

Self-Diffusion Measurements of Organic Molecules in PDMS and Water in Sodium Alginate Membranes

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ABSTRACT: The self-diffusion of some organic molecules in silicone rubber and of water and water–ethanol mixtures in sodium alginate membranes was investigated to obtain information on the transport behavior in these systems. The temperature dependence of self-diffusion was examined by the pulsed field gradient NMR technique. The experimental data confirm the homogeneous amorphous nature of PDMS and the affinity of silicone rubber to apolar solvents. The interrelations between solvent and polymer structures of the sodium alginate membrane varying the temperature have been obtained using differential scanning calorimetric. The results have been compared with the trend of self-diffusion coefficients, and structure modifications of the membranes have been evidenced. The overall results confirm the potentialities of the technique used in measuring transport parameter in polymeric membranes. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 1119–1128, 1999

Key words: self-diffusion; PDMS; sodium alginate membrane

INTRODUCTION

Membrane operations are extensively used today in various industrial separations processes, both in the gas and liquid phases. The transport mechanisms, which are at the origin of the membrane selectivity of dense polymeric films, are mainly described by a solubility model.¹ The overall permeability is given by the product of the various species in the polymeric phase multiplied by their diffusion coefficients in it. The relative contribution of these parameters on the permeability and selectivity can change, depending on the nature of the polymer and of the penetrants.^{2,3}

The availability of direct, fast, and sensitive methodology for independently measuring the solubility and the diffusion coefficient of various penetrants in the polymeric membrane and their variation with time is becoming important for correct design industrial operations.

The traditional way of studying the diffusion process in membranes is to follow the transient response of the adsorbate–adsorbent system after changing the pressure or the composition of the surrounding atmosphere.⁴ If it is possible to eliminate the influence of nondiffusive processes, either experimentally or through suitable data processing, from the analysis of the observed response curve the contributing diffusion coefficients may be calculated.⁵ A main feature of the sorption technique in all its modifications is the existence of sorbate concentration gradients within the sample. This state of nonequilibrium implies some difficulties with

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both the experimental procedure and the interpretation of results. Complications with the experimental procedure and the subsequent data processing are mainly due to the finite rate of sorption heat release⁶ and to external transport resistance in both the inlet (outlet) valves and the surrounding atmosphere as well as on the surface of the samples.⁷ An inherent limitation of the sorption technique is the change that may be induced by the sorbent in the membrane matrix.

Conformations of polymer molecular chains change successively by the thermal motion, resulting in the fluctuation of the occupation volume of the chains and the formation of "holes," which are effective transport channels allowing the small molecules to permeate easily. The "holes" size will fluctuate with the conformation change driven by ionic repulsion and stereo hindrance. Because swelling capacity often implies the expandability of the free volume, its marked increase means the expansion of the free volume and the "holes" size, and the components can permeate fast, so that the measured diffusion coefficient in many cases will result as an average of the "true" values at the two limiting sorbate loadings.

With the application of Nuclear Magnetic Resonance (NMR) to diffusion studies, these problems are overcome. The presence of preferential transport pathways or the features of heterogeneous media can be determined in many cases. In fact, the magnetic resonance methods are widely applied in the investigation of the matrix structure of polymeric and biological membranes, and of the diffusion mobility at the microscopic level.^{8,9}

Several NMR techniques have been used to study the submicrostructure of biological and polymeric membranes, yielding evidence of the presence of preferential transport pathways with dimensions from 0.3 to 5 nm.^{10,11} The Pulsed Field Gradient (PFG) NMR¹² is one of the most popular direct methods for the measurement of molecular and macromolecular translational mobility. Some modifications of this method are possible; they permit a direct measurement of molecular and ionic self-diffusion coefficients in these materials,¹³⁻¹⁷ as well as in microporous media¹⁸ and polymer solvent systems.^{18,19} PFG-NMR is a noninvasive analytical technique for studying transport phenomena at the microscopic scale. It measures molecular displacements in a fixed spatial direction during a diffusion time of the range of tens to hundreds of milliseconds. Its main ad-

vantages are that molecular diffusion rates are determined directly from the properties of nuclear spins of the target molecules, rather than having to be inferred indirectly from changes in the macroscopic properties of the system under study. Furthermore, an advantage of PFG-NMR is the possibility to investigate the self-diffusion process in a size ranging from 10^{-7} to 10^{-3} m, which is especially important in the case of restricted diffusion, as it enables one to find a correlation between structure and diffusion. In fact, this technique allows the determination of a critical range of diffusion rate that bridges the gap between methods better suited for studying diffusion over large molecular displacements and those for small molecular motions such as inelastic neutron scattering and laser interferometry. An other important feature of the technique is the possibility to separate the self-diffusion coefficients and solubilities of different penetrants in different microscopic environments in the case of a complicated self-diffusion processes.^{10, 11}

In some cases it has been shown that the membranes are nonhomogeneous,^{10, 11} and there are two channels in them. The diffusion property of the dense layer of a membrane is mainly determined by the self-diffusion in the channel slower.

In this study, the sequence used are the stimulated spin echo and the longitudinal eddy current delay. In the case of stimulated spin echo²⁰ (PGSTE) the sequence consists of three radio frequency (rf) 90° pulses and of two magnetic field gradient pulses. The rf pulses drive the spin system off the thermodynamic equilibrium, and the magnetic field pulses are applied to obtain information on the spin macroscopic spatial translation from the spin echo amplitude [Fig. 1(a)]. The longitudinal eddy current delay (PFGLED) sequence²¹ consists of seven pulses [see Fig. 1(b)]; five of them are (rf) 90° pulses. The other two pulses are the magnetic field gradient pulses. Accurate PFG-NMR studies of motions of slowly moving species at present are extremely difficult. The characteristically short traverse relaxation times of nuclear magnetization in some systems causes weak echo intensities in PFG spin echo experiments. In fact, for slowly moving species the required phase-encoding gradient pulses must have large amplitudes, resulting in eddy-current fields that can cause errors in the phase encoding. The PFGLED sequence permits the use of short traverse evolution times and the observation of accurate echo amplitudes and phases in the presence of large eddy-current field.

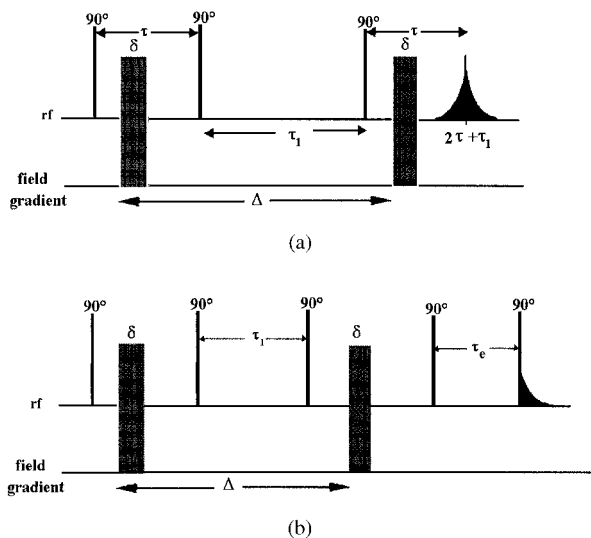


Figure 1 (a) Pulses scheme of the stimulated echo, and (b) of the longitudinal eddy currents sequences.

For molecules of penetrants undergoing unhindered an isotropic Brownian motion and for a vanishing steady field gradient, the evolution of spin echo amplitude due to self-diffusion is described by the following equation:²²

$$A(2\tau, \tau_1, \delta) = A(2\tau, \tau_1, 0) \exp[-(\gamma g \delta)^2 t_d D_s] \quad (1)$$

where γ is gyromagnetic ratio, $t_d = \Delta - \delta/3$ is the diffusion time, and D_s is the self-diffusion coefficient, $A(2\tau, \tau_1, 0)$ is the amplitude of the signal without gradient pulse, g represents the amplitude of the gradient pulses, and the meaning of times τ , τ_1 , τ_e , and δ is shown in Figure 1. During the experiment τ , τ_1 , g , and Δ are fixed, and only the dependence of A on δ is analyzed; the diffusion decay is expressed by the following equation

$$R = \frac{A(2\tau, \tau_1, \delta)}{A(2\tau, \tau_1, 0)} = \exp[-(\gamma g \delta)^2 t_d D_s] = \exp(-KD_s) \quad (2)$$

$$K = (\gamma g \delta)^2 t_d \quad (2\text{bis})$$

For a multiphase system and when the decay is nonexponential for a mixture of different penetrants, the diffusion decay is expressed by the following equation^{1,10}

$$R = \frac{A(2\tau, \tau_1, \delta)}{A(2\tau, \tau_1, 0)} = \sum_{i=1}^l \sum_{j=1}^m P^{ij} \exp[-KD_{sij}] \quad (3)$$

where D_{sij} is the self-diffusion coefficient of the i th component of penetrant in the j th transport channel of the membrane, if the membrane is not homogeneous. P^{ij} is the relative amount of nuclei of the i th component in channel j , and belongs to the molecules characterised by self-diffusion coefficient D_{sij} . In the case of two different transport channels or two components, eq. (3) becomes a biexponential equation,

$$R = \frac{A(2\tau, \tau_1, \delta)}{A(2\tau, \tau_1, 0)} = P \exp(-KD_{1s}) + (1 - P) \exp(-KD_{2s}) \quad (4)$$

For example, eq. (4) is useful when the resonance broadening due to the gradient pulses causes overlap of two resonances corresponding, for example, to the solvent inside and outside the polymer system.

The aim of this study is to validate the reliability of the PFG-NMR technique in bulk polymer/penetrant systems. For this reason the systems studied are two different polymers: a rubbery polymer, PDMS, and a glassy polymer, sodium alginate. The self-diffusion coefficients measured in bulk PDMS with this technique have been compared with the mean diffusion coefficient obtained by conventional methods on PDMS membranes. PDMS was chosen because a good amount of diffusion data on penetrants adsorbed in this amorphous polymer is available in the literature.²³⁻²⁵ This comparison was possible as the local diffusion rate, J_i , of penetrant i in a membrane can generally be depicted by Fick's first law. Under steady-state conditions this law takes the following form for one-dimensional diffusion:

$$J_i = D_i(C_{i,m}) \frac{dC_{i,m}}{dz}$$

where D_i is the local mutual diffusion coefficient of the penetrant/polymer system and $C_{i,m}$ is the penetrant concentration. Due to immobilization of the membrane D_i can be regarded as the self-diffusion coefficient.

The self-diffusion coefficient changes with temperature can give valuable information on changes in the membrane structure. In fact, the plot of the logarithm of the self-diffusion coefficient vs. the inverse absolute temperature usually follows a linear relationship when no structural change occur. The PFG-NMR technique has

already been used in determination of self-diffusion coefficient of water and ethanol/water mixtures in sodium alginate membranes. This preliminary study shows that the membranes are nonhomogeneous, and there are two different transport channels in them.

EXPERIMENTAL

Materials

The silicon rubber used in this study is a crosslinked polydimethylsiloxane (Sylgard 182 manufactured by Dow Corning). The samples were prepared by dissolving the polymer with 10 wt % curing agent in cyclohexane. The solution was placed in a 5-mm glass NMR test tube, the solvent was evaporated, and the solvent residue was dried in vacuum at 60°C for 12 h. The penetrants (reagent grade from Aldrich) were: toluene, benzene, *n*-hexane, *n*-heptane, *o*-xylene, *p*-xylene, acetone, isobutanol, ethyl acetate, and cyclohexanol. The solvents, used with no further purification, were added to the silicone sample, and the tube was sealed under nitrogen.

Sodium alginate (Kimitsu Chemical Industries, Japan) was an M (homopolymeric block of D-mannuronic acid)-rich polymer. An aqueous solution (2.7 wt %) was cast onto a glass plate after being filtered and degassed, and then dried at room temperature for 48 h. The membrane thickness was 20 μm . Water self-diffusion coefficient was measured on samples containing water (in the range of 25–125% wt of the dry membrane) and water + ethanol mixtures (in the ratios of 5 : 1 and 2 : 1). The penetrants were added to the membrane placed in a 5-mm glass NMR tube, and the tube was sealed under nitrogen.

Methods

The self-diffusion measurements were performed on a Bruker AM 300 NMR spectrometer operating at 300 MHz in the proton, using a pulsed field gradient experiment in a Fourier Transform mode (FT-PFG). In the case where PDMS systems were used, the echo stimulated the sequence (FT-PGSTE): the interval (Δ) between the magnetic field gradient pulse was kept constant and equal to 350 ms, while the intervals (τ and τ_1) between the rf 90° pulse were fixed to 150 and to 200 ms, respectively. The magnetic field gradient pulses duration (δ) was varied in the range of 2–20 ms.

The magnetic field gradient intensity (3.5 G/cm) was calibrated to 1% accuracy through parallel measurements on trace amounts of protons in D₂O, using established values from the literature.²⁶ The temperature was varied in the range 25–60°C, with a temperature controller (accuracy of about $\pm 0.2^\circ\text{C}$). The pulses current supply and the related thermostatic unit are commercial Bruker accessories.

A part of the measurements of PDMS were carried on a home-built NMR spectrometer operating at a proton resonance frequency of 16 MHz in the time domain using the classical PGSE sequence.¹² For these experiments the interval (Δ) between the magnetic field gradient pulse was varied, while the intervals between the rf 90° and 180° pulse was fixed to 20 ms. The magnetic field gradient pulses duration (δ) was kept constant and equal to 1 ms. A pulsed current supply, giving 7 A DC current, feeds the coil to obtain a 40.5-G/cm intensity field gradient. The gradient strength was calibrated with the self-diffusion coefficient of pure water at different temperatures and currents. The temperature was followed by a copper-constantan thermocouple, placed near the sample. The temperature was measured immediately before and after the spin-echo experiments; a stability of about $\pm 0.2^\circ\text{C}$ was obtained.

The self-diffusion in the PGSTE-NMR experiments is measured along the direction of the magnetic field gradient, that is, parallel to the sample tube axis in the 300-MHz spectrometer and perpendicular in the 16-MHz spectrometer.

PFG-NMR measurement in the sodium alginate membranes were carried out only with a Bruker AM 300 NMR spectrometer. The self-diffusion coefficients were determined using the PFGLED sequence. The interval Δ was fixed at 60 ms, while the intervals τ_1 and τ_e between the rf 90° pulse were fixed to 49.5 and 100 ms, respectively. The magnetic field pulses duration (δ) is kept constant and equal to 5 ms, while the magnetic field gradient intensity was varied in the range of 0–25 G/cm.

RESULTS AND DISCUSSION

The PDMS samples have been prepared by adding to the tubes the organic solvents (30 wt % of the dry polymer). In Table I the solvents used in this work and the temperature range of the measurements are reported.

Table I Organic Solvents (30% of the Dry Polymer) Adsorbed on PDMS Samples

Solvent	Temperature Range (°C)	
Toluene	25–60	Adsorbed
Benzene	25–60	Adsorbed
<i>o</i> -Xylene	25–60	Adsorbed
<i>p</i> -Xylene	25–60	Adsorbed
<i>m</i> -Xylene	25–60	Adsorbed
Cyclohexane	25–60	Adsorbed
Ethyl acetate	25–50	Adsorbed
Heptane	25–60	Adsorbed
Hexane	25–50	Adsorbed
Acetone	30–60	Partly adsorbed

The apolar solvents were entirely adsorbed by the polymer, but some polar solvents were also not completely adsorbed after some months.

The self-diffusion coefficient was measured when the solvent was completely adsorbed by PDMS at 25°C. In fact, when the solvent is not adsorbed, the spectrum shows more lines, stemming from different chemical neighborhoods that the solvent molecules experience.

By raising the temperature, the solvent is, in part, desorbed from the polymer to the vapor phase, because of the reduced capacity of the polymer to adsorb organic solvents when the temperature increases. The same effect was reported by Leemann et al.²⁷ in a study of vapor permeation and sorption of organic solvents in PDMS membranes.

The self-diffusion decay was analyzed with eqs. (1) and (4) to verify the presence of penetrant molecules with different mobility. The result, shown in Figure 2, indicates for the benzene one single self-diffusion coefficient, and therefore, an isotropic structure of PDMS at the microscopic level. The same result was obtained with the other solvents. In Figure 3 is shown the decay diffusion of toluene in Sylgard 182 by following aliphatic and aromatic protons. The best fit is exponential, in agreement with the homogeneous nature and the isotropic swelling of PDMS.

The diffusion behavior of toluene, *o*-xylene, *p*-xylene, and benzene in Sylgard 182 as a function of temperature is shown in Figure 4(a). The self-diffusion coefficient in both samples increases with increasing temperature. The temperature dependence approximately follows an Arrhenius relationship, and for benzene, toluene, and the other apolar solvents the diffusion is a slightly

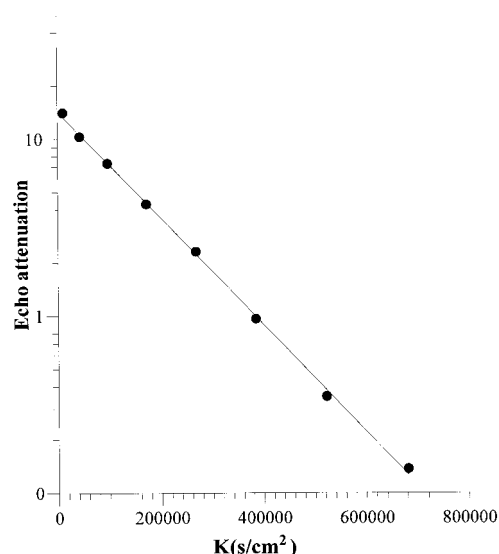


Figure 2 Diffusion decay of benzene in PDMS as a function of K performed on 16 MHz spectrometer using the classical PGSE sequence [see eq. (2) bis in the text]. The fitting of the data is obtained by using eq. (1), indicating that one single self-diffusion coefficient can describe the mass transport of benzene in PDMS.

endothermic process. In fact, the relative activation energies for diffusion (E_a) calculated for the apolar solvent using the well-known formula:

$$D(T) = D_0 \exp - (E_a/RT)$$

reported in Table II, are positive.

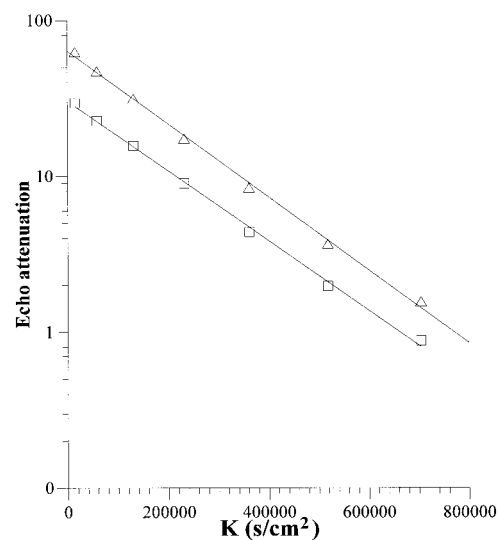
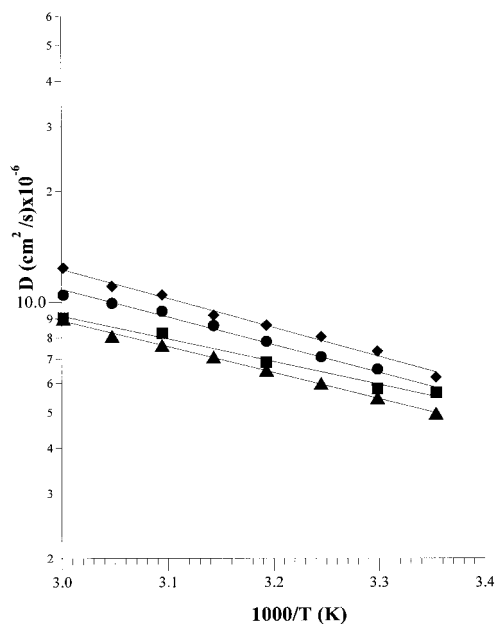
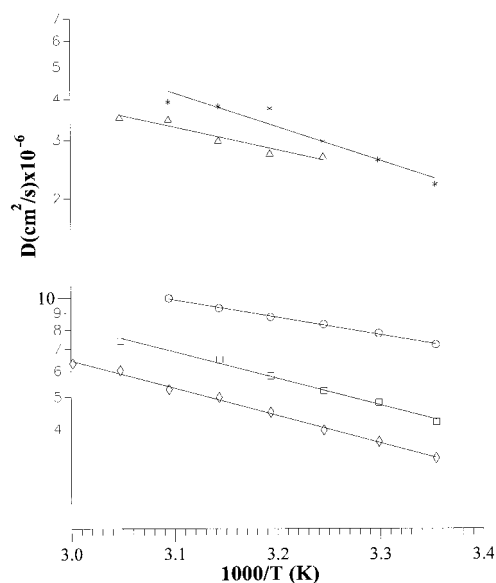


Figure 3 Diffusion decay of toluene in PDMS as a function of K performed on a Bruker AM300 spectrometer using the PGSTE sequence. Squares refer to the aromatic protons, triangles to aliphatic ones.

In addition, the diffusivity of the other aromatic solvents is, in most cases, higher than the diffusivity of toluene, even when, as in the case of *p*-xylene and *o*-xylene, masses and molecular di-



(a)



(b)

Figure 4 (a) Arrhenius plot of self-diffusion coefficients of aromatic solvents in PDMS. The symbols represent: \blacklozenge benzene, \blacktriangle toluene, \bullet *o*-xylene, \blacksquare *p*-xylene. (b) Arrhenius plot of self-diffusion coefficients of aliphatic solvents in PDMS. The symbols refer to: \square heptane, \triangle ethyl acetate, \circ *n*-hexane, $*$ acetone, and \diamond cyclohexane, respectively.

Table II Activation Energies for Apolar Organic Solvents in PDMS

Penetrant	E_a (KJ/mol)
<i>p</i> -Xylene	11.9
<i>o</i> -Xylene	14.5
Benzene	15.2
Toluene	13.6
Ethyl acetate	13.2
Acetone	19.6
Hexane	10.1
Heptane	15.4
Cyclohexane	15.9

mensions are larger. This effect is unusual, because the self-diffusion coefficient tends to decrease with increasing the permeant diameter, because it is necessary to displace larger number of segments of the polymer chain to open a larger opening between two different adsorption sites. The molecular dimensions are in the order benzene < toluene < *p*-xylene < *o*-xylene. The mobility of the molecules should be favored by the small size, but this is not the order that is found experimentally (benzene > xylenes > toluene). For what concerns the permeability, the effect is similar, as reported by Leemann et al.,²⁶ as toluene is less permeable than *p*-xylene.

Analyzing the solubility parameters can help to understand the inversion of mobility between toluene and xylenes: in fact, the order of molecular affinity according to the solubility parameters²⁷ is toluene \leq benzene < xylene.

The experimental results, therefore, demonstrate that the order of mobility is a compromise between molecular dimensions and chemical affinity.

The hypothesis could be made that, other things being equal, high chemical affinity of the solvent is more effective in decreasing the energy necessary to displace the macromolecular chains and to open a passage between two adsorption sites for the penetrant molecule.

The hypothesis is confirmed by comparing the activation energy for diffusion of the different penetrants examined (benzene > *o*-xylene > toluene > *p*-xylene). One difference with the order of chemical affinity with PDMS is given by *o*-xylene, whose position between benzene and toluene is justified by its high molecular dimensions and cross-section.

It is possible to derive the toluene diffusivity combining permeability and solubility from the

Table III Comparison between the NMR Organic Penetrant Self-Diffusion Coefficient Obtained in This Study and the Diffusion Reported in Literature

Penetrant	D (cm ² /s) (Reported in Literature)	D (cm ² /s) (in This Study)
Benzene	2.81×10^{-6} ^a	6.23×10^{-6}
<i>o</i> -Xylene	1.80×10^{-6} ^a	5.94×10^{-6}
<i>p</i> -Xylene	2.30×10^{-6} ^a	5.66×10^{-6}
Toluene	1.27×10^{-6} ^b	4.97×10^{-6}

^a Diffusion coefficients at zero concentration determined using a desorption technique at 20°C.

^b Diffusivity obtained combining permeability and solubility data at 40°C.³⁰

data of Leemann et al.,²⁷ and it has the same order of magnitude as the ones obtained with the NMR method. In the literature the diffusion coefficients at zero concentration of benzene, *o*-xylene and *p*-xylene in silicone rubber determined using a desorption technique are reported.²⁹ The data, reported in Table III and compared with our self-diffusion coefficients, are in good agreement.

When we consider nonaromatic molecules, especially with polarity beyond a certain value, the polymer adsorbed less and less solvent molecules. Consequently, in our experimental conditions it was impossible to measure a self-diffusion coefficient of alcohols in PDMS.

In Figure 4(b) the self-diffusion coefficients of some aliphatic solvents in PDMS are plotted vs. the reciprocal absolute temperature ($1/T$). Even in this case, the linearity of the data plotted is extended from room temperature to 60°C or less (boiling point of the solvent).

The order of mobility (acetone > ethyl acetate > *n*-hexane > *c*-hexane > heptane) closely follows the order of the chemical affinity derived from solubility parameters²⁷ (acetone < ethyl acetate < *n*-hexane, cyclohexane < heptane).

The marked difference in molecular dimensions explains the different mobility for hydrocarbons. If we look at the activation energies for diffusion they can generally be explain by considering both the chemical affinity with PDMS and the molecular size of the penetrants.

In the study of sodium alginate membranes the water decay diffusion was analyzed by eqs. (1) and (4). In Table IV the penetrant samples composition are reported. The best fit indicates the presence of two channels for diffusate movement

Table IV Penetrants Percentage Used in the Sodium Alginate Membrane

Sample 1	25% wt water
Sample 2	50% wt water
Sample 3	75% wt water
Sample 4	100% wt water
Sample 5	125% wt water
Sample a	100% wt water + 20% wt ethanol
Sample b	100% wt water + 50% wt ethanol

in sodium alginate membranes—in other words, a nonhomogeneous membrane structure on the contrary by PDMS samples.

In Figure 5 the plot for sample 4 is shown. It is evident that the presence of two different waters, in fact, the best fit is a biexponential function. In Figure 6 the values of two water self-diffusion coefficients obtained at 70°C by eq. (4) varying the water concentration are shown. The particular self-diffusion trend suggests the presence of membrane structural modification at changing of the water percentage. Those modification were confirmed by the DSC analysis, shown in Figure 7. In fact, when the sample contains more than 70% wt water, the transport looks Fickian; on the contrary, when it is less than 70% wt the self-diffusion coefficient decreases at higher water concen-

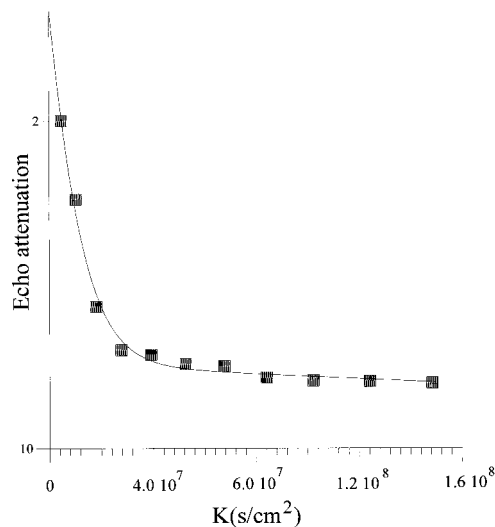


Figure 5 Diffusion decay of water in sodium alginate membrane (sample 4) as a function of K . The best fit is obtained by eq. (4), indicating that the presence of two different self-diffusion coefficient are necessary to describe the water mass transport in this system. The experimental data were performed on a Bruker AM300 using the PFGLED sequence.

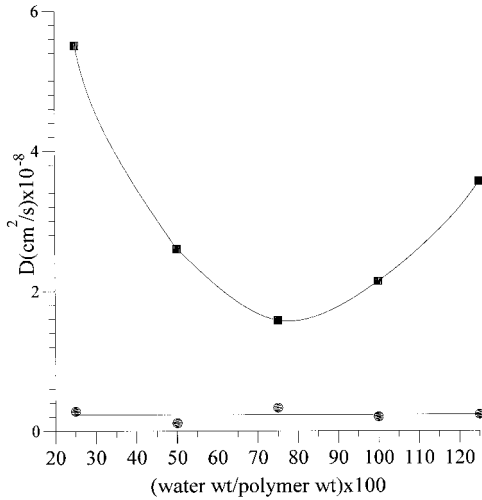


Figure 6 Water self-diffusion coefficient D_1 and D_2 in sodium alginate membranes, respectively, in channel 1 (■) and in channel 2 (●).

trations. This effect probably depends by gradual structural polymeric modification in the membrane that changes from crystalline to amorphous with increasing the water percentage. Beyond the 70% water, the structural modification is almost

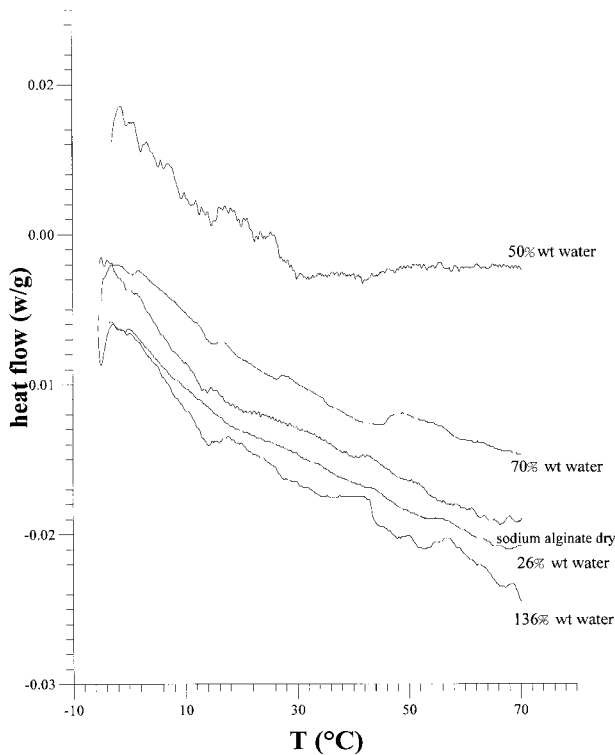


Figure 7 Differential scanning calorimetric sodium alginate membranes with different water percentage.

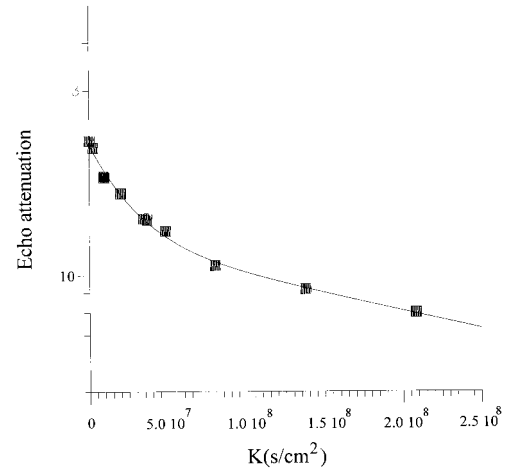


Figure 8 Water self-diffusion decay in sample a. The best fit is obtained by eq. (4), indicating that the presence of two different self-diffusion coefficient are necessary to describe the mass transport of water in this system. The experimental data were performed on a Bruker AM300 spectrometer using the PFGLED sequence.

complete, and although the system presents two different channels, the coefficient D_1 have a linear best fit, while D_2 is almost constant on the concentration penetrant range. In the sample containing the water/ethanol mixtures, the water percentage is fixed at 100% wt of the dry membrane, whereas ethanol is 20 and 50% wt. In sample a (Fig. 8), the decay trend indicates the presence of two different channels, while in sam-

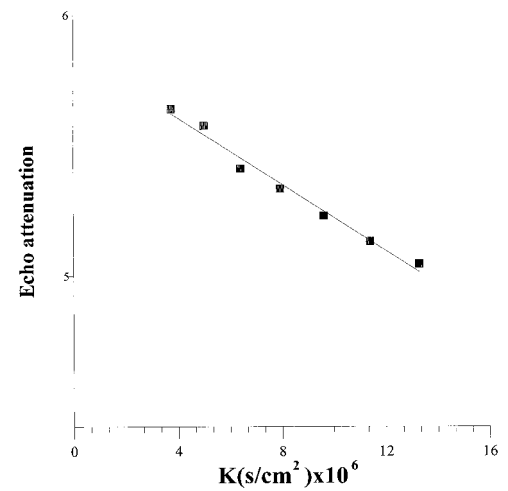


Figure 9 Water self-diffusion decay in sample b. The best fit is obtained by eq. (1). The experimental data were performed on a Bruker AM300 spectrometer using the PFGLED sequence.

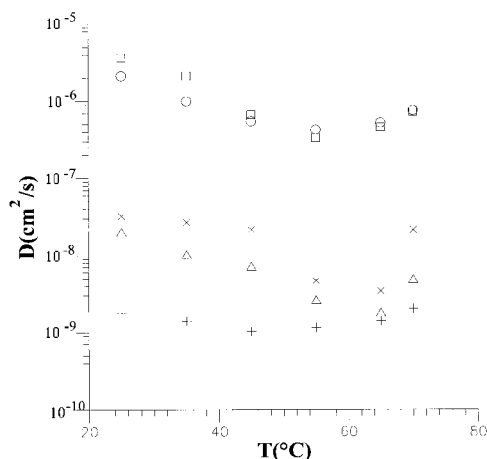


Figure 10 Temperature dependence of the water self-diffusion coefficient in sample 4 [channel 2 (+), the channel 1 (x)], in sample a [(□), channel 1; (△), channel 2 and in sample b (○)].

ple b the echo attenuation is fitted by a single exponential [(eq. (1), Fig. 9). The water self-diffusion coefficient obtained at different temperatures in samples a and b are compared with sample 4 (see Fig. 10 and Table V) with the same water percentage. In Table VI the water fraction that occupied the faster channel 1, in the different samples are reported. The data suggest that the channel 1 is more hydrophilic; in fact, the water fraction beyond 70% wt water when the structural modification are almost complete increase with increasing the water composition. Moreover, when the ethanol percentage is 50% (sample b) the water diffusion decay is a simple exponential function. This effect probably depends on the ethanol best affinity against the transport channel, which is more hydrophobic.

CONCLUSIONS

The self-diffusion of some penetrants in Sylgard 182 samples and sodium alginate membranes was measured by the PFG-NMR technique.

Table V Water Self-Diffusion Coefficient in the Different Channels for Sample 4, Sample a, and Sample b

T (°C)	Sample b	Sample a Channel 1	Sample a Channel 2	Sample 4 Channel 1	Sample 4 Channel 2
25	2.13e-6	3.68e-6	2.00e-8	3.20e-8	1.80e-10
35	1.00e-6	2.14e-6	1.02e-8	2.67e-8	1.40e-10
45	5.49e-7	6.72e-7	7.18e-9	2.13e-8	1.03e-10
55	4.25e-7	3.35e-7	2.64e-9	4.68e-9	1.15e-10
65	2.26e-7	4.59e-7	1.81e-9	3.46e-9	1.41e-10
70	7.63e-7	7.28e-7	4.93e-9	1.00e-8	2.03e-10

Table VI Water Fraction in the Channel Faster of Sodium Alginate Samples

	p_1 a 70°C
Sample 1	0.43
Sample 2	0.47
Sample 3	0.46
Sample 4	0.68
Sample 5	0.78
Sample a	0.97
Sample b	1

The PFG-NMR technique permits establishing a relation between the membrane structure and penetrants mobility. Owing to its ability to directly follow the individual stages of molecular migration, the PFG-NMR technique may provide unequivocal information on the mobility of the penetrant molecules as well as on the habit of the adsorbent particles as characterized, for example, by the accessibility of the active sites or the existence and intensity of surface barriers.

The transport of penetrants with a strong affinity for PDMS is characterized by a linearly increasing diffusion coefficient as is observed in the literature for other penetrant/rubber systems. The high diffusivity of organic solvent in Sylgard 182 depends on the high degree of polymer swelling.

The diffusivity plots as a function of inverse temperature follow an Arrhenius relationship, and the calculated activation energies are endothermic. In addition, the pattern of the spin echo decay shows that the polymer structure is homogeneous, with no preferential diffusion paths.

It was found that PDMS adsorbs preferentially apolar solvents. Polar molecules do not interact with the apolar polymer chains, resulting in a low solubility of the polar solvent in this material, but in a high mobility. A good agreement is found

with the order of permeability in PDMS membranes reported in the literature.

The water self-diffusion coefficients in sodium alginate membranes show a biexponential dependence, indicating the presence of two different transport channels for the water molecules. Upon increasing the water percentage in the system (membrane/penetrant) the self-diffusion coefficient trend, obtained at 70°C, indicates possible structure modifications of the membranes. These transitions are observed in the DSC analysis. The ethanol presence in mixture with water increases water mobility. Probably, this effect depends on perceptible changes in the swelling degree and by a greater water percentage that penetrates into channel 1 more hydrophilic.

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