

Influence of High Pressure Gases on Polymer-Solvent Thermodynamic and Transport Behavior

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ABSTRACT: Removal of residual solvent and monomers from a polymer through devolatilization can be the limiting step in production throughput. The process may be made more efficient by the addition of a cosolvent. In this work, the effects of two soluble gases, carbon dioxide, and ethylene, on the solubility and diffusivity of a number of solvents in poly(vinyl acetate) and poly(styrene) have been evaluated. The results indicate that in general the solubilities are reduced by the presence of the soluble gases and the diffusivity is significantly increased, with ethylene hav-

ing the most pronounced effect. Larger solvent molecules benefit more by the presence of the added gas. The implications of this work are that replacement of noninteracting gases such as air or nitrogen with soluble gases can reduce solvent removal times and increase production rates. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 1632–1641, 2008

Key words: diffusion; phase behavior; polystyrene; swelling; thermoplastics

INTRODUCTION

Devolatilization of polymers is critical to industrial applications such as film drying, foam production, microelectronics manufacturing, and bulk plastics processing. The mass transport and thermodynamics within such systems often limits production throughput. For example, a common method of devolatilization is ambient pressure desorption. In this situation, the diffusion of residual species from the polymer to the surrounding air is the limiting step in the manufacturing process. Therefore, the use of a cosolvent to affect the solubility and diffusion favorably is an area of interest to industry. Little data exist, however, showing the influences that occur when a cosolvent is added to a system and few models are capable of predicting these effects.

This work focuses on measuring and describing cosolvent effects in polymer-solvent systems. High pressure IGC (HPIGC) was used to study the influence of CO₂ and ethylene (C₂H₄) on polymer-solvent transport and thermodynamic behavior in poly(styrene) (PS) and poly(vinyl acetate) (PVAc) systems. The objective of the project was to determine which gas had a stronger influence on the solubility and diffusivity and if the influence of the gases increased or decreased based on the size of the solvent. The

gases are, of course, much easier to remove than the less volatile solvents.

BACKGROUND

IGC has been successfully used to measure the partition and diffusion coefficients in polymer-solvent systems.^{1–7} In addition to infinite dilution measurements, IGC has been extended to finite concentration measurements.^{8–14} Although Brockmeier et al.¹¹ showed that the technique could be operated at high pressure, there was little interest in its application until recently. Alessi et al.¹⁵ demonstrated that IGC operated with high pressure CO₂ could be used to measure reductions in the glass transition temperature. More recently, Zielinski et al.¹⁶ showed that IGC could be used to determine the influence of high pressure gases on the infinite dilution solubility and diffusivity of solvents in polymers.

EXPERIMENTAL

The IGC apparatus used for this study was originally built by Zielinski et al.¹⁶ and subsequently moved to the Center for the Study of Polymeric Systems. The basic unit was a Hewlett-Packard model 5890 chromatograph with a thermal conductivity detector (TCD). A modification was made in the design to overcome the temperature limitation they reported. A Tescom regulator with a maximum operating pressure of 27.6 MPa was used to control

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TABLE I
Capillary Column Specifications

Polymer	Length (cm)	Inner diameter (cm)	Coating thickness (μm)
PS	1562	0.053	10
PVAc	925	0.053	5

the pressure inside the column. The pressure was monitored using a Heise pressure transducer rated up to 20.7 MPa. To control the flow through the column, a Swagelok metering valve (model no. SS-SS1-MH) was fitted to the column exit tubing. This valve was installed outside the GC oven to permit testing systems at high temperatures. The line from the metering valve ran back inside the oven and into the detector inlet. Testing was performed to ensure the additional dead volume added by the valve placement did not contribute to peak spreading and erroneous diffusion results. The lines from the sample injector to the column were heated with heating tape. Temperatures in that zone were controlled with a Watlow Series 935A temperature controller. A standard Windows-based personal computer was used for control of the TCD and GC temperatures zones, as well as for collection of the data.

A Tylan model FC-260 mass flow controller along with a Tylan RO-28 controller module was used for delivery of gas to the reference line. The upper pressure limit of 1.04 MPa precluded use of the mass flow controller for use with the column supply lines. Before carrying out an injection, the system was allowed to equilibrate for 30 min after any change in pressure or temperature so that equilibrium was reached between the carrier gas and polymer.

MATERIALS

The poly(styrene) (PS) coated column was provided by Restek (Bellefonte, PA) with a 10 μm thick coating. The PVAc column was coated in the Center for the Study of Polymeric Systems. The column specifications are listed in Table I. The nine solvents used in this work (Table II) were received from Sigma Aldrich and used without further purification. Helium, CO_2 , and ethylene gases were UHP, bone dry, and chemically pure grade, respectively.

ANALYSIS OF DATA

The method of analyzing an elution profile obtained during an IGC experiment to obtain thermodynamic and transport parameters is well documented. The method employed in this work was that described by Hadj Romdhane and Danner.⁶ In the current work, for the cases where the carrier gas was soluble in the polymer, a key assumption in traditional IGC

TABLE II
Solvents Used in the Study

Solvent	Molar volume at 25°C (cm^3/mol)
Methanol	43.1
Isopropanol	81.5
Methyl acetate	85.5
Benzene	94.5
Vinyl acetate	99.2
Ethyl acetate	105.1
Toluene	112.1
Ethyl benzene	128.7
<i>p</i> -Xylene	129.8

is no longer valid. The finite solubility of the carrier gas in the polymer results in swelling which changes the film thickness of the polymer.

The film thickness was corrected by determining the binary solubility of the interacting carrier gases in the polymers. Experimental data from Sato et al.¹⁷ were used for CO_2 with PVAc and PS. Because of the lack of experimental data for ethylene in these polymers, the density and solubility were estimated at the experimental conditions using the group-contribution, lattice-fluid equation of state (GCLF-EoS).¹⁸ As shown in Figure 1 the solubility of ethylene in PVAc is significantly less than that of CO_2 .

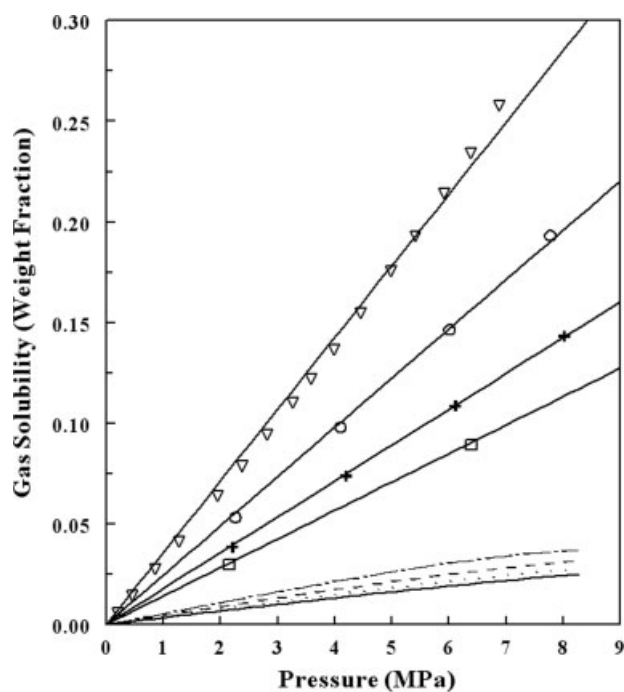


Figure 1 Solubility of the carrier gases in PVAc. Experimental data for CO_2 at 40 (∇), 60 (\circ), 80 ($+$), and 100°C (\square) taken from Sato et al.¹⁷ Lines are Henry Law correlations. Solubility of ethylene in PVAc was predicted with GCLF-EoS¹⁸ with a constant binary interaction parameter ($k_{ij} = 0.0264$). Predictions were made at 40 (---), 60 (---), 80 (---), and 100°C (—).

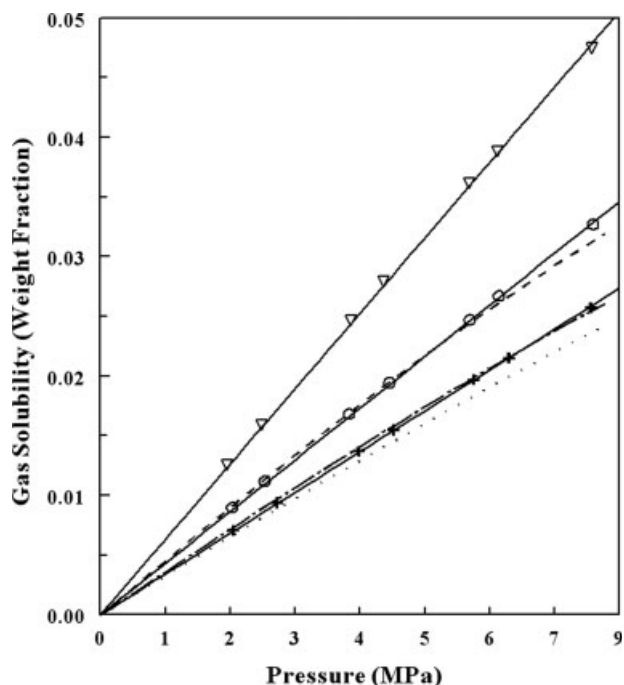


Figure 2 Solubility of the carrier gases in PS. Experimental data for CO₂ at 100 (▽), 150 (○), and 200°C (+) taken from Sato et al.¹⁷ Lines are Henry Law correlations. Solubility of ethylene in PS was predicted with GCLF-EoS¹⁸ with a constant binary interaction parameter ($k_{ij} = 0.0081$). Predictions were made at 100 (- - -), 150 (- · - ·), 200°C (· · · ·).

Figure 2 indicates that, while the same trend is apparent in PS (especially at the lower temperatures), the differences are not nearly as great.

The k_{ij} values used in the density and solubility predictions are those predicted from the GCLF-EoS. One would expect the error in the predicted solubilities of the ethylene to be greater than the error in the experimental data for CO₂. The differences between the ethylene and CO₂ on the polymer-solvent behavior are significantly greater, however, than can be explained based on expected errors. The largest swelling occurred for the PVAc-CO₂ system, where the film thickness changed as much as 17%. For PS-CO₂ the largest change was around 5%. Because the solubility of ethylene in the polymers is lower than that of CO₂, the swelling was lower. In PVAc, the change was about 3% while in PS it was only about 1%. The change in the film thickness in the capillary column is taken into account in the analysis of the data.

Neither polymer tends to crystallize and, thus, the absorption and desorption of the CO₂ and ethylene are not expected to change the morphology of the polymers. Irreversible changes could be expected if crystallization or phase separation (as in the case of copolymers) was an issue. Repeated experiments in the present work showed no signs of irreversibility.

RESULTS

In general, when a polymer absorbs gas it becomes plasticized resulting in a liquid of higher total free volume. With few exceptions this is true. It was expected that both CO₂ and ethylene would plasticize the polymer to varying degrees and increase the diffusion coefficient. It was unknown, however, whether the solvents would have stronger or weaker interactions in the polymer-gas mixtures compared with the polymer itself.

PVAc systems

Data were first obtained on the PVAc-vinyl acetate system with CO₂ or ethylene as the high pressure carrier gas. Zielinski et al.¹⁶ have observed that ethylene and CO₂ both led to lower partition coefficients of vinyl acetate in PVAc. Also they observed that the diffusion coefficients increased with both gases.

The partition coefficient (concentration in the polymer phase divided by the concentration in the vapor phase) results at 70°C are shown in Figure 3. Values indicated as being at zero pressure (i.e., partial pressure of either CO₂ or ethylene) were obtained using noninteracting helium as the carrier gas at ambient pressure. The data are plotted as a function of carrier gas pressure in the column. Within experimental error the data points collected in this work agree

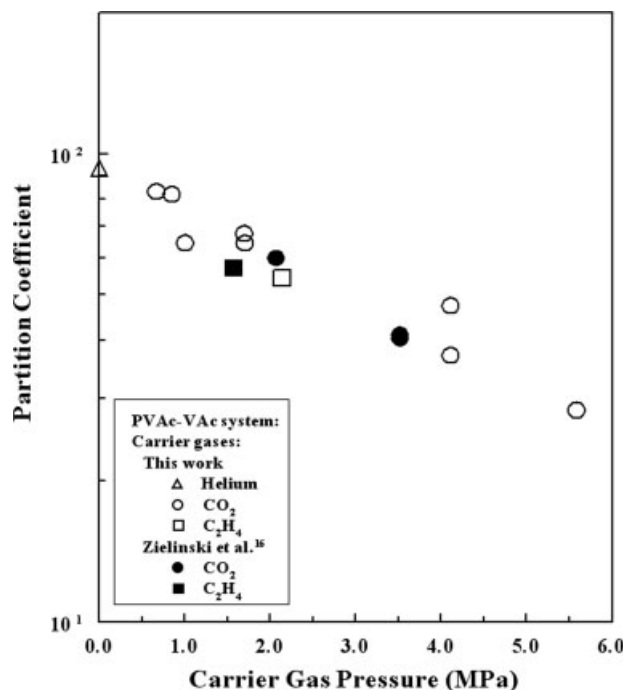


Figure 3 The partition coefficient of vinyl acetate on PVAc at 70°C as function of carrier gas pressure. Value at zero pressure (Δ) was taken using helium at ambient pressure as the carrier gas.

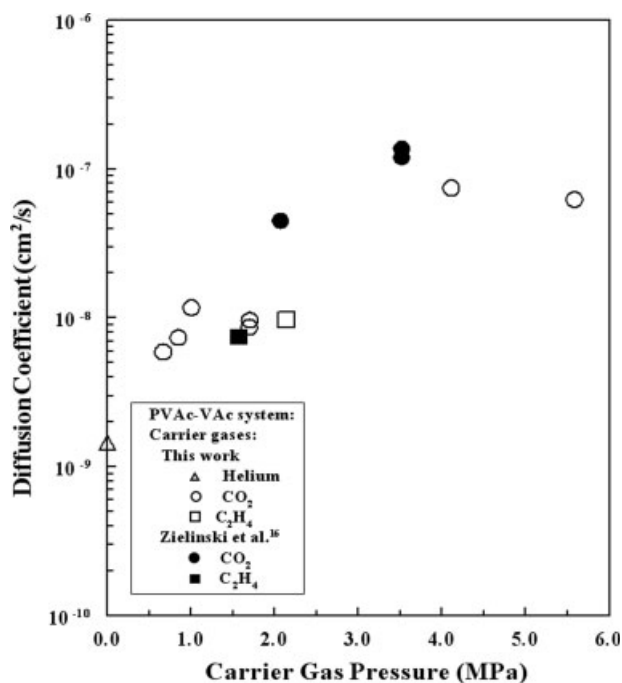


Figure 4 The diffusion coefficient of vinyl acetate on PVAc at 70°C as function of carrier gas pressure. Value at zero pressure (Δ) was taken using helium at ambient pressure as the carrier gas.

with the values obtained by Zielinski et al. at other pressures. Notice that the partition coefficient of vinyl acetate decreases as the pressure of CO₂ or ethylene is increased. This indicates that vinyl acetate has less favorable interactions in the polymer-gas mixture. The trend appears to be linear with pressure up to 6 MPa.

Corresponding values of the diffusion coefficient at 70°C are shown in Figure 4. The influence of pressure on diffusivity is much greater. The additional free volume added to the system by CO₂ or ethylene results in an increase of several orders of magnitude in the diffusion coefficient of vinyl acetate. The dependence of the diffusion coefficient on ethylene pressure appears comparable with that observed by Zielinski et al.¹⁶ The data obtained in the presence of CO₂, however, do not seem to show such a strong influence as they observed. In particular the data point at 5.58 MPa of CO₂ is slightly lower than the point at 4.11 MPa. This may illustrate the limitations of applying the existing IGC model to the data. The influence of the mass transfer resistance in the gas phase likely becomes significant at pressures of 4 MPa and higher and the apparent increase in diffusion within the polymer is lower.

The partition coefficients for the PVAc-methyl acetate (MAc) system with CO₂ as the carrier gas are shown in Figure 5. Data were collected at four pressures of CO₂ up to 5.58 MPa. For the data indicated as zero pressure helium at ambient pressure was

used as the carrier gas. The results indicate that, like vinyl acetate, the partition coefficient shows a continued decrease with increasing pressure. In addition, the influence is somewhat greater at lower temperatures. This is because at a given pressure the uptake of CO₂ is higher at lower temperatures and the influence on the partition and diffusion coefficient is more pronounced.

Results for the diffusion coefficient of methyl acetate with CO₂ as the carrier gas are shown in Figure 6. Again, the diffusion coefficient generally shows a proportional increase with increasing pressure up to 2.85 MPa. The value of the diffusion coefficient measured at 5.58 MPa, however, is essentially the same as that at 2.85 MPa. At higher pressures mass transfer resistance in the gas phase is likely to become a significant factor with CO₂. Notice that the plasticization effect starts to dominate the temperature effect at moderate pressures of CO₂. Typically, the diffusion coefficient decreases with decreasing temperature. The uptake of CO₂ with decreasing temperature, however, counteracts the temperature effect and produces this unique effect. The apparent activation energy of diffusion for the data at 1.70 MPa is lower than that at 0.83 MPa (i.e., the slope of the data at 1.70 MPa is smaller). At 40°C and 1.70 MPa the value of the diffusion coefficient is about two orders of magnitude higher than that observed in the normal polymer-solvent system.

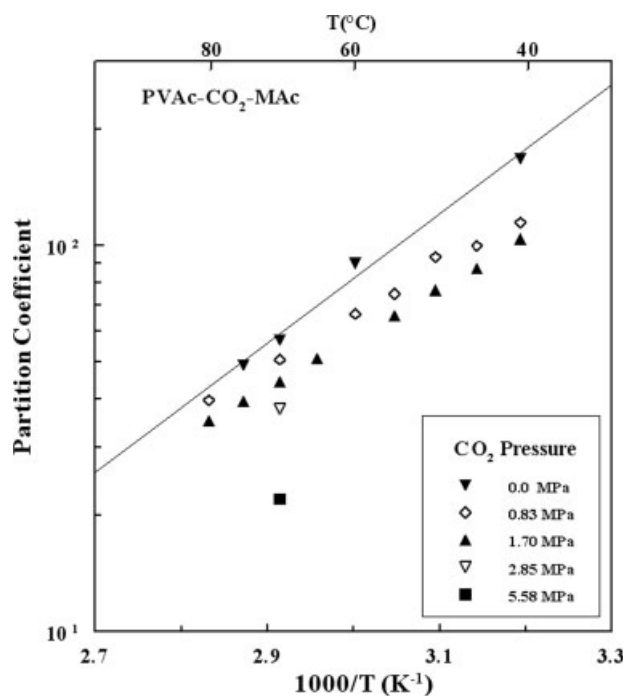


Figure 5 Partition coefficients of PVAc-methyl acetate as a function of temperature and CO₂ carrier gas pressure. Data at zero pressure were taken using helium at ambient pressure as the carrier gas.

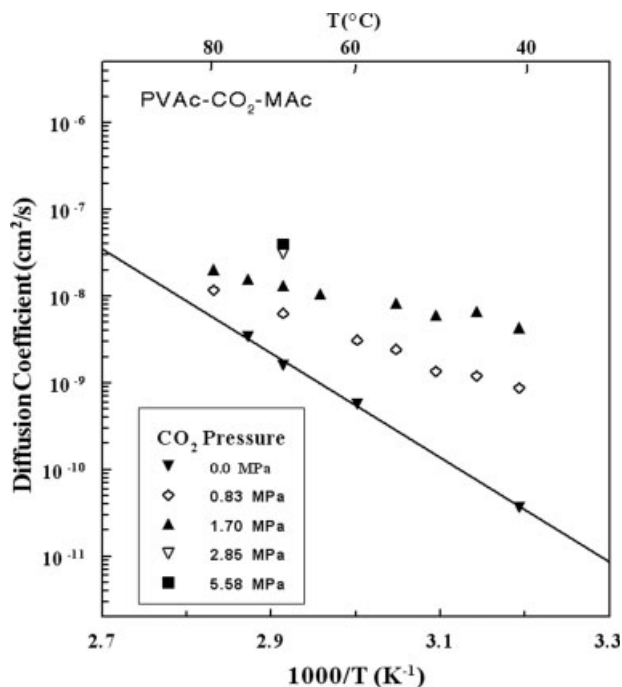


Figure 6 Diffusion coefficients of PVAc-methyl acetate as a function of temperature and CO₂ carrier gas pressure. Data at zero pressure were taken using helium at ambient pressure as the carrier gas.

Results in Figure 7 show the dependences of the partition coefficient of methyl acetate in PVAc on temperature and ethylene pressure. The results are

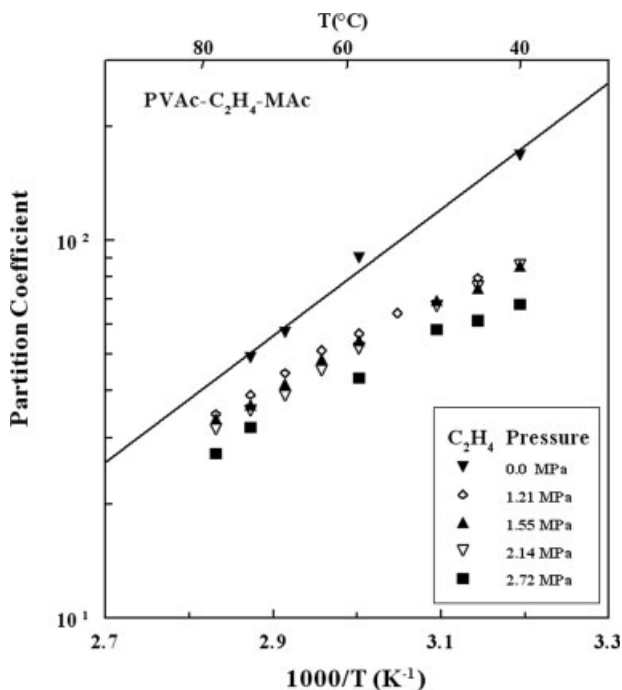


Figure 7 Partition coefficients of PVAc-methyl acetate as a function of inverse temperature and ethylene carrier gas pressure. Data at zero pressure were taken using helium at ambient pressure as the carrier gas.

similar to those observed with CO₂ for this same system. Ethylene more strongly hinders the interactions of methyl acetate with PVAc. The decrease again increases with increasing pressure of ethylene. Figure 8 gives the values of the diffusion coefficient for this system with ethylene. The effect as a function of temperature does not appear as pronounced as with CO₂. The influence on the diffusion, however, is still quite large with a change of nearly two orders of magnitude from those observed at the lower temperatures.

CORRELATION WITH SOLVENT SIZE

One of the objectives of this work was to determine if a strong correlation exists between solvent size and the influence of an absorbing carrier gas on the system. Solvents of different molar volumes (See Table II) were tested at the same temperature and pressure. The relative influence of an absorbing carrier gas on the thermodynamics was defined as the ratio of the partition coefficient when there was no absorbing carrier gas present (i.e., when helium at ambient pressure was used as the carrier gas) to that obtained in the presence of the high pressure absorbing gas. Because all the systems tested showed reduced interactions in the presence of CO₂ or ethylene (lower K values), the experimental values are greater than unity, as shown in Figure 9. (In

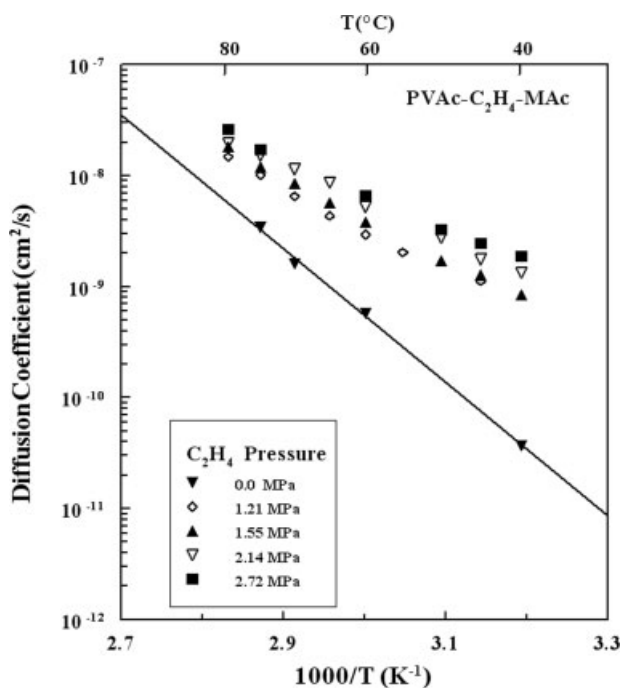


Figure 8 Diffusion coefficients of PVAc-methyl acetate as a function of inverse temperature and ethylene carrier gas pressure. Data at zero pressure were taken using helium at ambient pressure as the carrier gas.

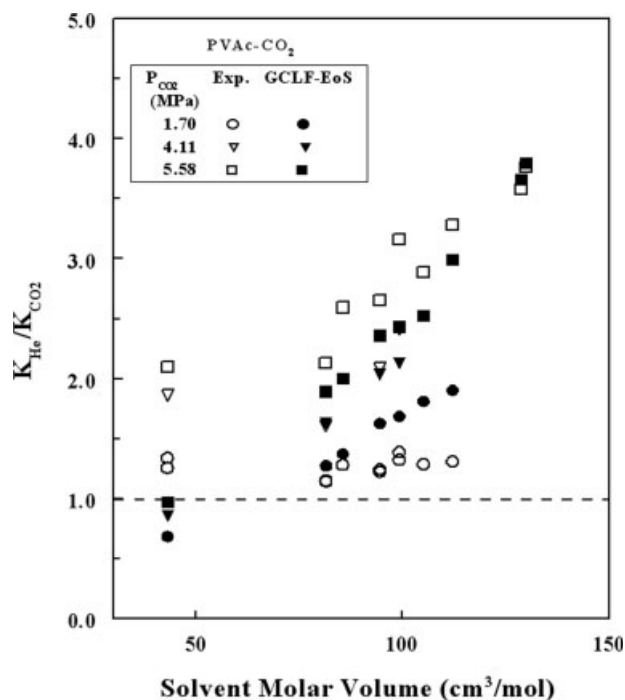


Figure 9 Experimental and predicted influence of CO₂ at 70°C in PVAc on the partitioning of solvents of different sizes.

the figures the molar volumes have been adjusted to the relevant temperature.)

The group-contribution, lattice-fluid equation of state¹⁸ (GCLF-EoS) was used to predict the influence on the partition coefficient. Values were calculated at 70°C and three pressures (1.70, 4.11, and 5.58 MPa) of CO₂. At the lowest pressure there appears to be no correlation with solvent size. At 4.11 and 5.58 MPa, however, there is an increase in the influence on the partition coefficient with increasing solvent size. The GCLF-EoS predicts that the influence of the high pressure gas on the solubility of the solvent will increase as the solvent size increases. The trend at 1.70 MPa is not as strong as predicted, but there is good agreement between the model and experimental results for isopropanol and methyl acetate (molar volumes 81.5 and 85.5 cm³/mol, respectively). At 4.11 MPa there is quite good agreement between the predictions and the observed influence, with the exception of the methanol results (molar volume 43.1 cm³/mol). Interestingly, GCLF-EoS predicts that there should be slightly higher solubility of methanol in the presence of the high pressure gas compared with the binary polymer-solvent system at the higher temperatures. This was not observed experimentally in the PVAc systems. The results at 5.58 MPa show generally good agreement with GCLF-EoS. The same trend with solvent size is observed with the predicted values being just slightly lower than the experimental ones.

Figure 10 shows a similar plot at 70°C of the partition coefficient ratios obtained with ethylene. The correlation between influence of the interacting gas and solvent size is quite clear in this plot. The increase in the partition coefficient in the presence of the high pressure gas shows a steady increase over the range of solvents tested. The effect that the gas has on the system is higher with bulkier molecules than smaller ones. The GCLF-EoS, however, predicts a much stronger dependence on solvent size than observed. The general trend is the same but the experimental values indicate that the partition coefficient in the presence of high pressure gas is only about 50% of the predicted values. This consistent trend suggests that the ethylene-solvent and ethylene-polymer segment parameters need refinement.

The influence of solvent size on the diffusion behavior was also determined. In this case, the ratio of the diffusion coefficient in the presence of the absorbing gases to that obtained at zero concentration of the absorbing gas (helium carrier) was calculated. In almost all cases the diffusion was observed to increase in the presence of the plasticizing gas, and therefore this ratio was greater than unity.

The results obtained with CO₂ as the high pressure gas are shown in Figure 11. Again the results at 1.70 MPa do not show any significant trend. There is a clear trend, however, with solvent size at higher pressures. The bulkier molecules are able to take advantage of the additional free volume brought to the system by CO₂. The smaller molecules which

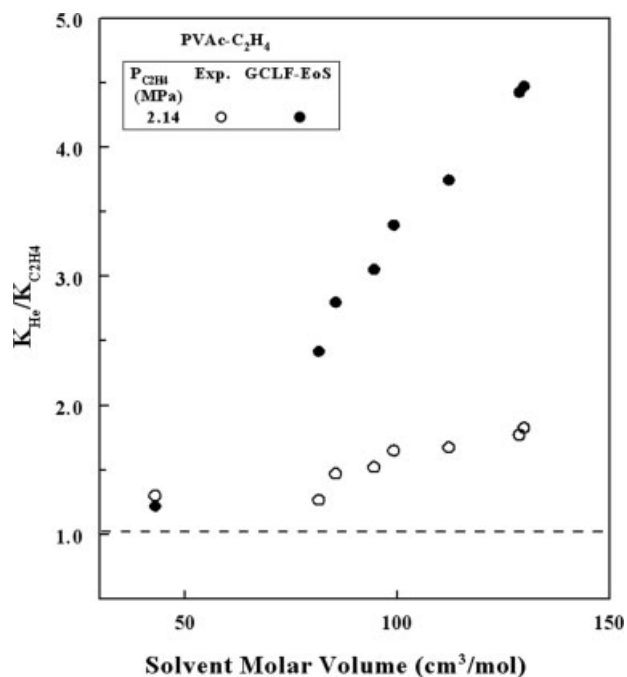


Figure 10 Experimental and predicted influence of ethylene at 70°C in PVAc on the partitioning of solvents of different sizes.

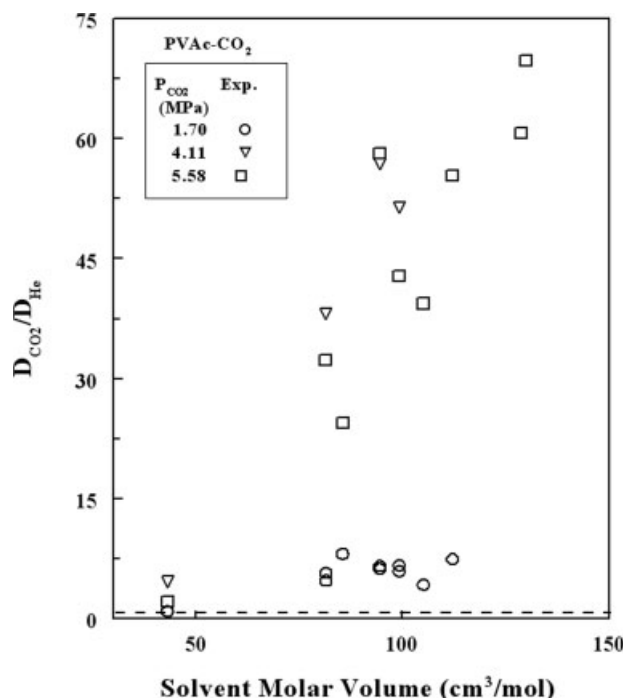


Figure 11 Influence of CO₂ at 70°C in PVAc on the diffusion of solvents of different sizes.

require less free volume for a diffusive “jump” are not as highly influenced by the additional free volume in the system.

Figure 12 indicates a similar trend for the data obtained in the presence of ethylene. Interestingly, values above 100 cm^3/mol all show similar behavior. The point for methanol (molar volume 43.1 cm^3/mol) falls below unity indicating slightly slower diffusion in the presence of methanol. The GC elution peak of methanol was by far the narrowest and slightly higher error was observed compared with the other solvents. It is not expected that the PVAc-methanol-ethylene system would exhibit antiplasticization behavior.

PS systems

As is evident from Figures 1 and 2 the solubility of CO₂ in PS is significantly lower than in PVAc. The solubility of ethylene in PS, however, is about the same as that in PVAc. Overall the uptake of the gases was lower compared to the PVAc systems because of the higher temperatures of the experiments for PS.

Data were obtained for benzene (C₆H₆) in PS with CO₂ and ethylene as carrier gases. Partition coefficients are presented in Figure 13 at two pressures for each carrier gas. Both gases have a pronounced influence on the thermodynamics of the system, with a significant reduction in the interactions between benzene and PS. The data indicates that

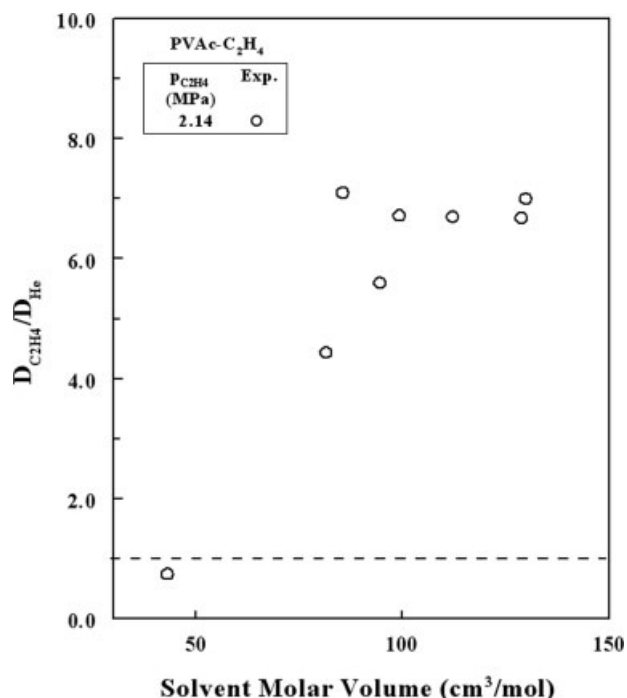


Figure 12 Influence of ethylene at 70°C in PVAc on the diffusion of solvents of different sizes.

ethylene at 2.34 MPa has the same influence on the partition coefficient as CO₂ does at 4.07 MPa. Considering that CO₂ has roughly 25% higher solubility than ethylene in PS at a given pressure, it is clear ethylene has a stronger influence on the thermodynamics of this system.

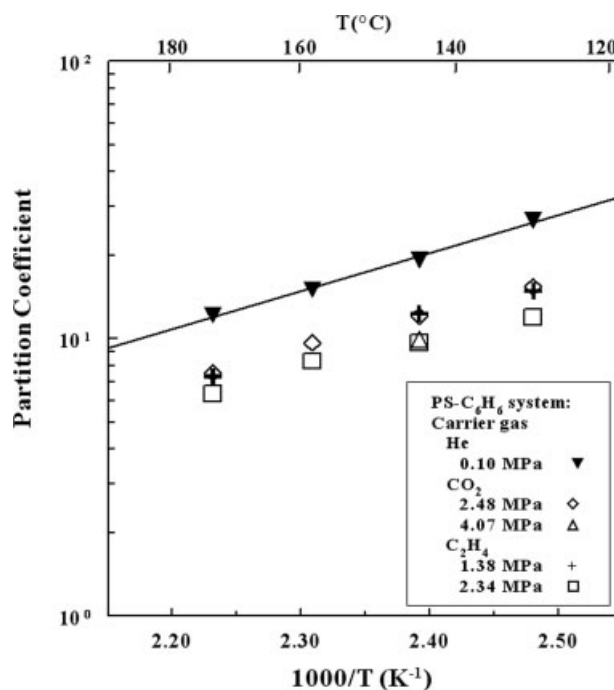


Figure 13 Partition coefficients of PS-benzene as a function of temperature and carrier gas pressure.

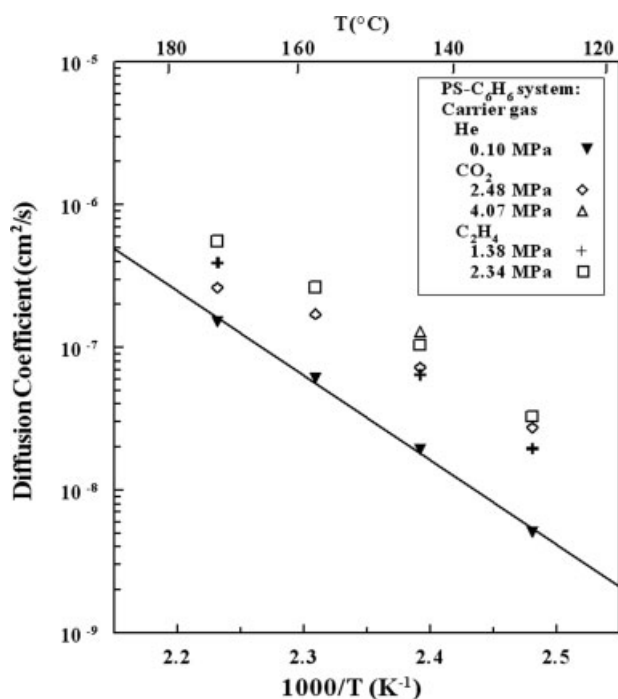


Figure 14 Diffusion coefficients of PS-benzene as a function of temperature and carrier gas pressure.

Diffusion coefficients are presented in Figure 14 at two pressures for each carrier gas. Again ethylene at 2.34 MPa and CO₂ at 4.07 MPa have the largest influence. The strong temperature effect observed in PVAc-methyl acetate is not present in this system because of the lower overall solubilities of the gases at the higher temperatures.

CORRELATION WITH SOLVENT SIZE

The influence of solvent size on the thermodynamics was also examined for PS with several solvents. The solvents tested were benzene, toluene, methanol, ethyl benzene, and *p*-xylene. Values were calculated at 160°C for CO₂ at 2.48 MPa and for ethylene at 2.34 MPa. In Figure 15 K_{Gas} refers to the partition coefficient with either CO₂ or ethylene as the carrier gas. Unfortunately, it was not possible to obtain reliable results for ethyl benzene and *p*-xylene in PS with ethylene. Figure 15 does not show a clear trend with solvent size for the ethylene results. Values calculated for the solvents in the presence of CO₂ indicate a higher influence on the bulkier molecules compared to methanol. There is no clear indication, however, that the thermodynamic influence increases with increasing solvent size for the PS systems. The GCLF-EoS indicates that the influence of the high pressure gas on the partition coefficient should increase for bulkier molecules. Except for the PS-benzene-CO₂ system there is little agreement between the model and the experimental results.

This could be due to inaccurate pure component parameters at the higher temperatures for the PS systems.

The influence of solvent size on the diffusion behavior is shown in Figure 16. Results were only obtained for the solvents in PS with CO₂ as a carrier gas. There appears to be a clear trend with solvent size which supports the results observed in the PVAc system.

CARRIER GAS INFLUENCE POTENTIAL

The last step in this project was to evaluate the carrier gas potential in terms of the thermodynamic and diffusion influences on a per mole basis. To do so, the partition and diffusion coefficient ratios were plotted as a function of carrier gas concentration in the polymer. For the case of CO₂, the concentration was determined from the data of Sato et al.¹⁷ For the ethylene data, the GCLF-EoS was used to estimate the concentrations at the experimental temperatures and pressures. It is assumed that this calculation may have contributed up to 10% error in the results. However, as will be shown, even with such an error the results clearly indicate the more effective gas.

Figure 17 shows a plot of the partition coefficient ratios for PVAc-methyl acetate as a function of carrier gas pressure at 70°C. The slope of the data indicates the strength of the carrier gas in terms of

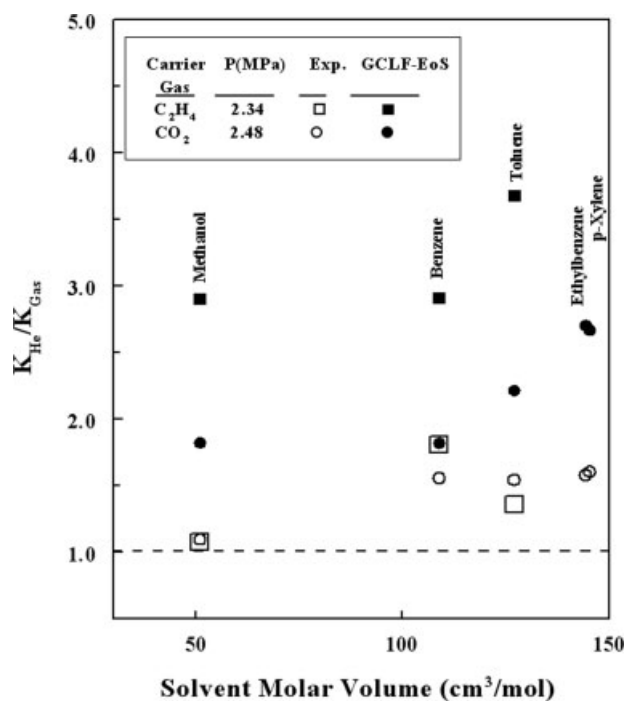


Figure 15 Experimental and predicted influence of the carrier gases at 160°C in PS on the partitioning of solvents of different sizes.

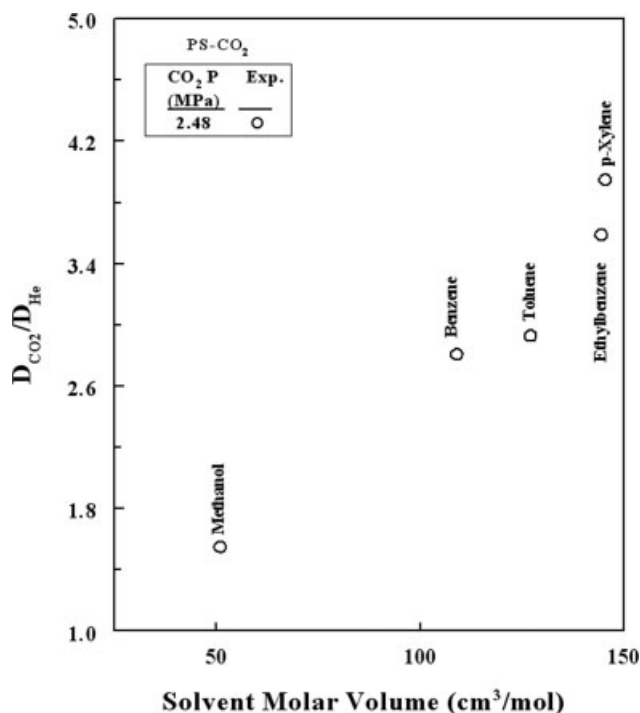


Figure 16 Influence of CO_2 at $160^\circ C$ in PS on the diffusion of solvents of different sizes.

influence on the thermodynamic behavior of the polymer-solvent system. It is clear that ethylene has a stronger influence per molecule on the thermodynamics than CO_2 .

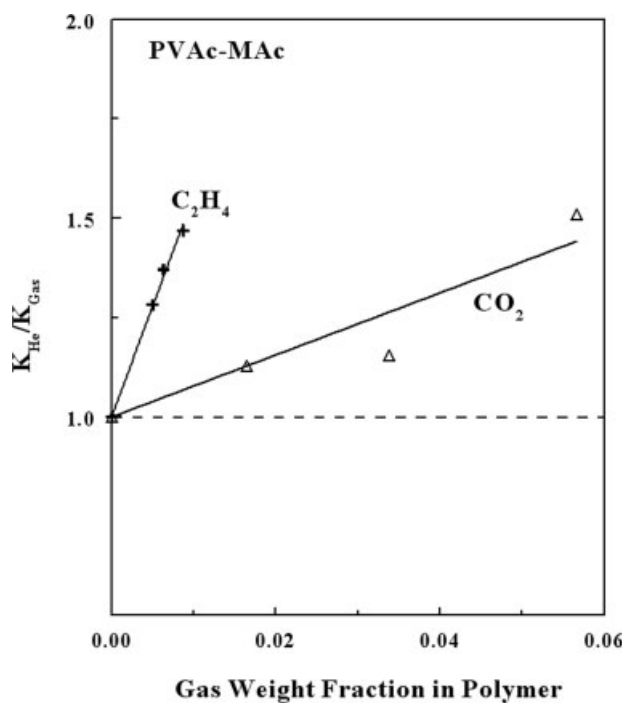


Figure 17 Comparison of carrier gas influence of ethylene (+) and CO_2 (Δ) on partitioning of PVAc-methyl acetate at $70^\circ C$.

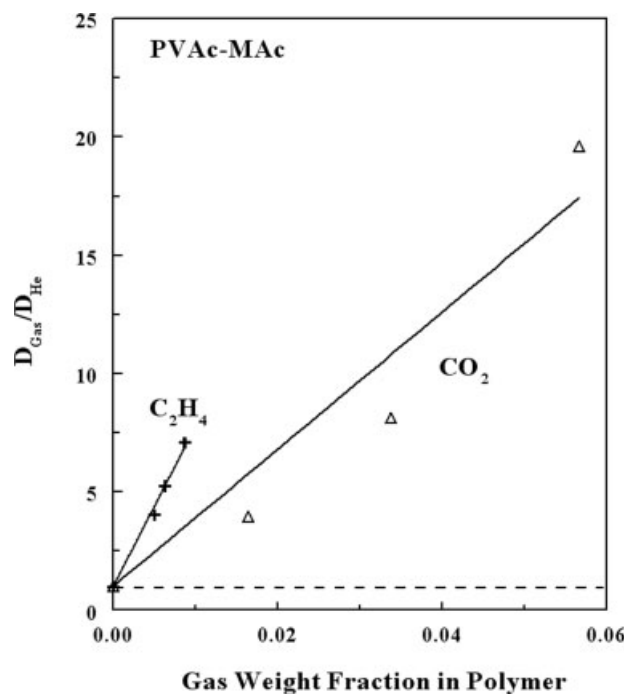


Figure 18 Comparison of carrier gas influence of ethylene (+) and CO_2 (Δ) on diffusion of PVAc-methyl acetate at $70^\circ C$.

Figure 18 shows a plot of the diffusion coefficient ratios for PVAc-methyl acetate as a function of carrier gas pressure. The slope of the data indicates the strength of the carrier gas in terms of its influence

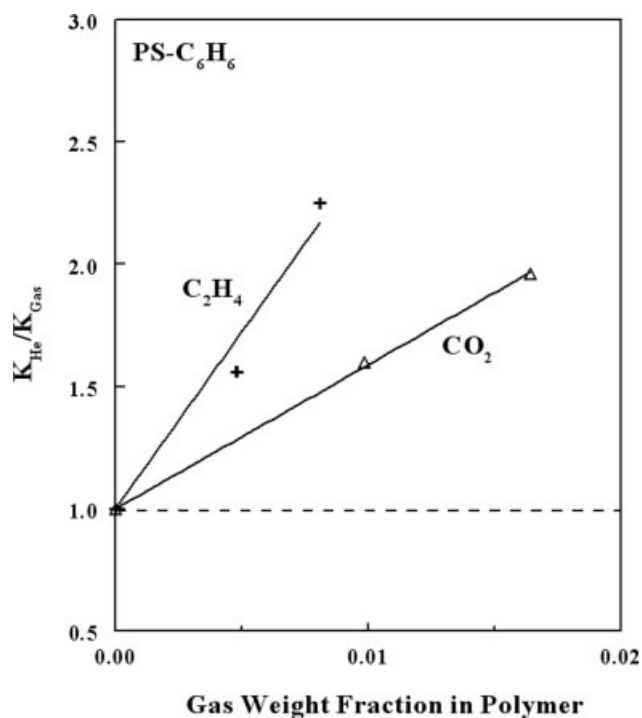


Figure 19 Comparison of carrier gas influence of ethylene (+) and CO_2 (Δ) on partitioning of PS-benzene at $145^\circ C$.

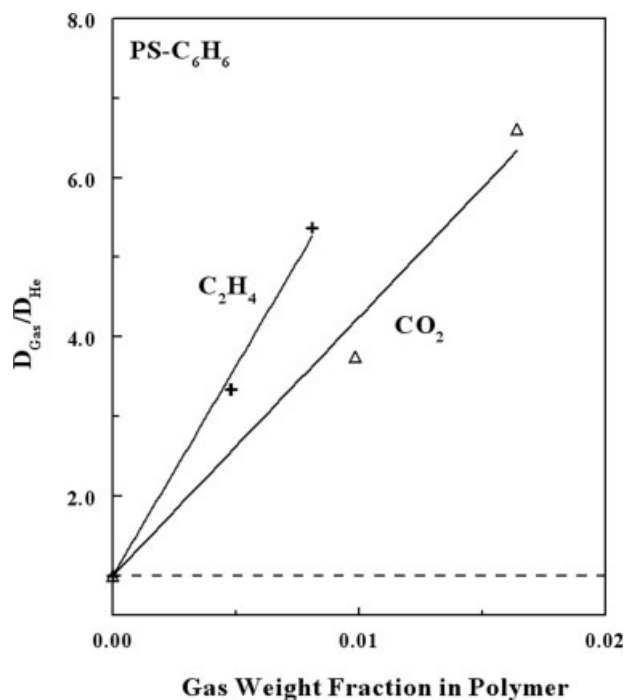


Figure 20 Comparison of carrier gas influence of ethylene (+) and CO₂ (Δ) on diffusion of PS-benzene at 145°C.

on the diffusion behavior of the polymer-solvent system. Again, based on these results it appears ethylene has a stronger plasticization potential. This is expected from the free volume theory of diffusion. Generally, a larger molecule will bring more free volume to the system and have a larger influence. The data in this study support that theory.

Figure 19 shows a similar comparison for the system PS-benzene at 145°C. As before the concentration in the CO₂ was determined from the data of Sato et al.¹⁷ and that in the ethylene from the GCLF-EoS. Figure 20 shows the diffusion coefficient ratios for PS-benzene as a function of carrier gas pressure. The slope of the data indicates the strength of the carrier gas in terms of influence on the diffusion behavior of the polymer-solvent system. The results indicate that ethylene has a more pronounced impact on both the solubility and diffusion than CO₂. The influence of small gases on the solubility of larger molecules is most likely attributable to entropic or steric effects. Physically, one can imagine that a larger molecule requires more volume for sorption. Therefore, presence of the ethylene or CO₂ is expected to have an increasing impact on solubility with increasing solvent molar volume. There are also specific interactions between the solvent-polymer and solvent-gas that may further enhance or hinder the solubility of the solvent in the polymer-solvent-gas matrix. However, as the data show the solvent size seems to be the dominant influence.

CONCLUSIONS

IGC has been shown to be a useful tool for examining the effects of high pressure gases on polymer-solvent behavior. In this work it was determined that ethylene (on a per mole basis) has a stronger influence on polymer-solvent solubility and diffusivity compared with CO₂. The GCLF-EoS was used to predict the influence of the high pressure gases on the thermodynamic behavior. The model predicts that the influence of the gases is higher for larger molecules. The experimental results for the PVAc systems confirm that the influence of these gases on the thermodynamics increases with increasing solvent size. Free-volume theory of diffusion predicts that molecules having larger free volume will plasticize the polymer to a higher extent. The influence of the carrier gases on the diffusion behavior increases as the size of the solvent molecules increases. The implications of this work are that CO₂ and ethylene have a pronounced effect on the thermodynamics and mass transport of polymer-solvent systems and devolatilization processes involving removal of higher molecular weight species such as aromatics and long chain paraffins will benefit the most from the use of such gases.

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