

# Elastic Effects on Solubility in Semicrystalline Polymers

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**ABSTRACT:** Capillary column inverse gas chromatography experiments at infinite solvent dilution were conducted for 15 polyethylene/solvent systems. Thermodynamic data were collected for various types of penetrant molecules (normal alkanes, 1-alkenes, isomers of hexane, and ring compounds). Theoretical predictions of the solubility data were made with an activity coefficient model (Universal Functional Group Activity-van der Waals-Free-Volume) (UNIFAC-vdw-FV) and an equation-of-state model (Group-Contribution, Lattice-Fluid, Equation of State) (GCLF-EoS). Although good agreement between the experimental data and theoretical predictions was obtained above the melting point of the polymer, at temperatures below the melting point, significant differences were found. This occurred

because at those temperatures, the polymer had a semicrystalline structure and the solubility of the solvent was reduced on account of the constraints on some of the chains in the amorphous phase by the polymer crystallites. The theory developed by Michaels and Haussein to account for such elastic effects on solubility was incorporated into the two predictive models. After these modifications, the new estimations of the solubility showed significantly improved agreement with the experimental results. Moreover, the elasticity effect resulted in elevated estimates of the crystallinity when inverse gas chromatography retention volumes were used. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 138–146, 2008

**Key words:** amorphous; melting point; polyethylene (PE)

## INTRODUCTION

The design of most equipment in the polymer industry requires knowledge of equilibrium data for polymer/solvent systems. However, experimental data are frequently not available, and theoretical predictions of the thermodynamic properties are needed.

In semicrystalline polymers such as polyethylene, two phases are present: amorphous and crystalline regions.<sup>1</sup> The crystalline region typically consists of crystal lamellae of regular folding chains, which are assumed to be impermeable to solvents; therefore, only the amorphous phase is accessible to the solvent molecules. In the amorphous region, different types of polymer chains are present: tie chains that are connected at both ends to different crystals, loops that exit and return to the same crystal, free ends that have one unattached end extending from the crystal, and, of course, floating chains that are not attached to a crystal. The tie chains are stretched when the solvent penetrates the amorphous polymer network; this makes them elastically deform, producing a constraint on the polymer crystallites and yielding a decrease in the sorption of the solvent in the polymer.<sup>2</sup>

Most of the theoretical models used to predict the solubility of solvents in polymers do not attempt to

account for the elastic effects in the amorphous region. When these models are applied to semicrystalline polymers below the melting point, significant deviations from the experimental values of solubility can occur. A number of authors have proposed methods to deal with the elastic factor: Michaels and Haussein,<sup>2</sup> Doong and Ho,<sup>3</sup> Castro et al.,<sup>4</sup> and Banaszak et al.<sup>5</sup>

Doong and Ho<sup>3</sup> used a theoretical model that considers four contributions to the total activity of the solvent when it penetrates the polymer network: the combinatorial, residual, free-volume, and elastic-factor contributions. UNIFAC<sup>6</sup> and solubility parameter methods were both combined with the Michaels–Haussein and Flory–Rehner theories for the prediction of the solubility for several polyethylene/solvent systems. For a series of aromatic compounds, the authors showed that for the UNIFAC model modified with the Michaels–Haussein theory, the resulting error was about 10%, whereas for the UNIFAC model modified with Flory–Rehner theory, the elastic factor was unable to mimic the temperature dependence of the solubility data.

Banaszak et al.<sup>5</sup> studied the sorption of ethylene and 1-hexene in linear low-density polyethylene. They ran molecular simulations to parameterize the perturbed-chain statistical associating fluid theory equation of state.<sup>7</sup> This equation of state does not take into account the elastic factors in semicrystalline polymers, so they adopted a modification following the Michaels–Haussein theory. They verified their

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predictions by comparison with the experimental results obtained by Novak et al.<sup>8</sup> for the same system. They concluded that these elastic constraints play an important role in the solvent solubility for temperatures below the melting point of the polymer.

Using a gravimetric sorption technique, Castro et al.<sup>4</sup> measured the sorption of several hydrocarbons in polyethylene and polypropylene. They used two models to predict the solvent solubility in these systems: UNIFAC-FV combined with the Michaels–Haussein theory and UNIFAC-FV combined with the Flory–Rehner theory. They concluded that the deviation of the predictions and the experimental results ranged from 4.7 to 10.8%.

### THEORETICAL BACKGROUND

In this work, two different methods have been used for the prediction of the weight fraction activity coefficient of solvents at infinite dilution. These models are extended forms of UNIFAC-vdw-FV<sup>9</sup> and GCLF-EoS.<sup>10</sup> The modified models have been tested with data for 15 solvents, including alkanes, alkenes, cycloalkanes, and aromatics.

#### UNIFAC-vdw-FV

The UNIFAC group contribution method, proposed by Fredenslund et al.<sup>6</sup> for the calculation of a solvent's activity coefficient, was later extended by Oishi and Prausnitz<sup>11</sup> to include a free-volume contribution. In this model, the activity coefficient of component  $i$  ( $\Omega_i$ ) in a solution has three contributions: combinatorial ( $\Omega_i^c$ ), residual ( $\Omega_i^r$ ), and free-volume ( $\Omega_i^{fv}$ ):

$$\ln \Omega_i = \ln \Omega_i^c + \ln \Omega_i^r + \ln \Omega_i^{fv} \quad (1)$$

The details of the combinatorial and residual terms are described in the original reference<sup>6</sup> and have been incorporated into many phase equilibrium calculation computer algorithms.

Following insights provided by Elbro et al.<sup>12</sup> and Flory,<sup>13</sup> Kannan et al.<sup>9</sup> revised the free-volume contribution based on the van der Waals partition function. This model was specifically developed to allow predictions in aqueous systems. The previous free-volume approach of Oishi and Prausnitz<sup>11</sup> failed because of the smaller free volume of water compared with that of most polymers. The UNIFAC-vdw-FV model has been shown to give predictions as good as or better than those of the former version for both aqueous and nonaqueous polymer systems.<sup>9</sup>

The term of Kannan et al.<sup>9</sup> to account for the free-volume effect is

$$\ln \Omega_i^{fv} = \ln \left[ \frac{\phi_i^{fv}}{\phi_i^h} \right] + \left[ \frac{\phi_i^h - \phi_i^{fv}}{x_i} \right] \quad (2)$$

where  $x_i$  is the molar fraction of species  $i$ ;  $\phi_i^{fv}$  and  $\phi_i^h$  denote volumetric fractions for species  $i$ ; and superscripts  $fv$  and  $h$  refer to the free-volume and hardcore molecular properties, respectively.

#### GCLF-EoS

The group contribution lattice–fluid equation of state was developed by Lee and Danner.<sup>10</sup> It is based on the lattice–fluid theory of Panayiotou and Vera<sup>14</sup> [Panayiotou–Vera equation of state (PV-EoS)], which comes from the lattice statistics model of Guggenheim.<sup>15</sup> The parameters for the PV-EoS are estimated with group contribution methods. These characteristic parameters are the hardcore volumes of the molecules, the molecular interaction energies, and, in a mixture, the binary interaction parameters.

The PV-EoS in terms of reduced variables is

$$\frac{\tilde{P}}{\tilde{T}} = \ln \left( \frac{\tilde{v}}{\tilde{v} - 1} \right) + \frac{z}{2} \ln \left( \frac{\tilde{v} + \frac{q}{r} - 1}{\tilde{v}} \right) - \frac{\theta^2}{\tilde{T}} \quad (3)$$

where  $\tilde{P}$  is the reduced pressure,  $\tilde{T}$  is the reduced temperature,  $\tilde{v}$  is the reduced volume,  $z$  is the lattice coordination number (10),  $r$  is the number of segments in the polymer molecule,  $\theta$  is the surface area fraction of the mixture, and  $q$  is the surface area parameter. Details of this equation of state and the group parameters are given in the original publication of Lee and Danner.<sup>10</sup>

#### Elastic effect

These theoretical models for predicting the solubility are not complete for semicrystalline polymers. In these cases, a new contribution due to the elastic effect that the crystalline phase has on the solubility of the solvent has to be incorporated.

With this goal, a correction based on the theory developed by Michaels and Haussein<sup>2</sup> was added to the models. Thus, the expression for the calculation of the solvent weight fraction activity coefficient taking into account the elastic contribution ( $\Omega_i^{el}$ ) becomes

$$\ln \Omega_i = \ln \Omega_i^c + \ln \Omega_i^r + \ln \Omega_i^{fv} + \ln \Omega_i^{el} \quad (4)$$

The relationship between the activity for species  $i$  ( $a_i$ ) and  $\Omega_i$  is expressed as follows:

$$a_i = \Omega_i \omega_i \quad (5)$$

where  $\omega_i$  represents the weight fraction for species  $i$ . The relation for the activity can therefore be expressed as follows:

$$a_i = a_i^c a_i^r a_i^{fv} a_i^{el} = \omega_i \Omega_i^c \Omega_i^r \Omega_i^{fv} \Omega_i^{el} \quad (6) \quad \mu_2^c = \mu_2^m + \mu_2^{el} \quad (13)$$

Because

$$a_i^c = \omega_i \Omega_i^c \quad (7)$$

it follows that, for the elastic contribution, the activity is equal to the activity coefficient:

$$a_i^{el} = \Omega_i^{el} \quad (8)$$

This relationship is useful in this work because all the predictions were made with activity coefficients at infinite solvent dilution.

In their theory, Michaels and Hausslein<sup>2</sup> suggested that the tension on the intercrystalline tie chains is in equilibrium with the free energy driving force of crystallization. Because solvent molecules are excluded from the crystals, thermodynamic equilibrium requires that the chemical potential of the solvent in the amorphous and vapor phases be equal:

$$\mu_1^v = \mu_1^a \quad (9)$$

Here  $\mu_1$  denotes the chemical potential of the solvent. The superscripts *v* and *a* represent the vapor and amorphous phases. The chemical potential in the amorphous phase can be expressed as the sum of two terms: the chemical potential of the solvent without the effect of the constraints of the chains ( $\mu_1^m$ ) and the chemical potential of the solvent taking into account the elastic constraints imposed by the crystallites on the tie chains ( $\mu_1^{el}$ ):

$$\mu_1^v = \mu_1^m + \mu_1^{el} \quad (10)$$

$\mu_1^v$  can be expressed as  $RT \ln a_1$ , and  $\mu_1^m$  can be expressed as  $RT(\ln \phi_1 + \phi_2 + \chi \phi_2^2)$ , where  $\phi_i$  represents the volume fractions of the solvent (1) and polymer (2),  $\chi$  is the Flory–Huggins interaction parameter, and  $R$  is the universal gas constant.<sup>13</sup> Thus,

$$\mu_1^{el} = RT[\ln a_1 - (\ln \phi_1 + \phi_2 + \chi \phi_2^2)] = RT \ln a_1^{el} \quad (11)$$

In the polymer phase, thermodynamic equilibrium also requires the equality of the chemical potential of the polymer in the amorphous and crystalline phases:

$$\mu_2^c = \mu_2^a \quad (12)$$

As before, the right-hand side of eq. (12) can be expressed as the sum of two terms: the chemical potential without the effect of the constraints of the chains ( $\mu_2^m$ ) and the chemical potential taking into account the elastic constraints imposed by the crystallites on the tie chains ( $\mu_2^{el}$ ):

As suggested by Flory,<sup>16</sup> the left-hand side of eq. (13) can be expressed in terms of the depression of the melting point of a crystalline polymer ( $T_m$ ) by a solvent:  $\mu_2^c = -\Delta H_2[1 - (T/T_m)]$ .  $\mu_2^m$  can be expressed as  $-RT(V_2/V_1)(\phi_1 - \chi \phi_1^2)$ .

Therefore, the elasticity term becomes

$$\mu_2^{el} = -RT \left[ \frac{\Delta H_2}{R} \left( \frac{1}{T} - \frac{1}{T_m} \right) - \frac{V_2}{V_1} (\phi_1 - \chi \phi_1^2) \right] \quad (14)$$

Using the assumption of Hookean behavior for the polymer tie chains, Michaels and Hausslein<sup>2</sup> developed an expression for the activity of the solvent. In this way, the following expression was obtained:

$$\ln a_1^{el} = \frac{\frac{\Delta H_2}{R} \frac{V_1}{V_2} \left( \frac{1}{T} - \frac{1}{T_m} \right) - (\phi_1 - \chi \phi_1^2)}{\frac{3}{2f\phi_2} - 1} \quad (15)$$

Here  $\Delta H_2$  is the molar heat of fusion for the crystalline polymer,  $V_i$  represents the molar volumes of the solvent ( $i = 1$ ) and polymer ( $i = 2$ ), and  $f$  is the fraction of elastically affected chains in the amorphous region. In general, in this region, all the different types of chains can be found: tie chains, loops, free ends, and floating chains. Only the former ones are stretched when the solvent penetrates the polymer network, and they become elastically deformed. This results in a decrease in the sorption of the solvent in the polymer compared with what occurs in a totally unconstrained amorphous polymer.

In eq. (15), the term  $\Delta H_2/V_2$  can be replaced by  $\Delta H_2^f \rho_a$ , where  $\Delta H_2^f$  is the specific heat of fusion per gram of crystalline polymer and  $\rho_a$  represents the density of the amorphous phase of the polymer.<sup>2,3</sup> The elastic contribution is given in terms of the activity, but according to eq. (8), this term can be considered either the activity or activity coefficient. In this work, it was used as an activity coefficient because the UNIFAC-vdw-FV and GCLF-EoS calculated the activity in terms of the activity coefficient, as expressed in eq. (4).

## EXPERIMENTAL

### Apparatus

A Varian 3400 gas chromatograph (Varian Inc., Palo Alto, CA) with a flame ionization detector was used for the determination of the partition coefficients. The flame ionization detector was supplied with hydrogen (30 mL/min) and compressed air (300 mL/min). The carrier gas was ultrahigh-purity helium.

The capillary column of polyethylene was prepared with the static coating technique as described

by Grob.<sup>17</sup> It had a polyethylene coating of 3  $\mu\text{m}$  and a length of 15 m. The thickness was based on the density of the polymer and confirmed with scanning electron microscopy pictures. For each analysis, an injection of 0.02  $\mu\text{L}$  was used. The inert marker gas used to determine the retention time was methane. Ten microliters was injected twice before each solvent injection. This retention time was used to calculate the linear velocity of the gas.

The resulting elution profiles reflect the interaction between the polymer and the given solvent. Peak retention times are related to the solubility, whereas diffusivity is related to the degree of spread of the eluted peak. The partition and diffusion coefficients were determined by the regression of a detailed model of the capillary column elution peak as described by Pawlish and coworkers<sup>18,19</sup> and Macris.<sup>20</sup> The partition coefficient is the equilibrium ratio of the concentration of the solvent in the polymer phase to the concentration of the solvent in the gas phase.

## Materials

The linear low-density polyethylene had a density of 0.9249  $\text{g}/\text{cm}^3$  at room temperature, a number-average molecular weight of 26,400  $\text{g}/\text{mol}$ , and a weight-average molecular weight of 145,600  $\text{g}/\text{mol}$ . To determine the crystallinity and melting point of the polymer, differential scanning calorimetry and inverse gas chromatography techniques were used. The crystallinity percentage by volume was found to be 45.5%. The melting point was about 110°C.

The solvents were *n*-pentane, *n*-hexane, *n*-octane, *n*-decane, 1-hexene, 1-octene, 1-decene, 2-methylpentane, 3-methylpentane, 2,2-dimethylbutane, 2,3-dimethylbutane, cyclohexane, cyclopentane, benzene, and toluene.

## RESULTS AND DISCUSSION

### Capillary column inverse gas chromatography experiments

Capillary column inverse gas chromatography experiments at infinite solvent dilution were conducted for 15 polyethylene/solvent systems. Most of the experiments were carried out at temperatures below the melting point of the polyethylene (see Table I). A few points were taken at 100°C and higher with cyclohexane and 1-octene to examine the behavior above the melting point. The partition coefficient ( $K_p$ ) had to be corrected to account for the crystallinity because the sorption was assumed to occur only in the amorphous phase. This correction was made as follows:

$$K_p = \frac{C_{\text{solvent in polymer}}}{C_{\text{solvent in vapor}}} \quad (16)$$

**TABLE I**  
 **$K_p$  Values at Infinite Solvent Dilution for Polyethylene/Solvent Systems (Corrected for 45.5% Crystallinity by Volume)**

Solvent	$K_p$		
	40°C (313 K)	60°C (333 K)	80°C (353 K)
<i>n</i> -Pentane	20.8	15.4	12.8
<i>n</i> -Hexane	61.4	38.8	29.0
<i>n</i> -Octane	492.5	246.4	152.1
<i>n</i> -Decane	3589.2	1463.1	725.5
1-Hexene	60.1	42.3	33.1
1-Octene	400.0	207.2	128.1
1-Decene	2982.9	1253.2	689.2
2-Methylpentane	48.3	36.4	29.3
3-Methylpentane	56.1	41.6	33.5
2,2-Dimethylbutane	30.9	28.2	24.0
2,3-Dimethylbutane	45.2	36.4	29.8
Cyclohexane	126.4	82.7	57.7
Cyclopentane	54.5	40.7	33.4
Benzene	129.0	84.1	62.1
Toluene	375.7	212.6	141.9

$$\phi_a = \frac{V_{\text{amorphous polymer}}}{V_{\text{total polymer}}} \quad (17)$$

$$K_p^{\text{corr}} = \frac{C_{\text{solvent in amorphous polymer}}}{C_{\text{solvent in vapor}}} = \frac{K_p}{\phi_a} \quad (18)$$

Here  $C$  denotes the concentration, and  $\phi_a$  is the volume fraction of the amorphous phase of the polymer. The experimental values of the partition coefficient corrected for the crystallinity ( $K_p^{\text{corr}}$ ) are given in Table I.

From the corrected values of  $K_p$  for each polyethylene/solvent system, the weight fraction activity coefficient at infinite dilution ( $\Omega_1^\infty$ ) was calculated:

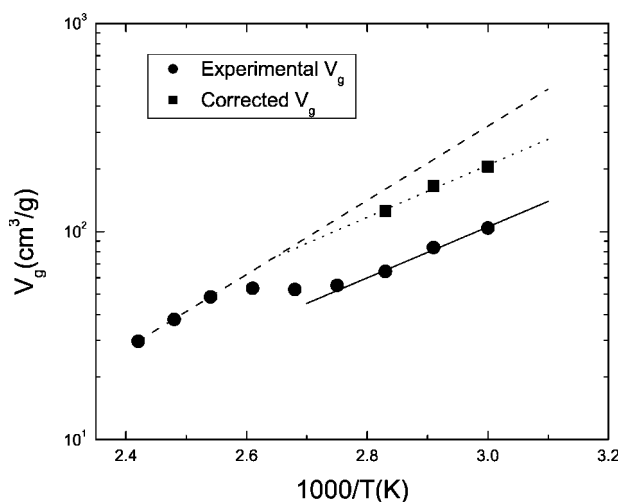
$$\Omega_1^\infty = \frac{RT\rho_2}{K_p^{\text{corr}}P_1^sM_1} \exp\left(\frac{-P_1^s(B_{11} - V_1)}{RT}\right) \quad (19)$$

Here  $\rho_2$  represents the density of the amorphous polymer,  $P_1^s$  is the vapor pressure of the solvent,  $M_1$  is the molecular weight of the solvent,  $B_{11}$  is the second virial coefficient of the solvent, and  $V_1$  is the molar volume of the solvent.

### Effect of elasticity on the crystallinity determination

Following the pioneer work of Guillet and Stein,<sup>21</sup> many researchers<sup>22-25</sup> have used the following equation to determine the degree of crystallinity in the polymers:

$$\text{Crystallinity (\%)} = 100 \left(1 - \frac{V_g}{V_e}\right) \quad (20)$$



**Figure 1** Relationship between the retention volume ( $V_g$ ) and temperature ( $T$ ) above and below the melting point for the 1-octene/linear low-density polyethylene system.

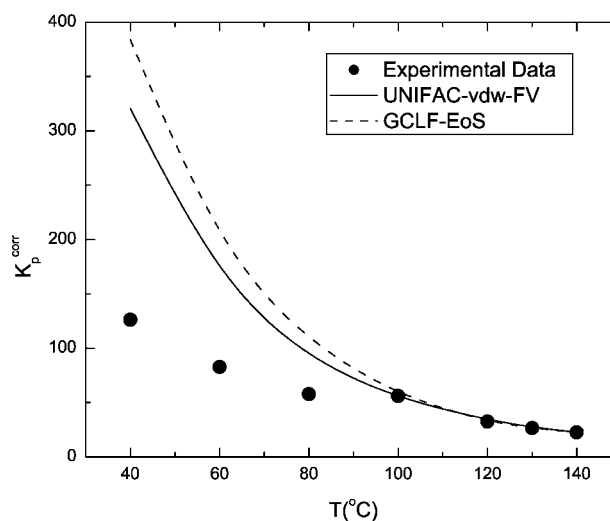
Here  $V_g$  is the measured retention volume at any temperature, and  $V_g^e$  is the extrapolation of the linear relationship between the logarithm of the retention volume and the reciprocal of temperature existing above  $T_m$  to temperatures below the melting point. Equation (20) is based on the assumption that crystalline regions are impenetrable and that the amorphous regions are fully penetrable to the probe molecules. It is also implicitly assumed that the thermodynamics of the melt are still valid in the semicrystalline region; that is, the amorphous chains between crystals are indistinguishable from those in the melt state.

To illustrate the unsuitability of eq. (20), the retention volume for 1-octene is plotted as a function of the reciprocal temperature in Figure 1 for temperatures that encompass the melting point. The experimental retention volumes are represented by circles, whereas the dashed line is the extrapolation of the retention volume from temperatures above  $T_m$  (i.e.,  $V_g^e$ ). The crystallinity is calculated from eq. (20) under the assumption that the experimental  $V_g$  values should be adjusted to match the values on the long-dash line. The crystallinity calculated in this way is about 60% by volume, whereas the value from differential scanning calorimetry is about 45% by volume. If the presence of crystals did not have any influence on the retention volume and subsequently on the solubility of 1-octene, the slope of the extrapolated values and the measured values (circles) below  $T_m$  would have been the same. In this work, those slopes were found to be different, and the same was found for other sources. Braun and Guillet<sup>26</sup> also pointed out that both slopes should be the same to calculate the sample's crystallinity. The deviations in their work were explained in terms of significant experimental surface retention in compar-

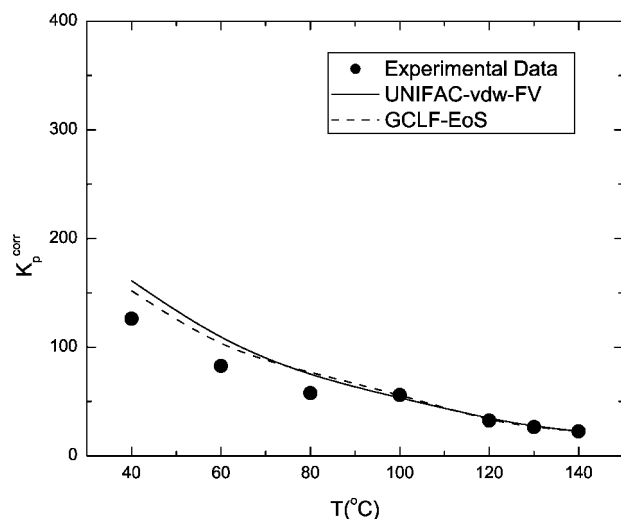
ison with the bulk sorption. At that time, the amorphous regions in the semicrystalline polymer were not considered to be affected by the tie chains. The second set of data in Figure 1 (squares) corresponds to the correction of the retention volume with the crystallinity value obtained from differential scanning calorimetry. They represent the true retention volume for the amorphous phase in the semicrystalline polymer, and they clearly show a decrease in the solubility with respect to the theoretical undisturbed amorphous phase. The area between the dashed lines shows the effect of the elastic contribution to the activity coefficient for a semicrystalline polymer. The extrapolation of the retention volume from the melt yields a larger value for  $V_g^e$  than is appropriate, resulting in an elevated estimate of the crystallinity.

#### Prediction of the weight fraction activity coefficients

Predictions of the weight fraction activity coefficient at infinite dilution were made with the UNIFAC-vdw-FV and GCLF-EoS models. These predictions were compared with the experimental results, and they showed big deviations below  $T_m$  (110°C). A typical example, polyethylene/cyclohexane, is shown in Figure 2. This figure shows that the models for the prediction of solubility are excellent above  $T_m$ . Below  $T_m$ , however, the solubility is seriously overestimated. For all 15 solvents, although the predictions with the UNIFAC-vdw-FV were somewhat better (40% average deviation vs 53% for the GCLF-EoS), neither method is adequate for temperatures below  $T_m$ .



**Figure 2** Solubility of the linear low-density polyethylene/cyclohexane system before the introduction of the Michaels–Hausslein model into the theoretical predictions.



**Figure 3** Solubility of the linear low-density polyethylene/cyclohexane system after the introduction of the Michaels–Haussein model into the theoretical predictions.

This discrepancy suggests the presence of elastic effects on the polymer, which could explain the decrease in the sorption of the solvent in the semicrystalline polymer from the value predicted by the thermodynamic models, which assume a typical amorphous phase. Thus, the results were compared with predictions from the modified models incorporating the Michaels–Haussein correction for elasticity.

The Michaels–Haussein theory contains the empirical parameter  $f$ , the fraction of elastically affected chains in the amorphous polymer. This parameter is difficult to determine because it depends on the crystallinity and history of the polymer.<sup>2</sup>

In this work, an optimum value of this parameter was estimated by correlation. This value corresponds to that which would yield the minimum error between the experimental and theoretical predictions for the values of solubility. This resulted in somewhat different optimum values for each of the solvent systems. However, an average  $f$  value for all the solvents for each model proved to be adequate.

One could anticipate that the  $f$  parameter is temperature-dependent. Thus, separate calculations were made in which  $f$  was assumed to be dependent or independent of temperature. In both cases, for the UNIFAC-vdw-FV model, the deviation was around 11%. Thus, it was concluded that no dependence on temperature of this parameter was needed, in agreement with the theory of Michaels and Haussein.<sup>2</sup>

For the UNIFAC-vdw-FV, the average optimum  $f$  value was 0.36, a result that is consistent with the value of 0.373 obtained for polyethylene by Doong and Ho<sup>3</sup> and in the range of 0.265–0.365 obtained by Michaels and Haussein<sup>2</sup> for several types of polyethylene. For the GCLF-EoS, the average optimum  $f$  value was 0.50.

To apply this theory, eq. (15) was used. In this equation, the heat of fusion of the crystalline polymer ( $\Delta H_2^f$ ) was calculated on the basis of the group contribution method of Van Krevelen and Hof-tyzer.<sup>27</sup> The resulting value of 65 cal/g agrees with that found by Doong and Ho.<sup>3</sup> The density of the amorphous polymer ( $\rho_a$ ) and the molar volume of the solvent ( $V_1$ ) depend on the temperature of the experiment. The calculation of the amorphous density was performed by extrapolation from temperatures above the melting point.<sup>28</sup> Because this work was done at infinite solvent dilution, the volumetric fraction of the solvent ( $\phi_1$ ) was considered to be zero, so the term  $\phi_1 - \chi\phi_1^2$  is also zero, and the volumetric fraction of the polymer ( $\phi_2$ ) is 1.

As shown in Figure 3 for the polyethylene/cyclohexane system, there was significant improvement in the predictions when the Michaels–Haussein correction was applied. No elastic contribution was taken into account above the melting point because only the amorphous phase is present. In this case, the fraction of elastically effective chains is zero, and so is the elastic contribution. This improvement was found for all the solvents. This confirms that these elastic effects significantly affect the sorption properties of polyethylene (or any semicrystalline polymer) below the melting point of the polymer.

Quantitative comparisons of experimental and predicted values for the weight fraction activity coefficient at infinite dilution are presented in Tables II and III. These tables correspond to the predictions made with the UNIFAC-vdw-FV and GCLF-EoS. The error in each case is calculated as follows:

**TABLE II**  
Comparison of the Solubility Values from the Experimental Data and from the UNIFAC-vdw-FV Model Incorporating the Michaels–Haussein Theory ( $f = 0.36$ )

Solvent	Solubility			
	40°C	60°C	80°C	Average
<i>n</i> -Pentane	25.3	23.0	15.3	21.2
<i>n</i> -Hexane	14.4	19.6	15.1	16.3
<i>n</i> -Octane	7.9	6.3	7.2	7.1
<i>n</i> -Decane	28.8	6.0	3.4	12.7
1-Hexene	0.47	4.8	15.6	6.9
1-Octene	5.5	6.9	8.8	7.0
1-Decene	26.6	5.3	4.7	12.2
2-Methylpentane	6.7	1.6	12.9	7.1
3-Methylpentane	3.2	5.3	17.8	8.8
2,2-Dimethylbutane	16.2	3.9	16.1	12.1
2,3-Dimethylbutane	8.2	5.0	17.0	10.0
Cyclohexane	26.2	22.6	18.4	22.4
Cyclopentane	13.7	6.1	7.1	8.9
Benzene	13.4	6.4	6.7	8.8
Toluene	0.78	0.14	8.4	3.1
Average error (%)	13.1	8.2	11.6	11.0

**TABLE III**  
**Comparison of the Solubility Values from the**  
**Experimental Data Incorporating the GCLF-EoS**  
**and Michaels–Hausslein Theory ( $f = 0.50$ )**

Solvent	Solubility			
	40°C	60°C	80°C	Average
<i>n</i> -Pentane	12.2	20.2	21.7	18.0
<i>n</i> -Hexane	9.6	10.5	16.5	12.2
<i>n</i> -Octane	58.5	15.9	0.97	25.1
<i>n</i> -Decane	115.	44.5	9.5	56.6
1-Hexene	15.7	5.9	4.0	8.5
1-Octene	42.6	7.5	8.6	19.6
2-Methylpentane	19.5	12.3	9.6	13.8
3-Methylpentane	22.7	15.7	13.9	17.5
2,2-Dimethylbutane	13.7	21.3	18.4	17.8
2,3-Dimethylbutane	23.3	21.7	19.0	21.3
Cyclohexane	10.6	16.1	20.1	15.6
Cyclopentane	4.5	7.0	3.8	5.1
Benzene	37.8	37.4	33.1	36.1
Toluene	18.8	26.3	26.2	23.7
Average error (%)	29.0	18.7	14.7	20.8

Error (%)

$$= \frac{\text{Experimental value} - \text{Predicted value}}{\text{Experimental value}} \times 100 \quad (21)$$

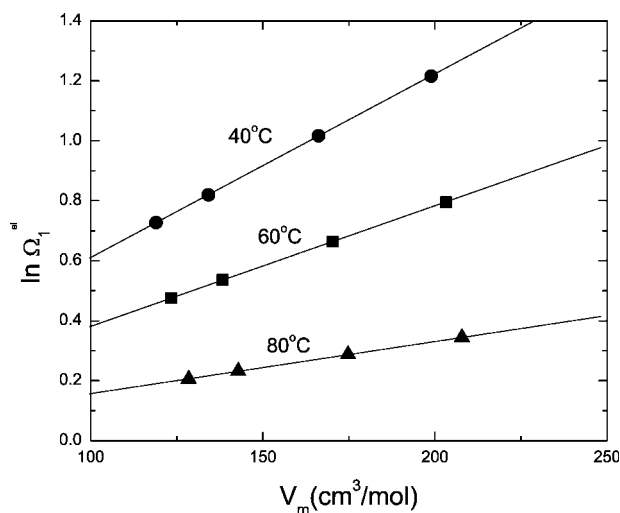
The average error is the arithmetic average:

$$\text{Average error (\%)} = \frac{1}{N} \sum_{n=1}^N \text{Error}_n(\%) \quad (22)$$

Here  $N$  is the total number of components. The deviations are generally larger at the lower temperature. The average deviation for the UNIFAC-vdw-FV approach falls from 40 to 11% with the introduction of the elasticity correction. The GCLF-EoS is again not as accurate. The average deviation improves, however, from 59 to 21%.

#### Effect of the molar volume and molecular weight of the solvent on the solubility

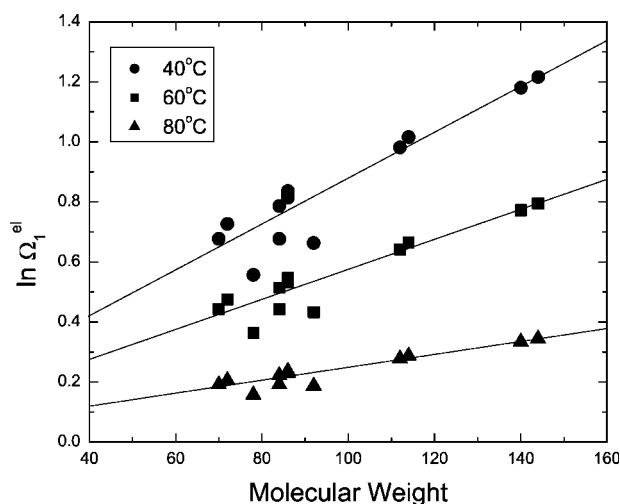
The size of the solvent that penetrates the polymer network has an influence on the elastic contribution of the activity, as can be seen in eq. (15). For all solvents, the elastic contribution is larger when the molecule of the penetrant has a higher molar volume. When the sorbed molecule is larger, it produces a bigger stress in the polymer chains, yielding a higher elastic deformation. As shown in Figure 4, the elastic contribution of the activity coefficient increases as the molar volumes of the  $n$ -alkanes increase. Note that as  $\Omega_i^{el}$  increases, the solubility decreases for the same activity. The rest of the solvents follow the same trend.



**Figure 4** Effect of the molar volume ( $V_m$ ) of  $n$ -alkanes on the elastic contribution ( $\Omega_1^{el}$ ) as calculated by UNIFAC-vdw-FV.

This effect was also studied by Doong and Ho<sup>3</sup> with a series of aromatic vapors and by Castro et al.<sup>29</sup> with the sorption of normal paraffins in polyethylene. They concluded that for the bulkier solvents, the solubilities were smaller because of the elastic factor, and their results are consistent with this work.

The effect of the molecular weight of the solvent on the elastic contribution of the activity coefficient was also studied. As expected, the results showed the same behavior as that for the variation of the elastic contribution with the molar volume. Figure 5 shows the increasing trend of the elastic contribution of the activity coefficient with an increase in the molecular weight or molar volume of all the solvents used in this study.



**Figure 5** Effect of the molecular weight of all the solvents on the elastic contribution ( $\Omega_1^{el}$ ) as calculated by UNIFAC-vdw-FV.

## CONCLUSIONS

Thermodynamic data were collected for 15 polyethylene/solvent systems by capillary column inverse gas chromatography experiments at infinite solvent dilution. Theoretical predictions of the solubility data were studied with the UNIFAC-vdw-FV activity coefficient model and the GCLF-EoS. These theories generally do not take into account the elastic effects on solubility in semicrystalline polymers, so it was necessary to incorporate the elastic contribution as predicted by the theory of Michaels and Hausslein.<sup>2</sup> After the incorporation of the elastic effect contribution, the predicted results showed significant improvements, going from 40% error before the correction to 11% error after the correction in the case of UNIFAC-vdw-FV.  $f$  was found to be essentially independent of the temperature or the solvent. The elastic contribution was shown to be larger in the case of bigger solvents (higher molar volume or higher molecular weight). If one uses the retention volumes in the usual manner [eq. (1)], the crystallinity percentage can be significantly overestimated.

## NOMENCLATURE

## Symbols

$a_i$	activity for component $i$
$B_{11}$	second virial coefficient of the solvent
$C$	concentration
$f$	fraction of elastically effected chains in the amorphous region
$\Delta H_2$	molar heat of fusion for the crystalline polymer
$\Delta H_2^f$	specific heat of fusion per gram of the crystalline polymer
$K_p$	partition coefficient
$K_p^{\text{corr}}$	partition coefficient corrected for the crystallinity
$M_1$	molecular weight of the solvent
$N$	total number of components
$\bar{P}$	reduced pressure
$P_1^s$	vapor pressure of the solvent
$q$	surface area parameter
$r$	number of segments in polymer molecule
$R$	universal gas constant
$\bar{T}$	reduced temperature
$T_m$	melting point of the crystalline polymer
$\bar{v}$	reduced volume
$V_g$	retention volume
$V_g^e$	estimated retention volume in the amorphous polymer
$V_i$	molar volume of component $i$
$x_i$	molar fraction of component $i$
$z$	lattice coordination number (10)

## Greek letters

$\theta$	surface area fraction of the mixture
$\mu_i^a$	chemical potential of component $i$ in the amorphous phase
$\mu_2^c$	chemical potential of the polymer in crystalline phase
$\mu_i^{el}$	chemical potential of component $i$ taking into account the elastic constraints
$\mu_i^m$	chemical potential of component $i$ without the effect of the constraints of the chains
$\mu_i^v$	chemical potential of component $i$ in the vapor phase
$\rho_a, \rho_2$	density of the amorphous phase of the polymer
$\phi_a$	volumetric fraction of the amorphous phase of the polymer
$\phi_i$	volumetric fraction of component $i$
$\phi_i^{fv}$	volumetric fraction for component $i$ with respect to the free-volume property
$\phi_i^h$	volumetric fraction for component $i$ with respect to the hardcore molecular property
$\chi$	Flory–Huggins interaction parameter
$\omega_i$	weight fraction for component $i$
$\Omega_1^\infty$	solvent weight fraction activity coefficient at infinite dilution
$\Omega_i$	weight fraction activity coefficient of component $i$

## Subscripts

1	solvent
2	polymer

## Superscripts

$a$	amorphous phase
$c$	combinatorial
$el$	elastic
$fv$	free-volume
$r$	residual
$v$	vapor phase

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