m$^{-2}$ (Fig. 3-8). In this frequency range, PDADMAC lines do not show a significant overlap with the strong water line. In order to further suppress the influence of water on the measured attenuation curves, we used gradients in the range of 0.4 T/m as the starting, viz. smallest value. It was observed that such gradients do not lead to any measurable decay of the PDADMAC lines. However, the intensity of the residual water line was sufficiently suppressed so that there was essentially no influence of water on the frequency-domain spectra in the measured range (3.8-1.8 ppm). In order to further verify that the attenuation curves shown in Fig. 3-8 correspond...
to the diffusion of PDADMAC only, the shapes of the frequency-domain spectra were compared at various gradient strengths, including those corresponding to the fast initial decay of $\psi$ measured at small diffusion times (Fig. 3-7). The shapes of the spectra provide information on the relationship between the apparent amplitude, the line width and the integral under the three lines in the range between 3.8 and 1.8 ppm. It was observed that these shapes, and hence also the PFG NMR attenuation curves for different lines, remained the same within the experimental uncertainty. Figure 3-7 shows an example of such shape comparison for two very different gradient strengths.

The attenuation curves in Fig. 3-8 show non-monoexponential behavior. The diminution of deviations from monoexponential behavior in the initial part of the attenuation curves with increasing diffusion time corresponds mainly to the gradual disappearance of the fast initial decay. However, even for large diffusion times (around 100 ms) the attenuation curves remain noticeably non-monoexponential. Such behavior was observed for all three samples. In general, monoexponential behavior of PFG NMR attenuation curves corresponds to the existence of a single diffusivity for all diffusing species under study (Eq.2.21). Deviations from the monoexponential behavior indicate that there is a distribution of diffusivities. Hence, the data in Fig. 3-8 suggest that there are different ensembles of PDADMAC ions with different effective diffusivities in the coacervate samples.

Changes in the shape of the attenuation curves in Fig. 3-8 with increasing diffusion time can arise from changing relative contributions of different ensembles of PDADMAC ions to the measured signal. This can happen if the characteristic longitudinal NMR relaxation times ($T_1$) vary for PDADMAC ensembles with different diffusivities and, in
addition, if these relaxation times are comparable with the diffusion times used in the measurements. In such case, the contribution of ensembles with smaller $T_i$ to the measured stimulated echo signal relative to those corresponding to larger $T_i$ would decrease with increasing diffusion time.\textsuperscript{10,13} As a result, the NMR signal of PDADMAC has to become smaller with increasing diffusion time. However, for the measured range of diffusion times, no significant reduction of the signal amplitude with increasing diffusion time was observed. Hence, we can conclude that the characteristic $T_i$ times are significantly larger than the diffusion times used, and the observed changes of the PFG NMR attenuation curves with increasing diffusion time were not due to the effects of $T_i$ relaxation.

In order to obtain quantitative information about PDADMAC diffusion the measured attenuation curves were fitted assuming the existence of several ensembles of PDADMAC ions having different diffusivities. In this case, the weighted sum of several exponential terms corresponding to PDADMAC ensembles with different diffusivities (Eq. 2.22) was used to fit the data. Fitting the attenuation curves revealed that the minimum number of the exponential terms in Eq. 2.22 is two for large diffusion times and three for small diffusion times.

The resulting best fit values of the diffusivities and the corresponding fractions of PDADMAC ions are presented in Table 3-4. This table shows that ensembles (a) and (b) with large diffusivities represent only a small fraction of all PDADMAC ions contributing to the measured NMR signal, an unexpected result since for the protein the large diffusivity mode was elsewhere (Ref.86) observed to be the dominant one. In comparison, at least 70% of the measured PDADMAC signal corresponds to the
slowest component \((c)\). The diffusivity of the slowest component remains mostly the same with increasing diffusion time and its relative contribution shows some tendency to decrease slowly with increasing time (Table 3-4). This decrease in the fraction of \((c)\) is compensated by the corresponding increase in the fraction of component \((b)\). Table 3-4 shows that the latter fraction increases very significantly in the measured range of diffusion times. Such behavior can be tentatively interpreted as a manifestation of exchange between these two fractions.

Table 3-4. Results of fitting of the PFG NMR attenuation curves shown in Fig. 3-8 for coacervate samples A1, A3 and A11. Eq. 2.22 with either two or three exponential terms corresponding to PDADMAC ensembles with different diffusivities was used to fit the curves.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(t_{\text{eff}}, \text{ms})</th>
<th>Fraction (a (A_a))</th>
<th>(D_a, \text{m}^2/\text{s})</th>
<th>Fraction (b (A_b))</th>
<th>(D_b, \text{m}^2/\text{s})</th>
<th>Fraction (c (A_c))</th>
<th>(D_c, \text{m}^2/\text{s})</th>
</tr>
</thead>
<tbody>
<tr>
<td>A2</td>
<td>28.85</td>
<td>0.11</td>
<td>(5.93\times10^{-12})</td>
<td>0.09</td>
<td>7.08\times10^{-13})</td>
<td>0.79</td>
<td>9.49\times10^{-14})</td>
</tr>
<tr>
<td></td>
<td>43.85</td>
<td>0.06</td>
<td>(4.17\times10^{-12})</td>
<td>0.08</td>
<td>6.83\times10^{-13})</td>
<td>0.86</td>
<td>9.30\times10^{-14})</td>
</tr>
<tr>
<td></td>
<td>58.85</td>
<td>N/A</td>
<td>N/A</td>
<td>0.12</td>
<td>6.75\times10^{-13})</td>
<td>0.88</td>
<td>8.96\times10^{-14})</td>
</tr>
<tr>
<td></td>
<td>73.85</td>
<td>N/A</td>
<td>N/A</td>
<td>0.13</td>
<td>6.39\times10^{-13})</td>
<td>0.87</td>
<td>8.70\times10^{-14})</td>
</tr>
<tr>
<td></td>
<td>98.85</td>
<td>N/A</td>
<td>N/A</td>
<td>0.16</td>
<td>4.89\times10^{-13})</td>
<td>0.84</td>
<td>8.13\times10^{-14})</td>
</tr>
<tr>
<td></td>
<td>198.85</td>
<td>N/A</td>
<td>N/A</td>
<td>0.19</td>
<td>3.99\times10^{-13})</td>
<td>0.81</td>
<td>7.60\times10^{-14})</td>
</tr>
<tr>
<td>A3</td>
<td>28.85</td>
<td>0.03</td>
<td>(6.44\times10^{-12})</td>
<td>0.17</td>
<td>7.32\times10^{-13})</td>
<td>0.80</td>
<td>1.87\times10^{-13})</td>
</tr>
<tr>
<td></td>
<td>43.85</td>
<td>N/A</td>
<td>N/A</td>
<td>0.18</td>
<td>8.36\times10^{-13})</td>
<td>0.82</td>
<td>1.92\times10^{-13})</td>
</tr>
<tr>
<td></td>
<td>58.85</td>
<td>N/A</td>
<td>N/A</td>
<td>0.22</td>
<td>7.18\times10^{-13})</td>
<td>0.78</td>
<td>1.85\times10^{-13})</td>
</tr>
<tr>
<td></td>
<td>73.85</td>
<td>N/A</td>
<td>N/A</td>
<td>0.28</td>
<td>5.74\times10^{-13})</td>
<td>0.72</td>
<td>1.77\times10^{-13})</td>
</tr>
<tr>
<td></td>
<td>98.85</td>
<td>N/A</td>
<td>N/A</td>
<td>0.29</td>
<td>5.36\times10^{-13})</td>
<td>0.71</td>
<td>1.76\times10^{-13})</td>
</tr>
<tr>
<td></td>
<td>198.85</td>
<td>N/A</td>
<td>N/A</td>
<td>0.25</td>
<td>6.14\times10^{-13})</td>
<td>0.75</td>
<td>1.89\times10^{-13})</td>
</tr>
<tr>
<td>A11</td>
<td>28.85</td>
<td>0.05</td>
<td>(4.65\times10^{-12})</td>
<td>0.03</td>
<td>4.88\times10^{-13})</td>
<td>0.92</td>
<td>4.91\times10^{-14})</td>
</tr>
<tr>
<td></td>
<td>43.85</td>
<td>N/A</td>
<td>N/A</td>
<td>0.06</td>
<td>5.67\times10^{-13})</td>
<td>0.94</td>
<td>5.53\times10^{-14})</td>
</tr>
<tr>
<td></td>
<td>58.85</td>
<td>N/A</td>
<td>N/A</td>
<td>0.07</td>
<td>6.10\times10^{-13})</td>
<td>0.93</td>
<td>5.64\times10^{-14})</td>
</tr>
<tr>
<td></td>
<td>73.85</td>
<td>N/A</td>
<td>N/A</td>
<td>0.09</td>
<td>4.92\times10^{-13})</td>
<td>0.91</td>
<td>5.43\times10^{-14})</td>
</tr>
<tr>
<td></td>
<td>98.85</td>
<td>N/A</td>
<td>N/A</td>
<td>0.12</td>
<td>4.19\times10^{-13})</td>
<td>0.88</td>
<td>5.13\times10^{-14})</td>
</tr>
</tbody>
</table>
Figure 3-9. Dependence of the effective diffusivities of PDADMAC shown in Table 3-4 on the root mean square displacements calculated using the Einstein relation (Eq. 1.11). Triangles, circles and squares show diffusivities for the coacervate samples A2, A3, and A11, respectively. Fractions (a), (b), and (c) are indicated by red, green and blue symbols, respectively.

Figure 3-9 shows dependencies of the diffusivities of the different ensembles of PDADMAC ions on the root mean square displacements (MSD) obtained using the Einstein relation (Eq. 1.11). This figure demonstrates that the application of high magnetic field gradients allowed us to probe diffusion of PDADMAC on the length scale of displacements smaller than 100 nm for fraction (c). Increase in the diffusion time of PFG NMR measurements resulted in an increase in the values of the measured root mean square displacements. It is seen in Fig. 3-9 that the diffusivities of fraction (c) were measured in the range of displacements between ca. 90 nm and 500 nm, while diffusivities of fractions (a) and (b) were measured for displacements up to ca. 1 µm.

The observation of fast diffusing PDADMAC fractions ((a)+(b)) and a slow diffusing fraction (c) can be discussed in relation to recent results, which suggest the
existence of two different types of domains in the coacervate samples: dense microdomains with a high concentration of BSA and dilute domains with a low concentration of BSA. Limited Cryo-TEM images of BSA-PDADMAC coacervates\textsuperscript{89,90} suggest that dilute domains form a continuous phase with volume fraction of ca. 0.85. This estimate is in agreement with the observation that the fast-diffusing component of BSA recorded by DLS in BSA-PDADMAC coacervates corresponds to around 75% of total BSA.

Protein-polyelectrolyte coacervate morphology suggested by Cryo-TEM involves irregular and partially interconnected solid-like regions with sizes between 100 nm and 1000 nm. In other systems exhibiting similar morphologies, viz. colloidal solutions of weakly charged colloidal silver\textsuperscript{95} and Boehmide rods,\textsuperscript{96} mesophase separation appears to arise from a combination of short-range attraction and long-range repulsion, which supports the hypothesis that aggregates of protein-polyelectrolyte on the order of 50 nm, and with residual net charge, can form clusters in the range of hundreds to thousands of nm. This scenario is consistent with the Cryo-TEM and small angle neutron scattering (SANS) data for the BSA/PDADMAC system\textsuperscript{89,90} and with SANS and electron microscopy data for the Lysozyme/poly(styrenesulfonate) system.\textsuperscript{97} It has further been proposed\textsuperscript{98} that Lys-NaPSS complexes phase separating from water consist of dense polyelectrolyte-protein "globules" (aka aggregates) of 30-40 nm in diameter separated by ca. 10 nm domains. These inter-aggregate regions consist of polyelectrolyte chains and their counter ions when the polyelectrolyte:protein charge ratio is 2-3 (this ratio is 4 for the coacervates of the present study), and are thus intracluster spaces from which excess polyelectrolyte can be released (see below). It is
expected that the rotational and conformational mobility of PDADMAC ions in the static aggregates and in the intracluster spaces between aggregates is significantly reduced in comparison to the dilute phase. As a result, rotation and/or change of conformation of PDADMAC polycations are likely to be too slow on the NMR time scale for averaging out the effect of proton dipole-dipole interaction on the $T_2$ NMR relaxation time, which is expected to be significantly reduced by such interactions. In particular, a pronounced decrease of proton $T_2$ NMR relaxation time due to hindered mobility of PDADMAC in related systems was recently reported in Ref. It is likely that the $T_2$ values of PDADMAC in dense domains are so small that no NMR signal from these PDADMAC polycations can be recorded by the stimulated echo sequence under our experimental conditions. This assumption is in agreement with the observation that the average line width of PDADMAC is larger for the FID measurements (Fig. 3-6) than for the measurements with the stimulated echo sequence by around 3%. In the former measurements the signal of essentially all PDADMAC ions can be recorded while in the latter measurements the PDADMAC signal is reduced due to $T_2$ NMR relaxation in the same way as discussed above for BSA.

Based on the discussion above, it is very likely that our PFG NMR measurements failed to detect PDADMAC ions in dense domains. The largest fraction ($c$) of PDADMAC ions can be attributed to diffusion in the dilute phase, which is expected to account for around 85% of the sample volume. PDADMAC ions with higher diffusivities ($((a) + (b))$) can be tentatively attributed to those released from a fraction of dense domains which are in the process of breaking up during the time window of diffusion measurements. Recent DLS data suggest that break up of dense domains
can occur on the time scale of dozens of milliseconds.\textsuperscript{89} This time scale is comparable with the diffusion time in the PFG NMR measurements (Table 3-4). A rapid break up of dense domains can lead to a massive release of PDADMAC ions, with the intracluster regions mentioned above acting as reservoirs for the release of excess PDADMAC. Once released, the PDADMAC ions are expected to move freely away from the newly created boundaries between dense and dilute domains. The effective diffusivity of the released PDADMAC at such boundaries can be larger than that in dilute domains far from the boundaries because the release of PDADMAC is expected to lead to a concentration gradient at the domain boundaries and hence short-range flow of PDADMAC into dilute domains. The existence of such flows can significantly increase effective diffusivity of PDADMAC because this diffusivity is determined from the measured MSD values using Eq. 1.11. For a sufficiently strong, homogeneous flow the effective diffusivity can be estimated as

\[ D = \frac{1}{6t_{eff}} \langle r^2(t_{eff}) \rangle \approx \frac{1}{6t_{eff}} \left( \int_0^{t_{eff}} v(t) \, dt \right)^2, \]  

(3.2)

where it was assumed that all PDADMAC ions move with the same velocity equal to the flow velocity \( v(t) \). In the coacervate samples a characteristic velocity of the PDADMAC flows is expected to become smaller with time because of leveling off of the concentration gradients. Consequently, the effective diffusivity as a function of time is expected to grow more slowly than the linear dependence given by Eq. 3.2 with a time-independent velocity. The diffusivity can even remain almost constant or decrease with increasing time. This expectation is in agreement with the results for the PDADMAC component \((b)\) in Table 3-4 which do not show any significant dependence of the
diffusivity of this component on diffusion time. The short-range flows discussed above are bound to include and carry with them some of the PDADMAC polycations located in the dilute domains near boundaries. Inclusion of polyelectrolyte from dilute domains into the flows explains why with increasing diffusion time, the fraction of rapidly diffusing component ($b$) increases, and the fraction of ($c$) decreases (Table 3-4).

A reduction in the volume of dense domains due to their break-up has to be compensated by new dense domain formation since the total volume of dense domains is expected to remain constant under the conditions of our measurements. Under these conditions the macroscopic NMR samples are expected to be in a steady state characterized by a constant free energy and the related constant volume fraction of dense domains because the sample was kept at the same temperature for at least several days before the measurements. Formation of dense domains within dilute domains can lead to transient local decrease in the concentration of PDADMAC and BSA in the dilute phase as these macroions are consumed in the process of dense domain formation. The latter is likely to lead to short-range flows and to the corresponding increase of the polyelectrolyte fractions with high effective diffusivities as measured by PFG NMR. Based on the discussion above we can conclude that the PFG NMR detection of highly mobile polyelectrolyte components ($a$) and ($b$) can be tentatively attributed to both break up and formation of dense domains.

Previous studies of PDADMAC-BSA coacervates using DLS and FRAP suggest that the stability of dense domains, i.e. the characteristic time scale of domain break up depends on the pH and ionic strength of the coacervate samples.$^{88,89}$ Under the conditions of strong interactions in the coacervates characterized by high pH and low
ionic strength (sample A11), large and stable dense domains are expected to exist. In contrast, dense domains in coacervates prepared at low pH and high ionic strength are expected to be less stable (sample A3). These expectations are consistent with the data in Table 3-4 showing that the sum of the relative contributions of components (a) and (b), which are attributed to the processes of break-up and formation of dense domains, is about twice as large for A3 than for A11 for all diffusion times used. The remaining sample A2 is also characterized by low pH and high ionic strength. However, the polyelectrolyte molecular weight for A2 is significantly larger, which is expected to lead to a reduced rate of domain break-up. This is in agreement with the observation that the sum of the fractions of the components (a) and (b) in A2 is slightly smaller than that in A3.

In addition to the stability of dense domains discussed above, ion diffusivities in the dilute phase can also show some dependence on coacervate pH and ionic strength. In particular, DLS data suggest that the diffusivity of BSA assigned to dilute domains in sample A3 (low pH, high ionic strength) is almost a factor of two higher than that in sample A11 (high pH, low ionic strength). This is in qualitative agreement with the observation that the polyelectrolyte diffusivity inside dilute domains, which are not affected by the short-range flows, is larger in A3 than in A11 (compare data for fraction (c) in Table 3-4 and in Fig. 3-9).

Summary

PFG NMR diffusion studies of PDADMAC polycations in several samples of PDADMAC-BSA coacervates reveal the existence of diffusion heterogeneity for PDADMAC on length scales from ca. 1000 nm down to 100 nm (see also Ref.\textsuperscript{100}). Such studies become possible due to the application of high (up to 30 T/m) magnetic field.
gradients. Observation of several ensembles of PDADMAC ions having different
diffusivities supports the hypothesis of the existence of microscopic domains in
coaacervates. The PDADMAC ensemble with the smallest diffusivity is attributed to
normal self-diffusion in dilute domains representing ca. 85% of the coacervate volume,
while the ensembles with large effective diffusivities are tentatively assigned to
PDADMAC transport arising from concentration gradient-driven flows in dilute domains.
Such flows are believed to occur due to constant break up and formation of dense
domains.

**Pure and Mixed Surfactant Systems**

**Influence of Breakup and Reformation of Micelles on Surfactant Diffusion**

**Motivation**

Properties of micelles that spontaneously form in ionic and nonionic surfactants
have been attracting a keen interest of the scientific community due to a variety of
applications of micellar systems which range from enhanced oil recovery $^{101}$ to
synthesis of porous materials where micelles are used as templates.$^{102}$ Mixing cationic
and anionic surfactants was recognized as a promising way to tune size, shape and
stability of micelles $^{103-108}$. In particular, flexible wormlike micelles can self-assemble in
aqueous solutions of cationic/anionic surfactant mixtures, $^{105,106}$ while spherical micelles
are often formed when only an anionic surfactant is present. An addition of small
amounts of cationic surfactants to aqueous solutions of an anionic surfactant is believed
to be able to promote formation of micelles, which are larger and also more stable than
those formed in the absence of the cationic surfactants $^{103,107}$.

Despite a large number of studies of micellar systems direct microscopic
investigations of surfactant diffusion as their aggregation state changes from micellar to
monomeric and back to micellar are still quite rare. An exchange between these two aggregation states can be characterized by two relaxation times, which can be measured by ultrasonic adsorption, pressure-jump, temperature-jump and other methods\textsuperscript{109,110}. The smaller of the two relaxation times with typical values in the microsecond range is attributed to fast association and dissociation of individual surfactant molecules or ions to and from micelles\textsuperscript{110}. This relaxation time is essentially equal to the average life time of any particular (labeled) surfactant molecules or ion in a micelle\textsuperscript{111}. The larger of the two times has typical values in the millisecond range. It is associated with the process of breakup and reformation of micelles\textsuperscript{110,111}. This work focuses on the study of an influence of the latter process on the diffusion behavior of surfactant ions. The ion diffusivities were monitored on the time scale comparable with the characteristic time of the micelle breakup and reformation. Diffusion measurements were performed using pulsed field gradient (PFG) NMR technique. An aqueous solution of a frequently used anionic surfactant, sodium dodecyl sulfate (SDS), as well as the corresponding solution where this surfactant was mixed with a small amount of the cationic surfactant N-dodecyltrimethylammonium bromide (C\textsubscript{12}TAB) were used as model micellar systems. C\textsubscript{12}TAB was chosen because this surfactant has equally long tails as those of SDS. The equality of the tail lengths is expected to maximize interactions between these two surfactants\textsuperscript{103,112}. Diffusion studies that are reported below were carried out for a broad range of diffusion times. Measurements at small diffusion times in the range of 15 ms were possible due to the ability to apply large (up to 20 T/m) magnetic field gradients. PFG NMR technique was applied previously to study diffusion in micellar systems with cationic and anionic surfactants\textsuperscript{113-118}. 
However, these studies were usually performed for large (≥ 100 ms) diffusion times and no dependence of the diffusion behavior of surfactants on the diffusion time was observed and/or reported. In this work the interpretation of the measured data was based on the concept of long-range diffusion, \textit{i.e.} diffusion under the conditions of fast exchange of diffusing species between different environments exhibiting different diffusivities in a macroscopic sample.

**Experimental Details**

**Sample preparations**

The PFG NMR samples were prepared in collaboration with the research group of Dr. Shah at University of Florida. Ultrapure sodium dodecyl sulfate (SDS) from MP Biomedicals, Inc. (Solon, OH) and N-dodecyltrimethylammonium bromide (C$_{12}$TAB) from Tokyo Kasei Kogyo Co. (Tokyo, Japan) were used without further purification. The compositions of the surfactant solutions were as follows: (i) 50 mM SDS and, (ii) 50 mM SDS + 12.5 mM C$_{12}$TAB. All solutions were prepared in D$_2$O (99.8 atom % D; Aldrich, Milwaukee, WI). The mixed micellar solutions of SDS/C$_{12}$TAB were prepared by adding the SDS and C$_{12}$TAB simultaneously and diluting them with D$_2$O. PFG NMR samples were prepared by introducing the micellar solutions into 5 mm NMR tubes using the procedure described earlier in the section on ionic liquids.

**PFG NMR measurements**

Diffusion studies were performed for a broad range of diffusion times (between around 15 and 120 ms) using the PFG NMR stimulated echo sequence \cite{10,13,21,22,67,119}. This sequence was employed to measure PFG NMR attenuation curves, \textit{i.e.} dependencies of the intensity of PFG NMR signal (A) on the amplitude of the magnetic
field gradients \( g \). The signal intensity was obtained by calculating the area under the selected line(s) of the NMR spectra. To obtain diffusivities in the studied samples the measured attenuation curves were fitted using an equation of the type of Eq. 2.22 with one or several weighted exponential terms corresponding to the existence of one or several different ensembles of the selected type of surfactant with different diffusivities.

Under our experimental conditions, \( \delta \) was always much smaller than the effective diffusion time, i.e. \( t_{\text{eff}} \approx \Delta \). The effective diffusion time was varied by changing the separation between the second and third \( \pi/2 \) r.f. pulses \( (\tau_2) \) of the PFG NMR stimulated echo sequence (Fig. 2-5) and keeping all other parameters of the sequence constant. In these measurements \( \delta \) was equal to 0.67 ms and the separation between the first and the second \( \pi/2 \) pulses \( (\tau_1) \) was equal to 2.17 ms. All measurements were performed at room temperature (293 K) to avoid an occurrence of disturbing convection effects.

**Experimental Results and their Discussion**

Figure 3-10 shows the \(^1\)H NMR spectra of the SDS (Fig. 3-10a) and SDS/C\(_{12}\)TAB (Fig. 3-10b) samples. The spectra were recorded by the stimulated echo PFG NMR sequence with small and intermediate gradient strengths. The three lines between 0.5 and 2 ppm and the line at around 3.9 ppm in the spectra of the SDS sample (Fig. 3-10a) are attributed to CH\(_3\)\(^-\), \(-\text{CH}_2\)\(^-\), and \(-\text{O-CH}_2\)\(^-\) groups of SDS. The lines at around 3.1 and 3.9 ppm in the spectra of the SDS/C\(_{12}\)TAB sample (Fig. 3-10b) are assigned to the N-methyl protons of C\(_{12}\)TAB and to the protons of \(-\text{O-CH}_2\)\(^-\) group of SDS, respectively.
Figure 3-10. Examples of $^1$H NMR spectra of the surfactant samples: pure SDS sample (a) and SDS/C$_{12}$TAB mixture (b). The spectra were recorded by the PFG NMR stimulated echo sequence for $t_{\text{eff}} = 14.78$ ms at small and intermediate gradient strengths $g$: 0.004 Tm$^{-1}$ (small), 0.57 Tm$^{-1}$ (intermediate) in figure (a), and 0.004 Tm$^{-1}$ (small), and 0.75 Tm$^{-1}$ (intermediate) in figure (b). Note that the relative amplitudes of the spectra recorded with the intermediate gradient strengths were significantly increased to facilitate comparison of these spectra with those obtained with the small gradient strength. The CH$_3$ line set at 0.88 ppm was used as an internal standard.
The lines between 0.5 and 2 ppm in these spectra are attributed to CH$_3$– and –CH$_2$– groups of both SDS and C$_{12}$TAB. The line at about 4.7 ppm is assigned to HDO.

The line assignments are summarized in Table 3-5.

Table 3-5. Assignment of the lines of the $^1$H NMR spectra for the surfactant samples shown in Fig. 3-10

<table>
<thead>
<tr>
<th>Frequency in ppm</th>
<th>Group</th>
<th>Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.88</td>
<td>CH$_3$</td>
<td>SDS+ C$_{12}$TAB</td>
</tr>
<tr>
<td>1.3</td>
<td>CH$_2$</td>
<td>SDS+ C$_{12}$TAB</td>
</tr>
<tr>
<td>1.6</td>
<td>CH$_2$</td>
<td>SDS+ C$_{12}$TAB</td>
</tr>
<tr>
<td>3.1</td>
<td>N-CH$_3$</td>
<td>C$_{12}$TAB</td>
</tr>
<tr>
<td>4.0</td>
<td>O-CH$_2$</td>
<td>SDS</td>
</tr>
<tr>
<td>4.7</td>
<td>HDO</td>
<td>Water</td>
</tr>
</tbody>
</table>

Figure 3-11 shows examples of the PFG NMR attenuation curves for the SDS and SDS/C$_{12}$TAB samples. The attenuation curves for the SDS sample were obtained by integrating the area under the CH$_3$–, –CH$_2$–, or O–CH$_2$– lines. Within the experimental uncertainty all lines yielded identical attenuation curves (not shown). This is an expected behavior because all three lines are assigned to SDS. For the SDS/C$_{12}$TAB sample the area under the N-methyl protons line was used to obtain the PFG NMR attenuation curves for C$_{12}$TAB and the area under the O–CH$_2$– line was used to determine the attenuation curves for SDS. In all cases the shape of the lines used for the diffusion studies was found to be independent of the gradient strength (Fig. 3-10). This observation is in agreement with the assignment of these lines to the pure lines of either SDS or C$_{12}$TAB.
Figure 3-11. Examples of $^1$H PFG NMR attenuation curves for diffusion of SDS and C$_{12}$TAB in the studied surfactant samples: diffusion of SDS in the pure SDS sample (a), diffusion of SDS in the SDS/C$_{12}$TAB sample (b), diffusion of C$_{12}$TAB in the SDS/C$_{12}$TAB sample (c). The curves are shown for different effective diffusion times: (■) 14.78 ms (●) 29.78 ms (▲) 59.78 ms (▼) 119.78 ms.

In the presentation of Fig. 3-11 the attenuation curves shown in each graph for different diffusion times are expected to coincide if the effective diffusivity(ies) of the corresponding type of surfactant ions do not change with increasing diffusion times. Non-coinciding attenuation curves in Fig. 3-11 indicate that there is a dependence of diffusion behavior on diffusion time. Fitting attenuation curves in Fig. 3-11 by Eq.2.22 showed that for sufficiently small diffusion times it is necessary to assume the existence of at least two ensembles of each type of surfactants with different diffusivities (i.e. $n=2$ in Eq. 2.22). The resulting best fit values for the diffusivities and the corresponding fractions of the surfactant ensembles are presented in Table 3-6.
This table shows that for both types of surfactants the fraction of the fast component ($a$) is quite small (around 10%) at the smallest diffusion time used (14.78 ms). Increase in the diffusion time leads to a significant increase (i.e., up to 100%) of this fraction. The diffusivities of the fast component decrease slightly with increasing diffusion time. In contrast, the diffusivities of the slow component ($b$) remain essentially the same at all diffusion times used (Table 3-6).

Table 3-6: Results of fitting of the PFG NMR attenuation curves for the surfactant samples shown in Fig. 3-11 by Eq. 2.22 with either one or two exponential terms corresponding to the presence of one or two ensembles of surfactant ions with different diffusivities.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ion</th>
<th>$t_{eff}$(ms)</th>
<th>$a$</th>
<th>$D_a$(m$^2$s$^{-1}$)</th>
<th>$b$</th>
<th>$D_b$(m$^2$s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure SDS</td>
<td>SDS</td>
<td>14.78</td>
<td>0.11±0.03</td>
<td>$(3.2±0.7)\times10^{-10}$</td>
<td>0.89±0.03</td>
<td>$(7.8±0.7)\times10^{-11}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>29.78</td>
<td>0.36±0.03</td>
<td>$(1.4±0.2)\times10^{-10}$</td>
<td>0.64±0.03</td>
<td>$(7.7±0.7)\times10^{-11}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>59.78</td>
<td>0.54±0.04</td>
<td>$(1.3±0.2)\times10^{-10}$</td>
<td>0.46±0.04</td>
<td>$(8.6±0.9)\times10^{-11}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>119.78</td>
<td>1.0±0.1</td>
<td>$(1.29±0.1)\times10^{-10}$</td>
<td>0.0±0.1</td>
<td>-</td>
</tr>
<tr>
<td>SDS/C$_{12}$TAB</td>
<td>SDS</td>
<td>14.78</td>
<td>0.10±0.03</td>
<td>$(3.6±0.7)\times10^{-10}$</td>
<td>0.90±0.03</td>
<td>$(5.9±0.6)\times10^{-11}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>29.78</td>
<td>0.19±0.03</td>
<td>$(1.7±0.2)\times10^{-10}$</td>
<td>0.81±0.03</td>
<td>$(6.3±0.6)\times10^{-11}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>59.78</td>
<td>0.30±0.04</td>
<td>$(1.4±0.2)\times10^{-10}$</td>
<td>0.70±0.04</td>
<td>$(7.1±0.7)\times10^{-11}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>119.78</td>
<td>0.43±0.04</td>
<td>$(1.4±0.2)\times10^{-10}$</td>
<td>0.57±0.04</td>
<td>$(8.0±0.8)\times10^{-11}$</td>
</tr>
<tr>
<td>C$_{12}$TAB</td>
<td>SDS</td>
<td>14.78</td>
<td>0.08±0.03</td>
<td>$(4.0±0.8)\times10^{-10}$</td>
<td>0.92±0.03</td>
<td>$(4.4±0.4)\times10^{-11}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>29.78</td>
<td>0.14±0.03</td>
<td>$(1.7±0.3)\times10^{-10}$</td>
<td>0.86±0.03</td>
<td>$(4.9±0.5)\times10^{-11}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>59.78</td>
<td>0.34±0.03</td>
<td>$(1.5±0.3)\times10^{-10}$</td>
<td>0.66±0.03</td>
<td>$(5.0±0.5)\times10^{-11}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>119.78</td>
<td>0.45±0.04</td>
<td>$(1.5±0.2)\times10^{-10}$</td>
<td>0.55±0.04</td>
<td>$(5.4±0.5)\times10^{-11}$</td>
</tr>
</tbody>
</table>

The PFG NMR attenuation curves for HDO, which were recorded using the line at around 4.7 ppm (Fig. 3-10), have shown monoexponential behavior with the diffusivity independent of the diffusion time in the studied range of the effective diffusion times (14.78 – 119.78 ms). This result confirms the absence of convection or other disturbing effects under the conditions of our PFG NMR measurements.

For diffusion times in the range of milliseconds the surfactant ions of both, viz. the slow and fast components of SDS and C$_{12}$TAB are expected to experience rapid
association and dissociation to and from micelles during the diffusion time because this
time is orders of magnitude larger than the expected average life time of any particular
ion in a micelle \(^{103}\). The slow components, which account for the vast majority of the
SDS and \(\text{C}_{12}\text{TAB}\) ions at small diffusion times, can be attributed to the surfactant ions
which do not experience break up or reformation of micelles during the diffusion time.
For both SDS and \(\text{C}_{12}\text{TAB}\) ions the measured diffusivity of the slow component \((D_b)\) can
be presented in the first approximation as

\[
D_b = p_{\text{mon}} D_{\text{mon}} + p_{\text{mic}} D_{\text{mic}},
\]

where \(D_{\text{mon}}\) and \(p_{\text{mon}}\) denote the diffusivity and fraction of monomeric surfactant ions,
respectively. \(D_{\text{mic}}\) and \(p_{\text{mic}}\) \((p_{\text{mon}} \cdot p_{\text{mic}} = 1)\) are the corresponding diffusivity and fraction of
surfactant ions aggregated into micelles. \(D_{\text{mic}}\) can be understood as a diffusivity of
micelles at sufficiently small diffusion times when micelles do not experience breakup
during the diffusion time. Eq. 3.3 inherently assumes that the aggregation into micelles
is the main type of aggregation and, as a result, the concentration of other types of
surfactant aggregates \(i.e.\) incomplete micelles, micellar aggregates, vesicles \(etc.\) is
negligibly small. For a well studied pure SDS system this assumption is expected to
hold \(^{117}\). Similarity between the values of \(D_b\) for SDS in the pure SDS and SDS/\(\text{C}_{12}\text{TAB}\)
samples (Table 3-6) suggests that this assumption can also be used for the
SDS/\(\text{C}_{12}\text{TAB}\) sample. Experimental evidence recently reported in Ref. 115 indicates that
for an aqueous solution of SDS the second term in Eq.3.3, which is associated with the
diffusion of micelles, is much larger than the first term. Hence, it determines the value of
the effective diffusivity of SDS. It is quite likely that also for the SDS/\(\text{C}_{12}\text{TAB}\) sample,
which exhibits similar value of $D_b$ for SDS, the second term is larger than the first one. Thus, also in this case the diffusivity of micelles determines the overall diffusivity of the slow component.

The fast component (i.e. components (a) in Table 3-6) can be tentatively attributed to the surfactant ions that experience at least one event of either breakup or formation of micelles. In complete analogy with Eq.3.3 the diffusivity of the fast component ($D_a$) can be written as

$$D_a = p_{	ext{mon}} D_{	ext{mon}} + p_{\text{mic}} D_{\text{mic}}/\text{breakup},$$

(3.4)

where $D_{\text{mic}}/\text{breakup}$ is the diffusivity of micelles under the conditions when each micelle has experienced at least one breakup/reformation event during the diffusion time. This diffusivity and its relationship with $D_{\text{mic}}$ can be understood based on the following considerations. A breakup of each micelle is expected to be followed by a micelle formation because the overall concentration of micelles in a macroscopic sample remains the same at all times under the considered steady-state conditions. The latter means that, on average, a surfactant molecule spend the same fraction of diffusion time diffusing as a monomer for all diffusion times, i.e. times larger and smaller than the life time of micelles. A breakup of one micelle occurring simultaneously with a formation of one micelle can be described as a breakup and reformation of the same micelle because the micelles are indistinguishable and there is a rapid exchange of surfactant ions between different micelles. For each such micelle the positions where breakup and reformation occur are usually separated by some non-zero distance. As a result, the value of MSD of all micelles in a macroscopic sample is expected to become larger due to the breakup and reformation events. Consequently, the effective micellar diffusivity,
which can be calculated from the MSD values of micelles using the Einstein relation (Eq. 1.11), is expected to increase with increasing diffusion time from $D_{\text{mic}}$ to $D_{\text{mic/breakup}}$.

The former diffusivity corresponds to diffusion of stable micelles, while the latter one corresponds to micellar diffusion occurring simultaneously with the breakup/reformation events.

In complete agreement with the discussion above, the fraction of the fast component ($a$) was observed to increase with increasing diffusion time (Table 3-6). Such behavior can be explained by an increase in the probability of the micellar breakup and reformation with increasing diffusion time. The data in Table 3-6 indicate that the diffusivity of the fast component shows some tendency to decrease in value with increasing diffusion time. Again, this is an expected behavior because a single breakup/reformation event is expected to lead to a larger relative change in the MSD and in the corresponding effective diffusivity at shorter times, when the displacements due to micelle diffusion are smaller, rather than at longer diffusion times, when such displacements are larger.

Table 3-6 shows that the effective diffusivities of the slow component ($b$) of SDS in the pure SDS sample are, on average, slightly larger the corresponding diffusivities of SDS and of C_{12}TAB in the SDS/C_{12}TAB sample. This is in agreement with the previous observation that an introduction of a small amount of C_{12}TAB to an aqueous solution of SDS can lead to a small increase in the size of micelles \textsuperscript{112}. The latter is expected to result in a decrease of $D_{\text{mic}}$ \textsuperscript{115}. 

Figure 3-12. Dependencies of the values of $b$ on $t_{\text{eff}}$ from Table 3-6 for SDS in the pure SDS sample (■), for SDS in the SDS/C$_{12}$TAB sample (□), and for C$_{12}$TAB in the SDS/C$_{12}$TAB sample (×). The solid lines show the best fit results using Eq. 3.5 with the values of $\tau_b$ equal to $43 \pm 10$ ms, $69 \pm 10$ ms, and $54 \pm 10$ ms for SDS in the pure SDS sample, SDS in the SDS/C$_{12}$TAB sample, and C$_{12}$TAB in the SDS/C$_{12}$TAB sample, respectively.

It is seen in Table 3-6 that a decrease in the fraction of the slow component ($b$) with increasing diffusion time occurs faster in the SDS sample than in the SDS/C$_{12}$TAB samples. Assuming a monoexponential dependence of the fraction ($b$) of the surfactant ions on the effective diffusion time

$$b = \exp\left(\frac{-t_{\text{eff}}}{\tau_b}\right),$$

the characteristic decay times ($\tau_b$) of $43 \pm 10$ ms and of $69 \pm 10$ were obtained for SDS in the SDS and SDS/C$_{12}$TAB samples, respectively. It was found that the characteristic decay time for C$_{12}$TAB in the SDS/C$_{12}$TAB sample ($\tau_b = 54 \pm 10$ ms) was similar to that of SDS in the same sample. The values of $\tau_b$ were obtained by fitting the dependencies
of $b$ on $t_{\text{eff}}$ using Eq. 3.5 (Fig. 3-12). It is important to note that Eq. 3.5 was used merely as an approximation of the dependence of $b$ on $t_{\text{eff}}$. This explains noticeable deviations between the measured and best fit curves for SDS in the pure SDS sample (Fig. 3-12).

The value of $\tau_b = 43 \pm 10$ ms obtained for SDS in the pure SDS sample can be compared with the slow relaxation time (around 150 ms) reported for such sample.\textsuperscript{120} The value of $\tau_b$ can be smaller than the slow relaxation time because $\tau_b$ describes the behavior of the fraction of surfactant ions which did not experience either breakup or formation of micelles, while the slow relaxation time correspond to the average life time of micelles. Clearly, multiple breakup/reformation events occurring with “the same” micelle are expected to make the value of $\tau_b$ shorter than that of the slow relaxation time. This consideration clarifies the origin of the difference between the values of $\tau_b$ and of the slow relaxation time.

An addition of small amount of C\textsubscript{12}TAB to SDS was shown to lead to an increase in the slow relaxation time.\textsuperscript{103} This is in a qualitative agreement with the observation that the value of $\tau_b$ is smaller in the SDS sample than in the SDS/C\textsubscript{12}TAB samples.

The NMR transverse ($T_2$) and longitudinal ($T_1$) relaxation times in the studied systems were sufficiently large (i.e. larger than around 8 ms and 700 ms, respectively) so that under the conditions of our measurements the PFG NMR signal was not significantly reduced by the NMR relaxation. Detailed studies of NMR relaxation behavior were previously used to gain insight on the micelle properties in aqueous solutions of SDS and other surfactants.\textsuperscript{113,114,121,122} It is important to note that such studies are not expected to provide similar type of data on the process of continuous
breakup and reformation of micelles as the diffusion data reported above. The rates of NMR relaxation are mostly determined by the average life time of individual surfactant ions in micelles and by the fractions of free and aggregated surfactant ions in the macroscopic micellar samples\textsuperscript{113,114,121,122}. In contrast to the effective diffusivities of surfactant ions (Fig. 3-11 and Table 3-6), these quantities are expected to remain constant with increasing observation time in the range of milliseconds and larger.

**Summary**

PFG NMR studies of diffusion of surfactant ions were carried out for the aqueous solutions of the anionic surfactant SDS and of the mixture of SDS with the cationic surfactant C\textsubscript{12}TAB (see also Ref.\textsuperscript{123}). For small diffusion times at least two surfactant components with different effective diffusivities were observed for each type of surfactant ions. The fast-diffusing component is tentatively assigned to the surfactant ions which experience breakup or reformation of micelles during the diffusion time of the PFG NMR measurements. The slow-diffusing component is assigned to the surfactant ions that do not experience such events during the diffusion time. This assignment was found to be in agreement with the observed patterns of change of the fractions and diffusivities of these components as diffusion time was increased from around 15 ms to around 120 ms. The fractions of the slow-diffusing component of SDS in the pure SDS sample were observed to be smaller than those in the SDS/C\textsubscript{12}TAB sample. This observation can be explained by stabilization of micelles due to an addition of the cationic surfactant C\textsubscript{12}TAB to the aqueous solution of the anionic surfactant SDS.
CHAPTER 4
SELECTED POROUS SYSTEMS

Transport of guest molecules in many types of materials containing meso- and/or micropores is of great importance for application of these materials in catalysis and separations. In many cases the transport through the meso-microporous network of these materials is the rate limiting step in catalysis and separations; however complete understanding of molecular transport in such situations is still lacking. The results presented in this chapter make a contribution to the development of such understanding. This is achieved by studies of sorbate diffusion and its relation to structure in the following two types of materials: 1) industrial zeolites of the types FAU, EMT, and FAU/EMT intergrowth, and 2) mesoporous silica SBA-15 containing micropores.

Observation of Intraparticle Transport Barriers in FAU/EMT Intergrowth by PFG NMR

Motivation

Intergrowth of a FAU-type zeolite and its hexagonal polymorph known as EMT is of high interest for applications in catalysis. In particular, FAU/EMT intergrowth shows promise as an active and selective cracking catalyst. Recent data indicate that this intergrowth is capable of a better catalytic performance in comparison to a pure FAU zeolite. The structures of FAU and EMT zeolites are closely related. The structure of the former zeolite is formed by the stacking of sodalite layers in a ABCABC sequence, while in the latter the stacking of such layers occurs in a ABABAB sequence. Both structures exhibit three-dimensional systems of relatively large (~1 nm) pores.

Properties of transport of reactant and product molecules in zeolites are of high
importance for applications of these materials in catalysis. Sorbate diffusion in FAU-type zeolites has been extensively investigated using a number of experimental techniques. As a result, detailed data on intracrystalline diffusivities of different types of sorbate molecules are available for this zeolite. In comparison, much less is known about diffusion properties of FAU/EMT intergrowth. A typical particle of this material usually consists of multilayer blocks with EMT structure sandwiched between multilayer blocks with FAU structure. Sorbate diffusion in such particles is expected to be complicated by the existence of the sandwich-like intergrowth structure. In particular, transport barriers can form at the interfaces between the intergrowth components. Transport barriers of this type were previously observed by the interference microscopy technique for MFI crystals exhibiting intergrowth structure. The existence of intracrystalline transport barriers was also observed by pulsed field gradient (PFG) NMR in MFI-type zeolites and in a FAU-type zeolite. Formation of intergrowth structures and other types of structural defects during the process of the crystal growth was discussed as the main reason for the appearance of such barriers. Discrepancies between the diffusion data obtained by PFG NMR and the quasieelastic neutron scattering (QENS) technique were also assigned to the formation of intracrystalline transport barriers in zeolites.

In the studies reported in this chapter PFG NMR was used to investigate sorbate transport inside particles of a FAU/EMT intergrowth. The discussion above indicates that intergrowth can lead to the occurrence of the intraparticle transport barriers. The PFG NMR data discussed below show that such barriers can indeed be observed for diffusion of isooctane in the studied sample of the FAU/EMT intergrowth. Analysis of
these data allowed estimating the characteristic size of the particle components separated by the barriers as well as the barrier permeability. Intraparticle diffusion was also investigated in the pure FAU- and EMT-type zeolites. The diffusion data obtained for these zeolites were used as a reference for the diffusion results obtained for the FAU/EMT intergrowth.

Experimental Details

Materials and material characterization

The zeolite samples were provided by Dr. Prabhakar, UOP LLC, Honeywell International. The details on the preparation of the zeolites and their characterization were obtained from Dr. Prabhakar. The EMT-type zeolite was synthesized as described in\textsuperscript{136} using 18-Crown-6 as template. The FAU-type zeolite was formed using a procedure similar to that reported in\textsuperscript{137}. The starting materials in the synthesis of the latter zeolite were sodium silicate, sodium aluminate, sodium hydroxide, and water. Synthesis of the FAU/EMT intergrowth was performed using mixed templates of 18-crown-6 and 15-crown-5. The Si-to-Al-ratio calculated from ICP ranged from 3 to 6. Powder XRD was used to confirm the formation of the zeolites. For scanning electron microscopy (SEM) images the zeolite samples were ground with mortar and pestle, and then suspended in isopropanol to de-aggregate. The samples were then deposited on a sample grid and lightly coated with Cr. SEM images were recorded at 1.0 kV using a JSM7401F field emission scanning electron microscope. The adsorption isotherms for iso-octane and isobutane were measured at 298.2K using McBein-Bakr balance.

PFG NMR samples were prepared as follows. Around 200 mg of zeolite was introduced into a 5 mm NMR tube. The NMR tube was connected to a custom-made vacuum system (assembled by the author) and the sample was activated, \textit{i.e.} made
sorbate-free, by keeping it under high vacuum at around 600 K for 24 hours. The loading was performed after the sample activation by exposing the zeolite sample to a certain sorbate pressure for at least 4 hours at 298 K. Upon loading, the NMR tube was flame sealed and separated from the vacuum system. Isooctane and isobutane were used as sorbates. For all studied samples the loading pressures were equal to 50 and 200 mbar for isooctane and isobutane, respectively. Such loading procedure resulted in the following sorbate concentrations at 298 K: 182 mg/g for the FAU/EMT intergrowth loaded with isooctane, 134 mg/g for the FAU/EMT intergrowth loaded with isobutane, 229 mg/g for the FAU zeolite loaded with isooctane, 142 mg/g for the FAU zeolite loaded with isobutane, 207 mg/g for the EMT zeolite loaded with isooctane, and 157 mg/g for the EMT zeolite loaded with isobutane. These loadings were estimated by using the isooctane and isobutane adsorption isotherms (not shown) measured for the three zeolites at 298 K.

**PFG NMR measurements**

The diffusion studies in most cases were carried out using the 13-interval PFG NMR sequence with bipolar gradients (Fig. 2-7). In addition, some measurements were performed using the PFG NMR stimulated echo sequence with the longitudinal eddy current delay (PGSTE-LED) (Fig. 2-6). The former sequence (as discussed earlier in Chapter 2) allows reducing or even completely eliminating the disturbing influence of magnetic susceptibility effects. Susceptibility effects are expected for heterogeneous porous materials such as zeolite beds studied in this work. The advantage of the latter sequence is related to the possibility of reducing influence of the transverse \( T_2 \) NMR relaxation on the measured signal (see Chapter 2). Such reduction
is achieved by keeping short the sequence time intervals \( (\tau_1) \) during which this relaxation process reduces the measured signal. Both sequences were used to measure PFG NMR attenuation curves, \textit{i.e.} dependencies of the intensity of PFG NMR signal \( (A) \) on the amplitude of the magnetic field gradient \( (g) \). The signal intensity was obtained by measuring amplitude of the proton NMR lines of the sorbate molecules. The proton NMR spectra of each type of sorbate consisted of a single line. It was verified that the line shape does not depend on the gradient amplitude. Contributions of different types of protons of sorbate molecules to these lines could not be resolved because of large line widths and the related short \( T_2 \) NMR relaxation time of the measured signals.

Effective diffusivities \( D_i \) were obtained from monoexponential (/biexponential) fit of the PFG NMR attenuation curves using Eq. 2.21 (/Eq. 2.22).

Values of the gradient duration \( (\delta) \) and the effective diffusion time \( (t_{eff}) \) were kept constant for measurement of each attenuation curve. The maximum gradient amplitude was around 30 T/m and the gradient duration was varied between around 0.3 and 1.1 ms. The separations between the first and second \( \pi/2 \) r.f. pulses of the 13-interval and PGSTE-LED sequences were between 1.6 and 5 ms. All other important parameters of the PFG NMR measurements are given in the next section below. Under the experimental conditions of the PFG NMR measurements the values of the proton transverse \( (T_2) \) NMR relaxation time were found to be in the range between 1.5 and 3 ms for isooctane and between ~1 and 2 ms for isobutane. The \( T_2 \) NMR relaxation times were determined using the standard Carr-Purcell-Meiboom-Gill (CPMG) sequence.\textsuperscript{16}
The corresponding values of the proton longitudinal ($T_1$) NMR relaxation times were between 300 and 600 ms for isooctane and close to 1 s for isobutane. The $T_1$ NMR relaxation measurements were performed using the inversion recovery pulse sequence.

**Experimental Results and their Discussion**

![SEM images](image)

Figure 4-1. SEM images of the samples of the FAU zeolite. (a), EMT zeolite (b), and FAU/EMT intergrowth (c). The SEM images were provided by the research group of Dr. Prabhakar at UOP LLC., Honeywell International.
Figure 4-1 shows representative SEM images of the three zeolite samples studied in this work. It is seen in Fig. 4-1a that the shape of individual crystals of the FAU zeolite resembles the typical octahedral shape for this zeolite, while the crystals of the EMT zeolite in Fig. 4-1b look like thin hexagonal plates. A typical particle of the FAU/EMT intergrowth, which is shown in Fig. 4-1c, can be described as a sandwich of blocks resembling the shapes of the pure FAU and EMT crystals. The characteristic sizes of individual blocks in the particles of the FAU/EMT intergrowth range between around 0.1 and 1 micron, while the characteristic size of the particles in this sample is found to be around 2.8 µm.

Figure 4-2a shows examples of the attenuation curves measured by the PFG NMR 13-interval sequence for isooctane diffusion in the FAU/EMT intergrowth. The measurements were performed at 264 K for different effective diffusion times in the range between 6 and 40.5 ms. In the presentation of this figure the initial parts of the attenuation curves measured for different effective diffusion times have to coincide (see Eq. 2.21) if the effective diffusivity defined by the initial slope of the attenuation curves does not depend on diffusion time. The results in Fig. 4-2a indicate that under the measurement condition used the effective diffusivity of isooctane is not time-independent because the initial slope of the attenuation curves changes with increasing effective diffusion time. The shape of the attenuation curves in the figure is relatively close to monoexponential in agreement with Eq. 2.21.
Figure 4-2. $^1$H PFG NMR attenuation curves measured for diffusion of isoctane in the FAU/EMT intergrowth. (a) The measurements were performed at $T = 264$ K for the following effective diffusion times: 6.0 ms (■), 10.5 ms (●), 20.5 ms (▲), and 40.5 ms (▼). The lines show the initial slopes of the attenuation curves, fit by Eq. 2.21. (b) The measurements were performed at $T = 289$ K for the following effective diffusion times: 5.7 ms (■), 10.2 ms (●), 40.1 ms (▼), 80.1 ms (□), and 120.1 ms (○). The lines show the best fit curves of the measured data by Eq. 2.22 with $n = 2$. (c) Additional measurements performed at $T = 289$ K with the maximum gradient amplitudes that were much larger than those used in (b) for the following effective diffusion times: 5.4 ms (■), 10.4 ms (●), 20.4 ms (▲), 80.4 ms (□). The measurements were carried for more precise determination of the intraparticle diffusivities. Hence, the initial gradient amplitudes were chosen to be sufficiently high for suppressing any noticeable contribution from the long-range diffusion. The lines show the initial slopes of the attenuation curves, fit by Eq. 2.21.
Table 4-1. Results of fitting of the initial parts of the attenuation curves in Fig. 4-2a by Eq. 2.21 and the corresponding effective diameters of the particle components surrounded by transport barriers ($d_{\text{eff}}$). The values of $d_{\text{eff}}$ were obtained by using Eq. 4.1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>T(K)</th>
<th>$t_{\text{eff}}$(ms)</th>
<th>$D_{\text{eff}}$(m$^2$s$^{-1}$)</th>
<th>Root MSD(µm)</th>
<th>$d_{\text{eff}}$ (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FAU/EMT intergrowth loaded with isoctane</td>
<td>6.0</td>
<td>(1.6±0.2)$\times10^{-12}$</td>
<td>0.24±0.2</td>
<td>0.44±0.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10.5</td>
<td>(9.0±1.4)$\times10^{-13}$</td>
<td>0.24±0.2</td>
<td>0.44±0.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20.5</td>
<td>(5.7±0.9)$\times10^{-13}$</td>
<td>0.26±0.2</td>
<td>0.48±0.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>40.5</td>
<td>(2.7±0.4)$\times10^{-13}$</td>
<td>0.26±0.2</td>
<td>0.48±0.5</td>
<td></td>
</tr>
</tbody>
</table>

The results of fitting of the initial parts of the attenuation curves in Fig. 4-2a by this equation are given in Table 4-1. The data in the table show that the effective diffusivity continuously decreases with increasing diffusion time, while the values of the root MSD remain independent of diffusion time within the experimental uncertainty. The latter values are much smaller than the characteristic size of the particles of the FAU/EMT intergrowth. At the same time, the root MSD values are comparable with the sizes of the individual FAU and EMT blocks forming these particles (see Fig. 4-1c and its discussion). These results can be explained by assuming transport barriers at the interfaces between intergrowth components in the particles of the FAU/EMT intergrowth. Under the measurement conditions used these barriers are essentially impermeable for isoctane molecules, as indicated by the unchanging values of the root MSD in Table 4-1. In the case of such restricted diffusion the probability density distribution is no longer Gaussian. This explains small deviations of the PFG NMR attenuation curves in Fig. 4-2a from the monoexponential behavior$^{10}$. An existence of a distribution over the sizes of the particle components surrounded by the transport barriers may also contribute to the non-monoexponential behavior of the attenuation curves. Assuming that all particle components separated by the transport barriers can
be approximated by spheres with the diameter $d_{\text{eff}}$, the following expression can be used to estimate the value of $d_{\text{eff}}^{10,67,138}:

$$D_{\text{eff}} = \frac{\langle r(t)^2 \rangle}{6t_{\text{eff}}} = \frac{d_{\text{eff}}^2}{20t_{\text{eff}}}.$$  

(4.1)

Table 4-1 presents the values of $d_{\text{eff}}$ that were obtained using Eq. 4.1. It is seen that these values obtained for different diffusion times are all the same within the experimental uncertainty. The values of $d_{\text{eff}}$ characterize the mean size of the particle components surrounded by the transport barriers. This size is found to be within the range of the sizes of the intergrowth components that can be seen in Fig. 4-1c.

Fig. 4-2b shows examples of the measured PFG NMR attenuation curves for isooctane in the FAU/EMT intergrowth at a higher temperature of 289 K. The measurements were performed by the 13-interval PFG NMR sequence. It is seen in Fig. 4-2b that the attenuation curves at large effective diffusion times show fast initial decay, which is followed by much slower signal attenuation at larger gradient strengths. The onset of the slow attenuation shifts to higher attenuation values with increasing diffusion time. Such behavior indicates a transition of the diffusion process from the intraparticle to long-range regimes as diffusion time increases$^{10}$. In the former regime sorbate displacements are smaller than or comparable with the particle sizes, while in the latter regime these displacements are larger than the particle sizes. The sorbate fractions and diffusivities corresponding to intraparticle (slow attenuation) and long-range (fast attenuation) diffusion can be obtained from the biexponential fit of the attenuation curves (Eq. 2.22 with $n = 2$)$^{10}$. Table 4-2 presents the resulting diffusivities and
molecular fractions for intraparticle diffusion ($D_1$ and $p_1$) and for long-range diffusion ($D_2$ and $p_2$).

Table 4-2. Results of fitting of the attenuation curves in Fig. 4-2b by Eq. 2.22 with $n = 2$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T$(K)</th>
<th>$t_{\text{eff}}$(ms)</th>
<th>$D_1$(m$^2$s$^{-1}$)</th>
<th>$p_1$</th>
<th>Root MSD 1 (µm)</th>
<th>$D_2$(m$^2$s$^{-1}$)</th>
<th>$p_2$</th>
<th>Root MSD 2 (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FAU/EMT intergrowth loaded</td>
<td>5.7</td>
<td>4×10$^{-9}$**</td>
<td>0.1±0.07</td>
<td>11**</td>
<td>8×10$^{-12}$*</td>
<td>0.9±0.07</td>
<td>0.5**</td>
<td></td>
</tr>
<tr>
<td>with isooctane</td>
<td>10.2</td>
<td>2×10$^{-9}$**</td>
<td>0.1±0.07</td>
<td>11**</td>
<td>4×10$^{-12}$*</td>
<td>0.9±0.07</td>
<td>0.5**</td>
<td></td>
</tr>
<tr>
<td>289</td>
<td>40.1</td>
<td>6(±3)×10$^{-9}$</td>
<td>0.5±0.1</td>
<td>39±10</td>
<td>2×10$^{-11}$**</td>
<td>0.5±0.1</td>
<td>2**</td>
<td></td>
</tr>
<tr>
<td></td>
<td>80.1</td>
<td>(1.1±0.3)×10$^{-8}$</td>
<td>0.7±0.1</td>
<td>74±11</td>
<td>2×10$^{-11}$***</td>
<td>0.3±0.1</td>
<td>4**</td>
<td></td>
</tr>
<tr>
<td></td>
<td>120.1</td>
<td>(1.3±0.5)×10$^{-8}$</td>
<td>0.8±0.1</td>
<td>96±20</td>
<td>6×10$^{-11}$***</td>
<td>0.2±0.1</td>
<td>6**</td>
<td></td>
</tr>
</tbody>
</table>

large experimental uncertainty in the range of a factor of 4

**large experimental uncertainty in the range of a factor of 2

***large experimental uncertainty in the range of a factor of 15

It is seen in the table that within the experimental uncertainty the values of long-range diffusivities $D_1$ do not depend on diffusion time. At the same time, the fraction of molecules $p_1$ corresponding to long-range diffusion increases significantly with increasing diffusion time. This is an expected behavior for the transition from the intraparticle to long-range diffusion regime with increasing diffusion time$^{10}$. Also, in agreement with the assignment of the ensemble 1 to molecules exhibiting long-range diffusion, the values of the root MSD for this ensemble (Table 4-2) are larger than the characteristic size of the particles of the FAU/EMT intergrowth (~ 2.8 µm). It is seen in Fig. 4-2b that the slopes of the slowly attenuating parts of the curves in this figure cannot be measured precisely because these parts of the curves are almost horizontal. This results in a large experimental uncertainty of the intraparticle diffusivities ($D_2$) in Table 4-2. In order to determine the intraparticle diffusivities with a better precision, the same types of the PFG NMR attenuation curves as those shown in Fig. 4-2b were
recorded for the ranges of the gradient amplitudes where the maximum amplitude was sufficiently large to allow for significant signal attenuation due to intraparticle diffusion and the smallest amplitude was sufficiently large to suppress any contribution from the long-range diffusion. The attenuation curves measured for such gradient ranges using the 13-interval PFG NMR sequence are shown in Fig. 4-2c. In complete analogy with the data in Fig. 4-2a, the initial slopes of the attenuation curves in Fig. 4-2c can be used to estimate intraparticle diffusivities. Table 4-3 shows these diffusivities and the corresponding values of the root MSD.

Table 4-3. Results of fitting of the initial parts of the attenuation curves in Fig. 4-2c by Eq. 2.21

<table>
<thead>
<tr>
<th>Sample</th>
<th>T(K)</th>
<th>$t_{\text{eff}}$(ms)</th>
<th>$D_{\text{eff}}$(m$^2$s$^{-1}$)</th>
<th>Root MSD(µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FAU/EMT intergrowth loaded with isoctane</td>
<td>5.37</td>
<td>(3.5±0.5)×10$^{-12}$</td>
<td>0.34±0.02</td>
<td></td>
</tr>
<tr>
<td>288</td>
<td>10.37</td>
<td>(2.5±0.4)×10$^{-12}$</td>
<td>0.39±0.03</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20.37</td>
<td>(1.5±0.2)×10$^{-12}$</td>
<td>0.43±0.03</td>
<td></td>
</tr>
<tr>
<td></td>
<td>80.37</td>
<td>(4.0±0.6)×10$^{-13}$</td>
<td>0.44±0.04</td>
<td></td>
</tr>
</tbody>
</table>

It is seen in the table that the effective intraparticle diffusivities continuously decrease with increasing diffusion time. This shows that also at a higher temperature of 289 K the intraparticle diffusion of isoctane has a mostly restricted character. The values of the root MSD obtained for this diffusion process increase slowly with increasing diffusion time (Table 4-3). Hence, in contrast to the behavior observed at 264 K, under our measurement conditions at 289 K isoctane molecules show an ability to gradually penetrate through the intraparticle transport barriers. The latter is also manifested by the existence of the molecular fraction exhibiting long-range diffusion. The dependence of this fraction on diffusion time shown in Table 4-2 allows estimating the permeability of the transport barriers that were most clearly observed experimentally.
at 264 K. This permeability can be obtained in the framework of the tracer desorption technique\textsuperscript{10} by estimating the value of the intraparticle mean life time (\( \tau_{\text{intra}} \))

\[
\tau_{\text{intra}} = \int_0^\infty (1 - p_1(t_{\text{eff}})) \, dt_{\text{eff}},
\]

where, in addition to the values of \( p_i \) given in Table 4-2, one can use that \( p_i(0) = 0 \) and \( p_i(\infty) = 1 \). The value of \( \tau_{\text{intra}} \) can be estimated using Eq. 4.2 and taking into account that for the tracer exchange processes strongly influenced by the penetration through the transport barriers \( p_i(t_{\text{eff}}) \approx 1 - \exp\left(-\frac{t_{\text{eff}}}{\tau_{\text{intra}}}\right) \)\textsuperscript{10}. Using this expression it was found that \( \tau_{\text{intra}} = 104 \pm 10 \) ms at 289 K. The intraparticle mean life time is related to the corresponding permeability (\( k_p \)) of the transport barriers\textsuperscript{10}, which separate the particle components with the characteristic diameters equal to \( d_{\text{eff}} \)

\[
\tau_{\text{intra}} \geq \frac{d_{\text{eff}}}{6k_p}.
\]

This relation is justified by the expectation that on their way out of the zeolite particles isooctane molecules have to cross over at least one of the transport barriers separating the particle components with the characteristic diameter \( d_{\text{eff}} \). Using Eq. 4.3 we find \( k_p \geq 0.8 \times 10^{-6} \) m/s at 289 K.

The transport properties of the FAU/EMT intergrowth were also investigated using isobutane as sorbate. Examples of the PFG NMR attenuation curves measured for this smaller sorbate by the 13-interval PFG NMR sequence at 231 K are presented in Fig. 4-3.
Figure 4-3. $^1$H PFG NMR attenuation curves measured for diffusion of isobutane in the FAU/EMT intergrowth at $T=231$ K. The measurements were performed for different effective diffusion times equal to 5.2 ms (■), 10.2 ms (●), 20.1 ms (▲), and 40.1 ms (▼). The lines show the best fit curves of the measured data by Eq.2.22 with $n = 2$.

The results in Fig. 4-3 show behavior corresponding to the transition from the intraparticle diffusion (slow signal attenuation) to the long range diffusion (fast attenuation) as diffusion time increases. Table 4-4 presents the best fit results of the data in Fig. 4-3 using Eq. 2.22 with $n = 2$.

Table 4-4. Results of fitting of the attenuation curves in Fig. 4-3 by Eq. 2.22 with $n = 2$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T$(K)</th>
<th>$t_{\text{eff}}$ (ms)</th>
<th>$D_1$(m$^2$s$^{-1}$)</th>
<th>$p_1$</th>
<th>Root MSD 1 (µm)</th>
<th>$D_2$(m$^2$s$^{-1}$)</th>
<th>$P_2$</th>
<th>Root MSD 2 (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FAU/EMT intergrowth</td>
<td>231</td>
<td>5.2</td>
<td>$(1.6\pm0.5)\times10^{-9}$</td>
<td>0.1±0.05</td>
<td>7±1</td>
<td>$(4.0\pm0.6)\times10^{-11}$</td>
<td>0.9±0.05</td>
<td>1.1±0.1</td>
</tr>
<tr>
<td>loaded with isobutane</td>
<td></td>
<td>10.2</td>
<td>$(1.9\pm0.6)\times10^{-9}$</td>
<td>0.1±0.05</td>
<td>11±2</td>
<td>$(4.8\pm0.7)\times10^{-11}$</td>
<td>0.9±0.05</td>
<td>1.7±0.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20.1</td>
<td>$(1.9\pm0.3)\times10^{-9}$</td>
<td>0.4±0.1</td>
<td>15±1</td>
<td>$(4.8\pm0.7)\times10^{-11}$</td>
<td>0.7±0.1</td>
<td>2.4±0.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>40.1</td>
<td>$(1.6\pm0.2)\times10^{-9}$</td>
<td>0.6±0.1</td>
<td>20±1</td>
<td>$(4.7\pm0.7)\times10^{-11}$</td>
<td>0.4±0.1</td>
<td>3.3±0.4</td>
</tr>
</tbody>
</table>
In complete analogy with the results in Table 4-2, the ensembles 1 and 2 in Table 4-4 can be assigned to the long-range and intraparticle diffusion, respectively. This assignment is consistent with the observation that the root MSD values for the ensembles 1 and 2 are, respectively, larger and comparable/smaller than the characteristic size of the zeolite particles (~2.8 µm). It is seen that within the experimental uncertainty the intraparticle diffusivities in Table 4-4 remain independent of diffusion time. Hence, no indications of a significant influence of the intraparticle transport barriers were observed in this case. The lack of a noticeable influence of the transport barriers on the isobutane diffusion is probably related to a smaller size of this sorbate in comparison to isooctane. It is important to note that for isooctane diffusion the diffusion restrictions by transport barriers were found for much smaller values of the root MSD (<0.5 µm) than those monitored for isobutane (>1.0 µm). PFG NMR diffusion measurements for displacements in the range of 0.5 µm could not be performed for isobutane due to limitations imposed by short $T_2$ NMR relaxation times. The measurements on the displacement length scale of 0.5 µm require temperatures ≤ 220 K, which are significantly lower than $T = 231$ K used in the studies reported above. It was verified that at $T \leq 220$ K the $T_2$ NMR relaxation time of isobutane becomes too short (<1 ms) for any meaningful PFG NMR measurements.

It is of interest to compare intraparticle diffusivities of isooctane and isobutane in the FAU/EMT intergrowth with the corresponding diffusivities in the pure FAU and pure EMT zeolites. Clearly, in the particles of the pure zeolites there is no intergrowth of different zeolite types and no corresponding transport barriers at the interfaces between alternating FAU and EMT blocks. PFG NMR diffusion measurements in the pure
zeolites were performed using the 13-interval PFG NMR sequence for isooctane and PGSTE-LED sequence for isobutane. The PFG NMR 13-interval sequence could not be used for isobutane measurements because under our experimental conditions the values of the $T_2$ NMR relaxation time were too short (~1 ms) for using this sequence. Estimates of the values of the intraparticle diffusivities for isooctane and isobutane in the FAU and EMT zeolites are shown in Table 4-5.

Table 4-5: Estimates of the intracrystalline diffusivities of isooctane and isobutane in the pure FAU and EMT zeolites. The diffusivities were obtained for the shown range of the effective diffusion times and the corresponding values of the root MSD by fitting the measured PFG NMR attenuation curves using Eq. 2.21 or Eq. 2.22 with $n = 2$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T$(K)</th>
<th>$D$(m$^2$s$^{-1}$)</th>
<th>The Range of $t_{eff}$ Values (ms)</th>
<th>The Range of Root MSD Values ($\mu$m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FAU loaded with isooctane</td>
<td>266</td>
<td>(3.7±0.7)$\times$10$^{-12}$</td>
<td>9.5 - 39.5</td>
<td>0.5 - 0.9</td>
</tr>
<tr>
<td>EMT loaded with isooctane</td>
<td>264</td>
<td>(1.7±0.3)$\times$10$^{-12}$</td>
<td>9.2 - 39.2</td>
<td>0.3 - 0.6</td>
</tr>
<tr>
<td>FAU loaded with isobutane</td>
<td>225</td>
<td>(1.0±0.8)$\times$10$^{-11}$</td>
<td>4.8*</td>
<td>0.5</td>
</tr>
<tr>
<td>EMT loaded with isobutane</td>
<td>233</td>
<td>(1.8±1.0)$\times$10$^{-11}$</td>
<td>2.8 - 4.8</td>
<td>0.6 - 0.7</td>
</tr>
</tbody>
</table>

*Intraparticle diffusivity was measured for a single diffusion time because the measurements required a significant signal averaging due to a low value of the $T_2$ NMR relaxation time (~ 1 ms).

These values were obtained in the same way as discussed above by fitting the measured PFG NMR curves using Eq. 2.21 for pure intraparticle diffusion or Eq. 2.22 with $n = 2$, for a transition range between the intraparticle and long-range diffusion. The data for the pure zeolites were obtained at the same or comparable temperatures as those used in the studies of the FAU/EMT intergrowth. In all cases no dependence of the intraparticle diffusivities on diffusion time was observed for the pure zeolite samples. The lack of such dependence indicates that for the measured range of the root MSDs there are no significant diffusion restrictions by transport barriers inside the particles of
the pure zeolite samples. It is seen from the data in Tables 4-4 and 4-5 that at around 230 K the intraparticle diffusivity of isobutane in the pure FAU and EMT zeolites was similar or even slightly lower than the corresponding diffusivity in the FAU/EMT intergrowth. It is expected that the effective diffusivity in the latter zeolite has to be much lower than those in the two former zeolites if the restricted diffusion effects due to intraparticle transport barriers are significant in the FAU/EMT intergrowth. The absence of such relationship between the isobutane diffusivities in the three zeolites confirms our conclusion about the lack of any large transport restrictions by intraparticle barriers in the case of isobutane diffusion in the FAU/EMT intergrowth. In contrast to the isobutane data, the effective intraparticle diffusivities of isooctane in the FAU and EMT samples were found to be significantly higher than that in the FAU/EMT intergrowth for large diffusion times at 264 K (compare data in Tables 4-1 and 4-5). Clearly, the isooctane data in Tables 4-1 and 4-5 are in agreement with the conclusion that the isooctane diffusion in the FAU/EMT intergrowth at 264 K is strongly influenced by the intraparticle transport resistances resulting in lower effective intraparticle diffusivities in the intergrowth in comparison to those in the pure zeolites.

It is quite likely that the intraparticle transport barriers, which are reported in this chapter, are located at the interfaces between intergrowth components of the FAU/EMT intergrowth. Similar intracrystalline transport barriers were observed previously in other zeolite types.\textsuperscript{130-133} It can be assumed that the reason for the existence of the barriers is a partial blockage of the channel openings at the interfaces. Such assumption is in agreement with the observed reduction of the influence of the transport barriers on the
overall diffusion process due to either temperature increase or decrease of the size of sorbate molecules.

The data in Table 4-5 show that the value of the intraparticle diffusivity of isooctane in the FAU zeolite is approximately a factor of two higher than that in the EMT zeolite. This observation correlates with the fact that the size of the channels connecting cages is somewhat smaller in the latter zeolite than in the former.\textsuperscript{125} For relatively bulky molecules, including isooctane, such difference in the channel sizes can be a reason of a slower diffusion in the EMT zeolite in comparison to that in the FAU zeolite. Similar analysis for isobutane was prevented by the large experimental uncertainty of the isobutane diffusivities (Table 4-5).

\textbf{Summary}

PFG NMR technique was used to study diffusion of isooctane and isobutane in a sample of FAU/EMT intergrowth (see also Ref.\textsuperscript{139}). The PFG NMR data obtained for diffusion of isooctane at a relatively low temperature (264 K) provide evidence for the existence of strong transport barriers inside particles of the intergrowth. It was found that when the same types of measurements are performed with isooctane at a higher temperature (289 K) or when using a smaller sorbate (isobutane) the influence of such barriers on the diffusion process becomes smaller or even nonexistent. Comparison of the diffusion data for the FAU/EMT intergrowth with the corresponding results obtained for the pure forms of the FAU and EMT zeolites confirms the conclusion about the existence of intraparticle transport barriers in the FAU/EMT intergrowth. A partial blockage of the channel openings at the interfaces between the intergrowth components of the FAU/EMT particles is suggested as a possible reason for the observed transport barriers.
Application of PFG NMR to Study Sorbate Diffusion in Mesoporous Silica SBA-15

Motivation

Mesoporous silica SBA-15\textsuperscript{140} attracts significant interest of the research community due to the possibility to use this type of mesoporous materials in catalysis and separations as well as for selective adsorption and immobilization of biomolecules\textsuperscript{141-143}. SBA-15 exhibits two-dimensional hexagonal p6mm symmetry with monodispersed cylindrical mesopores, which can be tailored to have diameters in the range between 4 and 22 nm. SBA-15 materials possess some intrawall porosity which may change from a corona of micropores to interconnecting small mesopores depending on synthesis conditions\textsuperscript{144,145}.

Properties of sorbate transport in SBA-15 are quite important for the majority of the potential applications of these materials. Despite their importance, these properties have not been studied as much as those of zeolites. Only a few recent investigations of molecular diffusion in SBA-15 materials can be found in the literature. In particular, in reference\textsuperscript{146} zero length column (ZLC) technique was applied to study diffusion of n-heptane in SBA-15 samples. Due to the limitation of this technique requiring that diffusion measurements are performed in the limiting case of low sorbate loadings, the data reported in this work corresponds, for the most part, to surface diffusion of n-heptane along the walls of mesoporous channels. A high content of micropores in these walls is expected to lead to the resemblance of the diffusion process along/in the mesopore walls to that in pure microporous materials. This expectation was found to be consistent with relatively low values of n-heptane diffusivities obtained by ZLC (10\textsuperscript{-14} m\textsuperscript{2}/s - 10\textsuperscript{-13} m\textsuperscript{2}/s) at temperatures close to 300 K\textsuperscript{146}. It was observed that a decrease in the micropore content results in an increase in the measured diffusivities.
Among the microscopic techniques used to study transport properties of porous materials pulsed field gradient (PFG) NMR was shown to be particularly useful. This technique was recently applied to study self-diffusion of benzene and nitrobenzene in the pore systems of SBA-15 under the conditions when the pores were fully saturated with the sorbate. In order to exclude contribution of sorbate diffusion in the gaps between SBA-15 particles to the recorded diffusion data, the PFG NMR measurements were performed at sufficiently low temperatures when the sorbate located between the SBA-15 particles was frozen. The measured diffusivities along the main mesoporous channels were found to be several orders of magnitude higher than those obtained by ZLC in . In particular, the PFG NMR measurements provided values around \(10^{-10}\) m\(^2\)/s for diffusion of nitrobenzene along the SBA-15 channels at 253 K. In contrast to the ZLC measurements, the PFG NMR studies were performed under conditions when the SBA-15 channels were completely saturated by the liquid sorbate. Hence, surface diffusion is not expected to play a dominant role in the overall diffusion process investigated by PFG NMR in Refs. At the same time, surface diffusion is likely to be the main contributor to the diffusion process investigated by ZLC in Ref. Such difference in the diffusion mechanism certainly contributes to the large difference between the diffusivities measured by the two techniques. Another contribution to this difference can arise from the fact that PFG NMR records self-diffusion coefficients while ZLC measures transport diffusivities.

In this work PFG NMR has been applied to study intraparticle diffusion of toluene in SBA-15 materials. Unlike previous studies, new diffusion measurements were performed under conditions where the adsorbed phase is in equilibrium with the
surrounding gas phase between the SBA-15 particles. Thus, the adsorbed sorbate molecules have a possibility to desorb and perform long range diffusion in the space between the particles. Diffusion data measured by PFG NMR will be compared with those obtained by tracer ZLC( TZLC), viz. a modified ZLC technique capable of self-diffusion measurements. The TZLC studies were performed by the research group of Dr. Mladen Eic, University of New Brunswick, Canada. TZLC results will not be discussed in this dissertation.

**Experimental Details**

**Materials and PFG NMR sample preparation**

Two samples of mesoporous silica SBA-15 were supplied by the research group of Dr. Eic. The samples were synthesized using the procedure reported by Zhao et al. The two samples are primarily distinguished from each other due to a difference in the pore sizes. Such difference was a consequence of using different temperatures for hydrothermal treatment (aging). The samples are denoted as SBA-15-\( T \) with the aging temperature \( T \) expressed in degrees Celsius. Sample characterization data (SEM and TEM) and nitrogen adsorption and desorption isotherms information were also provided to us by Dr. Eic and by another collaborator (Dr. Serge Kaliaguine, Université Laval, Canada). Table 4-6 shows the data obtained from Nitrogen adsorption/desorption isotherms. The pore system of SBA-15 materials consists of long monodispersed non intersecting mesopores. Presence of some small intrawall porosity in form of micropores, which may or may not interconnect the larger mesopore channels, has been suggested by additional data provided by Dr. Eic. Fig. 4-4 shows a schematic of pore system in SBA-15 materials.
Table 4-6. Textural properties for SBA-15 materials obtained from the measurements of the nitrogen adsorption/desorption isotherms.

<table>
<thead>
<tr>
<th>Materials</th>
<th>( S_{\text{BET}} )</th>
<th>( V_t )</th>
<th>( S_{\text{NL-DFT}} )</th>
<th>( V_{\text{NL-DFT}} )</th>
<th>( V_{\text{mNL-DFT}} )</th>
<th>( W_{\text{NL-DFT}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBA-15-80</td>
<td>717</td>
<td>0.81</td>
<td>671</td>
<td>0.77</td>
<td>0.057</td>
<td>6.8</td>
</tr>
<tr>
<td>SBA-15-130</td>
<td>493</td>
<td>1.15</td>
<td>450</td>
<td>1.10</td>
<td>-</td>
<td>9.3</td>
</tr>
</tbody>
</table>

\( S_{\text{BET}} \) is the nitrogen BET specific surface area calculated from the isotherm analysis in the relative pressure range of 0.10-0.20; \( V_t \) is the total pore volume at relative pressure 0.99. \( S_{\text{NL-DFT}} \) is the specific surface area; \( V_{\text{NL-DFT}} \) is the total pore volume, \( V_{\text{mNL-DFT}} \) is the micropore volume and \( W_{\text{NL-DFT}} \) is the mesopores diameter, calculated by the DFT method using the kernel of NL-DFT equilibrium capillary condensation isotherms of \( \text{N}_2 \) at 77 K on silica (cylinder, pore, NL-DFT adsorption branch model).

Table 4-6 shows results of the characterization of textural properties of the samples. The data in the table were obtained from the measurements of the nitrogen adsorption/desorption isotherms (not shown). These data indicate that in SBA-15-130 the diameter of the primary mesopores is larger and the thickness of the walls separating these mesopores is smaller in comparison to SBA-15-80. The total volume of micropores is also smaller in SBA-15-130 than in SBA-15-80. The essentially nil value for micropore volume in SBA-15-130 is fully expected\(^{10}\). The mean particle sizes, as provided by Dr Eic, for SBA-15-80 and SBA-15-130 are 7 and 9 µm respectively.
PFG NMR samples were prepared using the same approach described earlier for preparation of the zeolite samples. For the case of SBA-15 materials, a lower activation temperature of 403 K was used instead of 600 K used for the zeolites. For all studied samples the sorbate (toluene) loading pressure at 298 K was equal to 22 Torr. This pressure was selected based on the measurements of the adsorption isotherms for toluene in the studied SBA-15 samples at 298 K. The measured adsorption/desorption branches of the isotherms (not shown) indicate that for both samples the sorption equilibrium with 22 Torr of toluene corresponds to the situation when all meso- and micropores of the SBA-15 particles are completely filled with toluene but, at the same time, there is no capillary condensation of toluene in the gaps between the particles. The corresponding toluene loadings were found to be equal to 6.7 and 10 mmol/g for SBA-15-80 and SBA-15-130, respectively.
**PFG NMR measurements**

PFG NMR Diffusion studies were carried out for different diffusion times using the PFG NMR stimulated echo sequence with the longitudinal eddy current delay (PGSTE-LED) (Fig. 2-6)\(^{151}\). The sequence was used to measure PFG NMR attenuation curves, *i.e.* dependencies of the intensity of PFG NMR signal \( (A) \) on the amplitude of the magnetic field gradients \( (g) \). The signal intensity was obtained by integrating the area under the proton NMR line of toluene. The signal intensity was obtained by integrating the area under the two partially overlapping lines of toluene at approximately 7.2 and 2.2 ppm. It was verified that identical PFG NMR attenuation curves are recorded for each of the lines under the same measurement conditions.

In general, for diffusion of sorbate molecules in beds of porous particles the following two main types of transport can be observed: diffusion for displacements smaller than the size of individual porous particles (intraparticle diffusion), and diffusion for displacements much larger that the size of individual particles (long-range diffusion). For isotropic transport inside porous particles with the identical transport properties the intraparticle diffusion can be characterized by a single diffusivity. Values of this diffusivity are usually smaller than those for long-range diffusion. The diffusivities and fractions corresponding to these two types of sorbate transport can be obtained from biexponential fit of PFG NMR attenuation curves using Eq. 2.22 with \( n = 2 \). Here the two ensembles (see Eq. 2.22) \( p_1 \) and \( p_2 \) would correspond to the long-range diffusion and intraparticle diffusion.

In the case of diffusion in a bed of SBA-15 particles the intraparticle diffusivity in the direction of the main mesoporous channels and the corresponding diffusivity in the
direction perpendicular to these channels can be expected to be different. The latter
diffusivity can have a non-zero value if the primary cylindrical mesopores are
interconnected by additional meso- and/or micropores located in the walls of the
mesoporous channels. For such a case of anisotropic diffusion Eq. 2.22 is not expected
to provide the most accurate description of the signal attenuation. Instead the following
equation can be used:

\[
\psi = \psi_1 \exp \left( - \left( \gamma \delta g \right)^2 t_{\text{eff}} D_1 \right) + p_2 \frac{\sqrt{\pi}}{2} \exp \left( - \left( \gamma \delta g \right)^2 t_{\text{eff}} D_{\text{perp}} \right) \frac{\text{erf} \left( \sqrt{\left( \gamma \delta g \right)^2 t_{\text{eff}} \left[ D_{\text{par}} - D_{\text{perp}} \right]} \right)}{\sqrt{\left( \gamma \delta g \right)^2 t_{\text{eff}} \left[ D_{\text{par}} - D_{\text{perp}} \right]}},
\]

where \( D_{\text{perp}} \) and \( D_{\text{par}} \) denote respectively intraparticle diffusivities in the directions
perpendicular and parallel to the direction of the main mesoporous channels of the
SBA-15 particles. \( p_1 \) and \( p_2 \) are, respectively, the fractions of sorbate molecules
performing long range and intraparticle diffusion.

PFG NMR diffusion studies of porous materials are routinely performed using
pulse sequences with bipolar gradients, such as the 13-interval PFG NMR sequence
(Fig. 2-7). These sequences allow reducing or even completely eliminating the
disturbing influence of magnetic susceptibility effects that can be expected for beds of
porous particles. PFG NMR sequences with bipolar gradients were not used in the
present work because under our experimental conditions the values of the transverse
\( T_2 \) NMR relaxation time of toluene in the studied SBA-15 samples were found to be
too short (between 0.5 and 1 ms) for using such sequences. In order to verify that the
diffusion data obtained by the PGSTE-LED sequence were not distorted by the
susceptibility effects the measurements with this sequence were performed with
different values of the time interval between the first and the second $\pi/2$ r.f. pulses of the sequence $(\tau_1)$ and the same value of $t_{\text{eff}}$. In particular, it was observed that changing the value of $\tau_1$ from 0.75 ms to 1.0 ms does not influence the diffusion data. This observation indicates that under our experimental conditions the diffusion results were not perturbed by the susceptibility effects $^{94}$. Measurement of each PFG NMR attenuation curve was performed by changing the amplitude of the applied gradient and keeping all other parameters of the PGSTE-LED sequence constant. The duration of the gradient pulses used in our measurements was in the range between 0.1 and 0.3 ms.

**Experimental Results and their Discussion**

Figure 4-5 shows the PFG NMR attenuation curves measured at 298 K for the same toluene loadings in SBA-15-80 and SBA-15-130. The measurements were performed for different diffusion times. In the presentation of Fig. 4-5 the attenuation curves measured for different diffusion times have to coincide if the diffusion behavior and the corresponding sorbate diffusivities remain independent of diffusion time. Clearly, the data in Fig. 4-5 show strong dependence on diffusion time.

The pattern of changes of the attenuation curves with increasing diffusion time is similar to that observed for the transition from the intracrystalline to long-range diffusion regimes in beds of zeolite crystals $^{10}$. Thus, it can be assumed that the results in Fig. 4-5 correspond to the transition from intraparticle diffusion, which is expected for short diffusion times, to long-range diffusion, which is expected for large diffusion times.
Figure 4-5. $^1$H PFG NMR attenuation curves measured for diffusion of toluene in the samples of SBA15-80 (a), and SBA15-130 (b). The measurements were performed at $T = 298$ K for the following effective diffusion times: 1.9 ms (■), 5 ms (●), 10 ms (▲), 20 ms (▼), and 100 ms (○). Solid lines show the best fit curves obtained by using Eq. 2.22.
Table 4-7. Results of fitting of the PFG NMR attenuation curves in Fig. 4-5 by Eq. 2.22

The values of root MSD were obtained using Eq. 4.5 with $n = 3$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T$(K)</th>
<th>$t_{\text{eff}}$(ms)</th>
<th>$D_1$(m$^2$s$^{-1}$)</th>
<th>$p_1$</th>
<th>Root MSD 1 (µm)</th>
<th>$D_2$(m$^2$s$^{-1}$)</th>
<th>$P_2$</th>
<th>Root MSD 2 (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBA15-80</td>
<td>298</td>
<td>1.9</td>
<td>$6.2\pm0.8 \times 10^{-8}$</td>
<td>0.81±0.05</td>
<td>27±1</td>
<td>$(8.7\pm1.5)\times 10^{-9}$</td>
<td>0.19±0.05</td>
<td>10±1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.0</td>
<td>$6.7\pm0.7 \times 10^{-8}$</td>
<td>0.95±0.03</td>
<td>45±2</td>
<td>$(8.3\pm3)\times 10^{-9}$</td>
<td>0.05±0.03</td>
<td>16±4</td>
</tr>
<tr>
<td>SBA15-130</td>
<td>298</td>
<td>10.0</td>
<td>$6.3\pm0.6 \times 10^{-8}$</td>
<td>1</td>
<td>61±3</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20.0</td>
<td>$7.1\pm0.7 \times 10^{-8}$</td>
<td>1</td>
<td>92±6</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100.0</td>
<td>$8.1\pm0.8 \times 10^{-8}$</td>
<td>1</td>
<td>222±10</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.9</td>
<td>$8.2\pm0.9 \times 10^{-8}$</td>
<td>0.82±0.05</td>
<td>31±1</td>
<td>$(9\pm2)\times 10^{-9}$</td>
<td>0.18±0.05</td>
<td>10±1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.0</td>
<td>$9.3\pm0.9 \times 10^{-8}$</td>
<td>0.89±0.05</td>
<td>53±2</td>
<td>$(8\pm2)\times 10^{-9}$</td>
<td>0.11±0.05</td>
<td>15±2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10.0</td>
<td>$9.3\pm0.9 \times 10^{-8}$</td>
<td>0.92±0.03</td>
<td>75±3</td>
<td>$(9\pm3)\times 10^{-9}$</td>
<td>0.08±0.03</td>
<td>24±5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20.0</td>
<td>$1.5\pm0.2 \times 10^{-7}$</td>
<td>0.79±0.05</td>
<td>134±8</td>
<td>$(3.0\pm0.4)\times 10^{-8}$</td>
<td>0.21±0.05</td>
<td>60±4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100.0</td>
<td>$1.2\pm0.1 \times 10^{-7}$</td>
<td>1</td>
<td>268±11</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

It is important to note that the observed dependencies of the PFG NMR attenuation curves on diffusion time can be affected by the longitudinal NMR relaxation process if the time constant of this process ($T_1$) for toluene is smaller than or comparable with the diffusion time. However, under our experimental conditions $T_1 \geq 4$ s, i.e. much larger than the diffusion times used. Hence, we can conclude that the measured time dependencies of the attenuation curves were not perturbed by the $T_1$ relaxation effects.

Table 4-7 shows results of fitting of the attenuation curves in Fig. 4-5 by Eq. 2.22. This equation assumes isotropic 3-dimensional diffusion for two ensembles of sorbate molecules. In addition to the diffusivities and fractions of sorbate ensembles, Table 4-7 also presents the corresponding values of the square roots of the mean square displacements (MSD). The MSD values were calculated using the Einstein relation (see Eq. 1.11 and 1.12). The generalized form of this equation can be written as

$$ \left\langle r^2(t_{\text{eff}}) \right\rangle = 2nD t_{\text{eff}}, $$ (4.5)
where $n$ denotes dimensionality of the diffusion process ($n = 3$ for three-dimensional diffusion). The ensemble 1 in Table 4-7 can be assigned to long-range diffusion based on the following considerations. It is seen that the fraction of this ensemble increases with increasing diffusion time and the root MSD values are in all cases much larger than the characteristic sizes of SBA-15 particles in the studied samples. In contrast, the root MSD values of ensemble 2 are only slightly larger than that of the particle sizes. Hence, this ensemble corresponds to intraparticle diffusion with some contribution from the diffusion in the gas phase between the particles. The existence of such contribution of isotropic 3-dimensional diffusion in the gas phase makes the overall process of diffusion of ensemble 2 close to that of isotropic 3-dimensional diffusion, even when transport inside the particles is anisotropic. This consideration justifies application of Eq. 2.22, for fitting of signal attenuation, which assumes isotropic 3-dimensional diffusion for both ensembles 1 and 2.

Based on the discussion above it can be concluded that the intraparticle diffusivities at 298 K are expected to be smaller than the corresponding values of $D_i$ in Table 4-7. Obtaining more precise estimates of the intraparticle diffusivities would require PFG NMR measurements for diffusion times much smaller than the smallest effective diffusion time used (1.9 ms). Under our experimental conditions measurements at $t_{\text{eff}} < 1.9 \text{ ms}$ were not technically possible. However, it was possible to perform PFG NMR studies at lower temperatures resulting in a reduction of the measured root MSD values for the same smallest diffusion time of 1.9 ms. Data obtained from such studies at a lower temperature are discussed below.
Figure 4-6. $^1$H PFG NMR attenuation curves measured for diffusion of toluene in the samples of SBA15-80 (a), and SBA15-130 (b). The measurements were performed at $T = 273$ K for the following effective diffusion times: 1.9 ms (■), 3.4 ms (♦), 4.9 ms (●), 20 ms (▼), and 100 ms (○). Solid lines show the best fit curves obtained by using Eq. 2.22 with n=2.
Figure 4-6 presents measured PFG NMR attenuation curves for diffusion of toluene in the SBA-15 samples at 273 K. It was verified that limitations imposed by short $T_1$ NMR relaxation time prevent similar PFG NMR measurements at $T < 273 \text{K}$. In complete analogy with the data in Fig. 4-5, changes in the attenuation curves with increasing diffusion time in Fig. 4-6 show a familiar pattern of transition from intraparticle to long-range diffusion.

Table 4-8 shows the result of fitting of these curves by Eq. 2.22 with $n=2$. It is seen that in contrast to the data for 298 K, the root MSD values of the ensemble 2 obtained for the smallest diffusion time at 273 K are smaller than the characteristic particle sizes for both SBA-15 samples. Hence, the values of the corresponding diffusivities are expected to give satisfactory estimates of intraparticle diffusivities in the limiting case of isotropic 3-dimensional diffusion inside the particles. The diffusivity values for another limiting case of purely 1-dimensional diffusion inside the particles can be obtained by fitting the attenuation curves for the smallest diffusion time in Fig. 4-6 by Eq. 4.4 where $D_{\text{perp}}$ is assumed to be equal to zero. The resulting 1-dimensional
diffusivities and the corresponding values of the root MSD are given in Table 4-9. The root MSD values were calculated using Eq. 4.5 with $n = 1$. It was found that a significant contribution of long-range diffusion to the attenuation curves in Fig. 4-6 makes a procedure of direct determination of the values of $D_{\text{par}}$ and $D_{\text{perp}}$ from fitting the attenuation curves by Eq. 4.4 too uncertain. Therefore, the results of such fit are not shown.

Table 4-9. Results of fitting of the PFG NMR attenuation curves in Fig. 4-6 for $t_{\text{eff}} = 1.9$ ms by Eq. 4.4 with $D_{\text{perp}} = 0$. The values of root MSD were obtained using Eq. 4.5 with $n = 3$ and 1 for ensembles 1 and 2, respectively.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T$(K)</th>
<th>$t_{\text{eff}}$(ms)</th>
<th>$D_{f}$(m$^2$s$^{-1}$)</th>
<th>$p_{1}$</th>
<th>Root MSD 1 (µm)</th>
<th>$D_{\text{par}}$(m$^2$s$^{-1}$)</th>
<th>$P_{2}$</th>
<th>Root MSD 2 (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBA15-80</td>
<td>273</td>
<td>1.9</td>
<td>(3.6±0.4)$\times$10$^{-8}$</td>
<td>0.59±0.7</td>
<td>20±1</td>
<td>(3.4±0.7)$\times$10$^{-9}$</td>
<td>0.41±0.7</td>
<td>4±1</td>
</tr>
<tr>
<td>SBA15-130</td>
<td>273</td>
<td>1.9</td>
<td>(5.0±0.5)$\times$10$^{-8}$</td>
<td>0.37±0.7</td>
<td>24±1</td>
<td>(5.0±0.9)$\times$10$^{-8}$</td>
<td>0.63±0.7</td>
<td>14±2</td>
</tr>
</tbody>
</table>

Intraparticle diffusivities can also be obtained in the framework of the NMR tracer desorption technique by estimating the value of the intraparticle mean life time ($\tau_{\text{intra}}$)

$$
\tau_{\text{intra}} = \int_{0}^{\infty} \left(1 - p_{2}^* \left(t_{\text{eff}}\right)\right) dt_{\text{eff}},
$$

(4.6)

where $p_{2}^* \left(t_{\text{eff}}\right)$ denote the time-dependent fraction of sorbate molecules corresponding to intraparticle diffusion. Assuming that $p_{2}^* \left(t_{\text{eff}}\right) \approx 1 - \exp\left(t_{\text{eff}}/\tau_{\text{intra}}\right)$ and using the values of $p_{2}^* = p_{2}$ for the smallest diffusion time (1.9 ms) at 273 K in Table 4-8 we estimate $\tau_{\text{intra}} \approx 2$ ms for both samples. The intraparticle mean life time is related to the intraparticle diffusivity and the corresponding permeability of the external particle surface ($k_{p}$)

$$
\tau_{\text{intra}} = \frac{R^2}{15D_{2}} + \frac{R}{3k_{p}},
$$

(4.7)
where it was assumed that the intraparticle transport can be approximated as 3-dimensional isotropic diffusion with the diffusivity $D_2$ in spherical particles of radius $R$.

Using

$$D_2 \geq \frac{R^2}{15\tau_{\text{intra}}} \quad (4.8)$$

we obtain that $D_2 \geq 5 \times 10^{-10}$ m$^2$/s for SBA-15-80 and $D_2 \geq 6 \times 10^{-10}$ m$^2$/s for SBA-15-130 at 273 K. These estimates of intraparticle diffusivities are in agreement with the corresponding diffusion data in Table 4-8.

The estimates of intraparticle diffusivities of toluene obtained by the fitting of PFG NMR attenuation curves for the smallest diffusion time and by the NMR tracer exchange approach provide, respectively, the upper and lower estimates for the intraparticle diffusion coefficients of toluene. Using these considerations and assuming 3-dimensional intraparticle diffusion we obtain that the values of effective intraparticle diffusion coefficients in the SBA15 particles are $5 \times 10^{-10} \leq D \leq 8 \times 10^{-10}$ m$^2$/s for SBA15-80 and $6 \times 10^{-10} \leq D \leq 3.7 \times 10^{-9}$ for SBA-15-130. These estimates are in general agreement with the expectation that the intraparticle diffusivity in SBA15-130 can be somewhat larger than that in SBA15-80 because the mesopore diameter in the latter material (6.8 nm) is smaller than that in the former (9.3 nm) (see Table 4-6).

**Summary**

The reported above studies in SBA-15 materials are discussed in Ref.\textsuperscript{152} PFG NMR diffusion measurements were performed to study self-diffusion of toluene in two SBA-15 samples under the conditions when toluene completely fills all meso- and micropores of SBA-15 particles. Unlike previous measurements, where the sorbate
between the particles was frozen, these measurements were performed under conditions where the adsorbed phase is in equilibrium with the surrounding gas phase between the SBA-15 particles. Such a situation is most relevant to the potential application of these materials in separations and catalysis. Dependence of the PFG NMR attenuation curves on diffusion times and the pattern of their changes with increasing diffusion time are indicative of transition between intraparticle diffusion at small diffusion times to long range diffusion at sufficiently large diffusion times. Intraparticle diffusivities of toluene obtained by the two methods used (namely, by direct PFG NMR measurements and by using NMR tracer exchange approach) were found to be in good agreement.
CHAPTER 5
WORK IN PROGRESS

Many advances in industrial and scientific applications related to catalysis and separations rely on fundamental understanding of diffusion processes in porous materials. Such materials usually are structurally heterogeneous. Many types of porous membranes and catalyst particles contain microporous crystals, which are interconnected by larger meso and macropores. While diffusion inside the well ordered micropore systems of the microporous crystals (e.g. zeolites) has been a subject of large number of experimental and computational studies, properties of sorbate transport on length scales comparable to separations between microporous crystals in zeolite beds, membranes and catalyst particles have not been investigated sufficiently well. Transport of guest molecules through or near the external surface of microporous crystals can significantly affect the overall rate of transport in membranes and catalysts. Here a new experimental methodology is reported that was developed to study how often desorption of sorbate molecules from a microporous crystal is followed by fast re-adsorption into the same crystal. The experimental approach is based on application of continuous flow hyperpolarized $^{129}$Xe 2D NMR exchange spectroscopy (2D EXSY). First results of the study of desorption/re-adsorption events of Xe from/to NaY zeolite crystals are presented in this chapter.

The experimental data will be compared with the corresponding results of the dynamic Monte Carlo simulations. These simulations were developed by an undergraduate student Mr. Robert Muller, who worked under the author’s supervision.
Hyperpolarized $^{129}$Xenon 2D Exchange NMR Spectroscopy

Hyperpolarized $^{129}$Xe two-dimensional Exchange spectroscopy (Xe 2D EXSY) is a method that combines the use of enhanced NMR sensitivity of $^{129}$Xe hyperpolarization with two-dimensional (2D) exchange NMR spectroscopy to perform an NMR based tracer exchange experiment. Tracer exchange based experiments typically monitor the rate of release or uptake of a fraction of sorbate molecules, which are labeled in some way, from a region or domain of interest under the conditions of the overall sorption equilibrium for all (labeled and unlabeled) molecules. A time dependence of the normalized number of the labeled (unlabeled) molecules in a region of interest is usually referred to as the tracer exchange curve. Such curves can provide information on the permeability of surfaces/membranes, sticking coefficients, intraparticle diffusion coefficients, and some other related transport properties.

2D Exchange NMR Spectroscopy

Figure 5-1. Schematic of the two dimensional (2D) exchange NMR spectroscopy (EXSY) pulse sequence
2D exchange NMR spectroscopy is used to gain information about molecular
dynamics by monitoring exchange processes of nuclear spins in different environments
or states (e.g. adsorbed or desorbed state)\textsuperscript{153}. For this to work, the exchange processes
of the tracer molecules between different environments have to occur on time scales of
NMR, and the chemical shifts in the considered environments have to be sufficiently
different.

Figure 5-1 shows the schematic of the 2D Exchange NMR Spectroscopy (2D EXSY)
pulse sequence. The performance of 2D EXSY pulse sequence can be understood in
detail by treatment of product operators\textsuperscript{11,12,154}. However for the purposes of this text a
simpler qualitative explanation is provided below. Let us assume that at the time of the
start of the pulse sequence the nuclear spins in the sample belong to one of the two
possible ensembles associated with the two possible states $A$ and $B$ characterized by
its own chemical shift (and hence Larmor frequency $\omega_A$ and $\omega_B$ respectively). For
example, these two states can be associated with molecules adsorbed in porous
particles ($A$) and molecules located in the gas phase surrounding the particles ($B$)
under the conditions of sorption equilibrium. In the pulse sequence the first $\frac{\pi}{2}$ r.f.
pulse serves to bring the individual magnetization vectors in the transverse plane.
During the time interval $t_1$ between the first and the second $\frac{\pi}{2}$ r.f pulse, referred to as the evolution time, the individual spins precess in the transverse plane and thus
accumulate a phase proportional to the Larmor frequency associated with their state.
Spins in the state $A$ and $B$ will therefore accumulate phases $\theta_i = \omega_i \times t_1$ ($i = A, B$)
corresponding to their respective Larmor frequencies during the evolution time $t_1$. 
Application of the second $\frac{\pi}{2}$ r.f. pulse serves to send the magnetization along the $-z$ axis. This is done to store the magnetization, since the attenuation of the magnetization along the $z$ (longitudinal) direction is effected only by $T_1$ NMR relaxation. Relaxation of the net induced magnetization in NMR due to $T_1$ NMR relaxation process is typically much slower than $T_2$ NMR relaxation i.e. $(T_1 \gg T_2)$. After the application of the second $\frac{\pi}{2}$ r.f. pulse, a relatively long delay $\tau_m$, referred to as the mixing time, is introduced between the second and the third $\frac{\pi}{2}$ r.f. pulse. This delay serves to allow the nuclear spins (and the associated molecules/atoms/ions) to exchange positions between states $A$ and $B$. Application of the third $\frac{\pi}{2}$ r.f pulse brings the longitudinal magnetization components in the transverse plane. The individual spins again accumulate phases $\theta_i = \omega_i \times t_2 \ (i = A, B)$ associated with their new positions during the acquisition time $t_2$.

Even though there existed only two ensembles of spins at the start of the pulse sequence, at the end of time $t_2$, four ensembles of spins are found to exist. Two ensembles belong to nuclear spins that did not exchange their positions and, as a result remained in initial state $A$ or $B$ during the mixing time $\tau_m$. Such ensembles accumulated a net phase only with one Larmor frequency $\theta_i^{\text{net}} \propto \omega_i \times (t_1 + t_2) \ (i = A, B)$.

Two new ensembles belong to those nuclear spins that exchanged positions during the mixing time $\tau_m$ (i.e. they were either in state $A$ and exchanged to state $B$ or vice versa) and hence accumulated a net phase proportional to both Larmor frequencies

$\theta_i^{\text{net}} \propto (\omega_i \times t_1 + \omega_j \times t_2), \ i \neq j \ where \ (i, j = A, B)$. After Fourier transformation in both $t_1$ and
dimensions, four peaks arise in the resulting NMR spectrum. The area under each peak is proportional to the number of the corresponding spins contributing to the peak. Study of the changes in the peak intensities with increasing mixing time gives information about molecular exchange between the environments \( A \) and \( B \). Table 1 shows the different ensembles of spins at the beginning and end of a NMR 2D EXSY experiment.

<table>
<thead>
<tr>
<th>Initial State</th>
<th>Transition in mixing time ( \tau_m )</th>
<th>Final State</th>
<th>Net phase accumulated ( \theta_i^{\text{net}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A ) → ( A )</td>
<td>( A )</td>
<td>( \propto \omega_A \times (t_1 + t_2) )</td>
<td></td>
</tr>
<tr>
<td>( A ) → ( B )</td>
<td>( B )</td>
<td>( \propto \omega_A \times t_1 + \omega_B \times t_2 )</td>
<td></td>
</tr>
<tr>
<td>( B ) → ( B )</td>
<td>( B )</td>
<td>( \propto \omega_B \times (t_1 + t_2) )</td>
<td></td>
</tr>
<tr>
<td>( B ) → ( A )</td>
<td>( A )</td>
<td>( \propto \omega_B \times t_1 + \omega_A \times t_2 )</td>
<td></td>
</tr>
</tbody>
</table>

\( ^{129}\text{Xe as a Tracer Exchange Species and } ^{129}\text{Xe Hyperpolarization} \)

The \( ^{129}\text{Xe} \) isotope has a chemical shift that is highly sensitive to its environment. This happens due to a very large spherically symmetric electron cloud around the nucleus of \( ^{129}\text{Xe} \) atom. Any distortions in this electron cloud due to environment affect the effective magnetic field experienced by the \( ^{129}\text{Xe} \) nucleus and hence results in an environment dependent chemical shift. Further \( ^{129}\text{Xe} \) usually has very long \( T_1 \) NMR relaxation times. Therefore \( ^{129}\text{Xe} \) is a very good candidate for observing exchange of sorbate in beds of microporous particles (such as zeolite beds) between the adsorbed and gas phases using NMR 2D Exchange Spectroscopy discussed above.
One important consideration for the use of $^{129}\text{Xe}$ in 2D EXSY measurements is the possibility to hyperpolarize the spins. This idea will be briefly discussed below. The spin angular momentum $I$ associated with any spin is quantized and there exist $(2I + 1)$ sublevels that are degenerate. However in the presence of an external magnetic field the degeneracy breaks down. Therefore for a spin $\frac{1}{2}$ system such as $^1\text{H}$ and $^{129}\text{Xe}$, there are 2 possible spin states, called spin up and spin down. They are denoted by $|+1/2\rangle$ and $|-1/2\rangle$ respectively. The observed NMR signal from a sample containing such spins is proportional to the total number of nuclei with the observed spins in sample and a quantity called nuclear spin polarization $P^*$ defined by

$$P^* = \frac{N_\uparrow - N_\downarrow}{N_\uparrow + N_\downarrow} \quad (4.9)$$

where $N_\uparrow$ and $N_\downarrow$ are the populations in the spin $|+1/2\rangle$ and $|-1/2\rangle$ respectively. The difference in population of the two spin states is described by Boltzmann distribution. Under typical conditions of NMR experiments at room temperature such difference in population is very small. This results in a very small polarization $P^*$. For example the spin polarization of $^{129}\text{Xe}$ at 300 K in a 9.4 T magnetic field is ca. $9 \times 10^{-6}$. Low polarization under thermal equilibrium is not an issue with $^1\text{H}$ (proton) NMR since the $^1\text{H}$ nucleus has high gyromagnetic ratio ($\gamma = 2.675 \times 10^8 \text{ rad s}^{-1}\text{T}^{-1}$) and high natural abundance (99.99%). In contrast the low gyromagnetic ratio ($\gamma = -0.745 \times 10^8 \text{ rad s}^{-1}\text{T}^{-1}$), for $^{129}\text{Xe}$, combined with its low natural isotopic abundance (24.4% ) relative to $^1\text{H}$ results in a much lower sensitivity for $^{129}\text{Xe}$ in comparison to $^1\text{H}$ nuclei. Hence, using
thermally polarized \(^{129}\text{Xe}\) requires a large number of scans to get usable signal to noise ratios.

Polarization of spins of \(^{129}\text{Xe}\) nuclei can be modified in such a way that the populations of spins are concentrated in one of the two possible spin states, a phenomenon called ‘hyperpolarization’. Using hyperpolarization it is feasible to increase the value of the polarization factor \((P^*)\) to as large as ca. 0.7. As a result a signal enhancement of ca. 4 to 5 orders of magnitude can be achieved. This completely eliminates the need to use multiple scans and accumulations required for the case of thermally polarized \(^{129}\text{Xe}\).

Xenon hyperpolarization can be achieved by a variety of methods such as ‘cross-polarization’, \(^{155,156}\) ‘dynamic nuclear polarization’, \(^{157,158}\) ‘parahydrogen polarization’\(^{159-163}\) and ‘spin exchange optical pumping’.\(^{164,165}\)

**Study of Frequent Desorption/Re-adsorption Events for Sorbate at External Surfaces of Microporous Crystals**

**Motivation**

Porous membranes and catalyst particles often contain microporous crystals, which are interconnected by larger meso- and macropores. In many of the potential applications of such membranes and catalysts, transport of guest molecules through the external surface of microporous crystals can be the slowest and, as a result, the rate determining step. In such a case correlations between successive motions of molecules at or near the external surfaces of microporous crystals become important for the overall transport properties of the considered system. Very often desorption of molecules from a microporous crystal can be followed by a rapid re-adsorption into the same crystal. Such effects are typically thought to be negligibly small. However, not
much experimental data is available on the subject. In this work occurrence of frequent desorption and re-adsorption events at the external surfaces of microporous crystals has been investigated.

**Experimental Details and \(^{129}\text{Xe} \text{ 2D EXSY Studies}**

Use of \(^{129}\text{Xe} \text{ NMR for studies of porous materials, especially zeolites, has been reported previously.}^{166-170} \text{ Several models have been proposed to study relationship between chemical shift and the local environment in micro-meso porous materials}^{171-173}. \text{ Knowledge of the chemical shifts of }^{129}\text{Xe in the adsorbed and the gas phases has been used in PFG NMR diffusion studies on zeolites}^{174-176}. \text{ In this work a novel experimental approach has been developed. It is based on using continuous flow hyperpolarized (CFHP) }^{129}\text{Xe 2D Exchange NMR spectroscopy (2D EXSY) to investigate events of desorption of sorbate followed by rapid re-adsorption at the external surfaces of microporous zeolite crystals.}

\text{CFHP }^{129}\text{Xe 2D EXSY measurements were conducted at the research lab of Dr. Russell Bowers, Department of Chemistry, the University of Florida. Very well characterized samples of NaY type zeolite with particles sizes of ca. 1 µm were provided by Prof. Dr.-Ing. Jens Weitkamp, Stuttgart University, Germany. About 40 mg of sample were loaded into PEEK (polyetheretherketone) sample holder with an inside diameter of 1/8” and was activated under vacuum for 24hrs at 373 K. The experimental setup described in detail in Ref.}^{177} \text{ was used to achieve }^{129}\text{Xe hyperpolarization by spin exchange optical pumping (SEOP). The hyperpolarization was carried out in a glass chamber called the optical pumping cell. This pumping cell contains molten Rubidium (Rb) metal, which is optically excited by a circularly polarized laser light and as a result}
the pumping cell contains a vapor of optically excited Rb. vapor. The \(^{129}\text{Xe}\) gas is continuously circulated through the pumping cell. The interaction between the Rb vapor and \(^{129}\text{Xe}\) gas results in transfers of excitation to the thermally polarized \(^{129}\text{Xe}\) gas and effectively hyperpolarizes \(^{129}\text{Xe}\). This hyperpolarized gas is then passed through the sample chamber. The measurements were conducted using a 2\% Xe, 2\% N\(_2\) and 96\% He gas mixture. The application of \(^{129}\text{Xe}\) continuous flow hyperpolarized gas apparatus provides enormous NMR sensitivity and has the advantage of retaining a high spin polarization during the entire experiment.

Preliminary CFHP \(^{129}\text{Xe}\) 2D EXSY measurements on this sample were conducted for a 5 ms mixing time and a range of flow rates between 0 to 550 ml/min at a combined gas pressure of ca. 2300 Torr. The choice of gas pressure was governed by conditions that dictate maximum effective transfer of polarization of the Rb vapor to \(^{129}\text{Xe}\) gas\(^{177}\). Xenon atoms that enter the sample holder are present in the sample volume as either the adsorbed phase or as the gas phase in the space between the zeolite particles. In complete analogy with the description of 2D EXSY in the previous section four peaks were expected to be observed in the 2D NMR spectrum at the end of the experiment. The aim of the experiments was to study the effect of dependence of the adsorbed phase peak intensity on the flow rate of gas.
Preliminary Experimental Results

Figure 5-2. Example of continuous flow hyperpolarized $^{129}$Xe 2D exchange spectroscopy spectrum obtained for studies on NaY zeolite sample a): Normal view b): Oblique view. The spectrum was obtained at a flow rate of 247 ml/min.

Figure 5-2 shows an example of CFHP $^{129}$Xe 2D EXSY spectrum. Four peaks are seen in the spectrum. Two strongest peaks, which are referred to as the diagonal peaks in the spectrum correspond to those atoms that were present in the adsorbed (gas) phase at the beginning of mixing time and which are still in the same adsorbed (gas) phase at the end of the mixing time. Two additional peaks that are seen in the spectrum are referred to as the cross diagonal peaks. They correspond to those Xe atoms that were either present in the adsorbed phase at the beginning of mixing time ($\tau_m$) and were found to have exchanged into the gas phase at the end of the mixing time (denoted by ‘A to G’ in Fig. 5-2a) or vice versa (denoted by ‘G to A’ in the Fig. 5-2a). It is seen that the adsorbed phase peak is very large in comparison to all the other peaks. This is typical for microporous materials like zeolites, which are very strong adsorbents. Under our experimental conditions most of the Xe atoms in the bed are expected to be
located in the adsorbed phase at any given time. This work was aimed at observing how the absorbed phase intensity changes with changes in the flow rate of hyperpolarized $^{129}$Xe through the sample holder.

Figure 5-3. Dependence of the adsorbed peak intensity on the flow rate of gas in continuous flow hyperpolarized $^{129}$ Xe 2D exchange spectroscopy experiment. The mixing time $\tau_m$ was equal to 5 ms.

Figure 5-3 shows the dependence of the adsorbed phase peak intensity on the flow rate of hyperpolarized $^{129}$ Xe gas. It is observed that at relatively low flow rates (ca. \(\leq 200\) ml/min) within experimental error there is little or no dependence of the adsorbed phase peak intensity on the flow rate of hyperpolarized $^{129}$ Xe gas. However at sufficiently high flow rates a pronounced decrease in the adsorbed phase peak intensity from ca. 1 to 0.15 is observed.

Discussion of Experimental Results

Adsorbed phase line in the NMR spectrum of 2D EXSY experiment may arise from two kinds of $^{129}$Xe atoms 1) those that never left the parent adsorbent crystal during the
entire mixing time \( \tau_m \) or it may arise from molecules that desorbed and rapidly re-adsorbed into the parent crystal during the mixing time.

In general, any desorption event is expected to affect the chemical shift of the considered nuclear spins. If such events are frequent, and if the amount of time spent in both states (adsorbed and desorbed) are comparable then the exchange process will approach the fast exchange regime. The NMR spins from such ensemble of spins is expected to show either very broad peaks for the adsorbed and gas phases with considerable extent of overlap or just a single peak, depending on the frequency of exchange. No such effects were observed in the NMR spectrum. However, if the desorption of the Xe atoms followed by subsequent re-adsorption into the parent adsorbent crystal is such that the amount of time spent in the gas phase during time intervals \( t_1 \) and \( t_2 \) is very small as compared to the net time spent in the adsorbed phase (and if such events are infrequent), then the NMR signal coming from such atoms will essentially remain to be indistinguishable from the NMR signal of those molecules that never desorbed from the parent crystal during the entire time of the sequence. So, as mentioned earlier, the adsorbed phase peak signal can have contribution from molecules which desorbed and subsequently re-adsorbed into the parent adsorbent crystal without spending much time in the gas phase during time intervals \( t_1 \) and \( t_2 \).

Changes in the adsorbed phase signal intensity can be caused by a decrease in the mass of the sample. This can happen due to the gas flow that carries a fraction of microporous particles away from the volume of the sample holder where NMR signal is detected. Such a decrease in the mass was expected to be prevented by glass wool filters/mesh provided at each end of the sample holder. Further, such a decrease can
also be measured by monitoring the total NMR signal using a single r.f. pulse ‘zg’ experiment before and after a 2D EXSY measurement. Such experiments were carried out and it was observed that there is no change in the total signal intensity coming from the sample holder before and after a 2D EXSY measurement. Therefore, a loss of sample due to excessively high flow as a possible cause for decrease in the adsorbed phase peak intensity can be ruled out.

It should be noted that amount of $^{129}$Xe polarization achieved depends on the flow rate of the gas passing through the optical pumping cell. However after normalizing the peak intensities for different flow rates with the amount of polarization transfer, no dependence of the gas phase peak intensity on the flow rate of $^{129}$Xe gas was observed in a ‘zg’ experiment. Hence the decrease in the adsorbed phase intensity can’t be attributed to excessively high flow rate of the $^{129}$Xe gas through the sample holder. This fact is further corroborated by the observation that the mean residence time of molecules in the sample holder is expected to be in excess of 50 ms, which is much larger than the mixing time of 5 ms used in these studies.

Changes in the adsorbed phase peak intensity with increasing flow rate of gas may arise if there is a fraction of Xe atoms that for zero or sufficiently low flow rates, would have a tendency to desorb from the parent zeolite crystal into the gas phase and then rapidly re-adsorb into the same crystal. In the presence of strong gas flows, such a fraction of molecules would get swept away from the parent crystal and, as a result, would not be able to re-adsorb into the same crystal again. This consideration in combination with the quantitative data in Fig. 5-3 suggests that the fraction of molecules exhibiting such desorption-rapid-re-adsorption behavior in the studied sample must be
quite large. In conclusion, the reported results indicate that there is a large fraction of sorbate atoms that desorb from microporous crystals and rapidly re-adsorb into the same adsorbent crystals in the absence of a strong flow of a carrier gas.

**Dynamic Monte Carlo Simulations**

For qualitative studies of desorption/re-adsorption events discussed above, complementary 2D dynamic Monte Carlo (MC) simulation of molecular diffusion on a square lattice were carried out. The simulations were performed for a bed of zeolite crystals under conditions of sorption equilibrium between the Xe gas adsorbed in the zeolite crystals and the surrounding gas phase. This work was primarily done in collaboration with the undergraduate student (Mr. Robert Muller). The focus of the MC simulations was specifically on desorption and re-adsorption events at the external surfaces of the zeolite crystals in the simulated zeolite bed. Simulations of a similar type were previously performed by the author and his coworkers to extract the permeability of the domain boundaries and domain sizes in planar-supported lipid bilayers from the comparison of the measured PFG NMR data and the corresponding simulation results.\(^{178}\) Similar dynamic MC simulations were also previously performed for microporous materials.\(^{179-182}\)

**Simulation details**

In complete analogy with the simulation lattice described in the Ref.\(^{182}\), the two-dimensional simulation lattice used in this work is made up of four square domains representing zeolite microporous crystals and the inter-domain lattice, which represents the space between the zeolite crystals. A schematic representation of the same is shown in Fig 5-4.
Figure 5-4. Schematic of the simulation lattice used in the 2D dynamic Monte Carlo simulations. The periodic structure is formed by repetition of the simulation lattice of length $185\ell$. The square domains in grey represent the microporous zeolite crystals and the surrounding interdomain space represented the gas phase between the crystals. The inset shows various jump probabilities and the elementary diffusion step \( \ell \) used in the simulation model.

Periodic boundary conditions were applied at all margins of the lattice. The length of a side of the square simulation lattice (Fig. 5-4) used is set at $185\ell$ where \( \ell \) is the length of an elementary diffusion step. Each of the four square domains representing the microporous zeolite crystals have a side of length equal to $50\ell$. The intercrystalline space between any two neighboring crystal is set at $30\ell$. This particular choice was made to represent the approximate packing factor in a real bed of zeolite crystals. The molecular diffusion is modeled by random walk. In each diffusion step inside the crystals and in the gas phase between the crystals the random walkers move in one of the four orthogonal directions with equal probability $P_{x,y} = 0.25$. The differences in the
intracrystalline and gas phase diffusivities in experiments was approximated by choosing \( \tau_{\text{crystal}} / \tau_{\text{gas}} = 10 \), where \( \tau_{\text{crystal}} \) and \( \tau_{\text{gas}} \) represent the time for a single elementary diffusion step in the crystalline and gas phases respectively. If the diffusion step of the random walker, on a lattice site next to the crystal boundary, is normal to the external surface of the crystal then it may adsorb or desorb with probabilities \( P_A \) and \( P_D \) respectively. The desorption and adsorption probabilities which govern the desorption and the adsorption rates were assigned to be 4.14 % and 50% respectively. An order of magnitude difference between these probabilities represents the fact that the potential energy of the sorbate in the adsorbed phase inside a microporous crystal is much lower than that in the gas phase.

Under the conditions of sorption equilibrium, interfacial mass fluxes at the external surface in and out of the crystals are equal and opposite to each other. The fluxes in and out of the crystals are expected to be proportional to, respectively, the sorbate concentrations in the gas and intracrystalline phases. For desorption and adsorption probabilities discussed above this leads to a value of the concentration ratio

\[
\frac{c_{\text{crystal}}}{c_{\text{gas}}} \approx 121.
\]

This value is of the same order of magnitude as the ratio of the peak intensities corresponding to the adsorbed and gas phases for \(^{129}\text{Xe}\) in the experimental studies discussed above. Hence, it can be concluded that there is a good match between the conditions used in our experimental and computational studies.

Starting points of a total of \( N_T = 100000 \) random walkers were randomly selected on the simulation lattice. Final simulation results reported here are averages over 10 lattices with different configurations of starting points. The focus of the simulations was on gaining a qualitative understanding of sorbate transport near the external surfaces of
zeolite crystals, with particular attention to the occurrence of consecutive desorption and re-adsorption events from and to a zeolite crystal. The main quantity recorded in the simulations was the relative number of labeled random walkers, i.e. those that were inside the crystals at time $t=0$ and were still inside the same crystal at a certain latter time $t$, $N_c(t)/N_c^0$; where $N_c^0 = N_c(t=0)$. Other quantities recorded were the molecular trajectories, mean square displacements and the adsorption and desorption counts.

Selected simulation results

![Figure 5-5. Time dependence of normalized fraction of labeled molecules $N_c(t)/N_c^0$ denoted as $\gamma$, which started their trajectories inside the crystals at time $t=0$ and were still inside the crystal at a certain latter time $t$. The results were obtained using 2D dynamic Monte Carlo simulations. Data corresponding to molecules that never left their parent crystal (■) and those that never left+ those that left and returned to the parent crystal during the time between 0 and $t$ (●) are shown.](image)
Some selected results of the simulations relevant to the preliminary experimental results are presented in this section. The information about the complete work can be found in the undergraduate honors thesis of Robert Muller.

Figure 5-5 shows the main results of the simulations. The normalized fractions of the molecules $N_c(t)/N_c^0$ (denoted by $\gamma$ in the Fig. 5-5) which started their trajectories inside the crystals at time $t = 0$ and were still inside the crystal at a certain latter time $t$ are shown. The data points shown as black squares present the results for an ensemble of labeled molecules that never left the parent crystal. The red circles show the corresponding data for molecules that never left plus those that left and returned to the parent crystal by the time $t$ shown in the figure.

The difference between the two curves in Fig 5-5 represents the fraction of molecules that left and returned to the parent crystal. The results of simulations show that at sufficiently large simulation times, such a fraction can be much larger than the fraction of labeled molecules that never left the parent crystal. For instance, the dotted line on the left ($t \approx 75$) in Fig. 5-5 shows the diffusion time when the two fractions discussed above are both close to 100%. However, at sufficiently large diffusion times, such as that denoted in Fig 5-5 by the dotted line at $t \approx 5000$ the fraction of molecules that never left the parent crystal can be as small as 5%, while the corresponding fraction of those that left and returned can be close to 72%.

The time dependence of quantity $\gamma$ or $(1-\gamma)$, which is often referred to as the tracer exchange curve, can be obtained experimentally using different approaches including infrared spectroscopy, 2D ESXSY, tracer ZLC, and PFG NMR. Except for tracer ZLC, which employs a strong flow of a carrier gas in the sample volume, other
approaches mentioned above do not require experimental conditions that prevent re-adsorption of desorbed molecules into the same (parent) crystal. As a result, experimental tracer exchange curves, which are thought to be a representation of the black curve in Fig 5-5, may actually represent the red curve. In an event that the fraction of molecules that desorb and re-adsorb is very large, as seen from the results of simulations (Fig. 5-5), any quantitative estimates based on the experimentally observed tracer exchange curves should take into account the existence of this fraction. The mean distance travelled by the random walkers after desorption before they return to be re-adsorbed was also studied using the simulations (results not shown). It was seen that these mean distances travelled by molecules between desorption and re-adsorption events were very small in comparison to the crystal sizes and the intercrystalline distances. As a result, such events are expected to go virtually undetected in almost all tracer exchange based experimental studies other than the novel experimental approach using CFHP $^{129}$Xe 2D EXSY described earlier in this chapter.

From the knowledge of the diffusivities of sorbate molecules (random walkers) in experiments (simulations) and the corresponding sizes of the zeolite microporous crystals used in the experiments and their simulation counterparts it was determined that the mixing time ($\tau_m$) of 5 ms used in the experiments roughly corresponds to ca. 4000 in simulation time units. Using this information it is possible to show the superposition of the experimental data from CFHP $^{129}$Xe 2D EXSY measurement and the corresponding results of simulation presented in Fig. 5-5. Such superposition is presented in Fig. 5-6.
Figure 5-6. Superposition of experimental data obtained by continuous flow hyperpolarized $^{129}$Xe 2D exchange spectroscopy on the results of 2D dynamic Monte Carlo simulations. Tracer exchange curves for simulation data corresponding to molecules that never left their parent crystal (■) and those that never left+ those that left and returned to the parent crystal during the time between 0 and $t_0$ (●) are shown. Experimental data points denote adsorbed phase peak intensity obtained for various flow rates in ml/min: 45 (■), 120 (□), 171 (▲), 247 (▼), 330 (♦) and 502 (×).

In Fig. 5-6, the intensities of the adsorbed phase peak intensity from the experiments were normalized using the ratio of the adsorbed phase peak intensity at zero flow rates in the experiments and the corresponding value of $\gamma(t)$ represented by the red curve. It is seen in Fig. 5-6 that the experimental data points with the highest values of $\gamma$ overlap with the points of the red curve. The latter represents an ensemble of labeled random walkers in the simulations that are an aggregate of those which never left the parent crystal and those which desorbed and re-adsorbed into the same parent crystal. It is observed that (see Fig. 5-6) with increasing value of flow rates used in the experiments the experimental data points gradually approach the simulation data points.
represented by the black curve. The latter curve represents only those random walkers that never left the parent crystal. This result can be attributed to the expectation that at sufficiently low gas flow rates in the experiments there is a significant fraction of $^{129}$Xe atoms which desorb from and rapidly re-adsorb into the same adsorbent crystal. Hence, the experiment data points appear to be near the red curve obtained from simulations (see Fig. 5-6) However, at sufficiently high flow rates the fraction of molecules that desorb and re-adsorb approaches zero, since such molecules get swept away by the gas flow. As a result, the experimentally measured intensity of the adsorbed phase peak at such sufficiently high flow rate corresponds only to the molecules which never desorbed from the parent crystals. Hence, it is fully expected that the experimental data points at such flow rates appear close to the black curve obtained from the simulations.

Thus results of both experiments and the computer simulations are found to be in a qualitative agreement. It should be noted that the results of the simulations are purely qualitative in nature and entirely depend on the simulation parameters. Since the adsorption and desorption rates are determined by the adsorption and desorption probabilities, the significance of this observed effect can be different for different choices of parameters.

Summary

A novel approach to investigate frequent desorption/ re-adsorption events of sorbate at the external surfaces of microporous crystals is demonstrated. The approach is based on monitoring dependence of the adsorbed phase peak intensity on the flow rate of the carrier gas realized in continuous flow hyperpolarized $^{129}$Xe 2D exchange spectroscopy measurements. Preliminary experiments results, which were obtained for Xe diffusion in a zeolite bed under the conditions of sorption equilibrium, suggest the
presence of a large fraction of Xe atoms that desorb and rapidly re-adsorb into the same parent microporous crystal. The presence of such fraction is indicated by the decrease in the adsorbed phase peak intensity with increasing flow rates of the Xe gas through the sample chamber. Perhaps the most important significance of this work is related to the possibility of accurate determination of the surface permeability. Since it was shown that a significant fraction of sorbate may desorb from and re-adsorb back into the parent zeolite crystals, the real surface permeability might be larger than that predicted by using a traditional assumption that re-adsorption into the parent crystal can be neglected.

Results of complementary 2D dynamic Monte Carlo simulations corroborate the experimental data. Simulations indicate presence of a significant number of molecules that desorb from and rapidly re-adsorb into the parent crystals. It is seen that at certain diffusion times the fraction of sorbate species that never left the parent crystal might be much smaller than the fraction of those that desorbed and returned back. This suggests that the fraction of sorbate molecules/atoms that desorb and return back into the same crystal is not negligible, as is often assumed during the treatment of experimental data.

Both the results of experiments and the computer simulations are preliminary in nature. A more detailed experimental investigation and analysis of simulation data under varying conditions of simulation parameters will be required to quantify fully the effect of frequent desorption / re-adsorption events on the overall transport in a bed of microporous crystals or in a membrane containing microporous crystals.
CHAPTER 6
SUMMARY AND SIGNIFICANCE

New scientific developments in the field of chemical engineering rely heavily on the use of materials which show well-defined structural organization and/or hierarchy of structural order on small, i.e. micrometer and submicrometer, length scales. Emerging engineering areas ranging from advanced electronics to renewable energy as well as the age old traditional areas ranging from fossil fuel to pharmaceuticals are affected by the introduction of such materials. In many cases the traditional top down approach is rapidly losing ground to a new bottom up approach where tailoring of materials and processes on a microscopic length scale is the new standard. In many applications of interest molecular transport and its relation to structure on small length scales is the governing mechanism. Hence, there is an increasing need for fundamental understanding of transport on such length scales. This chapter is an attempt to summarize the studies reported in this work and to emphasize their significance.

This work presented relation between diffusion and structure in selected nanostructured materials/systems of scientific and industrial importance using NMR. For the most part diffusion studies were performed using pulsed field gradient (PFG) NMR, a powerful technique cable of measuring mean square displacements of molecules/ions. Part of the work presented development and implementation of this technique under conditions of high magnetic field (17.6 T) and ultra high gradient strengths (30 Tm$^{-1}$) with precise temperature control over a temperature range from 218 K to 423 K. Application of ultra high gradients resulted in a possibility of diffusion measurements on the length scale of displacements as small as 90 nanometers under
the conditions of high signal-to-noise ratios resulting from a high magnetic field. In some of the most recent work, exchange of the sorbate between different environments has been studied using continuous flow hyperpolarized $^{129}$Xe 2D exchange spectroscopy, a technique that works on the principle of NMR tracer exchange.

**Organized Soft Matter Systems**

Materials studied under this category were constituted by oppositely charged polyatomic ions and included the following types of systems: 1) room temperature ionic liquids 2) polyelectrolyte- protein coacervates 3) mixed micellar systems.

In the work on ionic liquids the diffusion of constituent ions and water in two imidazolium based ionic liquids was studied using PFG NMR. The effect of addition of water on the diffusion behavior of the anions and cations has been discussed in the context of presence of polar and nonpolar domains in the ionic liquids. A partial screening of electrostatic interaction between the cations and the anions in the polar domains by water is suggested to be responsible for the unique changes in diffusion behavior, which were observed experimentally. These included a) a significant increase in the ion diffusivities due to addition of a small amount of water into water free ILs, followed by not so dramatic increases in the ion diffusivities as a result of subsequent increase in water concentration; b) anomalous relation between the size and diffusivity of the diffusing ionic species in the absence of water, and the disappearance of this relationship due to addition of water.

The work on polyelectrolyte protein coacervates presented here, involves study of diffusion of polycation poly(diallyldimethylammoniumchloride) in the coacervates formed from this polycation and the protein bovine serum albumin (BSA). The diffusion studies point at the existence of several ensembles of the polycation. Existence of these
ensembles and the pattern of their changes with increasing diffusion time provide corroborative evidence for a previously proposed hypothesis about microscopic heterogeneity in these coacervates. This hypothesis states that the coacervates are comprised of dense domains rich in the protein and polycation that are suspended in a sea of diluted protein-polycation mixture. The data also provides evidence for dynamic disintegration and reformation of the dense domains in the coacervates.

PFG NMR experiments were also used to study the diffusion of surfactant ions in the following two micellar systems. a) aqueous solution of an anion surfactant sodium dodecyl sulfate (SDS) and b) aqueous solution of a mixture of SDS and a small amount of cationic surfactant N-dodecyltrimethylammonium bromide (C$_{12}$TAB). The PFG NMR measurements provided separate sets of data on diffusion of both types of surfactant ions. For each surfactant ion the PFG NMR diffusion data showed the existence of at least two components with different effective diffusivities at sufficiently small diffusion times. The observed changes in the fractions and diffusivities of these components with increasing diffusion time suggest that the faster of these two components corresponds to surfactant ions that have experienced breakup and reformation of micelles during the diffusion time and the slower component represents those that are yet to experience such events.

While all the organized soft matter systems may appear quite different from each other at the first glance, they all share common structural and diffusion characteristics. Microscopic heterogeneity due to dynamic agglomerations of the constituent polyatomic ions is the trait shared by all the soft matter systems studied in this work. All the systems exhibit formation of domains that influence the overall transport behavior of the
constituent ions and cause it to deviate from normal diffusion behavior that is expected in the case of homogenous liquids. Domain breakup and reformation events on time scales comparable to the measured diffusion times result in increased effective diffusion coefficients of constituent ions in these materials on the time scales of such breakup and reformation events. Observation of such very similar trends, which were reported for all the organized soft matter systems studied in this work, contribute towards developing a general understanding of diffusion and its relations to structure in such materials on sufficiently small time and length scales. These conditions are way beyond the reach of typical macroscopic techniques used for studies of molecular ionic transport.

**Porous Materials**

A significant part of the work reported in this thesis deals with studies of sorbate transport in micro-mesoporous materials. Materials covered under this category are 1) FAU/EMT zeolite intergrowth and corresponding pure zeolites, and 2) mesoporous silica SBA-15s.

In the zeolite related studies PFG NMR technique with high (upto 30 Tm⁻¹) gradient amplitudes was employed to study diffusion of isoctane and isobutane in FAU/EMT intergrowth as well as in the corresponding pure zeolites of the FAU and EMT types. The temperatures and diffusion times used in these studies were sufficiently small to allow performing diffusion studies for length scales of sorbate displacements smaller than the sizes of individual zeolite particles. Comparison of the PFG NMR data obtained for the intergrowth with the corresponding results of measurements of the pure zeolites revealed an existence of intraparticle transport barriers in FAU/EMT intergrowth. While a restriction in diffusion is clearly present for the larger sorbate *viz.*
isooctane, such effect is not observed for the diffusion of smaller isobutane molecules. Presence of partially blocked micropore openings at the interfaces between the intergrowth components of the FAU/EMT intergrowth is suggested to be the origin of observed transport barriers.

In the case of studies on mesoporous silica SBA-15s, PFG NMR experiments were conducted to study self diffusion of toluene in two sample of SBA-15 silica. Unlike previous studies of this type of materials, the measurements were performed under the conditions of dynamic equilibrium between the adsorbed phase in the SBA-15 particles and the surrounding gas phase in the space between the particles; a condition that is most relevant for potential applications in catalysis and separations. For all diffusion times used the measured PFG NMR attenuation curves showed deviation from monoexponential decay. The observed changes in the fraction and the diffusivities of these ensembles with increasing diffusion time, coupled with the analysis of the values of the mean squared displacements of these fractions, were suggestive of molecular exchange between ensembles performing long range diffusion and that corresponding to the transition from the intraparticle to long range diffusion. The data at sufficiently small diffusion times and temperatures allowed estimating intraparticle diffusion coefficients in all studied samples of SBA-15 silica.

The PFG NMR studies of the selected systems of porous materials mentioned above demonstrated the use of the PFG NMR under the conditions of high field and high gradient combined with precise temperature control to extract valuable information about transport of sorbate in materials that have previously been considered to be challenging to measure using PFG NMR. For instance, PFG NMR studies of
commercially synthesized zeolite materials are considered to be particularly challenging. However, the unique experimental capabilities developed as a part of this work allowed for the measurements of the PFG NMR signals from the isooctane (isobutane)-zeolite guest-host systems under conditions of extremely low $T_2^*\text{NMR}$ relaxation times (ca. <1 ms) and significantly reduced self diffusion coefficients (ca. $10^{-13}$ m$^2$s$^{-1}$) due to restricted diffusion. Such studies were made possible by the combined effect of high sensitivity provided by the high field, the very small gradient durations (consequently minimum relaxation effects) provided by the ability to apply very strong gradient pulses (up to 30 Tm$^{-1}$) and the ability to reduce the temperature sufficiently to measure intracrystalline diffusion in the case of isobutane. Due to the availability of such exceptional capabilities the presence of intracrystalline transport barriers in commercially synthesized FAU/EMT intergrowth could be detected.

**Work in Progress**

Continuous flow hyperpolarized $^{129}\text{Xe}$ 2D exchange spectroscopy measurements were conducted for a system of Xe adsorbed in a bed of zeolite crystals. The studies were aimed at observing frequent desorption / re-adsorption events at the external surfaces of microporous crystals. The preliminary results of the experimental studies verified the presence of such effects and also showed that the fraction of molecules that leave and return to the parent crystal can be quite large, contrary to infinitesimally small values, which are usually assumed in the literature. This can have a huge impact on the calculations of surface permeabilities because the real values might be quite large in comparison to a value calculated by assuming that the fraction of molecules that desorb and re-adsorb again in the parent crystal is negligibly small.
Dynamic Monte Carlo simulations co-developed by the author also suggest the presence of a significant fraction of molecules that desorb from and re-adsorb into a parent crystal. Thereby, the MC results support the experimental observations. More detailed work on the experiments and the simulations still needs to be done in a future.
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BIOGRAPHICAL SKETCH

Amrish Ramesh Menjoge was born in 1982 at Nagpur, India to Ramesh and Mangala Menjoge. He grew up there with his parents and elder sister Anupa Menjoge and all his early schooling was done in Nagpur. During his high school years, he was recognized for merit in district and state talent search exams and as a young athlete won championships in roller skating at state and national levels. He attended the Institute of Chemical Technology, Mumbai India (formerly UDCT) and earned a Bachelor of Chemical Engineering in 2004. Then, he attended graduate school at University of Florida (UF), Gainesville and earned a Master of Science in chemical engineering in 2006. He continued his enrollment at UF and earned a Doctorate in chemical engineering in 2010. While at UF, he got married to his long time friend and love interest, Shweta Mokashi in 2007.