J. Phys. Chem. A **2007,** *111,* 6131−6134 **6131**

ARTICLES

The Investigation of Water Diffusion into Teflon Copolymer Revealed by Fiber-optic Evanescent Wave Spectroscopy

Yosef Raichlin,[†,‡] **Sharon Marx,**[§] **and Abraham Katzir***[,†]

School of Physics and Astronomy, Sackler Faculty of Exact Sciences, Tel Aviv University, Tel Aviv, Israel, Department of Physics, College of Judea and Samaria, Ariel, Israel, and Department of Physical Chemistry, Israel Institute for Biological Research, Ness Ziona, Israel

Received: February 18, 2007; In Final Form: May 10, 2007

Fiber-optic evanescent wave infrared spectroscopy was used for the study of water diffusion in Teflon and has provided valuable information about the structure of water in amorphous hydrophobic polymers. Time-dependent absorption measurements were carried out in two spectral ranges: 3000−3800 cm^{-1}, associated with the O−H stretching mode, and 1620−1670 cm^{-1}, associated with the H−O−H bending mode of water. The results indicate that the IR spectra could be expressed as a superposition of spectra due to two species of water molecules: strongly and weakly hydrogen-bonded. We suggest that water molecules form clusters with strongly hydrogen-bonded molecules at the cores and with weakly hydrogen-bonded molecules at the external parts of the clusters. A mathematical model, based on a linear diffusion equation with a moving boundary, gave a ratio of 3.5 between the total number of molecules in a cluster and the number of water molecules at the core of the cluster.

1. Introduction

Water molecules incorporated in a polymer matrix (even in small concentrations) are known to influence the properties of the polymer. In addition, the physical state of these water molecules is significantly different from their state in liquid water.[1] The structure of water in polymer systems has been extensively studied by various methods, including spectroscopic techniques.[2−5] Among these, vibrational spectroscopy is a powerful tool for the investigation of the structure of water. In particular, the vibrational modes of the 0−1 transitions, which give rise to strong absorption in the middle infrared (mid-IR) range, have been useful for the analysis of the structure of water.[6]

Infrared absorption measurements can be performed during the penetration of water molecules into a polymer matrix. The time-dependent changes of the frequencies, intensities, and the shapes of water bands have been associated with changes in the structure of water in the polymers.[7−9] Unfortunately, the high absorption of water in the mid-IR has limited the use of transmission spectroscopy in this spectral range.

One of the methods proposed to overcome these difficulties is attenuated total reflectance (ATR) spectroscopy,[10,11] also called evanescent wave spectroscopy (EWS). ATR spectroscopy is based on the propagation of a beam of light inside a waveguide of index of refraction, n_1, which is surrounded by a medium (the sample) with a lower index of refraction, n_2. The beam makes a series of total internal reflections at the waveguide/sample interface. At each refraction, the electrical field penetrates into the sample and it decays exponentially with the distance from the interface. When the sample absorbs specific frequencies of light in the evanescent wave, the reflection is attenuated at these frequencies and the guided wave has a reduced intensity at these frequencies, resulting in an absorption spectrum, which is the basis of EWS. This technique can be realized by using an ATR-element which is frequently placed inside an FTIR spectrometer. With the development of optical fibers that are transparent in the mid-IR, it was realized that segments of these fibers may serve as ATR elements. This gave rise to fiberoptic evanescent wave spectroscopy (FEWS). The FEWS method in the mid-IR range can be successfully adapted[12−15] for the study of the diffusion of liquids in polymers.

2. Experimental Section

For the FTIR−FEWS measurements, we used silver halide fibers which have been developed in our laboratory. These fibers[16,17] are flexible and nonhygroscopic and they have a wide transmission window in the range of 3−20 μm. A segment of an unclad *AgClBr* fiber coated with a desirable polymer served as a sensor element. The polymer used in this study was Teflon AF 1600, a copolymer of TFE with 2,2-bistrifluoromethyl-4,5-difluoro-1,3-dioxole, made by Dupont. The perfluorinated structure renders the polymer hydrophobic in character. Silver-halide fiber segments of a diameter 0.9 mm and length of 10 cm were dip-coated, and the thickness of the coating was estimated to be $L = 7\ \mu$m

The experimental FEWS set up consisted of an FTIR spectrometer (Bruker, model Vector 22) with a homemade cell

---

* Corresponding author phone: +972-3-6408301; fax: +972-3-6415850; e-mail: katzir@post.tau.ac.il.

[†] Tel Aviv University.

[‡] College of Judea and Samaria.

[§] Israel Institute for Biological Research.

10.1021/jp071377v CCC: $37.00

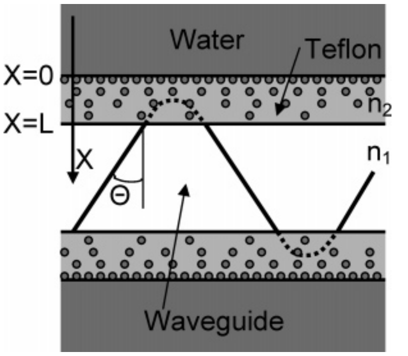

Figure 1. Evanescent wave at the interface between two media, under total internal reflection.

designed for liquid measurements. Radiation from the IR source of the spectrometer was focused on the input end of the sensor element, using a *ZnSe* lens of a focal length 1 in. Radiation collected from the output end of the fiber was focused, using a similar lens, onto the nitrogen-cooled MCT detector of the spectrometer. The FTIR spectrometer was kept at a constant temperature and was purged with dry nitrogen to eliminate water vapor absorption. Measurements on this fiber revealed the absorption spectrum of the polymer coating, and the result of these measurements served as a background for further measurements.

At time *t=0*, the coated sensor was immersed in water. Molecules of water penetrated into the polymer and reached the evanescent field region (see Figure 1). Measurements were taken continuously, and the background was subtracted from the results of each measurement. The difference between the results and the background showed the absorption due to water.

3. Spectral Measurements

We carried out spectral measurements of a polymer-coated fiber in water over a spectral range of 4000−600 cm^{-1}, but we were particularly interested in three narrower spectral regions: (1) The region of the stretching modes of water molecules (3800−3200 cm^{-1}); (2) The region of the bending modes of the water molecules (1700−1500 cm^{-1}); (3) The "fingerprint region" of the vibrational modes of Teflon (1050−1350 cm^{-1}).

The amplitudes of the absorption spectra of water increased during the diffusion process, as more and more water penetrated the polymer and reached the evanescent wave region near the silver-halide fiber. On the other hand, the amplitudes of the absorption spectra of the polymer itself decreased during the diffusion process.

The time-dependent changes in the spectra of water during the diffusion process are shown in Figures 2 and 3. Each of the absorption peaks exhibited a low-frequency and a high-frequency shoulder, and in each peak the shoulders showed a different time dependence.

In order to study the time-dependent behavior, we expanded each of the curves to two Gaussians. The stretching mode band was expanded to a low-frequency component centered at a wavenumber $\tilde{\lambda}_{\nu1} = 3260$ cm^{-1} and a high-frequency component centered at a wavenumber $\tilde{\lambda}_{\nu2} = 3400$ cm^{-1}. The bending mode band was expanded to a low-frequency component centered at a wavenumber $\tilde{\lambda}_{\delta1} = 1635$ cm^{-1} and a high-frequency component centered at a wavenumber $\tilde{\lambda}_{\delta2} = 1670$ cm^{-1}. The dependence of the normalized amplitudes of the four components on the square root of time is shown in Figure 4. One can see that the time dependence of the high-frequency component of the stretching mode is similar to that of the low-frequency component of the bending mode. Also, the time dependence of the low-frequency component of the stretching mode is similar to that of the high-frequency component of the bending mode. There is a significant difference in the time-dependent behavior of the two groups of modes. In Figure 5, we display the absorption spectra of the Teflon itself, in the "fingerprint region", during the diffusion process.

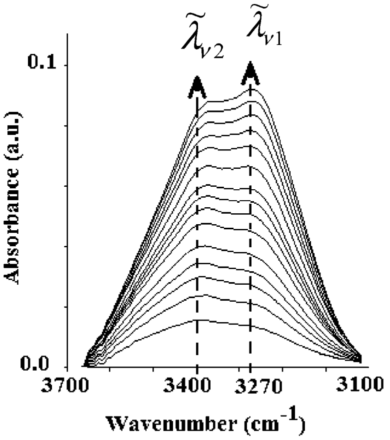

Figure 2. The evolution of the stretching band of water in the Teflon matrix during the first 500 s of the diffusion process (the interval between measurements was 30 s).

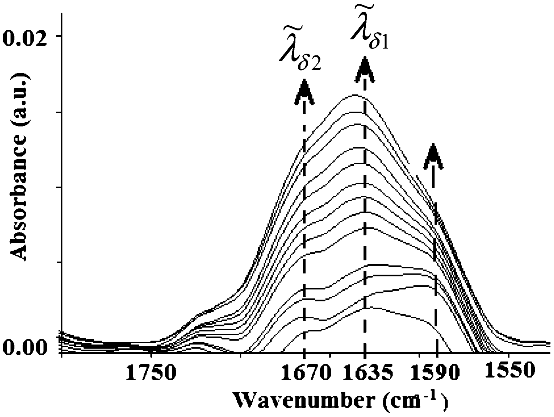

Figure 3. The evolution of the bending band of water in the Teflon matrix during the first 400 s of the diffusion process (the interval between measurements was 30 s).

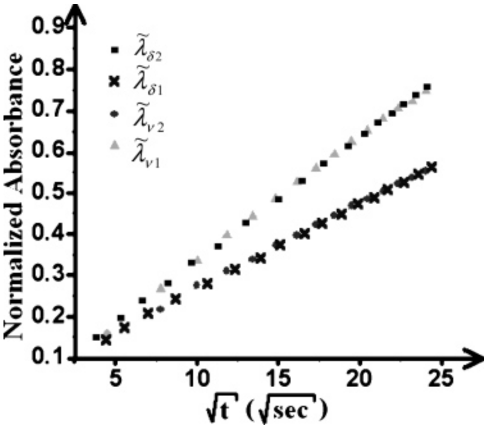

Figure 4. The dependence of normalized absorbance of the four components on the square root of time.

4. Discussion

According to the mixture model of the structure of water,[18−20] molecules of water which exhibit a high-frequency stretching

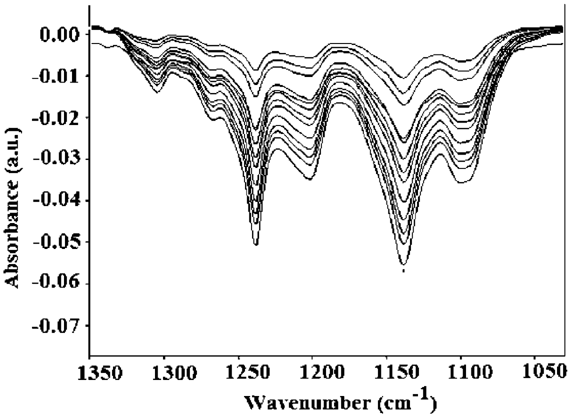

Figure 5. Time dependence of the absorption spectrum of Teflon during the diffusion process. The first 400 s are shown and measurements were carried out every 30 s.

mode (and a low-frequency bending mode) are weakly H-bonded water molecules and molecules of water which exhibit a low-frequency stretching mode (and high-frequency bending mode) are strongly H-bonded. The appearance of two species of water molecules with different rates of diffusion can be explained in the following way: water molecules form clusters. The strongly bonded species (which we called Water I), are situated at the cores of clusters, while the species with weakly bonded molecules (which we called Water II) form the external layers of the clusters. The diffusion rate of Water I should be slower than that of Water II, and this is indeed shown in Figures 4 and 5. The weakly H-bonded molecules are able to break their bonds with the cluster and execute individual diffusion motions. These molecules may become centers of new clusters formation. The wavenumber at 1590 cm^{-1} at the shoulder of the bending band (see Figure 3) can be attributed to the free water molecules.[21] This component increases significantly in the initial stages of the diffusion.

The "negative" bands of Teflon, shown in Figure 5, are probably due to a strong swelling of the polymer matrix, which is as a result of the water-diffusion process. It is unlikely that the small water molecules will cause such strong swelling of the polymer, especially at the very early stages of the diffusion process. Swelling was probably due to an aggregation of water molecules which penetrated into the Teflon, and this is additional evidence that water molecules did form clusters. As will be shown later, the absorption of IR-radiation is proportional to the mass of the molecules, which penetrate into the measurement area (i.e., the evanescent field area). The experiment shows a good linear dependence between the absorption signal and the square root of time, for the initial diffusion stage (the first 500 s). The kinetics of the diffusion process can be described in such a case either by Fick's law with a fixed coefficient of diffusion or by Fick's law for the case of a moving border. The first option can be ruled out because of the swelling of the polymer (see Figure 5). The diffusion of Water I molecules at the cluster core should, therefore, be described by means of a diffusion equation with a moving border (i.e., the moving of the clusters border).[22] Fick's law is termed one-dimensional in situations where the thickness of the polymer layer is much smaller than the radius of the fiber. In our case, the thickness of the polymer layer is indeed much smaller than the fiber radius (the ratio is 10^{-3}). Therefore, we can write

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}$$

where c is the concentration of Water I molecules in the polymer layer, D is the diffusion coefficient, and the axis x is normal to the surface of the fiber. We define $x = 0$ at the water-polymer interface, $x = L$ at the polymer-fiber interface (see Figure 1), and $x = \epsilon$ at the border of the clusters.

The diffusion equation is solved for the region $0 < x < \epsilon$ and for $x = \epsilon$:

$$-D\frac{dc}{dt_{x=\epsilon}} = \eta\frac{d\epsilon}{dt}$$

η is the concentration of the clusters in the polymer. The boundary conditions are $c = c_0$ for $x = 0$ (the border between polymer and water) and $c = 0$ for $x = \epsilon$.

The solution of the diffusion equation is

$$c = c_0\left[1 - \frac{\mathrm{erf}(x/2\sqrt{Dt})}{\mathrm{erf}(\beta)}\right]$$

β is a parameter that can be determined from the following equation:

$$\frac{\exp(-\beta^2)}{\sqrt{\pi}\,\mathrm{erf}(\beta)} = \frac{\eta}{c_0}\beta$$

The moving coordinate of the cluster's border is given by

$$\epsilon = 2\beta\sqrt{Dt}$$

The flux of water molecules into the polymer layer is given by

$$J = -D\frac{\partial c}{\partial x_{x=0}} = \frac{\eta\beta}{2\exp(-\beta^2)}\sqrt{\frac{4D}{t}}$$

The mass of water that penetrates into the polymer layer within a time t can be expressed as

$$M = \int_0^t J dt = 2\eta\beta\exp(\beta^2)\sqrt{Dt}$$

For this time, the mass of Water I in the polymer is calculated to be

$$M^{\mathrm{I}} = \eta\epsilon = 2\eta\beta\sqrt{Dt}$$

and the mass of Water II in the polymer is therefore

$$M^{\mathrm{II}} = M - M^{\mathrm{I}} = 2\eta\beta\{\exp(\beta^2) - 1\}\sqrt{Dt}$$

It can be shown[10] that evanescent field in the polymer (see Figure 1) can be expressed as $E(x) = E(L)\exp(x-L)/d_p$, where d_p, the penetration depth, is given by the expression

$$d_p = \frac{\lambda}{2\pi n_1\sqrt{\sin^2\theta - n_{21}{}^2}}$$

where λ is the wavelength of the light and $n_{21} = n_2/n_1$. Typically, d_p is on the order of the wavelength of the light in the sample.

The absorption of IR radiation in fiber-optic evanescent wave spectroscopy[12] is given by

$$A = K\exp\left(-\frac{2L}{d_p}\right)\int_\epsilon^0 c(x)\exp\left(\frac{2x}{d_p}\right)dx$$

K is a coefficient that depends on several factors: the total internal reflection of IR radiation at the fiber surface, the electrical field of the evanescent field at the fiber surface and the excitation coefficient of the molecular absorption mode.

During the early stages of the diffusion $\epsilon \ll d_p$ and the integral in the equation for A is proportional to the mass M. Therefore, A is also proportional to M and we can write

$$\frac{A^{I}}{A^{II}} = \frac{M^{I}}{M^{II}} = \exp(\beta^2) - 1$$

From the ratio of the experimental slopes in Figure 5, we can obtain the ratio $A^{I}/A^{II} \cong 1.5$ (for the initial state of diffusion), and therefore, $\beta = 0.96$ and $c_0/\eta = 3.5$. As mentioned, η is the concentration of cluster-forming centers, and therefore, c_0/η gives the ratio between the total number of molecules and the number of Water I molecules in the cluster. The simplest cluster that satisfies this ratio is the cluster of 14 molecules, with four molecules at its core.

5. Summary

FEWS−FTIR measurements were carried out using a $AgCl_xB_{1-x}$ fiber that was coated with a Teflon layer and immersed in water. This setup made it possible to carry out a very large number of measurements and to carefully study the diffusion of water in the Teflon layer. The high-quality spectra obtained enabled us to follow the kinetics of the diffusion process, including its very early stages. We hypothesize that there are two species of water molecules in the polymer matrix: strongly H-bonded molecules and weakly H-bonded ones. Water molecules that penetrate into the polymer form clusters. At the cores of the clusters there are four coordinate water molecules, and at the external parts of the clusters there are water molecules with destroyed H-bonds. These two species show different rates of diffusion in the Teflon. The simplest form of the cluster is a tetrahedral cluster with four water molecules at its core. The results of our studies make it possible to investigate the state of water in a hydrophobic amorphous polymer such as Teflon.

Acknowledgment. The help of Dr. Dan Grinstein is gratefully acknowledged.

References and Notes

(1) Coyle, F. M.; Martin, S. J.; McBrierty, V. J. *J. Mol. Liq*. **1996**, *69*, 95.

(2) Bagno, A.; Lovato, G.; Scorrano, G.; Wijnen, J. W. *J. Phys. Chem*. **1993**, *97*, 4601.

(3) Bradl, S.; Lang, E. W. *J. Phys. Chem*. **1993**, *97*, 10463.

(4) Nishikawa, S.; Ueda, M. *J. Phys. Chem*. **1993**, *97*, 3539.

(5) Tubergen, M. J.; Kuczkowski, R. L. *J. Am. Chem. Soc.* **1993**, *115*, 9263.

(6) Eisenberg, D.; Kauzmann, W. *The Structure and Properties of Water*; Oxford University Press: Oxford, 1969.

(7) Scherer, J. R.; Bailey, G. F.; Kint, S.; Young, R.; Malladi, D. P.; Bolton, B. *J. Phys. Chem.* **1985**, *89*, 312.

(8) Ononi, G.; Santucci, A. *J. Phys. Chem.* **1993**, *97*, 5430.

(9) Ostrovskii, D.; Paronen, M.; Sunholm, F.; Torell, L. M. *Solid State Ion* **1999**, *116*, 301.

(10) Harrick, N. J. *Internal Reflection Spectroscopy*; John Wiley: New York, 1967.

(11) Marechal, Y.; Chamel, A. J. *J. Phys. Chem.* **1996**, *100*, 8551.

(12) Fieldson, G. T.; Barbari, T. A. *Polymer* **1993**, *34*, 1146.

(13) Fieldson, G. T.; Barbari, T. A. *AIChE J.* **1995**, *41*, 795.

(14) Cava, D.; Sammon, C.; Lagaron, J. M. *Appl. Spectrosc*. **2006**, *60*, 1392.

(15) Yarwood, J.; Sammon, C.; Mura, C.; Pereira, M. *J. Mol. Liq.* **1999**, *80*, 93.

(16) Messica, A.; Grenstein, A.; Katzir, A. *Appl. Opt.* **1996**, *35*, 2274.

(17) Bormashenko, E.; Sheshnev, A.; Raichlin, Y.; Katzir. A. *Polym. Adv. Technol.* **2002**, *13*, 1039.

(18) Eisenberg, D. D.; Kauzmann, W. *The Structure and Properties of Water*; Oxford University Press: London, 1969.

(19) Walrafen, G. *J. Chem. Phys.* **1967**, *47*, 114.

(20) Raichlin, Y.; Millo, A.; Katzir, A. *Phys. Rew. Let.* **2004**, *29*, 185703.

(21) Shen, Y.; Wu, P. *J. Phys. Chem. B* **2003**, *107*, 4224.

(22) Crank, T. *The Mathematics of Diffusion*; Clarendon Press: Oxford, 1975.