Solubility of Gases in Amorphous Polyethylene

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ABSTRACT: The hypothetical polyethylene melt at room temperature is of interest for the purposes of developing the atomic level modeling of gas solubilities in rubbery polymers. In the present study, the gas solubilities in completely amorphous polyethylene are predicted by extrapolating alkane behavior to the long chain limit in a Flory−Huggins context. The results are seen to agree well with a recent simulation study.

1. Introduction

Polyethylene at room temperature is semicrystalline. This aspect of what is otherwise a "simple" polymer has led to complications in understanding its sorption of gases. Initially, a straightforward treatment was adopted where the contribution of the crystalline phase was neglected and the amorphous phase was treated as a liquid.[1] By extrapolating to zero crystallinity, such an approach permits the prediction of gas solubility in completely amorphous polyethylene. Subsequent work[2,3] demonstrated that the amorphous phase must be treated in a more realistic manner and, moreover, that the original extrapolation to zero crystallinity would substantially underestimate the solubility in the completely amorphous polymer. Contemporary studies[4,5] have refined the treatment of the semicrystalline state, but not surprisingly, interest in gas solubility in completely amorphous polyethylene waned as researchers focused on the complexities of the interplay of the crystalline and amorphous regions of the polymer.

Recently, interest in gas solubility in amorphous polyethylene has been rekindled by atomically detailed simulations[6,7] and theory[8] of simple gases in the polyethylene melt. Polyethylene was chosen in these studies as the host polymer not because of the intriguing complexities of experimental polyethylene but because the details of polyethylene's molecular model are well-known, at least at room temperature. Indeed, the modeling of rubbery polymers such as poly(dimethylsiloxane) and poly(isobutylene) are the eventual objectives of such studies, and amorphous polyethylene is essentially a test case.

Nonetheless, comparison with experimental measurements is an important component of both simulation and theory. For amorphous polyethylene, comparisons are commonly made with the Michaels and Bixler[1] extrapolation of semicrystalline polyethylenes which, as mentioned above, is suspect. In the present study, a different approach is adopted: an extrapolation based upon recent measurements of gas solubility in normal alkanes.[9] Somewhat higher gas solubilities are predicted, which should provide a more realistic basis of comparison with the predictions of simulations and theories.

Flory−Huggins theory[10,14] is the primary tool we use in this extrapolation, although the predicted solubilities should be independent of the Flory−Huggins formalism. Flory−Huggins theory is a generalization of regular solution theory,[11] and the analysis of the solubility of gases in liquids with regular solution theory has been a field of interest[12] since the 1940s. Despite suffering from a number of ambiguities associated with the physical meaning of the parameters used to describe the behavior,[13] it continues to be a popular approach.[15]

The largest data set for the implementation of regular solution theory for the permanent gases resulted from an extension by Yen and McKetta[16] of the earlier work of Prausnitz and Shair.[17] In the present study, we explore the use of the Yen−McKetta database in the prediction of the solubility of gases in amorphous polyethylene.

Recently measured gas sorption data in alkanes[9] are analyzed using the Yen−McKetta regular solution data set with the additional non-Bertholet mixing parameter, l_{12}, determined for each gas-alkane pair. The l_{12} for each gas then is extrapolated to the long chain limit, and the solubility in amorphous polyethylene is determined from the extrapolated l_{12}'s.

2. Flory−Huggins Theory

The equality of fugacities in the liquid−gas equilibrium is expressed[18] within Flory−Huggins theory as

$$f_{1,\mathrm{G}} = f_{1,\mathrm{L}}\phi_1\gamma_1 \qquad (2.1)$$

where $f_{1,\mathrm{G}}$ is the solute fugacity (usually taken as its partial pressure); $f_{1,\mathrm{L}}$, the fugacity of the solute in its pure state (usually envisioned as the vapor pressure); ϕ_1, the volume fraction of the solute; and γ_1, the solute activity. From Flory−Huggins theory, the activity coefficient is

$$\ln \gamma_1 = \left(1 - \frac{1}{N}\right)\phi_2 + \chi\phi_2^{\,2} \qquad (2.2)$$

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where ϕ_2 is the volume fraction of the polymer; χ, the Flory–Huggins interaction parameter; and N, the "chain length". The chain length is typically defined by the ratio of the molar volume of the polymer, V_2, to that of the solute (in the pure liquid state), $V_{1,L}$:

$$N = \frac{V_2}{V_{1,L}} \tag{2.3}$$

For polymers, N is very large so $1/N$ is usually taken to be zero. For relatively small concentrations, the logarithm of the activity coefficient is often linearized;[2,19] however, in the present study the full expression is retained.

Although eq 2.2 can be, and often is, adopted as a definition of χ, both regular solution and Flory–Huggins theories suggest that χ is given by

$$\chi = \frac{V_{1,L}}{RT}\,[(\delta_2 - \delta_1)^2 + 2l_{12}\delta_1\delta_2] \tag{2.4}$$

where R is the molar gas constant, T is the temperature, δ_1 is the solubility parameter of the gas, and δ_2, is the solubility parameter of the polymer. In principle, the solubility parameter is the square root of the cohesive energy density, although, in practice, it is used to fit equilibrium properties such as the solubility, S, which is of interest here. If true, eq 2.4 would be very useful since in this case all of the parameters are independent of concentration, and if l_{12} is zero, it would depend only upon the pure states of the gas and polymer. Combining the eqs 2.1, 2.2, and 2.4 results in

$$\frac{1}{\phi_1} = \frac{f_{1,L}}{f_{1,G}} \exp\left[\left(1 - \frac{1}{N}\right)\phi_2 + \frac{V_{1,L}}{RT}\,[(\delta_2 - \delta_1)^2 + 2l_{12}\delta_1\delta_2]\phi_2^{\,2}\right] \tag{2.5}$$

The solubility, per se, is related to the volume fraction by

$$S = \frac{\phi_1}{V_{1,L}P} \tag{2.6}$$

and to the mole fraction of the solute, X_1, by

$$S = \frac{X_1}{V_2 P} \tag{2.7}$$

where P is the pressure which is equal to 1 atm in this case.

For permanent gases, in which we are primarily interested here, there are four parameters required for the description of each gas type: $f_{1,L}$, $V_{1,L}$, δ_1, and l_{12}. Prausnitz and Shair,[17] in effect, assumed l_{12} to be zero and used experiments on liquids with a wide range of solubility parameters to fit the gas parameters. Yen and McKetta[16] refined the fit parameters and included more gases. Their reported pure state liquid fugacities can be fit for reduced temperatures in the range 0.7–2.6 by an equation of the Antoine form

$$\ln\left(\frac{f_{1,L}}{p_c}\right) = 2.8781 - \frac{2.2399}{T_r - 0.29889} \tag{2.8}$$

where P_c is the critical pressure and T_r is the temperature reduced by the critical temperature. Table 1 contains the parameters found by Yen and McKetta. In principle, these parameters, along with the solubility parameter of the solvent, permit the calculation of the solubility.

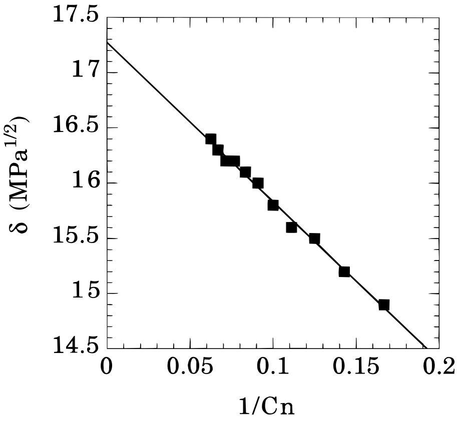

Figure 1. The variation of the solubility parameter of the normal alkanes with number of carbons in the chain.

Table 1. Gas Parameters from Yen–McKetta[16]

gas	$V_{1,L}$ (cm^3/mol)	δ (MPa$^{1/2}$)	f (atm)
N_2	40.0	6.56	201
Ar	55.0	10.25	224
O_2	49.6	9.64	225
CH_4	50.7	10.82	138
Kr	52.0	12.10	132
Xe	45.8	12.92	48.1
CO_2	62.0	12.30	48.4
C_2H_6	70.0	13.02	31.3

Usually the solubility parameter is calculated "directly" from the heat of vaporization; however, the negligible vapor pressure of polymers prohibits this approach. Instead, a number of indirect methods are employed, and, as a result, the solubility parameter for polyethylene, found experimentally, has values[20] between 16.3 and 17.9 (MPa)$^{0.5}$. Here, to have a straightforward method for obtaining δ_2, we extrapolate the solubility parameters of the liquid alkanes[15] (at room temperature) to the long chain limit as in Figure 1. This gives a value of $\delta_2 = 17.3$ (MPa)$^{0.5}$ which agrees well with the suggested experimental range.

To express the solubility coefficients in common units, the density of the polymer is needed. We use the ref 21 value of 0.855 g/cm^3 for amorphous polyethylene.

3. Results and Discussion

If l_{12} is assumed to be zero in eq 2.4, as would be done in traditional Flory–Huggins theory, the solubility of gases in both polyethylene and the alkanes would be greatly underestimated. The addition of a correction term to the χ parameter is justified in one of two ways for simple, nonpolar systems. It is attributed either to excess chain conformational entropy (indicating the addition of a temperature independent term) or to deviations from the van der Waals nature of the polymer-gas interaction (indicating the addition of a term proportional to $1/T$). The form of eq 2.4 assumes the latter; however, since only a single temperature is considered, the temperature dependence of l_{12} cannot be deduced.

Measurements[9] on simple gases in short alkane liquids provide the information needed in the extrapolation of the l_{12}'s in the long chain limit. The l_{12} required

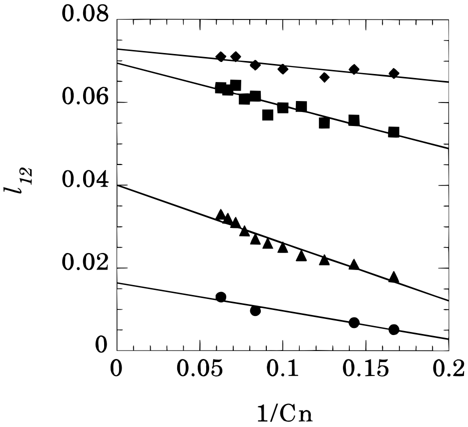

Figure 2. The variation of l_{12} with number of carbons in the chain, Cn. The circles are for ethane; the triangles, for xenon; the squares, for methane; and the diamonds, for carbon dioxide.

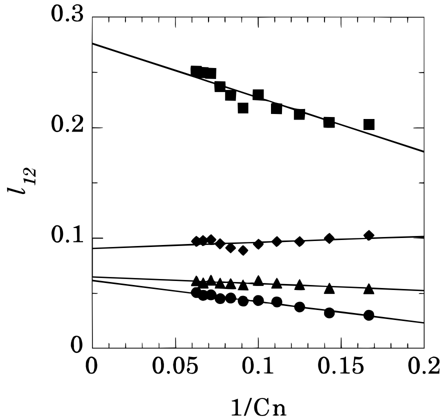

Figure 3. The variation of l_{12} with number of carbons in the chain. The circles are for krypton; the triangles, for argon; the diamonds, for oxygen; and the squares, for nitrogen.

Table 2. Extrapolation Parameters and Comparison with Previous Predictions

gas	slope	intercept: l_{12}	S (cm^3(STP)/ (cm^3 cmHg))	S/S_{MB}
nitrogen	−0.49	0.28 ± 0.01	0.000 904 61	1.67
argon	−0.063	0.065 ± 0.012	0.002 127	1.58
oxygen	0.068	0.096 ± 0.007	0.001 926 4	1.90
methane	−0.10	0.069 ± 0.002	0.004 671 8	1.75
krypton	−0.19	0.062 ± 0.007	0.006 410 2	
xenon	−0.14	0.040 ± 0.002	0.027 529	
carbon dioxide	−0.040	0.073 ± 0.002	0.012 97	2.19
ethane	−0.068	0.016 ± 0.003	0.027 226	1.62

in order to fit the solubility of each gas for a particular alkane is calculated. The resulting l_{12}'s then are plotted against one over the chain length as shown in Figures 2 and 3. The indicated linear fits are tabulated in Table 2 along with the extrapolated l_{12}'s for polyethylene.

The extrapolated l_{12}'s, when used in eq 2.5, yield gas solubilities for the amorphous polyethylene. These are shown in Figure 4 and reported in Table 2. The predicted solubilities are seen to be only slightly higher than those for natural rubber.[1]

The predicted gas solubilities from this approach are in disagreement with the extrapolation by Michaels and Bixler.[1] Their predicted amorphous solubilities, S_{MB}, found from an extrapolation of solubilities in semicrystalline polyethylenes, are approximately a factor of 2 lower than found in the current study (as seen in Table 2 as well as in Figure 4). Michaels and Bixler attributed all of the solubility to an unconstrained amorphous state which, as mentioned in the Introduction, is an oversimplified approximation.[2,3]

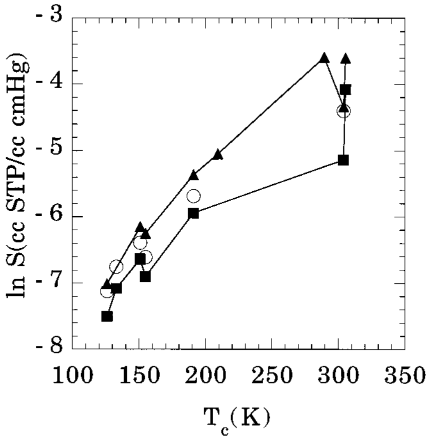

Figure 4. The solubility of various gases as a function of their critical temperature. The triangles are the results of the current study for amorphous polyethylene, the squares are the Michaels and Bixler values for amorphous polyethylene, and the circles are for natural rubber. Lines serve as guides for the eye.

The recent simulation of van der Vegt et al.,[6] when compared to the predictions of the present investigation, appear to describe the solubility of gases in amorphous polyethylene reasonably well. Six gases were studied (He, H_2, Ar, N_2, O_2, and CH_4) for two different sets of CH_2 potential parameters. In one case, the simulation predicted, on average, solubilities a factor of 3.5 higher than the Michaels and Bixler results and, in the other, a factor of 1.4 higher. It is possible, as was suggested,[6] that errors in the potential parameters or in the simulation methods caused these over predictions; however, when adjusted to the new gas solubilities presented here, these ratios take on the more reasonable values of 2.1 and 0.8. The large variability in the simulation results (of the same magnitude as the differences between the two extrapolation methods) indicates the need for more refinement in the modeling of the polyethylene/solute systems.

Polymer reference interaction site model (PRISM) theory has also been used to predict the solubility of gases in amorphous polyethylene,[8] and experimentally observed trends were predicted. First, the solubility was seen to increase with the increasing diameter of the gas due to the associated strengthening of the enthalpic interactions. Second, the solubility was seen to increase with temperature for gases with low critical temperatures and to decrease for gases with high critical temperatures.

The current investigation permits more detailed comparisons of PRISM with experiment. In particular, the sensitivity of the gas solubility to the interaction strength between CH_2 sites is currently being explored, and we will present these results in a separate paper.

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