Modeling High-Pressure Gas–Polymer Mixtures Using the Sanchez-Lacombe Equation of State

M. B. KISZKA, M. A. MEILCHEN, and M. A. McHUGH,*

Department of Chemical Engineering, The Johns Hopkins University, Baltimore, Maryland 21218

Synopsis

The Sanchez-Lacombe equation of state was used to model the sorption of high-pressure gases into solid, amorphous polymers and molten polymers. Only one adjustable parameter per binary pair, δ_{12}, was used in the mixing rules to correct the deviation of the characteristic pressure of the mixture, P_{12}^*, from the geometric mean. The values of δ_{12} which gave the best fit of the available literature data for the carbon dioxide–polymethyl methacrylate, carbon dioxide–silicone rubber, ethylene–low density polyethylene, methane–polyisobutylene, methane–low-density and high-density polyethylene, and methane–polystyrene systems ranged from -0.019 to 0.136. In all cases, the calculated sorption isotherms were in reasonably good agreement with the experimental data. The resultant swelling of polymethyl methacrylate and silicone rubber was also well represented by the Sanchez-Lacombe equation of state. Because the Sanchez-Lacombe theory is based on lattice-fluid theory, the sorption calculations are limited to polymers which are noncrystalline, not cross-linked or slightly crosslinked, above their glass transition temperature, or above their melting temperature. The sorption data for the amorphous polymers considered in this study were either at temperatures above the glass transition temperature of the polymer or were at sufficiently high pressures that the temperature was above the effective glass transition temperature as predicted from a theoretical relation presented by Chow.

INTRODUCTION

The solubility of a gas in an amorphous polymer is an important consideration in membrane and polymer processes. For instance, the efficacy of a membrane used for separating a gas mixture is dependent on the solubility of the various species in the membrane.[1] Although operating at high pressures can cause the solubility of one or more of the gas components from the gas mixture to increase in the membrane, a very high pressure can cause such high solubilities that the membrane will swell and the selectivity will decrease.[1] An estimate of the solubility of gases in the membrane over large ranges of pressures could be used to define the operating boundaries over which the membrane would effectively separate the mixture.

Swelling a solid polymer matrix with a high-pressure gas can, however, aid in the deposition of temperature-sensitive materials into the polymer. The supercritical fluid (SCF) swells the polymer[2] and, thus, allows the substance to migrate into the polymer matrix. Sand[3] has shown that substances such as fragrances, pest control agents, and pharmaceutical drugs can be impregnated

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*To whom correspondence should be addressed.

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in a solid polymer if the polymer is exposed to a supercritical fluid during the impregnation process. Swelling the polymer effectively increases the diffusion coefficient of the heavy dopant by several orders of magnitude and, thus, allows it to be transported into the polymer within a reasonable time. When the system is depressurized, the supercritical fluid is removed from the polymer and the heavy dopant, which is trapped in the matrix, slowly diffuses out of the solid at a rate which is now orders of magnitude slower than the rate at which it was put into the polymer. This technique could lead to the formation of novel controlled-release devices since very high molecular weight constituents could be impregnated into a swollen polymer matrix at operating temperatures low enough to avoid thermal degradation of the substituents if a supercritical fluid solvent is used as the swelling agent.

Of course polymers can be effectively stripped of low molecular weight impurities, including entrapped solvent, residual catalyst, or low molecular oligomers by contacting with a high-pressure gas or a supercritical fluid. In this instance, the supercritical fluid would swell the polymer, diffuse into the polymer matrix and dissolve the impurity, and then diffuse out of the swollen matrix thus removing the impurity. This supercritical fluid extraction process is somewhat analogous to those used for the decaffeination of coffee beans and the removal of low molecular weight constituents from solid coal particles.[4]

For any polymer–gas process which operates to high pressures, it is often necessary to be able to predict the solubility of the gas in the polymer. Fleming and Koros[5] recommend using the Flory–Huggins equation to calculate the sorption of high-pressure gases in rubbery polymers, such as carbon dioxide in silicone rubber. At pressures as high as 1000 psia, they calculate the activity of carbon dioxide as the ratio of system pressure to the vapor pressure of the gas. They recognize that at these high pressures the activity should be the ratio of the fugacity of the gas to the standard state fugacity. When the ratio of system pressure to the vapor pressure of the gas is used, it is necessary to determine a hypothetical vapor pressure of the gas if the gas is at conditions above its critical properties. The focus of this article is to report on the use of the Sanchez-Lacombe[6] equation of state for modeling the solubility of high-pressure gases in solid, amorphous polymers or molten polymers and the subsequent swelling of the polymer. The calculational methods that are described are applicable to polymers which are noncrystalline, not crosslinked or only slightly crosslinked, and are above their melting temperatures. The sorption data for the amorphous polymers considered in this study were either at temperatures above the glass transition temperature of the polymer or were at sufficiently high pressures that the temperature was above the effective glass transition temperature as predicted from a theoretical relation presented by Chow.[7] The systems modeled in this study include carbon dioxide–polymethyl methacrylate (PMMA),[2,8] carbon dioxide–silicone rubber,[5] ethylene–low-density polyethylene (LDPE),[9] methane–polyisobutylene (PIB),[10] methane–LDPE,[10] methane–high-density polyethylene (HDPE),[10] and methane–polystyrene (PS).[10]

MODELING

Bonner[11] presents a review of the available literature information on the solubility of supercritical fluids in polymers. He also presents the predictive

techniques available for calculating gas solubilities in polymers. Our methods closely follow those outlined by Bonner.[11]

Our approach is to model the polymer–gas system using the following assumptions:

1. the solubility of the gas in the polymer represents equilibrium data,
2. the solubility of the polymer in the high-pressure gas phase is essentially zero, *and*
3. the amorphous polymer above its T_g can be modeled as a liquid.

For the data modeled in this study it is assumed that enough time was allowed for each polymer–gas system to reach equilibrium so that assumption number one is valid. The second assumption, that the polymer is essentially insoluble in the high-pressure gas, is satisfied if the polymer has a very high molecular weight and if the molecular weight distribution is reasonably narrow. The small amount of data available in the literature on the solubility of polymers in supercritical fluids suggests that if the molecular weight of the polymer is above approximately 8,000 then the solubility will be very low;[4,12–14] hence, we will assume this assumption to be valid in our analysis. The third assumption is normally accepted as valid as long as the polymer is above its T_g. A number of studies have shown that if an amorphous polymer sorbs gas to any great amount, its glass transition temperature can be substantially lowered.[1,2,7,8,15] For the polymers considered in this article, either the system temperature is already above the polymer's T_g or the partial pressure of the gas is high enough that the system temperature is above the polymer's effective T_g as gas is solubilized in the polymer.

The equation of state of Sanchez-Lacombe[6] is based on lattice-fluid theory which assumes that the polymer has a flexible liquid structure. This equation of state is

$$\tilde{\rho}^2 + \tilde{P} + \tilde{T}\left\{\ln\{1 - \tilde{\rho}\} + \left\{1 - \frac{1}{r}\right\}\tilde{\rho}\right\} = 0 \tag{1}$$

where $\tilde{P}$, $\tilde{T}$, and $\tilde{\rho}$ are the reduced pressure, temperature, and density, respectively, and r represents the number of lattice sites occupied by a molecule. The reduced parameters for a pure component are defined as

$$\tilde{T} = T/T^* \qquad T^* = \epsilon^*/R \tag{2}$$

$$\tilde{P} = P/P^* \qquad P^* = \epsilon^*/v^* \tag{3}$$

$$\tilde{v} = 1/\tilde{\rho} = V/V^* \qquad V^* = N(rv^*) \tag{4}$$

$$\tilde{\rho} = \rho/\rho^* \qquad \rho^* = M/rv^* \tag{5}$$

where ϵ^* is the interaction energy per mer, R is the gas constant, v^* is the close-packed volume of a mer, V^* is the close-packed volume of the mixture, and M is the molecular weight. The characteristic parameters used for these reduced properties are obtained from pure-component, P-V-T data as described in the following paragraphs. It should be noted that there are only three adjustable characteristic parameters.

When using the equation of state for mixtures the mixing rules recommended by Sanchez and Lacombe[16] are used to obtain the mixture characteristic parameters. Sanchez and Lacombe[16] assume that the characteristic pressure, P^*, is pairwise additive

$$P^* = \sum_i \sum_j \phi_i \phi_j P_{ij}^* \tag{6}$$

The cross term, P_{ij}^*, is defined as

$$P_{ij}^* = \{P_i^* P_j^*\}^{1/2} \{1 - \delta_{ij}\} \tag{7}$$

The parameter δ_{ij} is a mixture parameter which is obtained by fitting gas–polymer data. A small value of δ_{ij} is used to correct the deviation of the characteristic pressure of the mixture, P_{ij}^*, from the geometric mean. The close-packed, volume fraction of component i, ϕ_i, is given by

$$\phi_i = \frac{m_i/\rho_i^*}{m_i/\rho_i^* + m_j/\rho_j^*} \tag{8}$$

where m_i is the weight fraction.

The mixing rule for v^* is

$$v^* = \phi_i^0 v_i^* + \phi_j^0 v_j^* \tag{9}$$

where

$$\phi_i^0 = \frac{m_i/(\rho_i^* v_i^*)}{m_i/(\rho_i^* v_i^*) + m_j/(\rho_j^* v_j^*)} \tag{10}$$

The number of lattice sites occupied by an r-mer in the pure state, r_i^o is obtained with the following relationship

$$r_i^o = \frac{P_i^* V_i^*}{RT_i^*} \tag{11}$$

The number of lattice sites occupied by an r-mer in the mixture is

$$r = \frac{r_i^0 x_i v_i^* + r_j^0 x_j v_j^*}{v^*} \tag{12}$$

where x_i is the mole fraction of component i.

The mixing rule for T^* is

$$\frac{T^*}{T} = \frac{\{\phi_i/\tilde{T}_i + \nu\phi_j/\tilde{T}_j\}}{\{\phi_i + \nu\phi_j\}} - \phi_i\phi_j\frac{\{P_i^* + P_j^* - 2P_{ij}^*\}v^*}{RT} \tag{13}$$

where

$$\nu = \frac{v_i^*}{v_j^*} \tag{14}$$

A detailed discussion of these mixing rules is given by Sanchez and Lacombe.[16]

At equilibrium, the chemical potential of the gas in the pure gas phase is equal to the chemical potential of the gas dissolved in the polymer

$$\mu_1^G(T, P) = \mu_1^P(T, P, \phi_i) \tag{15}$$

where the superscripts G and P represent the gas and polymer phases, respectively, subscript 1 represents the light gas, and ϕ_i represents the volume fraction of component i.

Using the Sanchez and Lacombe equation of state, the chemical potential of the gas dissolved in the polymer can be obtained

$$\mu_1^P = RT\left\{\ln \phi_1 + \left\{1 - \frac{r_1}{r_2}\right\}\phi_2 + r_1^o \tilde{\rho} X_1 \phi_2^2\right\}$$

$$+ r_1^o RT\left\{-\frac{\tilde{\rho}}{\tilde{T}_1} + \frac{\tilde{P}_1 \tilde{v}}{\tilde{T}_1} + \tilde{v}\left\{\{1 - \tilde{\rho}\}\ln\{1 - \tilde{\rho}\} + \frac{\tilde{\rho}}{r_1^o}\ln \tilde{\rho}\right\}\right\} \tag{16}$$

where r_1 is the number of lattice sites occupied by component 1 of the mixture and X_1 is

$$X_1 = \frac{\{P_1^* + P_2^* - 2P_{12}^*\}v_1^*}{RT} \tag{17}$$

The pure component parameters used in this study are listed in Table I. The characteristic parameters, ρ^*, T^*, and P^*, for PMMA, PIB, LDPE, HDPE, PS, and methane are obtained directly from Sanchez and Lacombe.[16] The characteristic parameters for PDMS are used as the characteristic parameters for silicone rubber, as explained later.

TABLE I
Characteristic Equation of State Parameters for the Light Gases and the Polymers as Tabulated by Sanchez and Lacombe, Unless Indicated Otherwise

Substance	ρ^* (g/cm^3)	T^* (K)	P^* (atm)
CH_4	0.500	224	2448
CO_2[a]	1.510	305	5670
C_2H_4[a]	0.515	327	2000
PMMA	1.269	696	4964
PDMS	1.104	476	2981
LDPE	0.887	673	3543
HDPE	0.904	649	4194
PIB	0.974	643	3494
PS	1.105	735	3523

[a] Parameters fit to the vapor–liquid equilibrium line and to liquid molar volume data.

The parameters for carbon dioxide were obtained by fitting molar volume data and the pure-component vapor–liquid equilibrium (VLE) curve to the equation of state with a standard regression routine. The pressure–temperature (P–T) conditions of the molar volume data were 40 to 60°C and 100 to 160 atm.[17] These P–T conditions were chosen so that the parameters would be based on the P–T space in which most of the experimental polymer–carbon dioxide data were obtained. We obtain a fair representation of the vapor–liquid equilibrium curve and the critical point for carbon dioxide (T_c^{calc} = 44.5°C, P_c^{calc} = 89.5 atm; T_c = 31.05°C, P_c = 72.8 atm). Kilpatrick and Chang,[18] who fit VLE data only, report slightly different parameters for carbon dioxide. With their parameters a better prediction of the critical point of carbon dioxide is obtained (T_c^{calc} = 36.8°C, P_c^{calc} = 85.7 atm). However, the molar volumes of carbon dioxide in the P–T region of the experimental polymer–carbon dioxide data are poorly predicted with the pure-component parameters reported by Kilpatrick and Chang.[18] In general, the calculated critical points for light gases are usually about 5% greater than the measured critical point.[6]

The pure component parameters for ethylene are also determined by fitting molar volumes and VLE data.[19] The P–T conditions chosen for the molar volume data (temperatures from 130°C to 140°C; pressures from 40 atm to 60 atm) are close to those for most of the ethylene–LDPE data. A fair representation of the VLE curve and the critical point for ethylene (T_c = 9.3°C, P_c = 49.7 atm; T_c^{calc} = 18.6°C, P_c^{calc} = 53.2 atm) is obtained using the parameters for ethylene. The difference between the calculated and experimental critical point of ethylene is consistent with the differences found for other similar light gases.[6,18]

Sorption isotherms were calculated with a given value of the adjusted mixture parameter, δ_{ij}, in the following manner. At a fixed temperature, pressure, and initial guess of the weight fraction of the gas in the polymer, the chemical potentials of the gas in the pure gas phase and in the polymer–rich liquid phase were determined. If equation (15) was not satisfied, then the weight fraction was adjusted and the chemical potentials were recalculated. The best-fit value of δ_{ij} was determined by minimizing the absolute value of the percentage residual error between calculated and experimental weight fractions for a given sorption isotherm.

RESULTS AND DISCUSSION

Sorption isotherms were calculated for the following systems: carbon dioxide–PMMA,[2,8] carbon dioxide–silicone rubber,[5] ethylene–LDPE,[9] methane–PIB,[10] methane–LDPE,[10] methane–HDPE,[10] and methane–PS.[10] The pure-component, characteristic parameters used in this analysis are tabulated in Table I and the mixture parameter, δ_{ij}, regressed from experimental data for each of the gas–polymer systems, is shown in Table II.

Figure 1 shows the model calculations for the carbon dioxide–PMMA system at 41.8, 58.1, and 68.0°C.[2,8] The δ_{ij} parameter obtained from the best fit of this data ranges from -0.001 to -0.019. For this system the fit of the sorption data is very dependent on the value of δ_{ij}. The values of δ_{ij} obtained for the carbon dioxide–PMMA system are negative, but this most likely is due

TABLE II
Values of the Mixture Parameter SL12 used in Sorption Calculations

System	Temperature (°C)	Pressure (atm)	Polymer M_w	SL12
CO_2/PMMA	41.8	0–250	60,600	− 0.001
CO_2/PMMA	58.1	0–250	60,600	− 0.004
CO_2/PMMA	68.0	0–275	60,600	− 0.019
CO_2/PDMS[a]	35.0	0–60	50,000	0.047
C_2H_4/LDPE	126.0	0–70	249,000	0.024
C_2H_4/LDPE	140.0	0–70	249,000	0.025
C_2H_4/LDPE	155.0	0–70	249,000	0.044
CH_4/PIB	155.4	0–350	1,300,000	0.114
CH_4/PS	125.4	0–700	500,000	0.136
CH_4/PS	155.4	0–700	500,000	0.119
CH_4/PS	188.4	0–700	500,000	0.090
CH_4/LDPE[a]	155.4	0–700	100,000	0.086
CH_4/HDPE[a]	140.0	0–350	100,000	0.044

[a] The M_w molecular weight for this system was assumed.

to specific interactions between the carbon dioxide and PMMA. Specific interactions normally decrease with increasing temperature and, thus, δ_{ij} is expected to decrease with increasing temperature. However, for the carbon dioxide–PMMA system the opposite temperature trend is observed for δ_{ij}. Since PMMA is being plasticized by carbon dioxide it may be possible that there is some vestige of order remaining in the PMMA on the time scale of the sorption experiment thus allowing for more complexing as carbon dioxide sorbs into the PMMA below the normal T_g. At temperatures which are greater than the normal T_g for PMMA, it is expected that δ_{ij} will decrease with increasing temperature as the liquid state of PMMA loses all vestiges of order.

Although Koros[1] reports sorption data for the carbon dioxide–PMMA system at 35°C and for pressures up to 20 atm, this data is not modeled well by the Sanchez-Lacombe equation of state. However, the failure of the Sanchez-Lacombe model at these P–T conditions is not unexpected. Polymers below their glass transition temperature have an additional unrelaxed volume, and PMMA is below its glass transition temperature at the P–T–x conditions investigated by Koros.[1] As shown in Figure 1(a), the carbon dioxide-PMMA data[2,8] is modeled reasonably well at a slightly higher temperature (41.8°C) and higher pressures (up to 300 atm) than the data of Koros.[1] Although the glass transition temperature of PMMA is 105°C, Chow[7] has shown that, in general, the glass transition temperature of a polymer can be significantly depressed if sufficient amounts of a high-pressure gas are sorbed in the polymer. Based on calculations with the expression developed by Chow,[7] it is found that almost all of the data reported by Liau and McHugh[2] are for PMMA at temperatures above its effective T_g.

As mentioned before, PMMA swells when in the presence of high-pressure carbon dioxide. Figure 2 shows the model calculations of this behavior. In these calculations, the δ_{ij} values obtained from the sorption calculations are used. A reasonable fit of the experimental data reported by Wissinger and
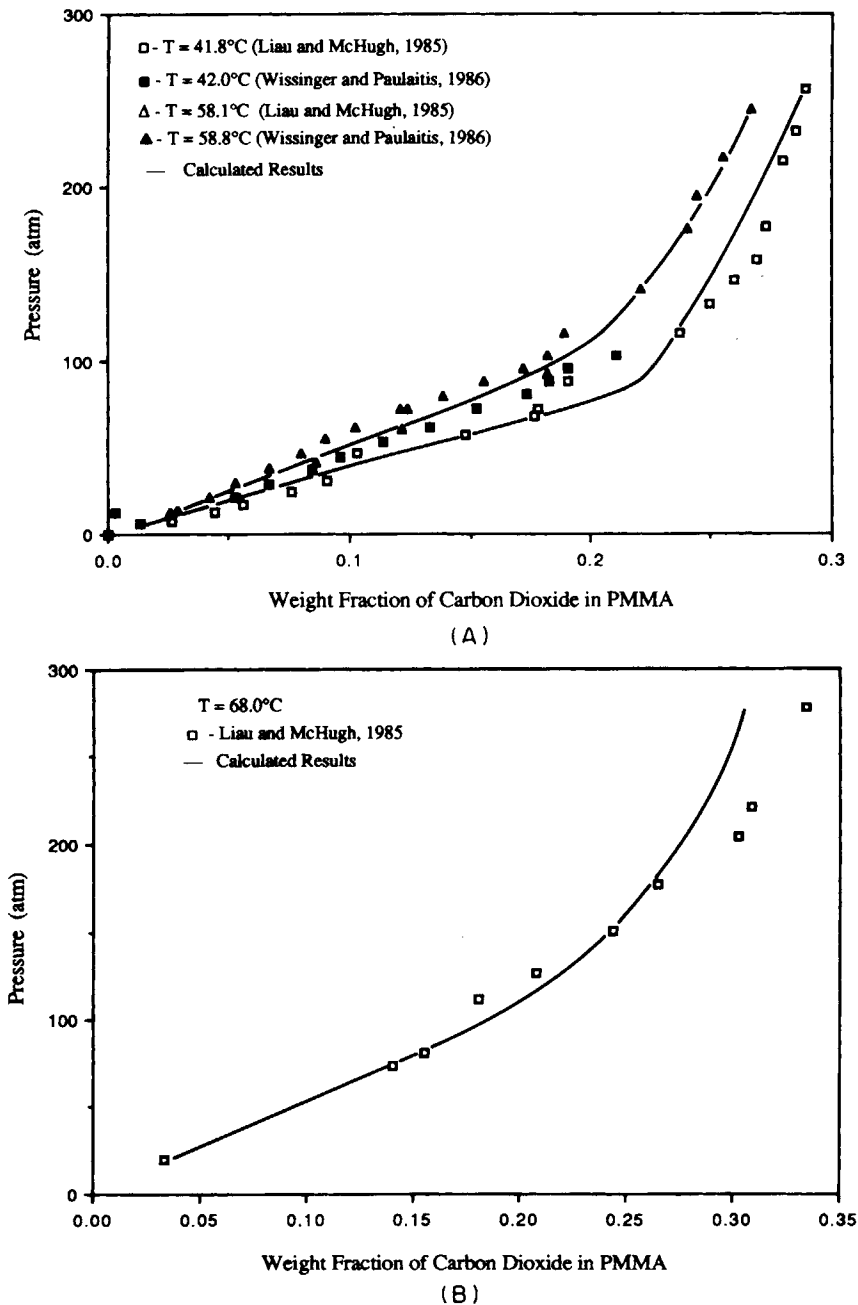
(A)

(B)

Fig. 1. Comparison of experimental and calculated sorption isotherms for the carbon dioxide–PMMA system. The calculated (—) isotherms at (A) (□, ref. 2) 41.8°C, (△, ref. 2) 58.1°C, and (B) 68.0°C (ref. 2) are determined with δ_{ij} equal to -0.001, -0.004, and -0.019, respectively. (■) 42.0°C (ref. 8), (▲) 58.8°C (ref. 8).
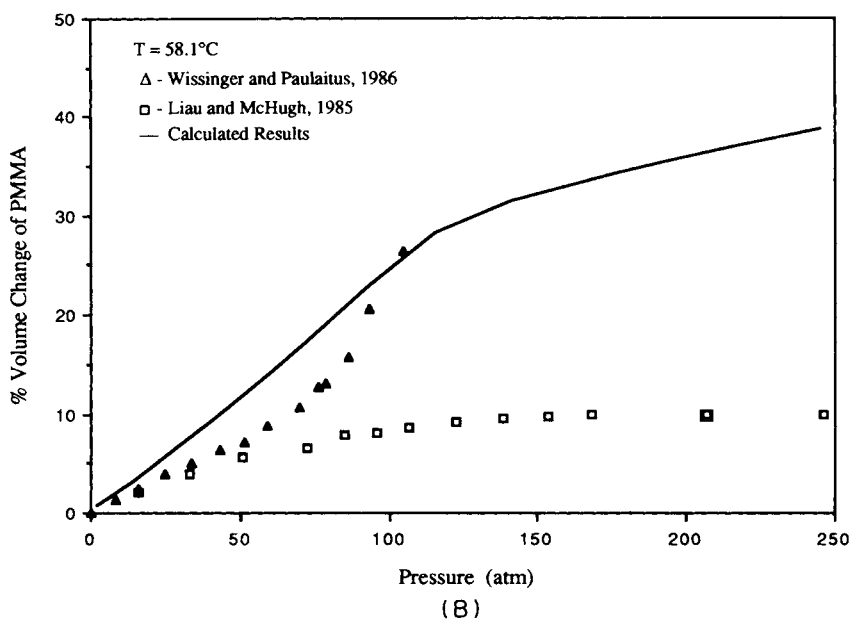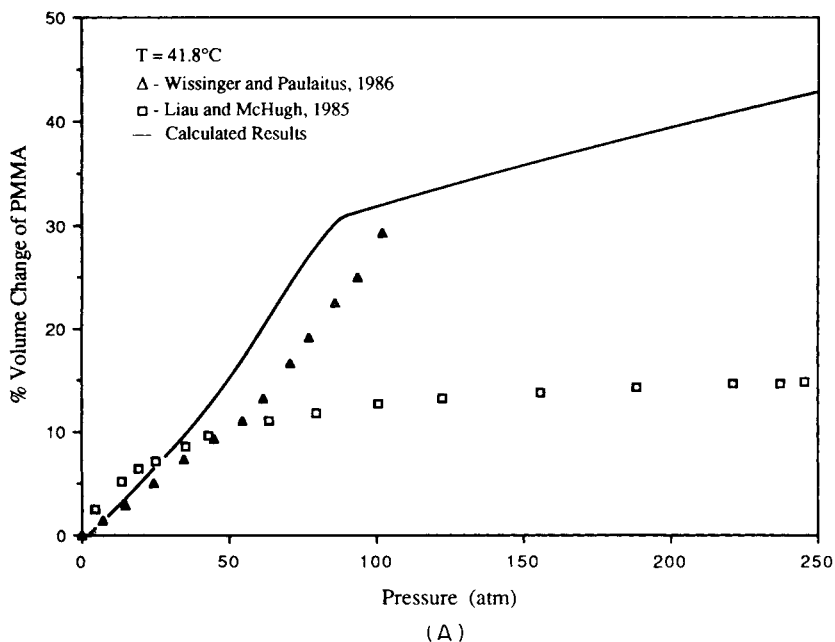
Fig. 2. The effect of carbon dioxide partial pressure on the volume of PMMA. The calculated results are obtained with the values of δ_{ij} listed in Figure 1.

Pauliatis[8] is obtained. The model predicts that if the data of Wissinger and Pauliatis were extended to higher pressures the swelling would level off. This trend is seen in the data reported by Liau and McHugh,[2] although the absolute value of their high-pressure swelling data differs considerably from the data of Wissinger and Pauliatus[8] and from the calculated results. We
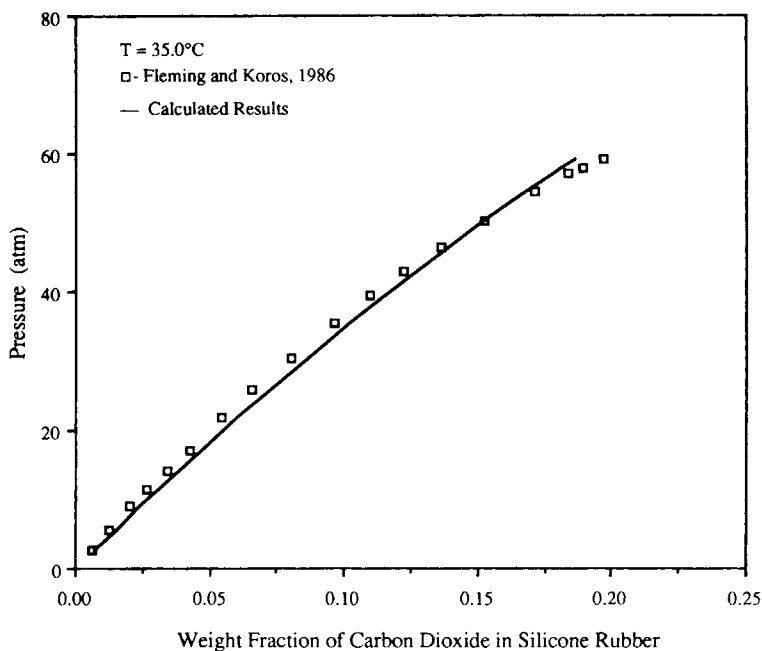
Fig. 3. Comparison of experimental and calculated (—) sorption isotherm for the carbon dioxide–silicone rubber system at 35.0°C. The value of δ_{ij} used for this isotherm is equal to 0.047. (□ ref. 5).

believe that the experimental method used by Liau and McHugh[2] was unrealiable for obtaining swelling data at pressures greater than about 80 atmospheres.

Figure 3 shows the carbon dioxide–silicone rubber data reported by Fleming and Koros.[5] The δ_{ij} parameter determined for this system is 0.047. Fleming and Koros indicate that the silicone rubber used in their study has a small amount of cross-linking. They assume that since the cross linking was minimal, the parameters for uncross-linked polydimethyl siloxane could be used in the analysis of their data. Hence, the same assumption is made in this study. An arbitrarily chosen molecular weight of 50,000 is used in our calculations. As shown in Figure 3, a good fit of the sorption isotherm is obtained. The swelling of the silicone rubber in the presence of carbon dioxide is also modeled using the value of δ_{ij} obtained from the sorption calculations. Figure 4 shows that a good fit of the swelling of the silicone rubber is obtained with the Sanchez-Lacombe equation of state. The calculated swelling for this system exhibits the same trends that were noted for the carbon dioxide–PMMA system. As the partial pressure of carbon dioxide increases, the swelling of silicone rubber increases monotonically until it eventually levels off at pressures greater than 80 atm.

The fit of the model to ethylene–LDPE isotherms at 126°C, 140°C, and 155°C[9] is shown in Figure 5. As with the carbon dioxide–PMMA system presented earlier, the three isotherms of the ethylene–LDPE system are best modeled with values of δ_{ij} which increase with increasing temperature (δ_{ij} = 0.024, 0.025, 0.044, respectively). Lundberg[10] argues that with branched poly-
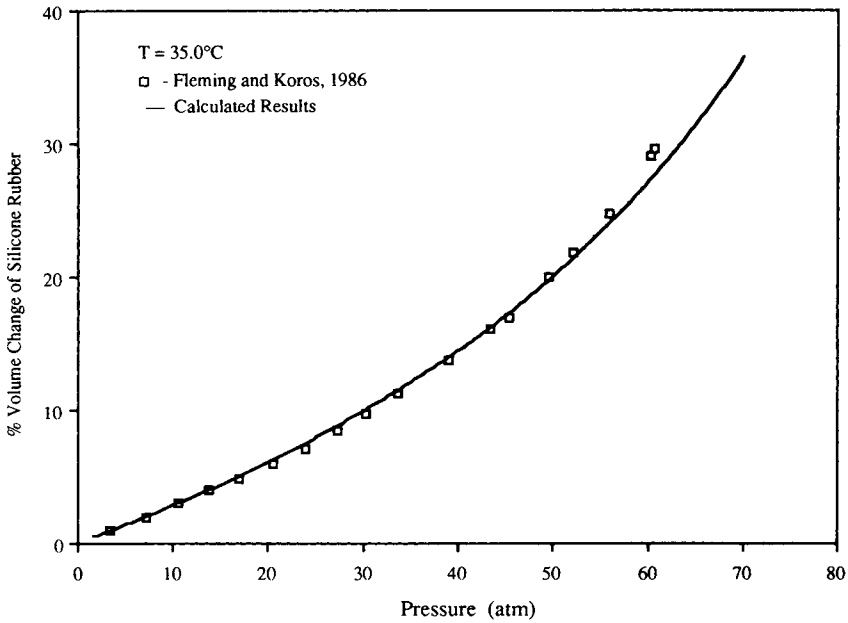
Fig. 4. The effect of carbon dioxide partial pressure on the volume of silicone rubber. The calculated results are obtained with the value of δ_{ij} listed in Figure 3. (□) ref. 5.
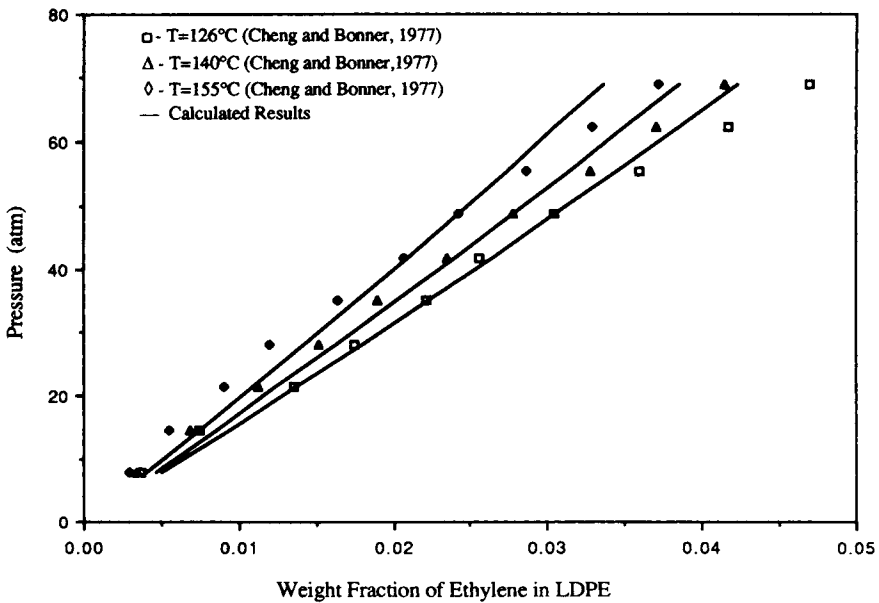

Fig. 5. Comparison of experimental and calculated sorption isotherms for the ethylene–LDPE system. The calculated isotherms at (□) 126.0°C, (△) 140.0°C, and (◇) 155.0°C are determined with δ_{ij} equal to 0.024, 0.025, and 0.044, respectively (ref. 9).
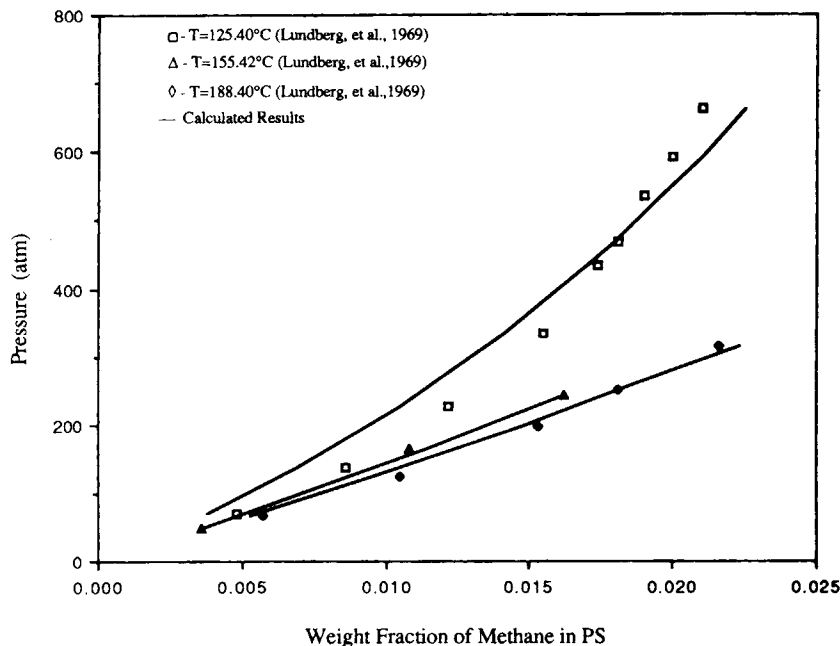
Fig. 6. Comparison of experimental and calculated sorption isotherms for the methane–polystyrene system. The calculated isotherms at (□) 125.4°C, (△) 155.4°C, and (◇) 188.4°C are determined with δ_{ij} equal to 0.136, 0.119, and 0.090, respectively (ref. 10).

ethylene there should not be any ordering in the liquid state at the temperatures investigated by Cheng and Bonner.[9] The reason that δ_{ij} increases with increasing temperature for the ethylene–LDPE system is not apparent at this time. Nevertheless, the Sanchez–Lacombe equation does a good job representing the sorption data with a small value of δ_{ij}.

Data on the solubility of methane in polystyrene and polyisobutylene are reported by Lundberg et al.[10] Figure 6 shows a comparison of experimental and calculated isotherms for the methane–polystyrene system at 126°C, 155°C, and 188°C. The best fit of the data is obtained by allowing δ_{ij} to vary as a function of temperature. In this instance δ_{ij} does decrease with increasing temperature as found for small molecule gas–liquid systems. It is speculated that at these temperatures the polystyrene is very mobile and lacks order and, therefore, will behave as a liquid. Figure 7 shows a comparison of the methane-polyisobutylene data at 155.41°C with the calculated results. Notice that even though the partial pressure of methane is very high for the methane–PIB and the methane–PS systems, the solubility of methane in the polymer is quite low. When the sorption isotherms for these two methane–polymer systems are calculated using pure component methane parameters obtained from fitting the methane VLE curve and molar volume data at P–T conditions near those of the experimental data, there is not a significant difference in the fit of the data nor in the values of δ_{ij}. Therefore, the characteristic parameters of methane given by Sanchez and Lacombe[6] are used in the calculations.
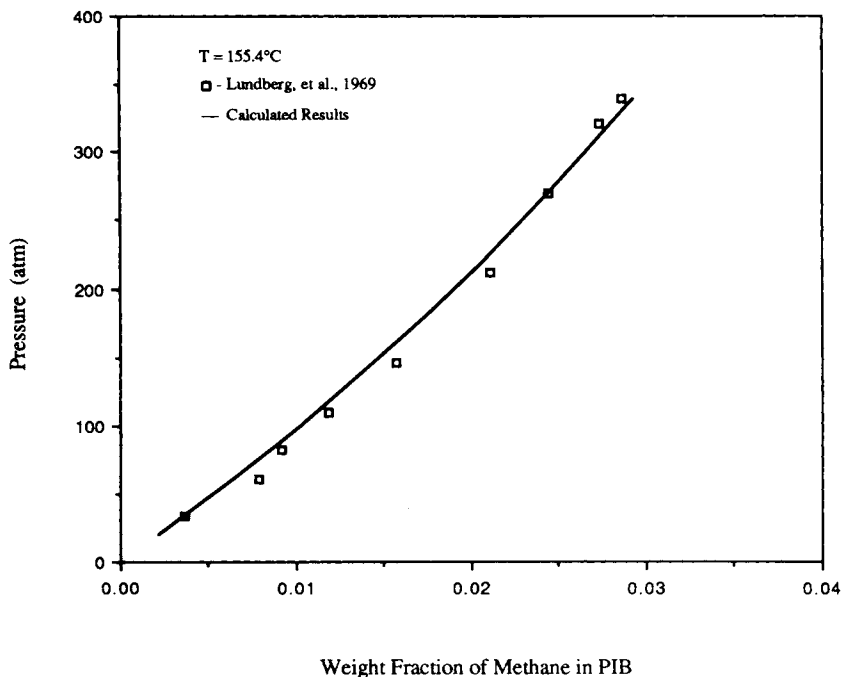
Weight Fraction of Methane in PIB

Fig. 7. Comparison of experimental and calculated sorption isotherm for the methane–poly-isobutylene system. The value of δ_{ij} used for this isotherm is equal to 0.114. T = 155.4°C. (□) ref. 10.
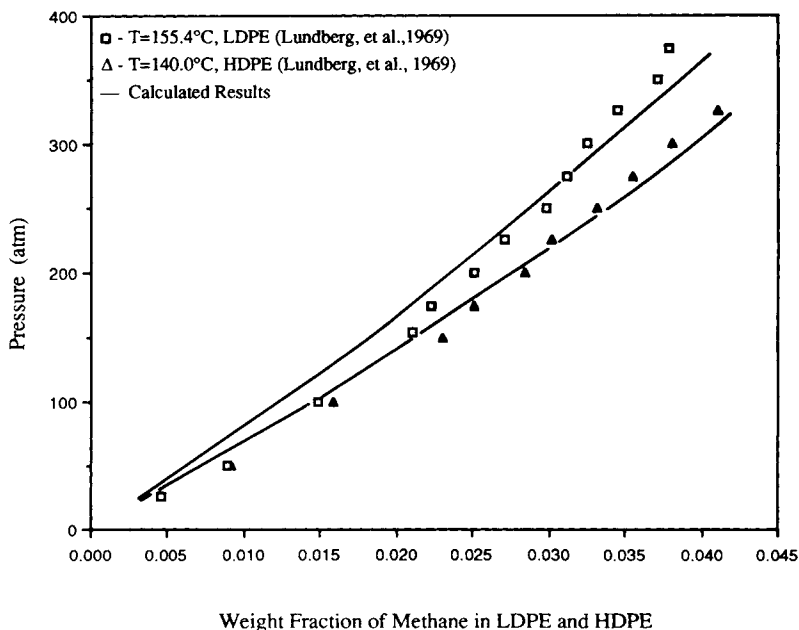

Weight Fraction of Methane in LDPE and HDPE

Fig. 8. Solubility of methane in low-density polyethylene (□, T = 155.4°C) (LDPE) and high-density polyethylene (△, T = 140.0°C) (HDPE). The calculated isotherms are determined with δ_{ij} equal to 0.086 and 0.044, respectively (ref. 10).

Figure 8 shows the model calculations for the methane–LDPE system[10] at 155.4°C and the methane–HDPE system[10] at 140.03°C. The values of δ_{ij} obtained from the best fit of the data are 0.086 and 0.044, respectively. It is not surprising that δ_{ij} is different for HDPE and LDPE since the structures of these polymers differ. Again, the Sanchez-Lacombe equation does a good job representing the sorption data with a small value of δ_{ij}.

CONCLUSIONS

The Sanchez-Lacombe equation of state with one mixture parameter can be used to effectively model the solubility of a high-pressure gas in an amorphous or molten polymer. Although the mixture parameter, δ_{ij}, must be fit to experimental data, the absolute value of δ_{ij} is small and it is of the same magnitude as the values found for the respective monomer–gas systems. The calculations decrease the amount of experimental data that is needed to define a sorption isotherm. The volume dilation of the polymer is also easily calculated. In certain instances it is speculated that there is still some ordering of the polymer in the molten state on the time scale of the sorption measurements. As such, the value for the fitted mixture parameter, δ_{ij}, does not decrease with increasing temperature as would be expected for small molecule–gas systems. It should be noted that it is straightforward to use the Sanchez-Lacombe equation of state to calculate ternary mixture behavior using only the values of δ_{ij} found for the binary pairs which make up the ternary mixture.

NOMENCLATURE

m = mass fraction
P = pressure
r = number of lattice sites occupied by a mer
T = temperature
v = molar volume
X = mixture parameter
x = mole fraction

Greek Letters

μ = chemical potential
ρ = reduced density
ϕ = close-packed volume fraction
δ = mixture parameter

Subscripts

c = critical properties
i = component i
1 = solvent
2 = polymer

Superscripts

calc = calculated values
G = gas
o = pure component
P = polymer
* = characteristic variable
~ = reduced variable

References

1. W. J. Koros, *J. Polym. Sci. Polym. Phys. Ed.*, **23**, 1611–1628 (1985).

2. I. S. Liau and M. A. McHugh, in *Supercritical Fluid Technology*, J. M. L. Penninger, M. Radosz, M. A. McHugh, and V. J. Krukonis, eds., Elsevier, Amsterdam, pp. 415–434, 1985.

3. M. L. Sand, "Method for Impregnating a Thermoplastic Polymer," U. S. Patent 4,598,006 (Jul. 1, 1986).

4. M. A. McHugh and V. J. Krukonis, *Supercritical Fluid Extraction: Principles and Practice*, Butterworths, Boston, 1986.

5. G. K. Fleming and W. J. Koros, *Macromolecules*, **19**, 2285–2291 (1986).

6. I. C. Sanchez and R. H. Lacombe, *J. Phys. Chem.*, **80**(21), 2352–2362 (1976).

7. T. S. Chow, *Macromolecules*, **13**, 362–364 (1980).

8. R. G. Wissinger and M. E. Paulaitis, presented at the Annual Meeting of the American Institute of Chemical Engineers, Miami Beach, Florida (November, 1986).

9. Y. L. Cheng and D. C. Bonner, *J. Polym. Sci. Polym. Phys. Ed.*, **15**, 593–603 (1977).

10. J. L. Lundberg, E. J. Mooney, and C. E. Rogers, *J. Polym. Sci. A-2*, **7**, 947–962 (1969).

11. D. C. Bonner, *Polym. Eng. Sci.*, **17**(2), 65–72 (1977).

12. P. Ehrlich and E. B. Graham, *J. Polym. Sci.*, **45**, 246 (1960).

13. J. P. Heller, D. K. Dandge, R. J. Card, and L. G. Donaruma, SPE 11789, presented at the International Symposium on Oilfield and Geothermal Chemistry, Denver (June 1983).

14. S. V. Dhalewadikar, M. A. McHugh, and T. L. Guckes, *J. Appl. Polym. Sci.*, **33**, 521–524 (1987).

15. W. V. Wang, E. J. Kramer, and W. H. Sachse, *J. Polym. Sci. Polym. Phys. Ed.*, **20**, 1371–1384 (1982).

16. I. C. Sanchez and R. H. Lacombe, *Macromolecules*, **11**(6), 1145–1156 (1978).

17. A. Michels and C. Michels, *Proc. R. Soc. London Ser. A.*, **160**, 348–357 (1937).

18. P. K. Kilpatrick and S.-H. Chang, *Fluid Phase Equil.*, **30**, 49–56 (1986).

19. S. Angus, B. Armstrong, and K. M. de Reuck, *International Thermodynamic Tables of the Fluid State, Ethylene*, Butterworths, London, 1974.