"Modeling High-Pressure Gas-Polymer Sorption Behavior Using the Sanchez-Lacombe Equation of State"

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Modeling High-Pressure Gas-Polymer Sorption Behavior Using the Sanchez-Lacombe Equation of State.

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Abstract:

The Sanchez-Lacombe equation of state was used to model the sorption of high-pressure gases into solid, amorphous polymers or molten polymers. One adjustable parameter per binary pair, $\delta_{12}$, was used in the mixing rule to correct the deviation of the characteristic pressure of the mixture, $P_{12}^*$, from the geometric mean. The values of $\delta_{12}$ 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 0.020 to 0.194, except for the methane-low density system which had a negative value of -0.183. 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 in the presence of high-pressure carbon dioxide was also well represented by the Sanchez-Lacombe equation of state. Because the Sanchez-Lacombe equation of state is based on lattice-fluid theory, the sorption calculations are limited to polymers which are non-crystalline, not cross-linked or slightly cross-linked, above their glass transition temperature, or above their melting temperature. All of the amorphous polymers considered in this study were above their glass transition temperature or their effective glass transition temperature as predicted from a theoretical relation presented by Chow.
Introduction:

The solubility of a gas in an amorphous or molten 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 (Koros, 1985). Although high-pressure gradients across the membrane can increase the solubility of one or more of the components from the gas mixture, a very high pressure gradient can cause the membrane to swell and the selectivity to decrease (Koros, 1985). 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 constituents in a gas 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 swells the polymer (Liau and McHugh, 1985) and, thus, allows the substance to migrate into the polymer matrix. Sand (1986) has shown that substances such as fragrances, pest control agents, and pharmaceutical drugs can be impregnated 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 weight 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 (McHugh and Krukonis, 1986) and the removal of low molecular weight constituents from solid coal particles (Whitehead and Williams, 1975).

For any polymer-gas process which operates at high pressures, it is often necessary to be able to predict the solubility of the gas in the polymer and the subsequent swelling of the polymer. Fleming and Koros (1986) 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 paper is to report on the use of the Sanchez-Lacombe equation of state (1976) for modeling the solubility of high-pressure gases in solid, amorphous polymers or molten polymers and the subsequent swelling of the polymer. By using an equation of state, we avoid the need to calculate a hypothetical vapor pressure and the activity of the high-pressure gas can be calculated in a thermodynamically rigorous manner. The calculational methods that are described are applicable to polymers which are non-crystalline, not cross-linked or slightly cross-linked, above their respective glass transition temperatures (T_g), or above their melting temperature. The systems modeled in this study include carbon dioxide-polymethyl methacrylate (PMMA) (Liau and McHugh, 1985), carbon dioxide-silicone rubber (Fleming and Koros, 1986), ethylene-

Modeling:

Bonner (1977) 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 follows those outlined by Bonner (1977).

Our approach is to model the polymer-gas system using the following assumptions:
1. the solubility data 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, solid polymer above its T_g can be modeled as a liquid.

The first assumption will only be true if the polymer is above its glass transition temperature and if sufficient time has been allowed for the system to reach equilibrium. 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 (Chow, 1980; Wang, Kramer, and Sachse, 1982; Liau and McHugh, 1985; Koros, 1985; Wissinger and Paulaitis, 1986). For the polymers considered in this paper, either the system temperature is already above the polymer's T_g, or the system temperature is above the polymer's effective T_g as gas is solubilized in the polymer.

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 (Ehrlich and Graham, 1960; Heller, et al., 1983; McHugh and Krukonis, 1986; Dhalewadikar, McHugh, and Guckes, 1987); hence, we will assume this assumption to be valid in our analysis.

The equation of state of Sanchez-Lacombe (1976) is based on the lattice-fluid theory which assumes that the polymer has a flexible liquid structure. This equation of state is

\[ \tilde{p}^2 + \tilde{p} + \tilde{T} \left\{ \ln \left( 1 - \tilde{\rho} \right) + \left\{ 1 - \frac{1}{x} \right\} \tilde{\rho} \right\} = 0 \]  

(1)

where \( \tilde{P} \), \( \tilde{T} \), and \( \tilde{\rho} \) are the reduced pressure, temperature, and density, respectively, and \( x \) represents the number of lattice sites occupied by a molecule. The characteristic reduction parameters used for these reduced properties are obtained from pure-component, P-V-T data as described in the following paragraphs.

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

\[ \mu^G_{1}(T,P) = \mu^P_{1}(T,P,\phi_i) \]  

(2)

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

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

\[ \mu^P_{1} = \kappa T \left\{ \ln \phi_1 + \left\{ 1 - \frac{r_1}{r_2} \right\} \phi_2 + r_1 \phi_1 X_1 \phi_2 X_2 \right\} + r_1 kT \left\{ \frac{-\tilde{P}}{T_1} + \frac{\tilde{T}}{T_1} \right\} + \right. \]

\[ \left. \tilde{v} \left\{ \left( 1 - \tilde{\rho} \right) \ln \left( 1 - \tilde{\rho} \right) + \frac{\tilde{\rho}}{r_1} \ln \tilde{\rho} \right\} \right\} \]  

(3)
where \( r_1 \) is the number of lattice sites occupied by molecule 1 and \( X_1 \) is a mixture parameter which is expressed as

\[
X_1 = \frac{\Delta P^* v_1^*}{kT}
\]  

(5)

where \( \Delta P^* \) is subsequently defined. The close-packed, volume fraction of component \( i \), \( \phi_i \), is given by

\[
\phi_i = \frac{m_i / \rho_i^*}{m_i / \rho_i^* + m_j / \rho_j^*}
\]

(4)

where \( m_i \) is the weight fraction and \( \rho_i^* \) is the characteristic density. Although Sanchez and Lacombe (1976) distinguish between \( r_1^0 \), the number of lattice sites occupied by a molecule in a pure state, and \( r_1 \), the number of lattice sites occupied by a molecule in a mixture, these quantities are assumed to be equal in our analysis.

The chemical potential of the gas in the pure gas phase is obtained by setting \( \phi_2 \) equal to zero in Equation (3). The amount of gas sorbed in the polymer can be determined by solving equation (2) with pure component characteristic parameters and with the appropriate mixing rules for the mixture characteristic parameters.

The pure component parameters used in this study are listed in Table 1. The characteristic parameters, \( \rho^* \), \( T^* \), and \( P^* \), for PMMA, PDMS, LDPE, HDPE, PIB, PS, and methane are obtained directly from Sanchez and Lacombe (1978). The characteristic parameters for PDMS are used as the characteristic parameters for the silicone rubber, as explained later.

As shown in Table 1, the characteristic parameters for carbon dioxide determined from a fit of the vapor-liquid equilibrium curve, did not follow the logical succession of pure-component parameters of other light gases given by Sanchez and Lacombe (1978). Thus, the parameters for carbon dioxide used in the calculations presented in this paper were obtained by fitting data on the liquid molar volume, the isothermal compressibility, and the thermal expansion coefficient of carbon dioxide at 50, 60, and 75 °C and 150 atm.
(Michels and Michels, 1937) to the equation of state. These pressure-temperature (P-T) conditions were chosen so the parameters would be based on the P-T space in which most of the experimental polymer-carbon dioxide data were obtained. Although the parameters for carbon dioxide found in this manner are more consistent with those recommended by Sanchez and Lacombe for similar light gases, we only obtain a fair representation of the vapor-liquid equilibrium curve and the critical point for carbon dioxide ($T_{c,\text{calc}}=42.9 \, ^\circ\text{C}$, $P_{c,\text{calc}}=96.5 \, \text{atm}$; $T_c=31.05 \, ^\circ\text{C}$, $P_c=72.8 \, \text{atm}$).

Contrary to the carbon dioxide case, the parameters for ethylene as determined from a fit of the vapor-liquid equilibrium line did follow the trends of the parameters tabulated by Sanchez and Lacombe (1976). However, when these parameters are used to calculate sorption isotherms, it is necessary to use a negative value for the mixture parameter, as described in the following paragraphs. Therefore, the pure component parameters for ethylene are determined by fitting the liquid molar volume, the isothermal compressibility, and the thermal expansion coefficient at 135 and 140 °C and 50 atm (Angus, Armstrong, and de Reuck, 1972) to the equation of state. These P-T conditions are close to those for most of the ethylene-LDPE experimental data. The parameters for ethylene found in this manner are consistent with those recommended by Sanchez and Lacombe for similar light gases, although they result in only a fair representation of the vapor-liquid equilibrium curve and the critical point for ethylene ($T_{c,\text{calc}}=18.6 \, ^\circ\text{C}$, $P_{c,\text{calc}}=54.5 \, \text{atm}$; $T_c=9.3 \, ^\circ\text{C}$, $P_c=49.7 \, \text{atm}$).

The mixing rules recommended by Sanchez and Lacombe (1978) are used to obtain the mixture characteristic parameters. These mixing rules are listed in Appendix A. There is only one adjustable parameter in these mixing rules, $\delta_{12}$, which is directly fitted to sorption data. A small value of $\delta_{12}$ is used to correct the deviation of the characteristic pressure of the mixture, $P_{12}^*$, from the geometric mean. All of the other parameters in the mixing rules are pure component parameters.
Sorption isotherms were calculated with a given value of $\delta_{12}$ in the following manner. At a fixed temperature, pressure, and initial estimate of the weight fraction of the gas in the polymer, equation (1) was solved to obtain the volumes of the pure gas phase and the polymer-rich liquid phase. If equation (2) was not satisfied, then the weight fraction was adjusted and the calculational procedure was repeated. The best-fit value of $\delta_{12}$ was determined by minimizing the 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 (Liau and McHugh, 1985), carbon dioxide-silicone rubber (Fleming and Koros, 1986), ethylene-LDPE (Cheng and Bonner, 1977), methane-PIB (Lundberg, et al., 1969), methane-LDPE (Lundberg, et al., 1969), methane-HDPE (Lundberg, et al., 1969), and methane-PS (Lundberg, et al., 1969). The pure-component, characteristic parameters used in this analysis are tabulated in Table 1 and the mixture parameter, $\delta_{12}$, regressed from experimental data for each of the gas-polymer systems is shown in Table 2.

Figure 1 shows the model calculations for the carbon dioxide-PMMA system at 41.8, 58.1, and 68.0°C (Liau and McHugh, 1985; Wissinger and Paulaites, 1986). The $\delta_{12}$ parameter obtained from the best fit of this data ranges from 0.019 to 0.035. For this system the fit of the sorption data is very dependent on the value of $\delta_{12}$. If $\delta_{12}$ is set equal to zero, a poor fit of the data is obtained. Various values of $\delta_{12}$ will give a reasonable fit of the low pressure portion of the sorption isotherms, but not necessarily of the higher pressure portion of the isotherms. Therefore, some data are needed at high pressures to define an appropriate value for $\delta_{12}$. Nevertheless, the Sanchez-Lacombe model reproduces the trends in the data and it provides a means for obtaining reasonable estimates of the solubility of carbon dioxide in PMMA at high pressures.
Although Koros (1985) 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-x conditions is not unexpected. Polymers below their glass transition temperature contain additional unrelaxed volume, and PMMA is below its effective glass transition temperature at the P-T-x conditions investigated by Fleming and Koros (1986). As shown in Figure 1 (a), the carbon dioxide-PMMA data (Liau and McHugh, 1985) is modeled reasonably well at a slightly higher temperature (41.8°C) and higher pressures (up to 300 atm). At the P-T-x conditions employed by Liau and McHugh (1985), the carbon dioxide-PMMA system is more than likely in its rubbery region. Although the glass transition temperature of PMMA is 105°C, Chow (1980) 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 (1980), it is found that almost all of the data reported by Liau and McHugh (1985) 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 $\delta_{12}$ values obtained from the sorption calculations are used. A reasonable fit of the experimental data reported by Wissinger and Pauliatis (1986) 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 (1985), although the absolute value of their swelling data differs considerably from the data of Wissinger and Pauliatis (1986) and from the calculated results.

Figure 3 shows the carbon dioxide-silicone rubber data reported by Fleming and Koros (1986). The $\delta_{12}$ parameter determined for this system is 0.125. 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. The molecular weight of the silicone rubber is not reported by Fleming and Koros, so an arbitrarily chosen molecular weight of 50,000 is used in our analysis. 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 \( \delta_{12} \) 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 (Cheng and Bonner, 1977) is shown in Figure 5. Like the carbon dioxide-PMMA system presented earlier, the three isotherms of the ethylene-LDPE system are best modeled with slightly different values of \( \delta_{12} \) (\( \delta_{12} = 0.026, 0.030, 0.041 \), respectively). A reasonable fit of all three isotherms is obtained as shown in Figure 5. As described earlier, the pure component parameters used for ethylene are obtained from fitting properties of ethylene in the P-T space of the experimental conditions. If the pure component parameters fit to the vapor-liquid equilibrium curve of ethylene are used to calculate sorption isotherms, a negative value of \( \delta_{12} \) is needed to fit the sorption isotherms.

Data on the solubility of methane in polystyrene and polyisobutylene are reported by Lundberg, et al. (1969). 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 \( \delta_{12} \) to vary as a function of temperature. 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 these two 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 methane properties 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 value of \( \delta_{12} \). Therefore, the methane characteristic parameters given by Sanchez and Lacombe (1976) are used in the calculations.

Figure 8 shows the model calculations for the methane-LDPE system (Lundberg, et al., 1969) at 155.4 °C and the methane-HDPE system (Lundberg, et al., 1969) at 140.03 °C. The values of \( \delta_{12} \) obtained from the best fit of the data are 0.0462 and -0.183, respectively. Notice that the \( \delta_{12} \) value for the methane-HDPE system is very negative. Even when the pure component characteristic parameters for methane are fit to properties in the P-T space of the experimental data, the \( \delta_{12} \) value remained negative.

Conclusions:

The solubility of high-pressure gases in amorphous polymers is becoming increasingly important as membrane separations are being performed at higher pressures. Solubility data are also important in polymer processes when polymers are used as controlled-release devices or when polymers are stripped of low molecular weight impurities. In this paper, we have shown that the Sanchez-Lacombe equation of state with only one mixture parameter can be used to effectively predict the solubility of a high-pressure gas in a solid amorphous polymer or a molten polymer. Although the mixture parameter, \( \delta_{12} \), must be fit to experimental data, the calculations do decrease the amount of experimental data that is needed to define a sorption isotherm. Compared to using Flory-Huggins theory to predict the isotherms, this method avoids the need to calculate hypothetical states and it rigorously calculates activities. Also, the volume dilation of the polymer is easily calculated.
Acknowledgements:

We would like to acknowledge Dr. Timothy Barbari for his helpful suggestions and critique of this work. This work was supported in part by the Office of Naval Research and the Battelle Foundation.
Appendix A. Mixing rules used with the Sanchez-Lacombe equation of state.

As stated before, the mixing rules presented by Sanchez and Lacombe are used in this analysis. The characteristic pressure for the mixture is given as

\[ P^* = \phi_1 P_{1*}^* + \phi_2 P_{2*}^* - \phi_1 \phi_2 \Delta P^* \]  

(A1)

where \( \Delta P^* \), a mixture parameter, is defined as

\[ \Delta P^* = P_{1*}^* + P_{2*}^* - 2P_{12*}^* \]  

(A2)

\[ P_{12*}^* = \left\{ P_{1*}^* P_{2*}^* \right\}^{1/2} \left\{ 1 - \delta_{12} \right\} \]  

(A3)

The mixing rules for \( r, v^*, \) and \( T^* \) are

\[ r = x_1 r_1 + x_2 r_2 \]  

(A4)

\[ v^* = \phi_1 v_{1*}^* + \phi_2 v_{2*}^* \]  

(A5)

\[ \frac{T^*}{T} = \frac{\{ \phi_1 / T_1^* + v \phi_1 / T_2^* \}}{\{ \phi_1 + v \phi_2 \}} - \phi_1 \phi_2 X \]  

(A6)

where

\[ v = \frac{v_{1*}^*}{v_{2*}^*} \]  

(A7)

\[ X = \frac{\Delta P^* v^*}{kT} \]  

(A8)

and \( x_i \) is the mole fraction of component \( i \). A detailed discussion of these mixing rules is presented by Sanchez and Lacombe (1978).
References:


Wissinger, R.G. and M.E. Paulaitis, presented at the Annual Meeting of the American Institute of Chemical Engineers, Miami Beach, Florida (November, 1986).
Nomenclature:
\( k \) = Boltzmann's constant
\( m \) = weight fraction
\( P \) = pressure
\( \tilde{P} \) = reduced pressure
\( P_{12}^* \) = mixture parameter
\( r \) = segment length
\( \delta_{12} \) = mixture parameter
\( T \) = temperature
\( \tilde{T} \) = reduced temperature
\( V \) = molar volume
\( \tilde{V} \) = reduced volume
\( X \) = mixture parameter
\( x \) = mole fraction

Greek Letters
\( \mu \) = chemical potential
\( \rho \) = density
\( \tilde{\rho} \) = reduced density
\( \phi \) = closed-packed volume fraction

Subscripts
\( c \) = critical properties
\( i \) = component \( i \)
\( 1 \) = solvent
\( 2 \) = polymer

Superscripts
\( \text{calc} \) = calculated values
\( G \) = gas
\( o \) = pure component
\( P \) = polymer
\( * \) = characteristic variable
Table 1. Characteristic equation of state parameters for the light gases and the polymers as tabulated by Sanchez and Lacombe (1978), unless indicated otherwise.

<table>
<thead>
<tr>
<th>Substance</th>
<th>( \rho^* \text{(g/cm}^3) )</th>
<th>( T^* \text{(K)} )</th>
<th>( P^* \text{(atm)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_4)</td>
<td>0.500</td>
<td>224</td>
<td>2450</td>
</tr>
<tr>
<td>CO(_2)*</td>
<td>1.389</td>
<td>346</td>
<td>3870</td>
</tr>
<tr>
<td>CO(_2)**</td>
<td>1.452</td>
<td>290</td>
<td>5880</td>
</tr>
<tr>
<td>C(_2)H(_4)*</td>
<td>0.511</td>
<td>336</td>
<td>1870</td>
</tr>
<tr>
<td>PMMA</td>
<td>1.269</td>
<td>696</td>
<td>4960</td>
</tr>
<tr>
<td>PDMS</td>
<td>1.104</td>
<td>476</td>
<td>2980</td>
</tr>
<tr>
<td>LDPE</td>
<td>0.887</td>
<td>673</td>
<td>3540</td>
</tr>
<tr>
<td>HDPE</td>
<td>0.904</td>
<td>649</td>
<td>4190</td>
</tr>
<tr>
<td>PIB</td>
<td>0.974</td>
<td>643</td>
<td>3490</td>
</tr>
<tr>
<td>PS</td>
<td>1.105</td>
<td>735</td>
<td>3520</td>
</tr>
</tbody>
</table>

* Parameters fit to the liquid molar volume, the isothermal compressibility, and the thermal expansion coefficient.
** Parameters fit to vapor-liquid equilibrium line.
Table 2. Values of the mixture parameter $\delta_{12}$ used in sorption calculations.

<table>
<thead>
<tr>
<th>System</th>
<th>Temperature (°C)</th>
<th>Pressure (atm)</th>
<th>Polymer $M_W$</th>
<th>$\delta_{12}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$CO_2/PMMA$</td>
<td>41.8</td>
<td>0-250</td>
<td>60,600</td>
<td>0.032</td>
</tr>
<tr>
<td>$CO_2/PMMA$</td>
<td>58.1</td>
<td>0-250</td>
<td>60,600</td>
<td>0.035</td>
</tr>
<tr>
<td>$CO_2/PMMA$</td>
<td>68.0</td>
<td>0-275</td>
<td>60,600</td>
<td>0.019</td>
</tr>
<tr>
<td>$CO_2/PDMS^{***}$</td>
<td>35.0</td>
<td>0-60</td>
<td>50,000</td>
<td>0.125</td>
</tr>
<tr>
<td>$C_2H_4/LDPE$</td>
<td>126.0</td>
<td>0-70</td>
<td>249,000</td>
<td>0.026</td>
</tr>
<tr>
<td>$C_2H_4/LDPE$</td>
<td>140.0</td>
<td>0-70</td>
<td>249,000</td>
<td>0.030</td>
</tr>
<tr>
<td>$C_2H_4/LDPE$</td>
<td>155.0</td>
<td>0-70</td>
<td>249,000</td>
<td>0.041</td>
</tr>
<tr>
<td>$CH_4/PIB$</td>
<td>155.4</td>
<td>0-350</td>
<td>1,300,000</td>
<td>0.135</td>
</tr>
<tr>
<td>$CH_4/PS$</td>
<td>125.40</td>
<td>0-700</td>
<td>500,000</td>
<td>0.194</td>
</tr>
<tr>
<td>$CH_4/PS$</td>
<td>155.42</td>
<td>0-700</td>
<td>500,000</td>
<td>0.123</td>
</tr>
<tr>
<td>$CH_4/PS$</td>
<td>188.40</td>
<td>0-700</td>
<td>500,000</td>
<td>0.099</td>
</tr>
<tr>
<td>$CH_4/LDPE^{***}$</td>
<td>155.4</td>
<td>0-700</td>
<td>100,000</td>
<td>0.046</td>
</tr>
<tr>
<td>$CH_4/HDPE^{***}$</td>
<td>140.03</td>
<td>0-350</td>
<td>100,000</td>
<td>-0.183</td>
</tr>
</tbody>
</table>

*** The molecular weight for this system the was assumed.
Figure 1. Comparison of experimental and calculated sorption isotherms for the CO$_2$-PMMA system. The calculated isotherms at 41.8°C, 58.1°C, and 68°C are determined with $\delta_{12}$ equal to 0.032, 0.035, and 0.019, respectively.
Figure 2. The effect of CO₂ partial pressure on the volume of PMMA.
Figure 3. Comparison of experimental and calculated sorption isotherms for the CO₂-silicone rubber system. The value of δ₁₂ used for this isotherm is 0.125.
Figure 4. The effect of CO$_2$ partial pressure on the volume of silicone rubber.
Figure 5. Comparison of experimental and calculated sorption isotherms for the $\text{C}_2\text{H}_4$ - LDPE system. The calculated isotherms at 126°C, 140°C, and 155°C are determined with $\delta_{12}$ equal to 0.026, 0.030, and 0.041, respectively.
Figure 6. Solubility of methane in PS at 125.4°C, 155.42°C, and 188.40°C. The calculated isotherms are determined with \( \delta_{12} \) equal to 0.194, 0.123, and 0.099, respectively.
Figure 7. Comparison of experimental and calculated sorption isotherms for the methane-PIB system. The calculated data is determined with $\delta_{12}$ equal to 0.135.
Figure 8. Solubility of methane in LDPE and HDPE. The calculated isotherms are determined with $\delta_{12}$ equal to 0.046 and -0.183, respectively.
END
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