

Nitrogen Solubilities in Low-Density Polyethylene at High Temperatures and High Pressures

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SYNOPSIS

An apparatus for the determination of the solubility of gases in polymers at high pressure and high temperature is described. The solubilities of nitrogen in low-density polyethylene (PE800E) at 394–450 K at pressures between 10 and 125 atm are reported. Empirical correlations are obtained which represent the Flory–Huggins interaction parameter χ , solubility coefficient K_H , and activity coefficient of dissolved gas Ω_2 as functions of temperature and pressure for the above system. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

With the ever-mounting environmental pressures, the polymer foaming industry is in crisis because existing process technologies are based largely on the use of chlorofluorocarbons (CFCs) and volatile organics (VOCs) as blowing agents.^{1,2} With the ratification of the Montreal protocol (signed by 24 nations in 1987; this agreement requires a sharp curtailment in CFC production and use), many foam producers switched from CFCs to volatile organic compounds (VOCs). These producers are now facing increasingly strict VOC regulations by EPA/OSHA and state regulatory agencies because VOCs are suspected carcinogens, are flammable, and contribute to smog. In many cases, existing process practices involve more art than science. The highly soluble CFCs and VOCs are very effective blowing agents, and their replacement by inert blowing agents (N_2 , CO_2 , Ar, etc.) is nontrivial. In most cases, these gases are less soluble and it is difficult to achieve the spectrum of densities and structures desired. Even with the more soluble gases (e.g., CO_2), melt rheology is affected and it is difficult to stabilize low-density foam films.

Reliable data on the solubility of gases (blowing agents) in liquids are not plentiful, especially at temperatures well removed from 25°C (Ref. 3, p. 389). At higher pressures and higher temperatures, the reliable solubility data are even more scarce. In considering the dissolved gas loading, the behavior of a gas–polymer solution (ideal or nonideal) are two of the key parameters in nucleation and bubble growth. To develop a reliable nucleation and bubble growth model, reliable solubility data and correlations are very important.

As part of the major effort of extending the knowledge base in the polymer foam processing area, extensive and reliable experimental as well as theoretical work has been conducted in our lab for several years.^{4–6} Following Prausnitz,³ the solubilities of gas-blowing agents in polymer melts were previously shown by Ruengphrathuengsuka.⁴ In this article, we show a slightly different approach and some empirical relationships of nitrogen solubilities in low-density polyethylene at higher temperatures and higher pressures. Our computational approach is applicable to other gas–molten polymer systems without modification.

EXPERIMENTAL

We obtained solubility data in this laboratory using a high-pressure, high-temperature Cahn balance.

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The approach is gravimetric, with the solubilities determined from polymer and dissolved gas weight measurements at different gas pressures and temperatures.⁴ In solubility tests in the Cahn balance, a cylindrical disk of the polymer is placed in a pan and is suspended from the balance arm into the test region containing the high-pressure, high-temperature gas.

In the experiments, the polymer sample was equilibrated with the gas at different temperatures and pressures and the uptake of the gas in the polymer was obtained from direct weight measurements. The pressure changes in the measurements were achieved through gas injection from a high-pressure hand pump.

Figure 1 shows the Cahn balance system used in the study.⁴ It is a high-temperature (up to 1366 K)/high-pressure (up to 140 atm) thermogravimetric system with the following key components:

1. A Cahn C-1100 pressure balance system. This high-pressure recording balance has a sensitivity of 0.01 mg at normal temperatures and pressures and 0.1 mg at high temperature and pressure (e.g., the maximum conditions noted above).
2. A furnace with multizone control. Specifically, this involves a specially designed system with a three-zone control system and as-

sociated controllers and a three-zone split tube furnace. This unit was custom built by Applied Test Systems.

3. A fluid pressurization, loading, and removal system. This consists of a Ruska high-pressure hand pump (Model 2250-801), a Precision vacuum pump (Model DD-90), plus a pressure transducer and associated electronic equipment (Validyne P305, 0-3,200 PSI).
4. Data acquisition/analysis system. This consists of an AT-286 computer with Labtech software (Model LTN-03) and an 8-channel A/D converter and timer interface (DAS-8) with an analog expansion multiplexer (Exp-16).

In Figure 2, we show the solubility vs. pressure at different temperatures for nitrogen in LDPE. Over the temperature range covered by the experiments, the behavior is quite nonlinear and Henry's law would be applicable only at very low pressures. The results also show that the solubility of N₂ in LDPE increases with temperature.

THEORETICAL BACKGROUND

When a gaseous component at fugacity f_2^g dissolved isothermally in a molten polymer, the solution pro-

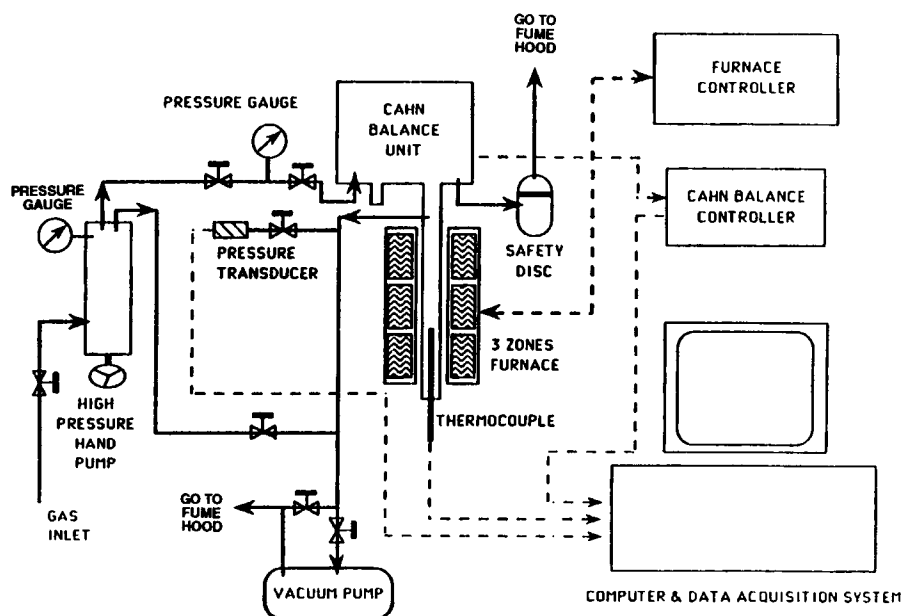


Figure 1 Cahn balance system: high-temperature and high-pressure solubility measurement.

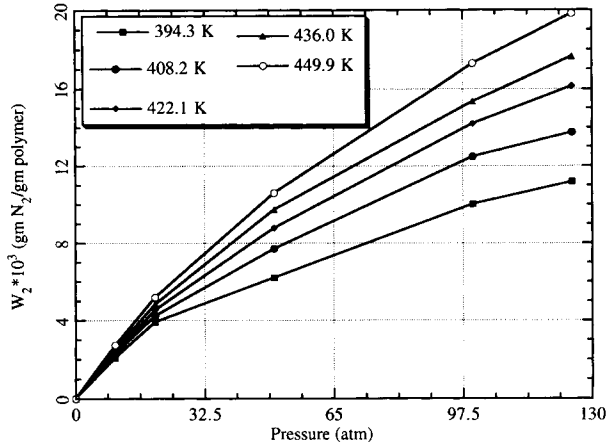


Figure 2 Solubility of N_2 in LDPE (PE800E).

cess can be considered as two steps: (1) gas isothermally “condenses” to a hypothetical state having a liquidlike volume close to the partial volume, which it has as a solute in molten polymer; (2) this hypothetical, liquidlike fluid dissolves in molten polymer (Ref. 3, p. 392). The solute in the molten polymer is in equilibrium with the gas, which is at the fugacity f_2^G ; then the equilibrium equation is³

$$\Delta g = 0 \quad (1)$$

where

$$\Delta g = \Delta g_I + \Delta \bar{g}_{II} \quad (2)$$

$$\Delta g_I = RT \ln \frac{f_{\text{pure}2}^L}{f_2^G} \quad (3)$$

$$\Delta \bar{g}_{II} = RT \ln \gamma_2 x_2 = RT \ln a_2 \quad (4)$$

Here $f_{\text{pure}2}^L$ is the fugacity of (hypothetical) pure liquid solute, γ_2 is the solute activity coefficient referred to the (hypothetical) pure liquid ($\gamma_2 \rightarrow 1$ as $x_2 \rightarrow 1$), and a_2 is the activity of the solute.³

We assume that the Flory–Huggins equation, or, say, the “modified” regular-solution equation, gives the activity for the liquidlike solute (Ref. 7, p. 82):

$$\ln a_2 = \ln \phi_2 + \left(1 - \frac{1}{r_1}\right) (1 - \phi_2) + \chi(1 - \phi_2)^2 \quad (5)$$

where ϕ_2 is the volume fraction of the solute; χ , the Flory–Huggins interaction parameter; and r_1 , the number of segments in the polymer molecule, each segment having the same size as that of the solute molecule. In our problem, $r_1 \gg 1$; then, we may write

$$\ln a_2 = \ln \phi_2 + (1 - \phi_2) + \chi(1 - \phi_2)^2 \quad (6)$$

Combining Eqs. (1)–(4) and (6) gives

$$\ln \frac{f_{\text{pure}2}^L}{f_2^G} + \ln \phi_2 + (1 - \phi_2) + \chi(1 - \phi_2)^2 = 0 \quad (7)$$

We may also write

$$\chi = - \frac{\ln \frac{f_{\text{pure}2}^L}{f_2^G} + \ln \phi_2 + (1 - \phi_2)}{(1 - \phi_2)^2} \quad (8)$$

The fugacity of the hypothetical pure liquid $f_{\text{pure}2}^L$ has been correlated in a corresponding-states plot as shown by Prausnitz (Ref. 3, p. 394). The fugacity of the solute, divided by its critical pressure, is shown as a function of the ratio of the solution temperature to the solute’s critical temperature. The fugacities in Prausnitz’s plot are for a total pressure of 1.013 bar. While the solution under consideration is at a considerably higher pressure, the Poynting correction is applied to the fugacity as read from Prausnitz’s plot. Thus,

$$f_{\text{pure}2(P,T)}^L = f_{\text{pure}2(1.013,T)}^L \exp \left[\frac{v_2^L (P - 1.013)}{\mathcal{R}T} \right] \quad (9)$$

where $f_{\text{pure}2(P,T)}^L$ is the fugacity at total pressure P , while $f_{\text{pure}2(1.013,T)}^L$ is the fugacity read from Prausnitz’s plot, i.e., at 1.013 bar. v_2^L is the molar “liquid” volume of the solute. As argued by Prausnitz from the regular solution theory, v_2^L is independent of temperature, e.g., $v_2^L = 32.4 \text{ cm}^3 \text{ mol}^{-1}$ for nitrogen.

The fugacity f_2^G can be expressed as (Ref. 3, p. 29)

$$f_2^G = P \exp \left[\frac{1}{RT} \int_0^P v_2^G dP - \int_0^P \frac{dP}{P} \right] \quad (10)$$

where v_2^G can be expressed from Peng–Robinson equation of state.

We denote w_2 as the experimental solubility, expressed as the gram of gas dissolved per gram of polymer. The volume fraction of dissolved gas ϕ_2 is expressed as

$$\phi_2 = \frac{w_2 v_2^L / M_2}{w_2 v_2^L / M_2 + v_1^L(P,T)} \quad (11)$$

where M_2 is the molecular weight of the dissolved gas; and $v_1^L(P,T)$, the specific volume ($\text{cm}^3 \text{ g}^{-1}$) of

the pure polymer melt at pressure P and temperature T .^{7,8}

By combining eqs. (9)–(11) with eq. (8), then the Flory–Huggins interaction parameter χ is available at various temperatures and pressures. We fit χ as a function of temperature and pressure, i.e., $\chi_{(T,P)}$, for a given system; here, it is N_2 –LDPE. By substituting this $\chi_{(T,P)}$ back to eq. (7), we can compute solubilities at any temperatures and pressures for this given system.

SOLUBILITY SAMPLE COMPUTATION

We compute the solubility of nitrogen in LDPE (PE800E) at $T = 394.31$ K and $P = 125$ atm:

Nitrogen: $T_{c2} = 126.2$ K, $P_{c2} = 33.9$ bar,

then $T/T_{c2} = 3.124$

From Figure 8–12 of Prausnitz (Ref. 3, p. 394), we have $[f_{\text{pure2}(1\text{atm})}^L/P_{c2}] = 6.0$; then $f_{\text{pure2}(1\text{atm})}^L$ is 203.4 bar and

$$f_{\text{pure2}(125\text{atm})}^L = 203.4 \exp \left[\frac{32.4 \times (125 - 1)}{82.057 \times 394.31} \right]$$

$$= 230.3 \text{ bar}$$

$$f_{\text{pure2}(\text{nitrogen}, 125\text{atm}, 394.31\text{K})}^G = 125$$

$$\times 1.013 \exp \left[\frac{1}{82.057 \times 394.31} \int_0^{125} v dP - \int_0^{125} \frac{dP}{P} \right]$$

$$= 129.9 \text{ bar}$$

$$\phi_2 = \frac{w_2 v_2^L / M_2}{w_2 v_2^L / M_2 + v_{1(P,T)}^L}$$

$$= \frac{1.1178 \times 10^{-2} \times 32.4 / 28.02}{1.1178 \times 10^{-2} \times 32.4 / 28.02 + 1.2403}$$

$$= 1.031 \times 10^{-2}$$

$$\chi = - \frac{\ln \frac{f_{\text{pure2}}^L}{f_2^G} + \ln \phi_2 + (1 - \phi_2)}{(1 - \phi_2)^2}$$

Table I Solubilities of Nitrogen in LDPE (PE800E)

Temp (K)	P (atm)	$f_{\text{pure2}}^{L(P,T)}$ (bar) [Eq. (9)]	$f_{\text{pure2}}^{G(P,T)}$ (bar) [Eq. (10)]	$w_2 \times 10^3$ (g/g) (Exptl)	$v_{1(P,T)}^L$ (cm ³ mol ⁻¹)	$\phi_2 \times 10^3$ (Exptl) [Eq. (11)]	χ [Eq. (8)]	χ [Eq. (12)]	$\phi_2 \times 10^3$ (Predicted) [Eq. (7)]
394.3	10	205.2	10.14	2.085	1.2525	1.921	2.258	2.348	1.754
394.3	20	207.3	20.32	3.915	1.2514	3.604	2.323	2.424	3.255
394.3	50	213.6	51.04	6.208	1.2481	5.718	2.770	2.698	6.156
394.3	100	224.6	103.2	10.02	1.2428	9.238	2.971	2.915	9.795
394.3	125	230.3	129.9	11.18	1.2403	10.31	3.075	3.011	11.04
408.2	10	203.5	10.15	2.292	1.2670	2.087	2.185	2.236	1.982
408.2	20	205.4	20.33	4.239	1.2658	3.857	2.361	2.313	3.679
408.2	50	211.5	51.14	7.708	1.2623	7.011	2.584	2.586	7.000
408.2	100	222.0	103.5	12.48	1.2566	11.35	2.799	2.803	11.19
408.2	125	227.4	130.3	13.740	1.2539	12.51	2.909	2.899	12.65
422.1	10	210.7	10.15	2.333	1.2810	2.102	2.187	2.142	2.199
422.1	20	203.6	20.34	4.540	1.2797	4.086	2.219	2.218	4.085
422.1	50	209.4	51.21	8.784	1.2759	7.898	2.480	2.492	7.896
422.1	100	219.4	103.8	14.20	1.2698	12.77	2.693	2.708	12.57
422.1	125	224.6	130.7	16.15	1.2668	14.53	2.785	2.804	14.24
436.0	10	198.2	10.15	2.521	1.2943	2.247	2.138	2.095	2.347
436.0	20	200.0	20.35	4.819	1.2929	4.291	2.189	2.171	4.370
436.0	50	205.5	51.30	9.735	1.2888	8.659	2.412	2.444	8.374
436.0	100	215.0	104.0	15.35	1.2822	13.65	2.653	2.661	13.54
436.0	125	220.0	131.1	17.64	1.2791	15.70	2.737	2.758	15.20
449.9	10	191.3	10.15	2.722	1.3069	2.403	2.107	2.054	2.540
449.9	20	193.0	20.36	5.182	1.3054	4.569	2.164	2.130	4.728
449.9	50	198.1	51.33	10.59	1.3010	9.324	2.378	2.404	9.077
449.9	100	207.0	104.2	17.29	1.2940	15.22	2.592	2.620	14.78
449.9	125	211.6	131.4	19.81	1.2907	17.44	2.683	2.716	16.82

$$\ln \frac{230.3}{129.9} + \ln(1.031 \times 10^{-2})$$

$$= - \frac{+ (1 - 1.031 \times 10^{-2})}{(1 - 1.031 \times 10^{-2})^2} = 3.075$$

When the Flory–Huggins interaction parameter χ is available at various experimental temperatures and pressures (Table I), curve-fitting χ as a function of temperature and pressure, we got the following phenomenological relation:

$$\chi = 1.722 \times 10^5 + \frac{8.439}{P} - 1.164 \times 10^{-2}P$$

$$+ 3.729 \times 10^{-5}P^2 - \frac{4.531 \times 10^6}{T} + 73.82T$$

$$- 2.919 \times 10^{-2}T^2 + 0.87041 \ln P - 3.107$$

$$\times 10^4 \ln T \quad (12)$$

where P is in atm, and T , in Kelvin. The plot of χ vs. T and P is Figure 3 [eq. (12)].

When substituting this $\chi_{(T,P)}$ [eq. (12)] back to eq. (7), we can compute solubilities at any temperatures and pressures, as shown in Table I. The comparison of predicted [eq. (7)] and experimental [eq. (11)] solubilities is shown in Figure 4.

SOLUBILITY COEFFICIENT K_H

At a certain temperature T and pressure P , we assume that the solubility c (mol cm⁻³) of gas in the polymer melt follows the form of

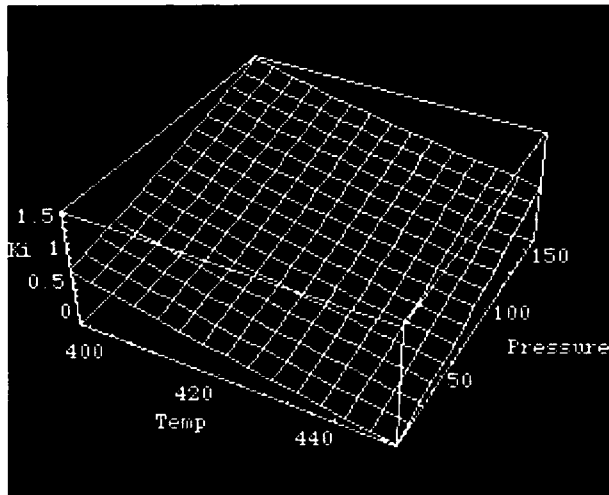


Figure 3 The Flory–Huggins interaction parameter χ vs. temperature and pressure for the N₂–LDPE system.

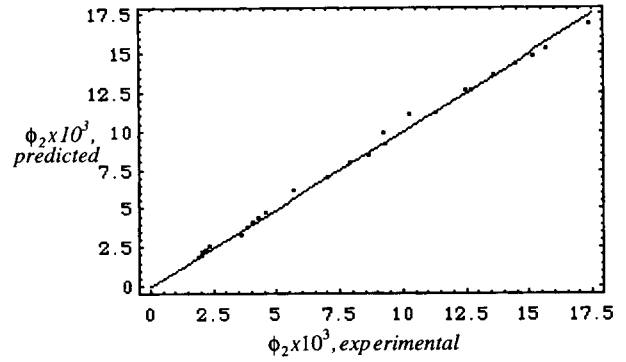


Figure 4 Comparison of predicted and experimental volume fraction of dissolved nitrogen on LDPE (PE800E).

$$c = K_H P \quad (13)$$

Here, K_H is the solubility coefficient. Also,

$$c = \frac{w_2/M_2}{w_2 v_2^L/M_2 + v_1^L(P,T)} = \frac{\phi_2}{v_2^L} \quad (14)$$

Then, we have (Table II):

$$K_H = \frac{c}{P} = \frac{\phi_2}{v_2^L P} \quad (15)$$

Fitting K_H s as a function of temperature and pressure, we have eq. (16). While plotting K_H vs. T and P , we got Figure 5. K_H values predicted by eq. (16) are also listed in Table II. The comparison of predicted and experimental solubility coefficient K_H s is shown in Figure 6:

$$K_H = 9.919 \times 10^3 - 5.519 \times 10^{-2}P + 2.057$$

$$\times 10^{-4}P^2 - \frac{3.532}{T} \times 10^5 + 1.923T$$

$$- 1636 \ln T \quad (16)$$

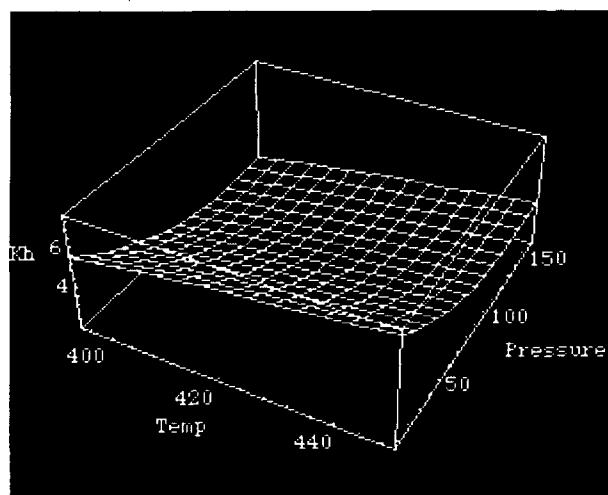
where P is in atm, T in Kelvin, and K_H in mole dyne⁻¹ cm⁻¹ × 10⁻¹².

ACTIVITY COEFFICIENT OF DISSOLVED GAS IN POLYMER MELT

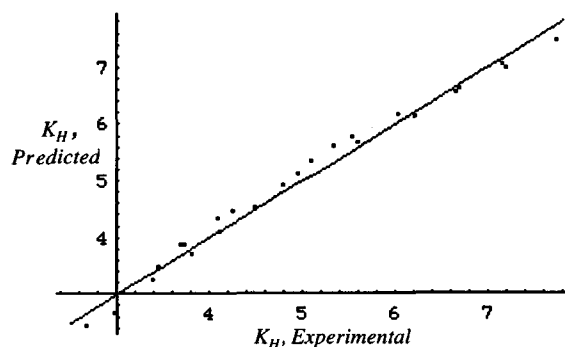
At a fixed temperature, for any given solute and solvent, when pressure approaches zero, we assume that

Table II Solubility Coefficients and Activity Coefficients of Nitrogen in LDPE (PE800E)

Temperature (K)	Pressure (atm)	Solubility Coefficient ($K_H \times 10^{12}$) (Exptl) [Eq. (15)]	Solubility Coefficient ($K_H \times 10^{12}$) (Predicted) [Eq. (16)]	Activity Coefficient Ω_2 (Exptl) [Eq. (17)]	Activity Coefficient Ω_2 (Predicted) [Eq. (18)]
394.31	10	5.343	5.589	0.913	0.877
394.31	20	4.957	5.099	0.833	0.808
394.31	50	3.750	3.875	0.633	0.635
394.31	100	2.984	2.658	0.434	0.460
394.31	125	2.690	2.436	0.398	0.427
408.20	10	6.037	6.157	0.921	0.908
408.20	20	5.693	5.666	0.847	0.839
408.20	50	4.264	4.443	0.664	0.665
408.20	100	3.408	3.226	0.482	0.491
408.20	125	3.083	3.004	0.449	0.450
422.10	10	6.698	6.614	0.926	0.929
422.10	20	6.222	6.123	0.857	0.860
422.10	50	4.810	4.900	0.686	0.686
422.10	100	3.829	3.683	0.515	0.512
422.10	125	3.470	3.460	0.484	0.479
435.98	10	7.149	7.028	0.930	0.946
435.98	20	6.656	6.537	0.865	0.876
435.98	50	5.102	5.314	0.703	0.703
435.98	100	4.124	4.097	0.542	0.529
435.98	125	3.704	3.874	0.512	0.495
449.87	10	7.737	7.457	0.934	0.962
449.87	20	7.201	6.966	0.872	0.892
449.87	50	5.530	5.743	0.719	0.719
449.87	100	4.502	4.526	0.567	0.544
449.87	125	4.099	4.303	0.539	0.511

**Figure 5** The solubility coefficient K_H vs. temperature and pressure for the N_2 -LDPE system.

Henry's law is perfectly satisfied, i.e., $c = kP$; here, k is a constant (Ref. 3, p. 374). When pressure is increased, the deviation of the solubility coefficient K_H from k indicates the nonideality. In other words, the activity coefficient Ω_2 is given by

**Figure 6** Comparison of predicted and experimental solubility coefficient K_H for N_2 -LDPE system.

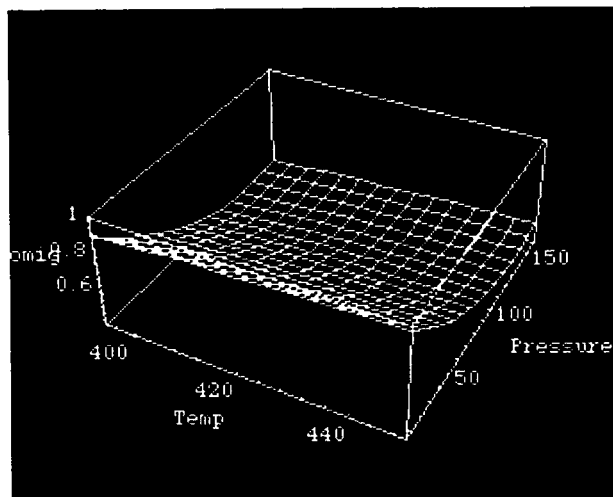


Figure 7 Activity coefficient of dissolved nitrogen Ω_2 vs. temperature and pressure for N_2 -LDPE system.

$$\Omega_2 = \frac{K_H}{k} = \frac{K_H}{\lim_{P \rightarrow 0} K_H} \quad (17)$$

where K_H is given by eq. (16). The results are shown in Table II.

Fitting the obtained Ω_2 as a function of temperature and pressure, we have now eq. (18). While plotting Ω_2 vs. T and P , we got Figure 7. The Ω_2 values predicted by eq. (18) are listed in Table II. The comparison of the predicted and experimental activity coefficient Ω_2 is shown in Figure 8:

$$\Omega_2 = 637.1 - 7.790 \times 10^{-3}P + 2.870 \times 10^{-5}P^2 - \frac{2.295}{T} \times 10^4 + 0.1204T - 104.6T \quad (18)$$

where P is in atm, and T , in Kelvin.

CONCLUSION

The solubility of nitrogen in low-density polyethylene (PE800E) increasing with temperature shows that the mixing of a gas and a polymer is an endothermic process which is opposite to what is observed for the low-pressure range. Empirical correlations obtained which represent the Flory-Huggins inter-

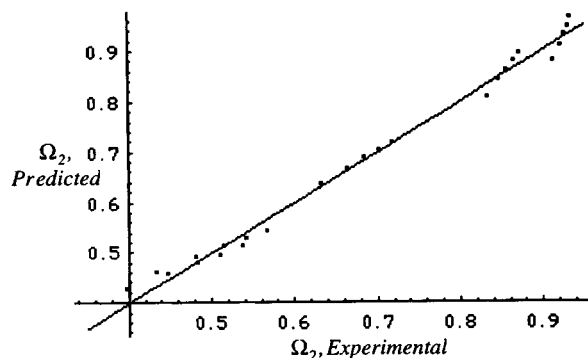


Figure 8 Comparison of predicted and experimental activity coefficient Ω_2 of dissolved nitrogen for N_2 -LDPE system.

action parameter χ , solubility coefficient K_H , and activity coefficient of dissolved gas Ω_2 as functions of temperature and pressure for above system represent the experimental results quite well.

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