Diffusion Coefficients of Xenon in Polystyrene Determined by Xenon-129 NMR Spectroscopy

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ABSTRACT: A new experimental approach for measuring diffusion coefficients of sorbed gas in polymers has been developed based on a combination of NMR spectroscopy and the use of polymer microspheres. The system chosen to demonstrate the technique is xenon gas sorbed into polystyrene beads of micron size. Pressures in the range of 10−15 atm are sealed in NMR tubes containing a gram or so of polymer. Chemical shift exchange of the xenon gas is easily monitored in either one or two dimensions through the xenon-129 resonances since well-separated signals are observed for the sorbed and free gas. To quantitatively determine diffusion coefficients, selective saturation of the gas phase resonance is used to reduced that signal to zero. Then the decay of the sorbed signal is monitored as a function of saturation time to determine the rate of diffusion of gas out of the polymer microsphere. Diffusion in this case is simply described mathematically by diffusion out of a sphere. A model has been developed to take into account the effects of diffusion in combination with spin−lattice relaxation of the xenon-129 sorbed in the polymer. The diffusion coefficient of xenon in polystyrene at 25 °C is $(1.9 \pm 0.4) \times 10^{-9}$ cm^2/s. Measurements were made up to 115 °C and an apparent activation energy of 36 kJ/mol was found for diffusion in glassy polystyrene with a sharp increase in the diffusion coefficient when the glass transition region was reached.

I. Introduction

In recent years there has been an increasing number of reports on xenon-129 NMR spectroscopy for investigating microporous materials including zeolites,[1−3] clathrates,[4,5] polymers,[6−11] and biological substances.[12−14] The application of xenon-129 NMR has been reviewed,[15−18] including the xenon optical pumping with dramatic enhancement in sensitivity.[19,20]

In this article we wish to describe a new method for measuring the diffusion coefficients of xenon in polymer beads using ^{129}Xe NMR. The technique has the potential to be applied to other nuclei as long as resolved signals are obtained for the sorbed gas and the free gas. Xenon-129 is a favorable nucleus in this regard because of the large shifts observed between sorbed xenon and free xenon.[12] This experiment may have general utility for chemists since NMR equipment is ubiquitous and only a vacuum line is required for sample preparation. The concept of using polymer microspheres to expedite diffusion studies is also well established so that the prospect of obtaining appropriate polymer samples is reasonable. The technique has the potential to be extended to study diffusion in polymer spheres with treated surfaces which are also commonly available as chromatographic materials.

The experiment is based on the presence of a dynamic equilibrium between free and sorbed gas. When gases are in dynamic equilibrium with polymers, the penetrant molecules are expected to exchange between the sorbed and gas phase. We have tailored a gas/polymer system to measure this exchange and extracted the diffusion coefficients for the process as a function of temperature. The key relationship to be achieved is to match the exchange rate of the gas between the sorbed and free state to the chemical shift separation between the resonance line measured in hertz. When this occurs, exchange processes are easily monitored by NMR spectroscopy. The rate of exchange in the polymer bead is controlled by two factors. The first, and the property to be studied, is diffusion of the gas in the polymer. The second factor controlling exchange is the size of the microsphere and spheres of varying, well-characterized sizes are available.

For bulk polymers with millimeter dimensions below their glass transition temperatures (T_g), the exchange of interest will be very slow on the NMR time scale and thus inaccessible to NMR spectroscopy. Berens[21,22] and Hopfenberg[22−28] pioneered the use of polymer microspheres for sorption experiments in order to control surface area and shoften the observation time. The approach taken here is an extension of their work incorporating the NMR spectrometer as the means to detect gas exchange.

Recently, Tomaselli et al.[10] studied polymer blend systems with 2D ^{129}Xe NMR to probe microheterogeneity and to obtain an average diffusion coefficient for two different polymers.

In a recent publication,[29] we reported observations from 1D and 2D chemical exchange ^{129}Xe NMR (NOESY) experiments which clearly indicated exchange between molecules in the gas phase and those sorbed in polystyrene beads. In addition, we obtained a value for the diffusion coefficient of xenon sorbed in polystyrene. In this paper, we present more extensive results and a more complete interpretational model applicable to the results from the ^{129}Xe NMR selective saturation experiment.[30]

II. Experimental Section

(a) Sample Preparation. Polystyrene (PS) beads ("uniform latex particles") of different and well-controlled sizes were

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Table 1. Spin−Lattice Relaxation Times of ^{129}Xe in Polystyrene

T (°C)	T_1 (s)
25	17.6
55	16.8
85	15.0
100	11.7
115	10.3

obtained from Bangs Laboratories, Inc. of Carmel, IN ($T_g \sim$ 100 °C). They were spheres of diameters 10.5, 18, and 64 μm with densities of 1.062−1.066 g/cm^3. For the purpose of comparison, we also used PS pellets (molecular weight 250 000; density 1.047 g/cm^3) as a bulk sample, which were cylinders of length 3 mm and diameter 2 mm and supplied by Aldrich Chemical Co.

The gas employed for our experiment was ^{129}Xe with 26.44% natural abundance from Matheson Gas Products. PS samples were placed in heavy-walled, 10 mm NMR tubes (with a 7 mm i.d.) and packed to a depth of 55−60 mm. This corresponded to sample masses of between 1.1 and 1.5 g. The tubes were then connected to a vacuum line with a transducer electrometer system to monitor the pressure. After removal of the sorbed air, xenon gas was introduced into the entire manifold. Placing the tubes into liquid nitrogen cryopumped xenon quantitatively into the tubes, and the tubes were then flame sealed to give final pressures in the range of 10−15 atm at ambient temperature.

(b) NMR Spectroscopy. A selective rf pulse is applied to saturate the ^{129}Xe in the gas phase for varying duration time (t) just prior to the observing 90° pulse. Saturating the spins in the gaseous state for a longer period of time will result in a greater attenuation of the sorbed ^{129}Xe resonance. This is due to the fact that the unsaturated sorbed ^{129}Xe undergoes exchange with the saturated ^{129}Xe in the gas phase. The newly sorbed, saturated (formerly gaseous) ^{129}Xe nuclei do not contribute to the signal intensity if they have not had time to relax back to equilibrium by spin−lattice relaxation (T_1). Thus the decay rate of the integrated intensity of the sorbed ^{129}Xe peak is a measure of the rate of exchange out of the bead.

All NMR experiments were performed with a Varian Unity 500 NMR spectrometer interfaced to a Sun IPX workstation running the VNMRS 4.1A software package. A two-channel, 10 mm broad-band probe was employed. Samples were spun at 12 Hz to improve field homogeneity, and the sample temperature was monitored closely during the experiments.

The ^{129}Xe NMR spectra were acquired at 138.3 MHz with a 20 μs 90° pulse and a relaxation delay of 130 s for 1D spectra and 75 s for 2D spectra. The spectral width was typically 40 kHz (289 ppm). 2K data points were collected for both 1D and 2D spectra. The time-domain data were apodized using a shifted, squared sine-bell, and the 1D data were zero-filled to a total size of 8K prior to Fourier transformation. The ^{129}Xe sorbed gas resonance was integrated using a constant integral scaling factor from 226 to 210 ppm after applying baseline correction. The integral of the peak at zero saturation time for free gas was obtained and an average value of this quantity used as a fixed value in the fitting procedure. In addition, this averaging also yielded a standard deviation, which is taken as the uncertainty of the measurements.

III. Results and Discussion

(a) Spin−Lattice Relaxation. The ^{129}Xe nuclei have much longer T_1 in the gaseous state than in the sorbed state (a value of 257 s was obtained for neat gas under our conditions). During a T_1 measurement a certain amount of diffusion takes place across the surface of the polymer bead so that the observed T_1 for ^{129}Xe in the sorbed state will be slightly longer than for ^{129}Xe sorbed in, say, a large solid block of PS where surface area is low and hence exchange is slow. Likewise, the T_1 for the gas surrounded by PS powder will be observed to be much shorter than in the neat gas due to the diffusional exchange. The T_1 determination

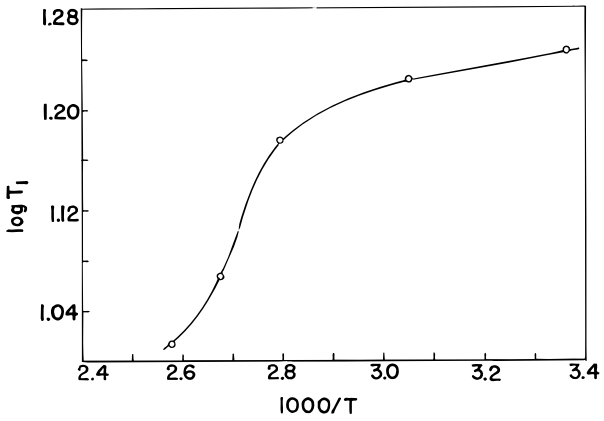

Figure 1. Spin−lattice relaxation time (T_1) versus reciprocal temperature for ^{129}Xe sorbed in polystyrene pellets.

Table 2. Sorbed ^{129}Xe Chemical Shifts and Line Widths as a Function of Temperature and Polystyrene Bead Diameter

bead diam (μm)	temp (°C)						
	25	40	55	70	85	100	115
10	215.9[a] (657)[b]						
18	219.7 (808)	217.1 (576)	214.2 (405)	212.6 (318)	210.4 (241)	209.0 (200)	
64	218.8 (884)	217.3 (610)	214.9 (417)	213.5 (324)	212.0 (249)		206.6 (200)
375	215.1 (817)						
2000−3000	218.0 (1448)		213.6 (618)		211.9 (311)	209.1 (247)	

[a] Chemical shifts are in ppm with respect to the gas peak set at 0 ppm. [b] Line widths are in hertz and given inside the parentheses.

gave estimates of 18.8 and 26.2 s for the sorbed and gaseous ^{129}Xe, respectively in the 18 μm spheres. As indicated, the accuracy of these determinations is compromised by the presence of the diffusional exchange. We have, therefore, measured the T_1 values of ^{129}Xe in the PS pellets as a function of temperature (see Table 1 and Figure 1) and assumed these values to be valid as the sorbed value for all PS beads regardless of their diameters. Note that the largest change in T_1 as a function of temperature occurs at about 100 °C in the vicinity of the glass transition of the polystyrene.

(b) Chemical Shifts and Line Widths. For ^{129}Xe in PS the separation of the sorbed gas resonance and the free gas resonance is 220 ppm, while the line widths are 802 and 207 Hz (5.8 and 1.5 ppm), respectively, at 25 °C. The data for sorbed xenon chemical shifts and line widths are given in Table 2 as a function of temperature and PS bead diameter. The uncertainty in the values for the line width is about 10−30 Hz.

(c) Treatment of the Selective Saturation Data. In Crank's formulation of diffusion out of a sphere,[31] the concentration C_p of xenon gas in the polymer phase as a function of time t is given by

$$\partial C_p/\partial t = D\nabla^2 C_p \qquad (1)$$

where D is the diffusion coefficient of the xenon within the polymer sphere. Once xenon exits a polymer sphere, its nuclear resonance is quickly saturated. The xenon magnetization within the polymer, M_z, is depleted since the xenon gas diffusing in from the gas phase has zero magnetization. The deficiency of xenon magnetization at point r from the center of the polymer sphere at time

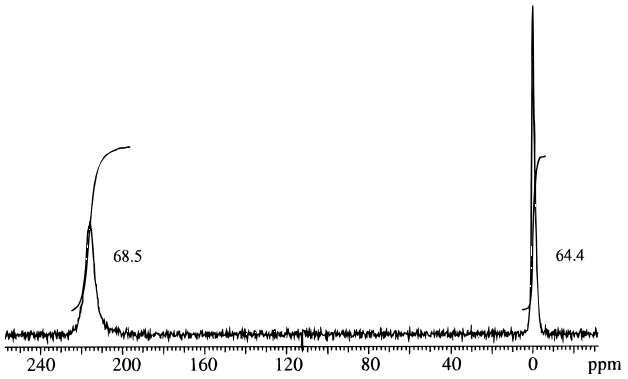

Figure 2. NMR spectrum of ^{129}Xe sorbed in polystyrene beads of 10 μm diameter at 25 °C. The gas phase peak is set at zero ppm.

t is $M_0 - M_z(r,t)$, where $M_z(r,t)$ is the z magnetization due to the xenon sorbed in the polymer sphere at distance r from the center at time t and M_0 is the magnetization at that point at time zero before the saturation experiment began. Since the modification of the xenon nuclear spin population cannot alter the chemical equilibrium between the gas and the polymer, the amount of xenon lost at each point in the polymer must be exactly balanced by the amount of gas phase xenon that has entered the polymer sphere in the time t. Insomuch as the sorbed xenon is not in equilibrium given by the quantity $M_0 - M_z(r,t)$, it will recover by spin−lattice relaxation.

Equation 1 can be written in terms of magnetization taking into account both diffusion and spin−lattice relaxation as

$$\partial M_z(r,t)/\partial t = D\nabla^2 M_z(r,t) + (M_0 - M_z(r,t))/T_1 \quad (2)$$

It is convenient to define a new variable

$$y = M_0 - M_z(r,t) \quad (3)$$

so that eq 2 becomes

$$\partial y(r,t)/\partial t = D\nabla^2 y(r,t) - y(r,t)/T_1 \quad (4)$$

which is near to the form discussed by Crank.[32]

Let us first consider the case of pure diffusion with no T_1 effects (i.e., $T_1 \rightarrow \infty$); then the last term in (4) is dropped and because of radial symmetry a new variable is introduced, $H = yr = r(M_0 - M_z(r,t))$. Equation 4 then becomes

$$\partial H(r,t)/\partial t = D\partial^2 H(r,t)/\partial r^2 \quad (5)$$

and boundary conditions may be expressed as

$$H = 0 \quad \text{at } r = 0 \text{ for } t > 0$$

$$H = aM_0 \quad \text{at } r = a \text{ for } t > 0$$

and

$$H = 0 \quad \text{for } 0 < r < a \text{ at } t = 0$$

where a is the radius of the polymer sphere. The solution of eq 5 with the boundary conditions given above can be obtained from eq 6.18 on p 91 of Crank[31] as

$$\frac{M_z(r,t)}{M_0} = -\frac{2a}{\pi r}\sum_{n=1}^{\infty}\frac{(-1)^n}{n}\sin\left[\frac{n\pi r}{a}\right]\exp\left[\frac{-D\pi^2 n^2 t}{a^2}\right] \quad (6)$$

The general solution of (4) ($T_1 \neq \infty$) is given by eq 14.24 on p 332 of Crank[31] as

$$\frac{M_z(r,t)}{M_0} = -\frac{2a}{\pi r}\sum_{n=1}^{\infty}\frac{(-1)^n}{n}\sin\left[\frac{n\pi r}{a}\right]\left\{\frac{k + v\exp(-t(k+v))}{k+v}\right\} \quad (7)$$

where we have defined

$$k = 1/T_1$$

and

$$v = Dn^2\pi^2/a^2$$

In the limit that $t \rightarrow \infty$, the solution in eq 7 becomes

$$\frac{M_z(r,\infty)}{M_0} = -\frac{2a}{\pi r}\sum_{n=1}^{\infty}\frac{(-1)^n}{n}\sin\left[\frac{n\pi r}{a}\right]\left\{\frac{k}{k+v}\right\} \quad (8)$$

Equations 7 and 8 give the reduced magnetization of xenon in the polymer bead at time t at radial position r. What is measured experimentally is $M_z(r,t)/M_0$ averaged over the polymer sphere radius. Defining the mean penetrant magnetization

$$m(t) = \frac{4\pi\int_0^a\left[\frac{M_z(r,t)}{M_0}\right]r^2\,\mathrm{d}r}{\frac{4\pi a^3}{3}} \quad (9)$$

we finally obtain

$$m(t) = \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\left\{\frac{k + v\exp(-t(k+v))}{k+v}\right\} \quad (10)$$

which has the limits of $m(0) = 1$ and

$$m(\infty) = \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\left\{\frac{k}{k+v}\right\} \quad (11)$$

In order to determine the diffusion coefficient, D, of xenon in PS beads of diameter $2a$, first we substitute an appropriate T_1 value from Table 1 into eq 10, where $k = 1/T_1$. Then the time course of the measured magnetization, $m(t)$, is fitted to the expression (10) to yield the value of D. (See Figure 3 for an example.) The long-time limit can be evaluated directly from eq 11 and is shown as a dashed line in Figure 3. In Table 3 our results for the diffusion coefficients of xenon (10−15 atm) sorbed in PS beads of different sizes at various temperatures are listed. It is a one-parameter fit and the uncertainty in our determined diffusion coefficients is estimated to be 20%.

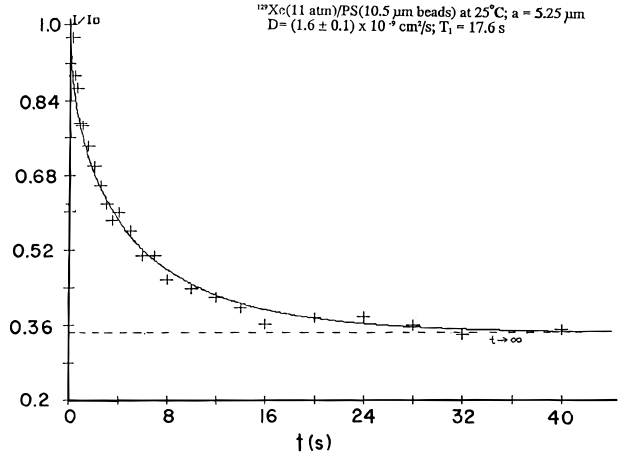

Figure 3. Observed relative magnetization intensity M_z/M_0 plotted as a function of duration time (t) for the selective saturation pulse for ^{129}Xe (11 atm) in PS (10 μm) at 25 °C.

Table 3. Diffusion Coefficients of Xenon (10−15 atm) Sorbed in Polystyrene Beads of Different Diameters at Various Temperatures

	$D \times 10^9$ (cm^2/s)		
T (°C)	10 μm	18 μm	64 μm
25	1.6	2.2	
40		3.6	3.6
55		6.5	8.3
70		11	13
85		20.5	21.6
100		38	
107.5			115
115			165

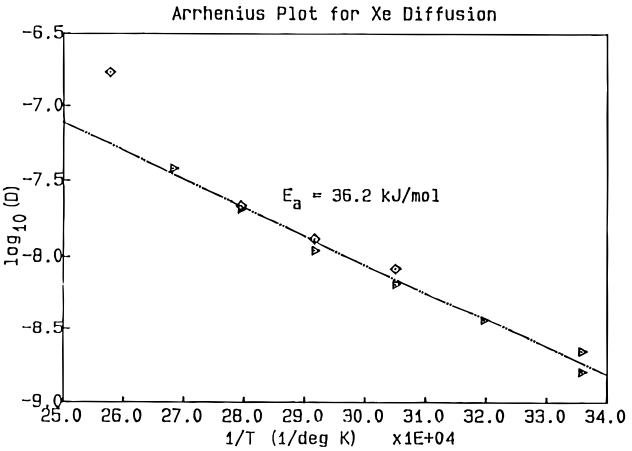

Figure 4. Arrhenius plot of log D vs $1/T$ for xenon in polystyrene.

For the time t much shorter than T_1, we may let $T_1 \rightarrow \infty$ or $k \rightarrow 0$ in eq 10 and obtain

$$\lim\ m(t) = (6/\pi^2)\sum(1/n^2)\exp[-Dn^2\pi^2/a^2t] \quad (12)$$

Equation 12 may be used to obtain an approximate value of D when the value of T_1 is either unknown or known to be large. In other words, the initial time period of the measured magnetization $m(t)$ may be fitted to eq 12 to yield an approximate diffusion coefficient of sorbed xenon.

In Figure 4 we present a plot of log D vs $1/T$ for temperatures below the glass transition to obtain an activation energy E_D for Xe in glassy PS. The diffusion constant at ambient temperature is (1.6−2.2) × 10^{-9} cm^2/s and the activation energy for diffusion of xenon in polystyrene below T_g is found to be about 36 kJ/mol. The values for both the ambient temperature diffusion coefficient and the activation energy can be compared with other literature determinations.[10,32] Tomaselli et al.[10] give a value of (13 ± 7) × 10^{-9} cm^2/s, though this is an effective diffusion constant for diffusion between lamellae of PS and PVME and is an average value for both polymer components. Odani et al.[32] quote a value of 0.6 × 10^{-9} cm^2/s and an activation energy of 50.2 kJ/mol for a low pressure of xenon (<2 atm) using transient time lag measurements. In spite of the lack of data on pure PS with a high concentration of sorbed xenon, the agreement is generally encouraging. The effect of sorbed xenon on the value of T_g for polystyrene shows the presence of modest plasticization as can be seen from the temperature dependence of T_1 (Figure 1), which indicates an inflection at approximately 100 °C. Likewise the diffusion constants increase significantly above 100 °C, reflecting more rapid translational motion in rubbery PS.

IV. Conclusion

The selective saturation method may be applied to other synthetic polymers and biopolymers for measuring diffusion coefficients of the sorbed xenon. There are, however, some obvious limitations: (i) a sample of interest has to be prepared as uniform spheres of controlled diameters; (ii) the sorbed ^{129}Xe NMR has to appear as a reasonably narrow and distinct peak. The line width of the peak is not easy to predict. For example, a very broad NMR peak is found for the xenon sorbed in PMMA beads. It is also possible to consider applying the experiment to nuclei other than xenon-129. The experiment can be applied to either glassy or rubbery polymers if the sphere size is adjusted to compensate for changes in the diffusion constant. If one has a known distribution of bead sizes, the diffusion constant can still, in theory, be extracted from the data since an analytical form (eq 10) is available and can be treated as a summation for the different radii (a). However, the sensitivity of the fit in such a situation may limit the precision to which D can be estimated.

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