

Measurement of the Solubility and Diffusivity of Blowing Agents in Polystyrene

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ABSTRACT: The solubility and diffusivity of several gases in polystyrene (PS) and styrene acrylonitrile copolymer (SAN) were studied with the pressure decay method. Data were collected for carbon dioxide, isobutane, and 1,1,1,2-tetrafluoroethane (R-134a) in PS and for R-134a in SAN. The temperature range was between 30 and 200°C, and the gas pressures ranged from approximately 0.2 to 8.2 MPa. To cover these ranges, both the absolute and differential pressure decay methods were required. Henry's law was found

to adequately represent all the gas solubilities. Isobutane and R-134a were found to have a plasticizing effect on PS and SAN; that is, the diffusivity increased significantly as the pressure (and mass uptake) increased. CO₂ in PS had the highest diffusivity and lowest solubility and did not affect the diffusivity in PS over the pressure range studied. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 2359–2365, 2010

Key words: diffusion; polystyrene; blowing agents

INTRODUCTION

Isobutane and 1,1,1,2-tetrafluoroethane (R-134a) are blowing agents used in the production of polystyrene (PS) foams. Supercritical CO₂ has been explored as a more environmentally friendly blowing agent. The diffusivities and solubilities of blowing agents at high pressure are of interest because these properties affect their performance and applicability. In this research, we studied and compared the sorption of some blowing agents potentially useful for PS or styrene acrylonitrile copolymer (SAN). The pressure decay method was used at conditions ranging from atmospheric conditions to high temperatures and pressures.

When gas pressures are high, the pressure decay method is the most widely used method for sorption measurements.¹ Diffusivities and solubilities were determined as early as 1962 by Lundberg et al.² In this technique, gas fills a chamber containing the absorbing sample. The pressure inside the isolated chamber is monitored and recorded over the course of the experiment as the sample absorbs gas. With an appropriate equation of state, the mass of gas remaining can be calculated from the chamber volume, pressure, and temperature. Typically, the temperature is controlled, and the gas density is calculated from an equation of state.

A pressure decay apparatus, which makes use of the higher precision of a differential pressure transducer, was created by Sato et al.³ An improved version, which compares the pressure in the sample chamber with a reference chamber with the differential transducer, was created by Pourdarvish et al.⁴

Sato and coworkers^{3,5,6} reported data for the solubilities of CO₂/PS and isobutane/PS systems. The R-134a/PS system has received considerable attention, with data contributed by Sato et al.,⁷ Wong et al.,⁸ and Daigneault et al.⁹ A correlation of Henry's law coefficient with temperature for different gases was explored by Stiel and Harnish.¹⁰

In this study, we extended the pressure and temperature ranges of the previous studies. We also improved the data analysis by using a more exact equation of state. The experimental apparatus and methods and improvements in the treatment of the experimental data are described.

EXPERIMENTAL

Apparatus

The experimental equipment and techniques used in this research were developed by Davis et al.¹ for absolute pressure decay and by Pourdarvish et al.⁴ for differential pressure decay. The absolute pressure decay apparatus (Fig. 1) consisted of a sample chamber, capsule, and gas supply system. The sample chamber and capsule were both enclosed in an oven, which was temperature controlled (up to 200°C) and had forced air convection. The sample chamber housed the polymer sample and the absorbate gas.

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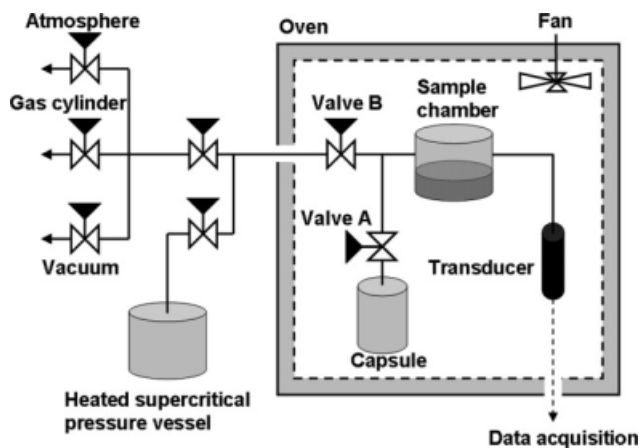


Figure 1 Absolute pressure decay apparatus.

The capsule was used to calibrate the sample chamber volume with expanding gas at a known pressure from one chamber to the other with valve A. The gas supply system provided absorbate from commercial gas cylinders or from the heated supercritical vessel. The latter was used to condition the pressure of vapors, including isobutane and R-134a, that had low vapor pressures at room temperature. The vessel temperature (and, hence, the inside pressure) was controlled via a type-J thermocouple and a CN76000 microprocessor-based proportional-integral-derivative (PID) controller. Simple pressure regulators were used to control the supply cylinders.

The pressure decay experiments required a setup that was leak-tight to prevent large errors. A P053HD pressure transducer (TransMetrics, Division of United Electric Controls, Watertown, MA), rated up to 232°C and 13.8 MPa with an accuracy of 0.15% full scale, was used. The transducer was connected to a PDAQ 56 data acquisition unit (IOtech, Cleveland, OH), and the data were stored on a PC.

As noted by Lundberg and Mooney,¹¹ it is difficult to determine the gas density at the start of an experiment. The uncertainty in the density results from the Joule effect, that is, the expansion of a gas at a constant internal energy, which causes the temperature of the gas to decrease upon expansion into the sample chamber. As the gas returns to the temperature of the experiment, a pressure change is observed. Only after the temperature has equalized can accurate densities be calculated. The traditional method for preventing this problem is the use of a dual chamber for the purpose of calibrating the mass of expanded gas.^{12,13} A more efficient way was developed by Michaels et al.¹⁴ and used by Davis et al.;¹ this method makes use of an extrapolation of the initial density. The adsorption data at short times, which are linear with respect to the square root of time, are extrapolated to zero time to determine the initial gas-phase density.

All the high-pressure, high-temperature experiments (up to 200°C and 8.2 MPa) were performed in the setup shown in Figure 1. The differential pressure decay apparatus (Fig. 2) was used when conditions required a more sensitive pressure measurement than that afforded by the absolute pressure decay apparatus. For instance, in the case of the isobutane/PS system at 30°C, the amount of gas absorbed and, therefore, the pressure change were quite small and hard to measure accurately. Resorting to a differential technique gave us a solution to this measurement challenge. The setup also consisted of an oven, but in addition to the sample chamber, the oven enclosed a reservoir and a reference chamber. The reservoir chamber supplied conditioned gas to the sample and reference chambers. The absolute pressure transducer was used to determine the pressure of gas that was expanded into the chambers, which were then isolated by closed valves. The differential pressure transducer measured the pressure differential between the sample and reference chambers with substantial accuracy. The differential and absolute pressure data were used to compute the absolute pressure in the sample chamber as a function of time.

The oven temperature was controlled with a CN76000 microprocessor-based PID controller (Omega Engineering, Stamford, CT). The oven temperature was measured with an accuracy of $\pm 1^\circ\text{C}$ by a type-J thermocouple. The differential pressure transducer was a PX821-005DV (Omega Engineering) with a range of 34.5 kPa, an error of $\pm 0.1\%$ full scale, and a high temperature limit of 80°C. A DBK2000 data acquisition board and LabView (National Instruments, Austin, TX) software were used to record the transducer signal on a computer.

In both setups, tubing 0.25 in. in diameter was used to connect the sample chamber, transducer, capsule, and reference and reservoir chambers. The

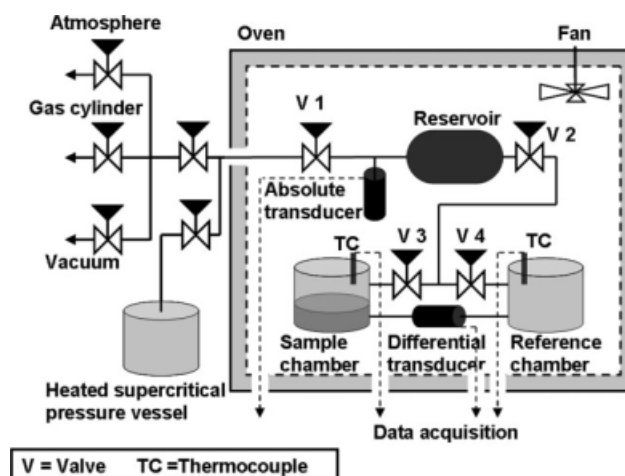


Figure 2 Differential pressure decay apparatus.

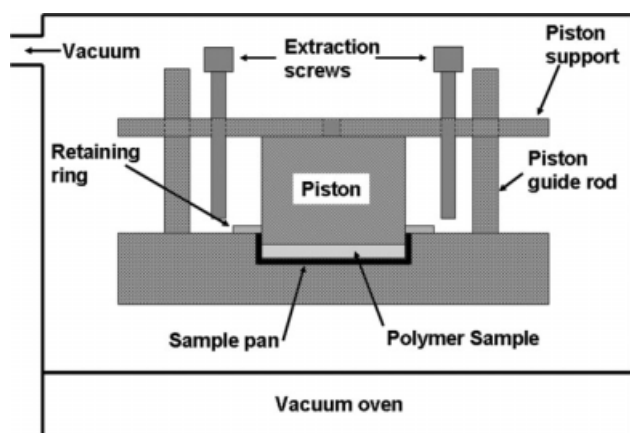


Figure 3 Sample molding press.

tubing, chambers, and valves were all made of grade 316 stainless steel. The sample chamber design reflected the high pressures and temperatures required by this research: a solid cylindrical shell 2 in. in inside diameter and 3.5 in. in outside diameter was accessible from the top via a 0.50-in. flange fastened to the shell with six bolts 5/16 in. in diameter. The bottom wall was 0.50 in. thick as well and was welded to the shell.

Polymer samples for the high-temperature, molten-phase diffusion experiments were prepared with compression molding in a press designed specifically for this purpose (Fig. 3). The desired mass of polymer (in pellet form) was placed in a cylindrical metal pan 3.1 cm in diameter and compression-molded into a flat slab by the piston. The assembly was placed in a vacuum oven at 160°C for 4 h. After extraction from the oven and subsequent cooling, the sample mass was determined by weighing, and the sample thickness was determined via the polymer density, ascertained with the Tait equation.¹⁵

To calculate the density of the gas phase, accurate equations of state were critical. The Benedict-Webb-Rubin (BWR) equation¹⁶ was used by Davis et al.¹ and Pourdarvish et al.⁴ for gas-phase density in pressure decay experiments. The BWR equation had significant errors within the temperature and pressure ranges used in this research. In addition, BWR coefficients for R-134a are not available. Therefore, the equations of state developed by Span and Wagner¹⁷⁻¹⁹ for polar and nonpolar fluids were used. The functional forms for R-134a, carbon dioxide, and isobutane had 12 substance specific parameters. Span and Wagner^{18,19} showed that their equation correlated the experimental density of carbon dioxide with an accuracy of 0.5% or better for pressures up to 100 MPa and temperatures from 260 to 600 K. A comparison of the predictions of the BWR equation for the density of CO₂ and those of the Span-

Wagner equation is shown in Figure 4. At high pressures and moderate temperatures, as found in this study, the percentage error approached 30%.

The equations of state were used to determine the mass of gas in the known volumes at specified pressures and temperatures. The volumes of the capsule and sample were carefully determined with expansion or gravimetric techniques. Values within ± 0.12 cm³ and within ± 1 cm³ were obtained for the capsule (~ 7 cm³) and the sample chamber (~ 60 cm³), respectively. The actual volumes varied slightly and depended on the sample sizes. We reduced the vapor space of the sample chamber by the placement of a block of stainless steel of known volume, thereby increasing the sensitivity.

Materials

The PS used in the experiments was atactic and had a molecular weight of approximately 168,000 and a polydispersity of 2.2. The density was 1.07 g/cm³, and the glass-transition temperature was 104°C. The SAN was a random copolymer containing 15 wt % acrylonitrile. It had a molecular weight of approximately 118,000 with a polydispersity of 2.2. Its density was 1.09 g/cm³, and the glass-transition temperature was 105.5°C. The CO₂ was bone dry, the isobutane had a purity of 99%, and the R-134a was greater than 99.8% pure.

Experimental procedure and data analysis

In the pressure decay setup (Fig. 1), the sample chamber was evacuated and kept under continual vacuum to degas the sample while the oven temperature reached its set point. The absorbate gas was expanded into the sample chamber via valve B, and pressure data collection continued until sorption equilibrium was reached. The initial pressure was increased in steps to obtain solubility and diffusivity data over a wide range of pressures. The initial gas density was calculated with the method of Michaels et al.,¹⁴ and the final gas density, calculated from the

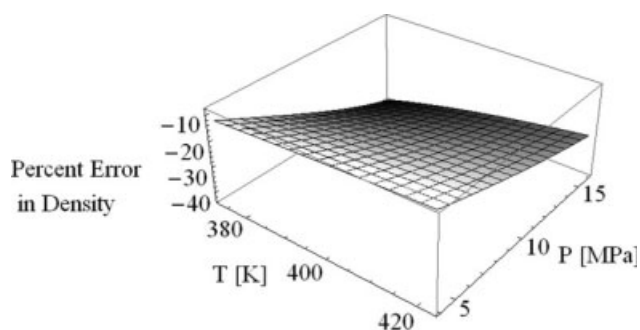


Figure 4 Difference between the BWR and Span-Wagner equations of state for the density of CO₂ (P = pressure; T = temperature).

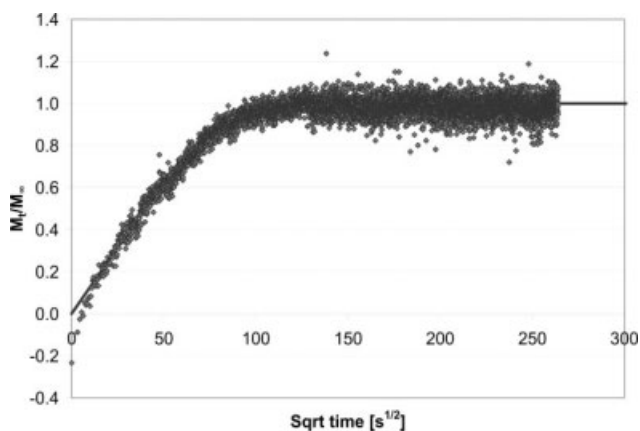


Figure 5 Mass uptake curve of the sorption of isobutane in PS at 125°C and 2.23 MPa.

Span–Wagner equation of state, was used to calculate the total mass uptake and solubility.

The initial slope method was used to determine the diffusivity. In this approach, the mass uptake in a film with diffusion from only one side was predicted to increase linearly with the square root of time at early times. The operative equation as given by Crank²⁰ is

$$\frac{M_t}{M_\infty} = 2 \left[\frac{D_p t}{\pi \ell^2} \right]^{1/2}$$

where M_t is the mass uptake at any time, M_∞ is the mass uptake at equilibrium, D_p is the mutual diffusion coefficient, t is the time, and ℓ is the thickness of the film.

The differential pressure apparatus (Fig. 2) required for the isobutane in PS measurements at 30°C was used for two different types of experiments. The diffusion rate in this case was very slow, and equilibrium could not be reached within a reasonable time for samples with a diffusion length greater than 25 μm . It was difficult to produce PS films of this thickness. Instead, we first determined the solubility by absorbing gas into a powder sample with a small diffusion length. This powder was cryogenically ground to a maximum particle diameter of about 25 μm . Approximately 0.3 g of the PS powder (inside a fine steel mesh enclosure) was placed in the sample chamber. We calculated the gas volume by subtracting the volume of all of the contents of the chamber from its volume. The solubility was determined from the calculated mass uptake at equilibrium. Even with the decreased diffusion length afforded by the powder, the sorption experiments took about 1 month to reach equilibrium.

Because the powder was not uniform, it could not be used to determine the diffusivity. Instead, PS films with a thickness of approximately 0.5 mm

were prepared with the molding press (Fig. 3). The experiment was run in the same way as with the powder, except that it was terminated when enough data were collected to determine the initial slope (usually after 48–72 h). The value for equilibrium mass uptake was calculated from the solubility data obtained for the powder in the first type of experiment. The initial mass uptake data were used to find the initial slope. Hence, excessively long times for the slab to reach equilibrium were avoided.

RESULTS AND DISCUSSION

Typical pressure decay curves for the two apparatuses

The absolute pressure decay apparatus operated over a wide pressure range, which generated some experimental uncertainty. An example of the fractional absorption (M_t/M_∞) versus the square root of time is shown in Figure 5 for isobutane in PS at 125°C and 2.23 MPa. The characteristic rapid initial pressure change, which was the result of the Joule effect, was observed in the first several minutes of the experiment. The initial slope of this trace was well defined, and the values of diffusivity could be determined with little difficulty. At equilibrium, there was some scatter, and the average value was taken. Much of this scatter was attributed to the noise in the pressure transducer, which was particularly evident once saturation was reached.

The differential pressure decay apparatus operated over a much narrower pressure range than that of the absolute pressure decay setup, and the scattering was reduced considerably. An example is shown in Figure 6 for one of the PS films at 30°C and 0.207 MPa. The adsorption process occurred slowly with a well-defined, linear trend. After 50 h 10 min elapsed (corresponding to 425 $\text{s}^{1/2}$ in Fig. 6), the fractional mass uptake was still under 3%. Thus, it was clear

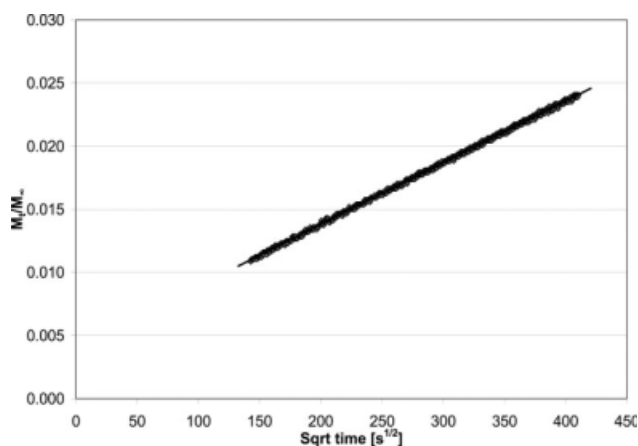


Figure 6 Mass uptake curve of the sorption of isobutane in PS at 30°C and 0.207 MPa.

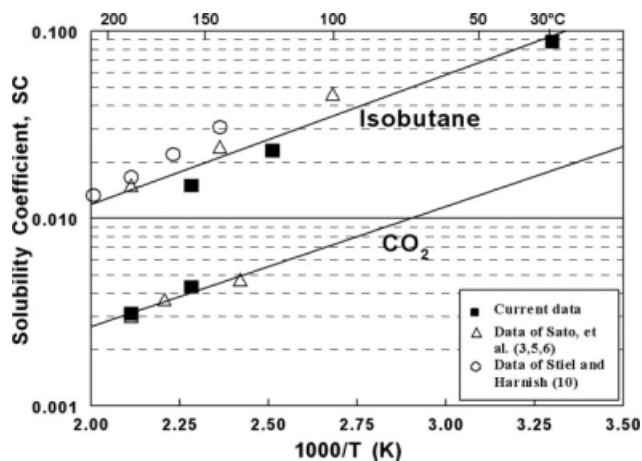


Figure 7 SCs for isobutane and CO₂ in PS ($T =$ temperature).

that it was not feasible to conduct an equilibrium sorption experiment within any reasonable time limit with a film sample.

Solubility of the gases in PS

In all cases, the solubility of the gases in PS exhibited linear behavior as a function of pressure at a given temperature. Here, this was characterized as the solubility coefficient (SC), which is the reciprocal of the Henry's law constant as it is usually defined:

$$SC = \frac{\text{Mass fraction of gas}}{\text{Pressure (MPa)}}$$

The logarithms of the SCs in PS are plotted in Figures 7 and 8 as a function of reciprocal temperature. The SCs increased as the temperature decreased. As expected, the CO₂ was much less soluble than either the isobutane or the R-134a. These data are also compared with literature data in the figures. There was relatively good agreement between these data and the data of Sato and coworkers^{3,5,6} for isobutane and CO₂, as shown in Figure 7. Stiel and Harnish¹⁰ collected data on numerous solvents using inverse gas chromatography. From the retention volumes, they estimated SCs at infinite dilution (zero pressure). Although the procedure was correct in theory, the results were less reliable than those taken over a range of pressures and concentrations. The values obtained appeared to be somewhat high and were not included in the regression for the isobutane line shown in Figure 7. The experimental data for the solubility of R-134a/PS shown in Figure 8 showed more scatter than those for the other two gases, but the trends in these data and those of the literature were essentially the same. SC for isobutane gas in PS was larger than that for R-134a in PS.

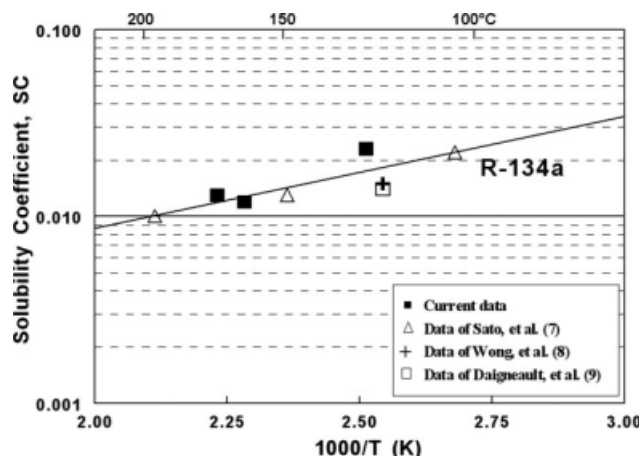


Figure 8 SCs for R-134a in PS ($T =$ temperature).

In Figure 7, SC of isobutane at 30°C is included. This is noteworthy because this point was taken with the differential pressure apparatus. As described in the Experimental section, the diffusivity for this case was so low that different types of samples had to be used to measure the solubility and the diffusivity. The extrapolated results for the higher temperatures show good agreement with this low-temperature value. As expected, SC was significantly higher than at higher temperatures. Of course, the actual mass uptake would normally be far below the uptake at the higher temperatures because the gas pressure cannot exceed the saturation pressure of isobutane (0.406 MPa at 30°C).

Diffusivity of the gases in PS

The diffusivities measured for carbon dioxide in PS are shown in Figure 9. All of the data fell within a small range of diffusivity. The pressure had no discernible effect on the diffusivity, as would be expected for such a small molecule at these higher

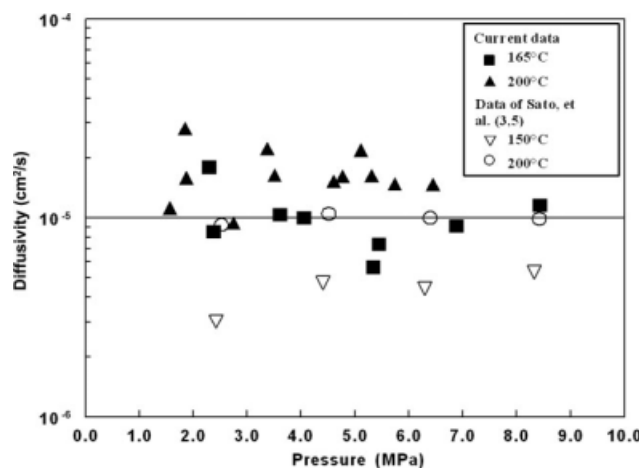


Figure 9 Diffusivity of CO₂ in PS.

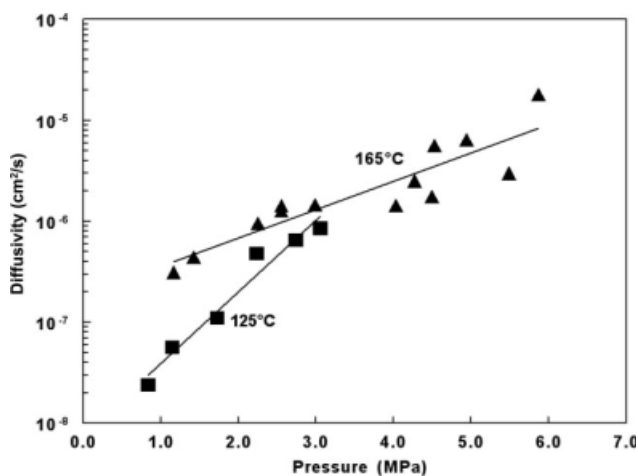


Figure 10 Diffusivity of isobutane in PS.

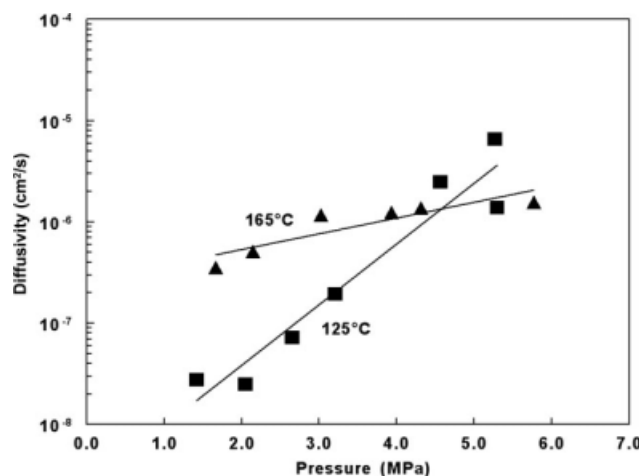


Figure 12 Diffusivity of R-134a in SAN.

temperatures. Because of the low solubility and high diffusivity of the CO_2 in PS, there was some scatter in these diffusivity measurements. The trend, however, was as expected, i.e., the diffusivity increased as the temperature increased from 150 to 165 to 200°C. The diffusivity values were consistently higher than the values reported by Sato et al.⁵ The diffusivity in the polymers could be increased by the presence of solvents, which is called *plasticization*. Carbon dioxide apparently had no plasticizing effect on PS in the pressure and temperature ranges of these experiments.

The diffusivities calculated for isobutane in PS at 125 and 165°C are given in Figure 10. The data showed linear behavior of the logarithm of the diffusivity with pressure at a set temperature. As expected, the diffusivity of isobutane at low pressures was higher at 165 than at 125°C. At 125°C, however, SC was significantly larger than at 165°C. Thus, as the pressure increased, the mass fraction of isobutane

in the PS increased at a faster rate. The resulting plasticizing effect on the polymer also increased the diffusivity such that the diffusivity would eventually be greater at the lower temperature.

For isobutane-PS at 30°C, the diffusivity as determined with the differential apparatus was essentially $5 \times 10^{-12} \text{ cm}^2/\text{s}$, which was orders of magnitude lower than at 165°C. Because the gas pressures at 30°C were necessarily low, the mass uptake was small, and no plasticization was observed.

The diffusivities for R-134a in PS at 125 and 165°C are shown in Figure 11. Although there was more scatter in the data, the same trend as observed with the isobutane was observed: the lower temperature diffusivity approached that of the higher temperature as the pressure and, thus, the mass fraction of R-134a increased. In comparison with these results, Wong et al.⁸ reported that at 120°C, the diffusivity of R-134a was about $1.2 \times 10^{-8} \text{ cm}^2/\text{s}$ with R-134a at infinite dilution and $3.6 \times 10^{-8} \text{ cm}^2/\text{s}$ at 3.5 MPa. These values of Wong et al. suggested a smaller plasticization effect than we observed in this study.

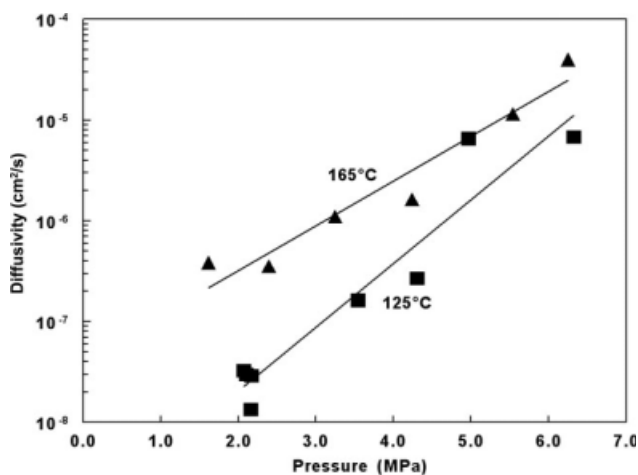


Figure 11 Diffusivity of R-134a in PS.

Solubility and diffusivity of the gases in SAN

The same properties of R-134a in SAN were studied. A literature search did not uncover any previous data for the sorption of R-134a in SAN. The solubilities measured in this study were higher at 125°C than at 165°C and were again linear with pressure; this led to SCs of 0.023 and 0.010 MPa^{-1} at 125 and 165°C, respectively

The diffusivities are shown in Figure 12. At low pressures, the diffusivity of R-134a was higher at 165°C than at 125°C and then inverted at higher pressures. This was once again the effect of the higher SC and increased solubility at the lower temperature. This increased mass fraction and resultant

plasticization affected the reversal of the diffusivity values.

CONCLUSIONS

The experimental method was improved by the use of a more accurate equation of state, and thus, we obtained more reliable density estimates than those afforded by the BWR equation of state. The use of both powders and films of the same polymer in the differential pressure decay method allowed measurements at low temperature and pressure, with a diffusivity in the 10^{-12} cm²/s range.

In this study, we extended the range of solubilities and diffusivities available for four systems, namely, CO₂/PS, isobutane/PS, R-134a/PS, and R-134a/SAN. At 125°C, the solubilities of R-134a in PS and SAN were almost identical, and the solubility of isobutane was somewhat higher. Of the gases studied, the solubility of carbon dioxide in PS was significantly lower, regardless of temperature.

The diffusivity of isobutane was consistently higher at all pressures than the diffusivity of R-134a in either polymer. Also, the diffusivity of R-134a was higher in SAN than in PS. The diffusivities of carbon dioxide in PS were overall about two orders of magnitude higher than the diffusivities of isobutane or R-134a in either PS or SAN.

The solute concentration had a clear effect on the diffusivity in most systems. The increase in the diffusivity due to the pressure-dependent plasticization was similar for isobutane in PS and R-134a in both PS and SAN.

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