

# An attenuated total reflectance cell for analysis of small molecule diffusion in polymer thin films with Fourier-transform infrared spectroscopy

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(Received 1 August 1997; revised 10 November 1997; accepted 17 November 1997)

A cell is described for characterizing the diffusion of small molecules through thin polymer films using attenuated total reflectance (ATR) Fourier-transform infrared spectroscopy. The cell is designed to be used with precast (commercially extruded) polymer films, removing the need to cast the film directly onto the ATR crystal and allowing the as-processed transport properties of the film to be assessed. Pressurized gas is used to maintain contact between the polymer film and the ATR crystal during the diffusion experiment. Data are presented to demonstrate the use of this cell for measuring the diffusion of a gas (CO<sub>2</sub>), two liquids (amyl acetate and limonene), and simultaneous diffusion of individual components from a liquid mixture (50/50 amyl acetate/limonene) through thin polymer films. In the last case, it was found that pure penetrant transport rates do not necessarily apply to diffusion of the same penetrants from a mixture. Diffusion coefficients obtained from the ATR cell compare favourably with values obtained gravimetrically for the same polymers and penetrants. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: diffusion; polymers; small molecules)

## INTRODUCTION

Diffusion coefficients of small molecules in polymers are readily measured using gravimetric techniques<sup>1,2</sup>. In these methods, the sample geometry is adjusted so that analytical solutions to the time-dependent diffusion equation can be obtained, and experiments can be completed in a reasonable time. The time required for a small molecule undergoing Fickian diffusion to move a distance  $x$  is approximately given by  $x^2/D$ , where  $D$  is the diffusion coefficient. For small gaseous diffusants,  $D$  is high, which allows for a larger diffusion path length and sample size. Large organic molecules have smaller  $D$  values, and a short diffusion path length is desirable. This can usually be achieved with thin polymer films or monodisperse spherical latex particles, which enable diffusion coefficients as low as  $10^{-18}$  cm<sup>2</sup> s<sup>-1</sup> to be measured<sup>3</sup>.

When the diffusant molecule is infrared active, the attenuated total reflectance (ATR) sampling method coupled with Fourier-transform infrared spectroscopy can also be used to measure small molecule diffusion in polymer thin films. Penetrant molecules are placed in contact with the side of the polymer film opposite the ATR crystal, and infrared spectra are collected as a function of time as the penetrant molecules diffuse toward the film/crystal interface. The evanescent wave in an ATR experiment samples only the first several  $\mu$ m of the polymer surface in contact with the ATR crystal, thus providing a short diffusion path length for larger diffusing molecules. Proper analysis of the time-dependent intensity of the diffusant infrared peaks as the diffusant moves into or out of the polymer film yields a diffusion coefficient. This method is especially useful for in

situ analysis of liquid diffusion in polymers, as it overcomes the problems associated with 'blot and weigh' immersion techniques that are normally applied in this case.

Analysis of small molecule diffusion in polymers with ATR is not new. Use of this method for studying diffusion of acetone into poly(isobutylene) was reported by Lavrent'ev *et al.* more than 20 years ago<sup>4</sup>. The ATR method was also suggested for analyzing individual diffusivities of components of a mixture, to observe various stages of diffusion in multilayer systems, and to assess the delamination of adhesive joints in a 1983 publication<sup>5</sup>. In a 1988 publication, we reported use of ATR methods to measure diffusion of CaCO<sub>3</sub> out of paint films exposed to sulfurous acid<sup>6</sup>. The samples in this work were immersed in the acid for various amounts of time and then removed, thus they contained 'frozen' CaCO<sub>3</sub> concentration profiles and the analysis was not conducted in real time. Nevertheless, excellent agreement was obtained between diffusion coefficients obtained with the ATR method and real-time bulk weight loss measurements. The mathematical methodology for extracting diffusion coefficients from the ATR data using an iterative numerical technique was also developed in this paper. In a later publication (1994), we conducted real time measurements with the ATR technique, which allowed simultaneous, independent measurement of water diffusion into the paint, diffusion of CaCO<sub>3</sub> out of the paint, and the swelling kinetics of the paint resulting from water uptake<sup>7</sup>.

Other groups have also exploited the ATR method. In 1992, Scholttter and Furan reported the diffusion of additives in polyolefins and attempted to relate the infrared absorbance of the additives to their mass uptake<sup>8</sup>. Fieldson and Barbari have studied the diffusion of water in polyacrylonitrile, acetone in poly(methyl methacrylate) and polypropylene, and methanol in polystyrene and

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poly(methyl methacrylate)<sup>9-11</sup>. They showed that the ATR method could be applied to polymer/penetrant systems which follow Case II diffusion kinetics as well as Fickian systems. Finally, the ATR technique has been used by a number of groups for studying polymer-polymer interdiffusion<sup>12-15</sup>.

Experimentally, the ATR method has in the past required the polymer film to be solution-cast or hot-pressed directly onto the ATR crystal in order to obtain the intimate contact necessary for evanescent field spectroscopy. This is undesirable for a number of reasons. (1) The casting or hot-pressing process affects the morphology of the polymer film, and can alter its transport properties as well. For commercially extruded films intended for specific barrier applications, the properties of the as-extruded film are desired. (2) Delamination can occur at the polymer-ATR crystal interface due to stresses imposed by the penetrant as it diffuses into the polymer. This is especially true for high-solubility liquid penetrants that can swell the polymer. In these cases, contact of the polymer with the ATR crystal can be lost, diffusant can accumulate between the polymer and the ATR crystal, and the diffusant peak intensities will no longer be proportional to the concentration of diffusant in the polymer. (3) Background spectra cannot be recorded through the ATR accessory after the polymer film is applied. (4) Complete removal of the polymer film and cleaning/polishing of the ATR crystal after the experiment can be tedious.

In this paper, an ATR cell designed for analysis of small molecule diffusion in polymers is described that overcomes the above difficulties. It utilizes commercial or pre-cast polymer films, and can be used for measuring diffusion of gaseous or liquid penetrants. Contact between the polymer film and the ATR crystal is maintained throughout the experiment via pressurized gas. Results are presented for diffusion of a gas, two liquids, and simultaneous measurement of the diffusivities of two liquids in a mixture through polymer films. For the first two cases, the ATR data are compared with gravimetric sorption data collected for the same polymer/penetrant systems.

## ATR CELL DESIGN

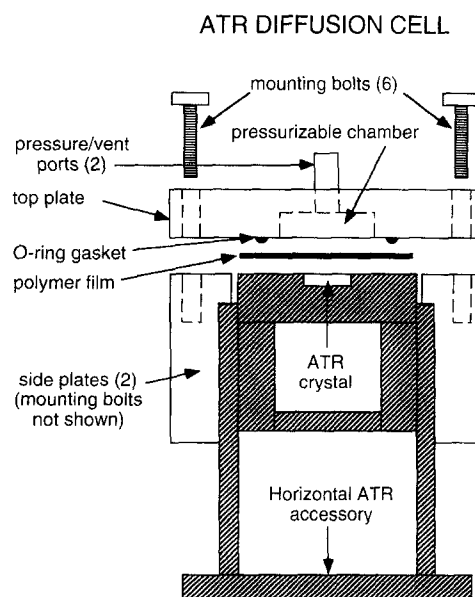
A cross-sectional drawing of the ATR cell is shown *Figure 1*. The cell is essentially a modification of a commercially available horizontal ATR accessory (shaded portion of *Figure 1*). Most horizontal ATR accessories could be similarly modified for this purpose. Stainless steel side and top plates were added to the original ATR accessory. The top plate contains a hollowed-out rectangular pressurizable chamber that covers and surrounds the ATR crystal. Two ports open into this chamber; one is attached to a gas cylinder, while the other is fitted with a valve to vent the chamber and to allow addition of liquid penetrants. The chamber is pressure-sealed against the top surface of the ATR accessory by a rectangular O-ring gasket. The polymer film sample is held in place between the O-ring and the top surface of the ATR accessory when the top plate is bolted down. The dimensions of the polymer film must be large enough to extend beyond the O-ring gasket, and are typically 1.75" × 4.5" for our prototype. Somewhat smaller films could be accommodated by reducing the size of the pressurizable chamber, which is ultimately limited by the dimensions of the ATR crystal.

The key element in the design of this cell is the use of pressurized gas in the sealed chamber above the ATR crystal to achieve and maintain intimate contact between the

polymer film and the ATR crystal. The use of hydrostatic pressure for this purpose is unique to our knowledge, and ensures uniform and reproducible contact of the polymer film across the entire ATR crystal surface. The amount of gas pressure needed to achieve good polymer/crystal contact depends on the thickness and compliance of the polymer sample. Good results have been obtained with gas pressures from 15 to 50 p.s.i. for a number of different polymers having thicknesses from 25 to 100 μm. At these low pressures, both polymers and liquids are essentially incompressible, thus the pressure will not affect the measured diffusivities. Since the ATR crystal is not mounted with an airtight seal, the bottom surface of the polymer film is at atmospheric pressure, which creates a pressure differential across the polymer film. This is important, as it keeps the polymer film in contact with the ATR crystal throughout the diffusion process, even when liquid penetrants that swell the polymer are used.

The type of pressurizing gas used depends on the intended application. If a conventional ATR spectrum of the polymer alone is desired, an infrared-inactive gas such as nitrogen or argon can be used. By venting the chamber, contact between the polymer film and the ATR crystal is lost, which allows background spectra to be conveniently collected without removing the ATR cell or polymer sample from the spectrometer. Use of an infrared-active gas such as CO<sub>2</sub> to pressurize the cell allows measurement of diffusion of that gas through the polymer. If diffusion of a liquid into the polymer is being studied, the liquid is first added through the vent port, followed by pressurization with an infrared-inactive gas.

Although not incorporated into our prototype device described here, temperature control could be added by fitting the top plate of the ATR crystal plate with cartridge heaters, or by drilling holes lengthwise through the top plate to admit a thermostatted fluid from a constant-temperature bath. In experiments where liquid flow is required across the polymer sample (e.g. diffusion/leaching of compounds out of a polymer film), the liquid could be pumped through the chamber using the two ports. In this case, the liquid itself would supply the necessary pressure to maintain the



**Figure 1** End view of the horizontal ATR accessory modified for ATR diffusion measurements. The infrared beam path is perpendicular to the plane of the paper

polymer film/ATR crystal contact. The inlet and outlet port diameters would have to be designed to maintain an elevated pressure inside the chamber.

## EXPERIMENTAL

### Materials

Commercial polymer films were used. High-density polyethylene film (HDPE, 26.3  $\mu\text{m}$  thick) was obtained from Amoco Corp., and low-density polyethylene film (LDPE, 97.5  $\mu\text{m}$  thick) was obtained from Hunstman Film (Carrollton, OH). Polyethylene is especially well-suited for ATR diffusion experiments since its infrared spectrum is very simple and contains wide spectral regions with nearly zero absorbance, thus providing several 'windows' for monitoring penetrant infrared absorbances. Polystyrene film (PS, 52.5  $\mu\text{m}$  thick) was obtained from Dow Plastics. Amyl acetate (*n*-pentyl acetate) and limonene were obtained from Aldrich Chemical Co. and used as received.

### ATR diffusion measurements

The ATR diffusion cell was mounted in an Analect model FX-6260 FT-i.r. spectrometer. A ZnSe ATR element with a 45° incidence angle was used. Although the cell temperature was not directly controlled, the heat generated within the sample compartment raised and maintained the cell temperature at  $33 \pm 1^\circ\text{C}$ . Background spectra were collected just prior to each diffusion experiment with the diffusion cell depressurized and polymer sample in place as noted above. Nitrogen at 25–40 p.s.i. was used as the pressurizing gas during diffusion experiments conducted with amyl acetate and limonene. The spectrometer was programmed to acquire approximately one spectrum per second, and to average blocks of 10–30 spectra for each data point to improve the signal-to-noise ratio.

### Gravimetric diffusion measurements

Gravimetric sorption/diffusion experiments using gaseous or vaporizable penetrants were carried out using a conventional electrobalance (Cahn C2000) interfaced with a computerized data acquisition system. The electrobalance was enclosed in a glass vacuum system at a controlled temperature and penetrant pressure. The experimental procedure involved hanging a thin film polymer sample on the electrobalance, evacuating the chamber until the sample was completely degassed, and then backfilling with the desired experimental gas or vapour to a fixed pressure. Weight gain *versus* time data was collected, and all experiments were conducted at 30°C.

### Data analysis

The equation describing Fickian diffusion of a penetrant through a thin film polymer sample, measured at one side of the film using the FT-i.r.-ATR method has been developed by ourselves<sup>7</sup> and by Fieldson and Barbari<sup>9–11</sup>. The contribution to the intensity of a selected penetrant infrared band at time  $t$  from penetrant molecules located at distance  $x$  from the ATR crystal is proportional to the product of the penetrant concentration  $c(x,t)$  and the square of the evanescent field amplitude,  $E^2(x)$ . The evanescent field amplitude drops off exponentially with distance from the ATR crystal:

$$E(x) = E_0 \exp\left(-\frac{x}{d_p}\right) \quad (1)$$

In this equation,  $E_0$  is the evanescent field amplitude at the

surface of the ATR crystal, and  $d_p$  is the penetration depth of the evanescent wave into the sample, which is a function of the refractive indices of the polymer and the ATR element, the angle of incidence of the infrared beam, and the infrared wavelength ( $\lambda$ ). For most typical cases,  $d_p$  is less than  $\lambda/3$ . The total time-dependent integrated absorbance  $A(t)$  of the selected penetrant infrared band is proportional to the product  $c(x,t) \cdot E^2(x)$  integrated over the entire film thickness ( $h$ ), after substituting the appropriate (Fickian) concentration profile for  $c(x,t)$ . The result is conveniently expressed as an absorbance ratio:

$$\frac{A(t)}{A(\infty)} = 1 - \frac{64}{\pi} \sum_0^{\infty} \left[ \frac{(-1)^n}{2n+1} \right] \left[ \frac{r^2}{16r^2 + \pi^2(2n+1)^2} \right] \times \exp\left(\frac{-\pi^2(2n+1)^2 D t}{4h^2}\right) \quad (2)$$

where  $A(\infty)$  is the integrated penetrant absorbance at equilibrium,  $D$  is the penetrant diffusivity, and  $r = h/d_p$ . In deriving equation (2), it is assumed that  $r \geq 5$ , which simplifies the equation somewhat and will hold for most cases of practical interest. We have further assumed that  $d_p$  (and therefore  $r$ ) remains constant during the diffusion process. This is not strictly true, since the composition and thus the refractive index of the region sampled by the evanescent wave is changing with time as the penetrant diffuses into the polymer. However,  $A(t)/A(\infty)$  as calculated by equation (2) is very insensitive to changes in  $r$  when  $r \geq 5$ . For film thicknesses greater than 25  $\mu\text{m}$ , this covers  $d_p$  values that correspond to any wavelength in the mid-infrared region. Under these conditions, diffusion coefficients obtained from fits of equation (2) to experimental data will be independent of the choice of infrared wavelength and changes in the sample refractive index. In practice, a five-term version of equation (2) is fitted to the  $A(t)$  *versus*  $t$  data using nonlinear regression methods, with  $D$  and  $A(\infty)$  as the adjustable parameters. The five-term version of the infinite series is sufficient to determine  $D$  to three significant figures.

Sorption of organic liquids by polymers is often accompanied by polymer swelling. This causes a reduction in the intensities of all of the polymer infrared bands during the ATR sorption experiment since the density of polymer segments in the region probed by the evanescent wave is decreasing. To account for this, the penetrant infrared band chosen for monitoring the sorption kinetics was always ratioed with a polymer reference peak in each spectrum to obtain a number which is more representative of the actual concentration of penetrant in the polymer. The quantities  $A(t)$  and  $A(\infty)$  are therefore redefined as penetrant/polymer peak intensity ratios. Although swelling did not occur in all cases reported here, penetrant/polymer peak ratioing was used in all cases for consistency.

In a gravimetric experiment, Fickian diffusion of small molecules into or out of a thin polymer film can be described by either of the following two equations:

$$\frac{M(t)}{M(\infty)} = 4 \left(\frac{z}{\pi}\right)^{1/2} = f(z) \quad (3)$$

$$\frac{M(t)}{M(\infty)} = 1 - \frac{8}{\pi^2} \exp(-\pi^2 z) = g(z) \quad (4)$$

Here  $M(t)$  is the total mass of penetrant sorbed or desorbed at time  $t$ ,  $M(\infty)$  is the mass sorbed or desorbed at equilibrium, and  $z = Dt/h^2$ . Equation (3) is the one-term approximation to the infinite series solution of the time-

**Table 1** Diffusivities from ATR and gravimetric data

System and method	$D$ (ATR) ( $\text{cm}^2 \text{s}^{-1}$ )	$D$ (gravimetric), $\text{cm}^2/\text{s}$
Amyl acetate/HDPE		
ATR	$3.05 \times 10^{-9}$	—
Gravimetric sorption, run 1	—	$10.7 \times 10^{-9}$
Gravimetric desorption, run 1	—	$7.59 \times 10^{-9}$
Average, run 1	—	$9.14 \times 10^{-9}$
Gravimetric sorption, run 2	—	$8.94 \times 10^{-9}$
Gravimetric desorption, run 2	—	$9.30 \times 10^{-9}$
Average, run 2	—	$9.12 \times 10^{-9}$
CO <sub>2</sub> /PS		
ATR, run 1	$6.66 \times 10^{-8}$	—
ATR, run 2	$7.12 \times 10^{-8}$	—
Average, runs 1 and 2	$6.89 \times 10^{-8}$	—
Gravimetric sorption	—	$3.09 \times 10^{-8}$

dependent diffusion equation that converges rapidly at short times, while equation (4) is the one-term approximation for the series solution that converges rapidly at long times<sup>16</sup>. To extract  $D$  and  $M(\infty)$  from experimental  $M(t)$  versus  $t$  data, we have developed a numerical method (the 'hybrid one-term method') which involves a weighted sum of the two r.h. terms in equation (3) and equation (4):

$$\frac{M(t)}{M(\infty)} = \phi(z)f(z) + [1 - \phi(z)]g(z) \quad (5)$$

The weighting function  $f(z) = 1$  at short times, and switches rapidly to  $f(z) = 0$  when  $f(z)$  becomes inaccurate and  $g(z)$  applies. Details have been published elsewhere<sup>17</sup>. The weighting function is:

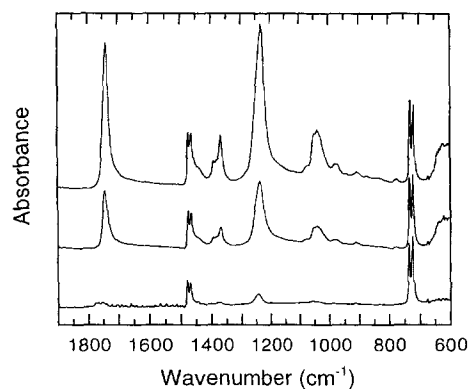
$$\phi(z) = \frac{1}{1 + \exp\left(\frac{z-a}{b}\right)} \quad (6)$$

with  $a = 0.05326$  and  $b = 0.001$ . Again nonlinear regression methods are used with equation (5) to obtain  $D$  and  $M(\infty)$  from the experimental data. The hybrid one-term method has the advantages of using all of the data, is an excellent approximation to the full infinite series solution with a true zero intercept at  $t = 0$ , converges more rapidly than truncated versions of the series solution, and has been shown to provide more reliable estimates of  $D$  and  $M(\infty)$  from scattered data, or data that have not yet reached equilibrium, compared to other commonly used methods<sup>17</sup>.

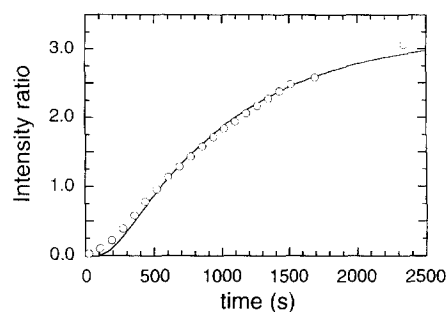
## RESULTS

### Liquid diffusion: amyl acetate/HDPE

Three ATR spectra collected during diffusion of amyl acetate into HDPE are displayed in Figure 2 and clearly



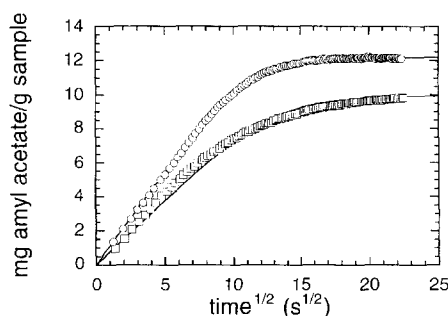
**Figure 2** Representative ATR spectra acquired at  $t = 26, 603,$  and  $1592$  s (bottom to top) during diffusion of amyl acetate into HDPE. The ATR cell was pressurized at 25 p.s.i. with nitrogen



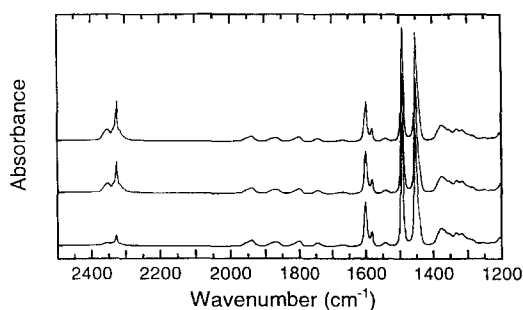
**Figure 3** Variation in the integrated intensity ratio for the  $1744 \text{ cm}^{-1}$  amyl acetate carbonyl band and the  $720 \text{ cm}^{-1}$  HDPE band during diffusion of amyl acetate into HDPE. The solid line is the fit of equation (2) to the data

show increasing intensities of the amyl acetate peaks with time. The amyl acetate carbonyl band at  $1744 \text{ cm}^{-1}$ , integrated from  $1700$  to  $1775 \text{ cm}^{-1}$ , was chosen for monitoring its sorption kinetics, and the polyethylene doublet at  $720 \text{ cm}^{-1}$ , integrated from  $700$  to  $740 \text{ cm}^{-1}$ , was chosen as the polymer reference peak. The integrated intensity ratio for all spectra collected during the diffusion process is plotted against time in Figure 3. The solid line represents the fit to equation (2), and shows that diffusion of amyl acetate into HDPE is essentially Fickian with a diffusion coefficient of  $3.05 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$  (Table 1). No evidence for polymer swelling was seen in the data, or in the appearance of the sample after it was removed from the ATR cell.

The corresponding gravimetric sorption and desorption data for saturated amyl acetate vapour at  $30^\circ\text{C}$  and 3.5 Torr are shown in Figure 4. Solid lines are curve fits using the hybrid one-term method (equation (5)). Sorption and desorption of amyl acetate vapour in HDPE also follows Fickian kinetics. The sorption curve lies above the desorption curve, which is typical for concentration-dependent diffusion<sup>1</sup>, suggesting that some swelling of the polymer is taking place. However, the  $D$  values obtained from the sorption and desorption curves were very similar (see Table 1), which indicates that the degree of swelling is small. This conclusion is supported by a second run with a different HDPE sample, for which the sorption and desorption  $D$  values were nearly equal (see Table 1). The average of the sorption and desorption  $D$  values is often taken as more representative of the diffusivity that should apply over that range of penetrant concentrations. The average  $D$  values for the two gravimetric runs listed in Table 1 are nearly identical (approximately  $9.1 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ ), but are larger by a factor of 3 than the value obtained for liquid amyl acetate using the ATR technique. Theoretically, it would be expected that the rates of transport of a liquid



**Figure 4** Gravimetric sorption (circles) and desorption data (squares) for saturated amyl acetate vapour (vapour pressure = 3.5 Torr) into HDPE at  $30^\circ\text{C}$ . Solid lines are fits of equation (5) to the data



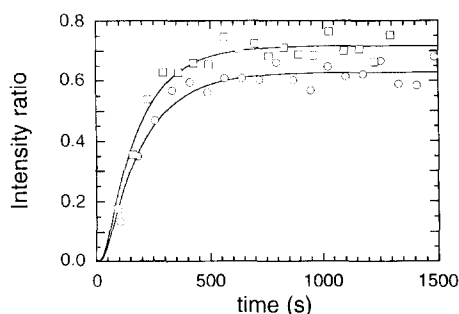
**Figure 5** Representative ATR spectra acquired at  $t = 103, 257,$  and  $717$  s (bottom to top) during diffusion of  $\text{CO}_2$  into PS. The ATR cell was pressurized at 40 p.s.i. with  $\text{CO}_2$ .

and its saturated vapour through the same polymer film would be equal since both are at unit activity. In practice, this often turns out not to be the case, with the liquid diffusivity exceeding the saturated vapour diffusivity<sup>18</sup>. However, just the opposite trend has been observed here. At present we have no explanation for this, although agreement within an order of magnitude in  $D$  values obtained by different techniques is often considered satisfactory.

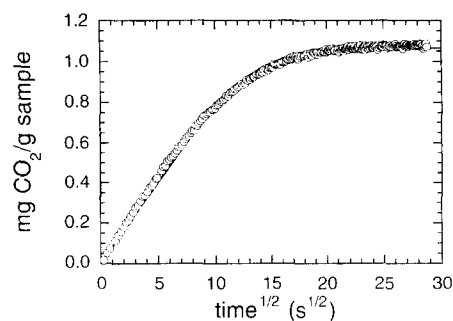
#### Gaseous diffusion: $\text{CO}_2$ /polystyrene

The sorption of  $\text{CO}_2$  by polystyrene has been well characterized and is known to follow Fickian kinetics at low pressures ( $< 20$  atm.). Carbon dioxide also has a strong carbonyl stretching absorbance around  $2350\text{ cm}^{-1}$ , making it a good candidate for studying gaseous diffusion with the ATR cell. A complication that must be considered in this case is the 'background  $\text{CO}_2$ ' that is always present in the spectrometer chamber. If the purging conditions remain constant during acquisition of the background and sample spectra, the contribution of the 'background  $\text{CO}_2$ ' to the spectra acquired during diffusion is eliminated during the spectral ratioing process. The ability to acquire background spectra through the ATR cell without removing the cell from the spectrometer, as described earlier, makes this possible. The ATR cell was pressurized at 40 p.s.i.  $\text{CO}_2$  for these measurements.

Three ATR spectra collected during diffusion of  $\text{CO}_2$  in polystyrene (PS) are shown in *Figure 5*. The  $\text{CO}_2$  band was integrated from  $2283$  to  $2395\text{ cm}^{-1}$ , and was ratioed against the PS band located at  $1450\text{ cm}^{-1}$ , which was integrated from  $1424$  to  $1470\text{ cm}^{-1}$ . This intensity ratio is plotted against time for two different  $\text{CO}_2$ /PS runs in *Figure 6*. Although this data is somewhat scattered and the ultimate intensity ratio reached in each run is different, the  $D$  values obtained from the curve fits to equation (2) (solid lines) are nearly equal (see *Table 1*). The data fit the Fickian model



**Figure 6** Variation in the integrated intensity ratio for the  $2350\text{ cm}^{-1}$   $\text{CO}_2$  carbonyl stretching band and the  $1450\text{ cm}^{-1}$  PS band during diffusion of  $\text{CO}_2$  into PS. Two separate runs are shown. The solid lines are fits of equation (2) to each data set



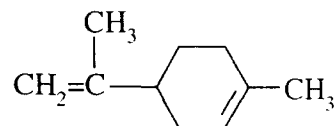
**Figure 7** Gravimetric sorption data for  $\text{CO}_2$  at 447 Torr into PS at  $30^\circ\text{C}$ . Solid lines are fits of equation (5) to the data

reasonably well, and the two runs yielded an average  $D = 6.89 \times 10^{-8}\text{ cm}^2\text{ s}^{-1}$ .

Gravimetric sorption of  $\text{CO}_2$  in PS was carried out with the same sample at  $30^\circ\text{C}$  and is displayed in *Figure 7*. The data exhibit classical Fickian behaviour, and the diffusivity obtained from a fit of equation (5) to the data was  $D = 3.09 \times 10^{-8}\text{ cm}^2\text{ s}^{-1}$ , which compares well with the ATR value. The pressure at which this experiment was conducted was 447 Torr, which is much lower than the pressure used in the ATR experiment. However, the solubility of  $\text{CO}_2$  in PS is very low and its diffusivity is independent of pressure (or concentration) over this range. Comparison of  $D$  values should be valid in spite of the pressure difference between the two techniques. The discrepancy in these two diffusivities also cannot be accounted for by the  $3^\circ\text{C}$  temperature difference between the gravimetric and ATR experiments. If measured at  $33^\circ\text{C}$ , it is estimated that the gravimetric value would increase by only 15%, using a literature value for the activation energy for diffusion of  $\text{CO}_2$  in PS<sup>19</sup>.

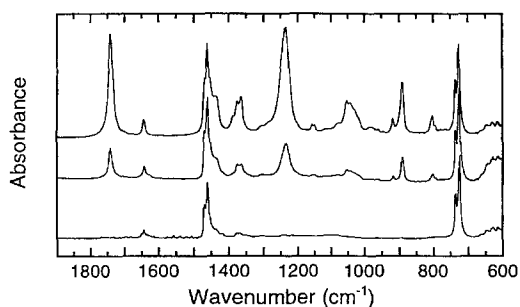
#### Liquid mixture/LDPE

As a final illustration of the capabilities of the ATR cell, we consider diffusion of a 50/50 (v/v) mixture of two liquids, amyl acetate and limonene, into low-density polyethylene (LDPE). Limonene is used as a flavouring compound in drinks such as orange juice, and its transport behaviour in polyethylene is of concern when this polymer is used in drink packaging<sup>20</sup>. Limonene is 10-carbon unsaturated cyclic compound having the following structure:



These two liquids and LDPE are of interest for illustrating the ATR method because each has an infrared peak in a region where the other components have no absorption: limonene at  $886\text{ cm}^{-1}$ , amyl acetate at  $1744\text{ cm}^{-1}$ , and the LDPE reference peak at  $720\text{ cm}^{-1}$ . The ATR cell was pressurized at 25 p.s.i. with nitrogen for these measurements. The diffusion of the two neat liquids in LDPE was also recorded. Three representative spectra obtained during diffusion of the liquid mixture into LDPE are shown in *Figure 8*, where it can be seen that the three peaks chosen above appear in non-overlapping regions of the spectrum. Each penetrant peak was ratioed separately with the LDPE reference peak and the results have been plotted in *Figure 9* (filled symbols), along with ATR diffusion data from each pure liquid (open symbols).

Limonene has a relatively high solubility in LDPE and causes significant swelling. This was confirmed by

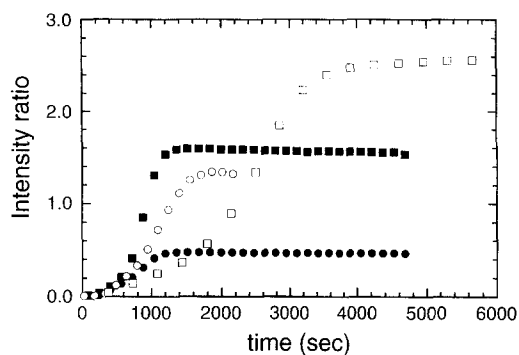


**Figure 8** Representative ATR spectra acquired at  $t = 26, 660,$  and  $1452$  s (bottom to top) during diffusion of a 50/50 (v/v) mixture of amyl acetate/limonene into LDPE. The ATR cell was pressurized at 25 p.s.i. with nitrogen

removing and examining the film from the ATR cell at the end of the sorption experiment. Being more polar, amyl acetate is less soluble in LDPE, and induces a lower degree of swelling. The Fickian model did not fit any of the ATR data for LDPE sorption, due presumably to the fact that swelling and diffusion occur on approximately the same time scale, complicating the transport kinetics. Nevertheless, the data in *Figure 9* still provide a relative comparison of transport rates of the two liquids in LDPE, as neat liquids and as components of a mixture. It is clear that neat limonene diffuses more rapidly than neat amyl acetate, as can be seen by comparing the time it takes for each penetrant to reach equilibrium. This behaviour is consistent with the observation that limonene swells LDPE more than amyl acetate. However, when these two penetrants are sorbed simultaneously from a 50/50 mixture, amyl acetate diffusion is facilitated by the presence of limonene and occurs much faster, reaching equilibrium at the same time as limonene. In fact, both components of the mixture appear to reach equilibrium in a shorter time than either pure component alone. The important conclusion to be drawn from these results is that pure penetrant diffusivities or transport rates do not necessarily apply to diffusion of the same penetrants from a mixture. The ATR method is a unique and powerful way to study this very fundamental concept.

## CONCLUSIONS

An infrared cell for studying diffusion of small molecules through thin polymer films using the ATR technique has been described. The cell utilizes pressurized gas to maintain contact between the polymer film and the ATR crystal. The principal features of this cell are: (1) commercially processed polymer films can be used in as-received form; (2) either gaseous or liquid penetrants can be studied; (3) background spectra can be collected through the ATR cell without removing the cell or the polymer sample from the spectrometer; and (4) the same polymer samples can be used for complimentary gravimetric sorption/desorption experiments. Use of this cell has been demonstrated for liquid penetrants, a gaseous penetrant, and simultaneous measurement of the transport of two liquids in a mixture through a polymer film. Diffusion coefficients measured with the ATR technique compared favourably with values obtained from gravimetric measurements with the same penetrants and



**Figure 9** Sorption of limonene (circles) and amyl acetate (squares) into LDPE as neat liquids (open symbols) and as components of a 50/50 (v/v) mixture (filled symbols) using the ATR method. Integrated intensity ratios were calculated by ratioing the  $1744\text{ cm}^{-1}$  amyl acetate band and the  $886\text{ cm}^{-1}$  limonene band against the  $720\text{ cm}^{-1}$  LDPE band

polymer samples. Although not incorporated in our prototype, temperature control could easily be added to this ATR cell design.

The ATR method itself offers the advantages of in situ analysis of liquid transport in polymers (which is preferable to 'blot and weigh' methods), and the ability to probe the transport of individual components of a mixture through polymers.

## ACKNOWLEDGEMENTS

The authors thank Dr Andy Wnuk and the Procter and Gamble Company, Cincinnati, OH, for partial support of this work.

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