

# The analysis of sorption data of organic vapors in polymeric membranes through novel theories

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## Abstract

Analysis of sorption data of hydrocarbon vapors in polyethylene and polypropylene films using Flory–Huggins, UNIFAC, Michael–Hausslein and Flory–Rehner theories are presented. Basically two models are used, one deduced with UNIFAC and Michael–Hausslein (UNIFAC-M-H) approach and the other with UNIFAC and Flory–Rehner (UNIFAC-F-R) theory. Prediction of penetrant activity values through these theories fit quite well the experimental results with errors ranging between 4.7 and 10.8%. The mean arithmetic values of the fraction of elastically effective chain in the amorphous region are  $f=0.4915$  and  $f=0.3354$  for polypropylene (PP) and polyethylene (PE), respectively. The experimental results with polypropylene are correlated, establishing a unique expression to predict solubility and solubility coefficient. The dependence of solubility in polypropylene over the whole range of temperature it is also presented.

*Keywords:* Vapors solubility; Penetrant activity; Polyethylene; Polypropylene; Thermodynamics; Hydrocarbons

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## 1. Introduction

Gas and vapor solubility predictions are becoming increasingly important, for designing purposes, in many operations such as separation and packaging and also for separative membrane characterization. The Flory–Huggins [1] theory was mostly used in the past. The resulting expression, to predict solubilities of gases and vapors, is based on two main contributions. The lattice model to account for the mixing entropy and the introduction of the parameter  $\chi$  to take into account the mixing enthalpic effect. Although the Flory–Huggins [1] model was widely used, its main recognized drawback results in the strong temperature and penetrant concentration dependence on the parameter  $\chi$ . As a whole, the experimental results can only be fitted with

the introduction of at least two adjustable parameters for each set of penetrant–polymer system.

Group contribution models have been successfully applied to predict activity coefficients in solutions. Oishi and Prausnitz [2] extended the UNIFAC procedure (Fredenslund et al. [3]) to polymer solutions finding fairly accurate results. By correcting the UNIFAC predictions with the free-volume concept (UNIFAC-FV model) they were able to produce activity coefficient estimates with maximum deviations, in regards with experimental findings, below 10%. The main advantage of Oishi and Prausnitz [2] procedure is that no experimental information of the solvent–polymer mixture is required to perform activity predictions.

Another interesting model results by applying Hildebrand regular solution theory in conjunction with

Flory–Huggins [1] model. In this particular case, the interaction parameter  $\chi$  becomes closely related to the well-known solubility parameters. From this point of view, also with this combined model, no experimental information is required to produce predictions. However the validity of the produced results will rely on the validity of the regular solution behavior when compared with the actual penetrant–polymer system. Nevertheless, solubility parameters of ordinary polymers can be easily estimated (Barton [4]) or either calculated through group contribution methods (van Krevelen and Hoftyzer [5]).

Nowadays, however, it is widely recognized that these theoretical models are only truly applicable to amorphous polymers. Even if the crystalline region of the polymer is not accessible to penetrant, the sorption phenomena will be affected by the presence of these rigid zones located within the polymeric network. Recently, Doong and Ho [6] were able to construct a novel model in which this effect is taken into account. They assumed that the resulting free energy of mixing is a combined result of four different types of interactions. The so called combinatorial entropy factor which takes into account the great differences in size and shape of the two molecules. The free-volume factor that accounts for the different liquid structure between penetrant and polymer. The interactional enthalpy factor to include the heat of mixing contribution to the free energy. The fourth interaction is the elastic effect to account for the additional elastic free energy contribution, caused by the restriction imposed by crystalline regions in the swelling or shrinking of the amorphous phase. The first three contributions can be estimated theoretically, while the fourth need the knowledge of an unknown parameter. Doong and Ho [6] have shown that two models can be used to predict the so-called elastic interaction. The first one is due to Roger et al [7,8], based on Flory–Rehner theory, which introduces an unknown parameter that should be characteristic of the polymer since it is related to the mean molecular weight of the chains between two crystallites in the polymer. The second one is based on Michaels and Hausslein [9] theory in which, also, an undetermined parameter, characteristic of the polymer, has to be found through experimental measurements. This parameter  $f$  has the meaning of the elastically effective chains in the amorphous fraction in which the sorption phenomena take place.

Doong and Ho [6] used their own experimental sorption data of benzenic hydrocarbons in polyethylene (PE) and also previous results of Castro et al. [10] to conclude that Michaels and Hausslein [9] model produces more reliable estimates of the penetrant activities than the corresponding one derived from Flory–Rehner theory. This last model was not able to predict the experimental activity temperature dependence.

In this contribution our previous results (Castro et al., [10]) of paraffin sorption in PE and new findings of *n*-pentane and *n*-hexane vapor solubilities in polypropylene (PP) will be used to discuss the main conclusions of Doong and Ho [6]. Since PP structure has a greater degree of crystallinity than the corresponding PE polymer it should be expected that the restriction imposed in the model by the crystalline region would enhance the elastic effects on solubility predictions. A comparison among results obtained with different models will also be discussed to increase the knowledge on the behavior of Doong and Ho [6] proposed model.

## 2. Theoretical models

A detailed discussion of the novel models can be seen elsewhere [6]. Basically the activity of the penetrant,  $a_1$ , can be predicted using the following expression:

$$\ln a_1 = \ln a_{1c} + \ln a_{1fv} + \ln a_{1inte} + \ln a_{1el} \quad (1)$$

where the subindexes *c*, *fv*, *inte* and *el* are to denote the combinatorial, free volume, interactional and elastic contributions. The first three factors are similar to the Oishi and Prausnitz [2] model deduced from UNIFAC-FV concepts. The last contribution is to account for the effect of restrain in the swelling phenomena caused by the crystalline regions located within the polymeric network. Thus the following expressions were used:

$$\ln a_{1c} = \ln \phi'_1 + (1 - \phi'_1) \quad (2)$$

where  $\phi'_1$  denotes the segment weight fraction of the penetrant in the mixture. As discussed by Doong and Ho [6] expression (2) predicts values of  $a_{1c}$  in close agreement with the more complex expression deduced with UNIFAC method. In our calculations this statement was confirmed.

Free-volume contribution can be estimated as follows:

$$\ln a_{fv} = 3C_1 \ln \left[ \frac{\bar{V}_1^{1/3} - 1}{\bar{V}_m^{1/3} - 1} \right] - C_1 \left[ \left( \frac{\bar{V}_1}{\bar{V}_m} - 1 \right) \left( 1 - \frac{1}{\bar{V}_1^{1/3}} \right)^{-1} \right] \quad (3)$$

where:

$$\bar{V}_m = V_m \left[ \frac{W_1}{V_1^*} + \frac{W_2}{V_2^*} \right] \quad (4)$$

$$\bar{V}_1 = \frac{V_1}{V_1^*}, \bar{V}_m = \frac{V_m}{V_m^*} \quad (5)$$

$V_1^*$  and  $V_2^*$  denote specific hard-core volumes for penetrant and polymer respectively,  $w_1$  and  $w_2$  the weight fractions for penetrant and polymer respectively and  $V_1$  the specific volume for penetrant.  $C_1$  is a constant taken equal to 1.1, with carbon numbers 4–10, after Oishi and Prausnitz [2].

The interactional contribution can be estimated from the following expression:

$$\ln a_{inte} = \sum_k \nu_{1k} (\ln \Gamma_k - \ln \Gamma_{1k}) \quad (6)$$

where  $\nu_{1k}$  is the number of group  $k$  in the penetrant molecule and  $\Gamma_k$  and  $\Gamma_{1k}$  the interactional activities of group  $k$  in the penetrant–polymer mixture and of group  $k$  in the pure penetrant compound, respectively. The values of  $\ln \Gamma_k$  and  $\ln \Gamma_{1k}$  can be calculated from UNIQUAC equations and data bank coefficients. A second approach based on Hildebrand's regular solution theory could be used but will not be considered here since it was already shown [6] that the resulting expression is not able to fit experimental findings in the whole range of penetrant activities, suggesting that regular solution rules are not fully obeyed by these systems.

Finally there are two alternative models to predict the effect of crystalline region restrains on the amorphous sorbing zones within the polymeric membrane network. The first one is due to Michaels and Hausslein [9] who, by assuming Hookean like behavior to account for the force elongation phenomena of the chain polymer segments, deduced the following expression:

$$\ln a_{el} = \frac{\left[ \frac{M_1 \rho_a}{\rho_1} \frac{\Delta H_M}{R} \left( \frac{1}{T} - \frac{1}{T_M} \right) - (\phi_1 - \chi \phi_1^2) \right]}{\left[ \frac{3}{2f\phi_2} - 1 \right]} \quad (7)$$

$\Delta H_M$  denotes the polymer melting change of enthalpy.  $T$  the absolute temperature and  $\phi$  the volume measured fraction. Subindexes 1 and 2 stand for penetrant and polymer repeating unit species and  $M$  for identifying the melting point. The Flory parameter  $\chi$  can be approximately calculated following Flory–Huggins [1] theory:

$$\chi = \frac{(\ln a_{inte} + \ln a_{fv})}{\phi_2^2} \quad (8)$$

It should be noticed that the unknown parameter  $f$  has been defined as the fraction of elastic effective chains in the amorphous region.

The second alternative model is derived from the early Flory–Rehner theory of swelling of cross-linked polymers. Roger et al. [7,8] applied the theory to semicrystalline polymers like PE and PP. Their expression is:

$$\ln a_{el} = \left( \frac{\rho_a M_1}{\rho_1 M_c} \right) \phi_2^{1/3} \quad (9)$$

$\rho_a$  being the density of the amorphous phase of the polymer,  $\rho_1$  the penetrant density,  $M_1$  molecular weight of penetrant and  $M_c$  the molecular weight of the chain between two crystallites.

In all cases experimental results were used to estimate, with each data point, values of  $f$  or  $M_c$ . Then a linear average was taken and this resulting mean value, of  $f$  or  $M_c$ , used to correlate all the experimental results. Finally a mean average error was calculated in order to compare the ability of each model in fitting experimental findings.

### 3. Experimental

#### 3.1. Materials

Low density polyethylene (PE) and polypropylene (PP) films were used in this study. Both had a thickness of 25  $\mu\text{m}$ . The density of PE and PP at 30°C, were

0.9157 and 0.9030 g/cm<sup>3</sup>, respectively. They were determined by pycnometry according to the ASTM D 792-66 method. The volume fraction of amorphous polymer of PE was calculated as  $\alpha=0.57$  at 30°C. It was estimated from the density measurement assuming crystalline- and amorphous-phase specific volumes of 1.003 and 1.171 cm<sup>3</sup>/g, respectively, according to the expression given by Michaels and Bixler [11]. The resulting value of  $\alpha$  for PP was 0.31 assuming that the densities of crystalline and amorphous phases are 0.935 and 0.854 g/cm<sup>3</sup>, according to Lee and Rutherford [12]. The nominal average molecular weight was  $M_n=24\,900$  g/mol for the PE and  $M_n=52\,000$  g/mol for the PP, as determined by GPC chromatography.

Four saturated hydrocarbons were used as penetrants. They were chromatograph quality (Merck) *n*-pentane, *n*-hexane and *n*-heptane. These compounds were used as provided, while 98% *n*-butane was dried before use.

### 3.2. Apparatus and procedure

In the gravimetric sorption apparatus, a Cahn RG high vacuum electrobalance was used to monitor weight changes. More details about the apparatus used and the experimental procedure to obtain solubilities of hydrocarbon vapors have been described elsewhere [10].

## 4. Results and discussion

### 4.1. Isotherms

The absorption data obtained with the different hydrocarbon in PE were shown elsewhere [10]. In this work results obtained with PP are presented. All the data with PE and PP will be analyzed with the described novel theory. Absorption isotherms for *n*-hexane and *n*-pentane in PP are shown in Figs. 1 and 2. As can be seen the solubility depends on temperature and, almost linearly, on pressure. Thus, the solubility coefficient of each hydrocarbons in PP is independent on pressure, showing a remarkable difference with the behavior in PE [10].

In Figs. 3 and 4 experimental solubility data points as a function of relative pressure ( $P/P^0$ ) are shown. Although solubility points are slightly inverted with

respect to temperature, all the experimental data can be well correlated by a single curve that reveals that the heat of mixing is almost negligible. This being another remarkable difference in regards with the observed behavior with PE [10].

### 4.2. Temperature dependence of solubility in PP

As shown in Fig. 5, the temperature dependence of *n*-pentane solubility in PP, over the whole range of temperatures studied, obeys the Arrhenius law:

$$S = S' \exp(-B/T) \quad (10)$$

$B$  and  $S'$  being specific constants for each hydrocarbon,  $\Delta H_s$  (cal/mol) =  $B$ .  $R$ , the apparent heat of solution and  $R$  the universal gas constant. Values of  $B$  for *n*-pentane and *n*-hexane are 3293 and 3694 (1/K), respectively. This apparent heat of solution is found to be insensitive to total penetrant pressure.

Since the heat of mixing is negligible, by considering that in the sorption process the penetrant vapor is first

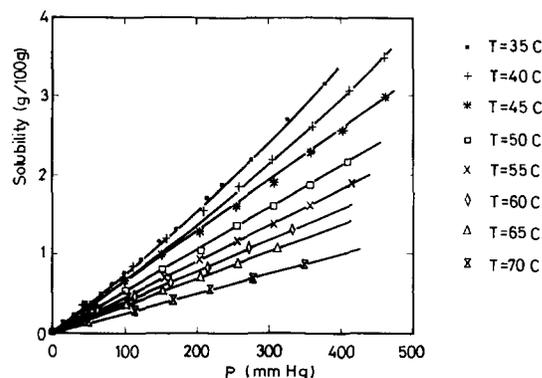


Fig. 1. *n*-Pentane sorption isotherms in PP.

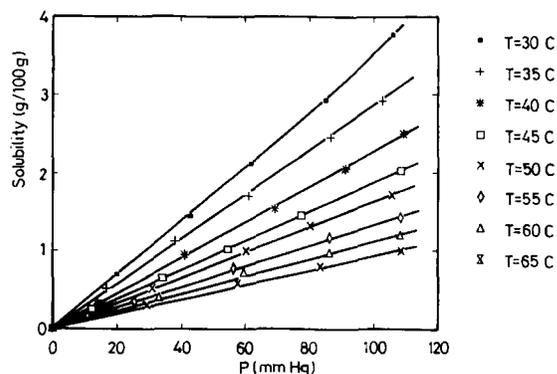


Fig. 2. *n*-Hexane sorption isotherms in PP.

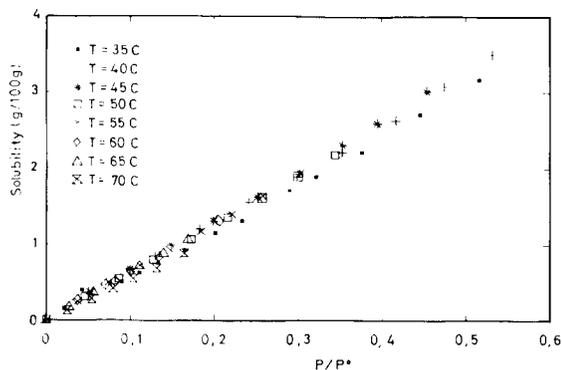


Fig. 3. Solubility of *n*-pentane in PP at various temperatures as a function of the relative pressure.

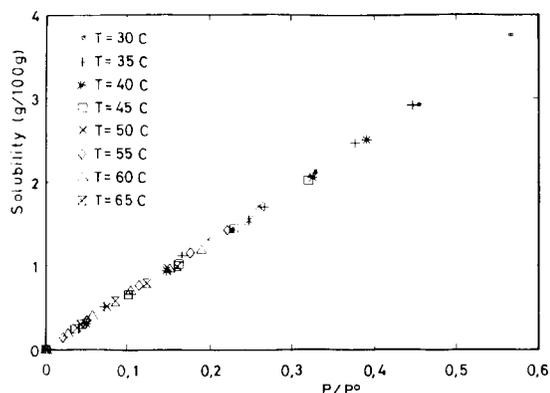


Fig. 4. Solubility of *n*-hexane in PP as a function of the relative pressure at different temperatures.

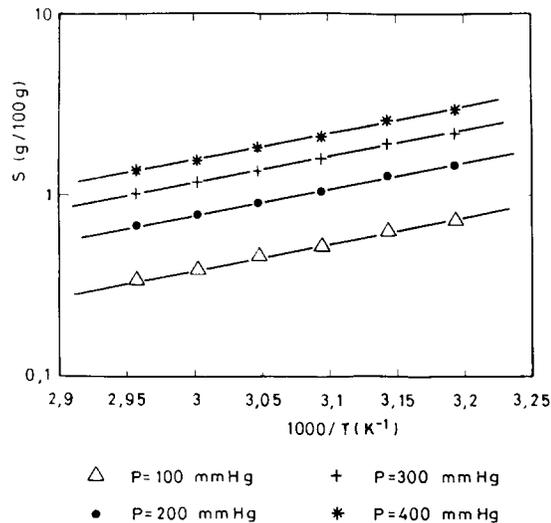


Fig. 5. Effect of temperature on pentane solubility in PP.

condensed on the polymer surface and is then solubilized, the apparent heat of solution should be equal to

the heat of condensation. In fact, with the values of  $B$  given above,  $(-\Delta H_{\text{cond}}) = 6520$  and  $7314$  (cal/g mol) are calculated for *n*-pentane and *n*-hexane, respectively. These figures compare fairly well with tabulated values for the same species  $[(-\Delta H_{\text{cond}}) = 6005$  and  $7250$  (cal/g mol)] within the same range of temperature.

#### 4.3. Solubility in PP

With the aim of predicting the molar solubility per gram of total polymer ( $S^\circ$ ), for each penetrant, experimental  $S^\circ$  values were plotted vs. penetrant activity on a log–log scale (Fig. 6). The fugacity of pure solvent, at each experimental temperature, was taken as the standard state for activity ( $a_1$ ) calculations and the fugacity coefficients were calculated with the Redlich–Kwong equation of state.

The resulting correlation expressions is:

$$S^\circ \text{ (mol/g)} = (8.01 \pm 0.62) \times 10^{-4} a_1^{(0.99 \pm 0.01)} \quad (11)$$

being unique and valid for all hydrocarbons with a regression coefficient of 0.9895 and a confidence level of 95%.

#### 4.4. Solubility coefficient in PP

Since the solubility in PP is shown to depend linearly on pressure, the solubility coefficient ( $K_{s^\circ}$ ) will only be a function of  $T$  and the nature of the penetrant. Thus, as shown by Castro et al. [10] a simple empirical

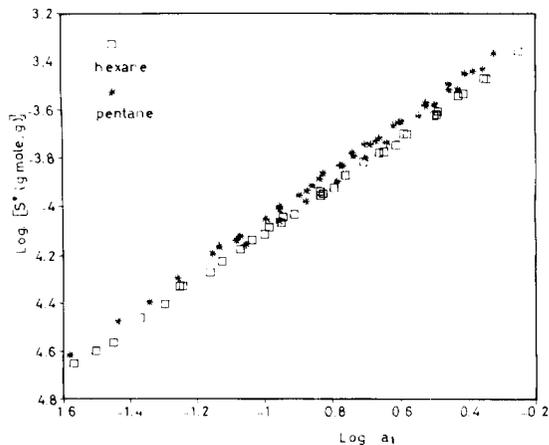


Fig. 6. Effect of activity on molar solubility.

Table 1  
Comparison of activity data with theoretical predictions

Solubility data	Error <sup>a</sup> (%)			
	Polyethylene		Polypropylene	
	UNIFAC-M-H $f=0.3354$	UNIFAC-F-R $M_c=106.33$	UNIFAC-M-H $f=0.4915$	UNIFAC-F-R $M_c=124.15$
<i>n</i> -Butane	6.07	9.56		
<i>n</i> -Pentane	6.02	7.13	7.43	7.09
<i>n</i> -Hexane	5.09	7.73	8.29	9.20
<i>n</i> -Heptane	4.69	10.80		

<sup>a</sup> Error =  $\{ (1/n) \sum_i [\text{calculated activity value} - \text{experimental activity value}]^2 / (\text{experimental activity value}) \}^{1/2}$ .

expression can be found to correlate all experimental results:

$$\log K_*^\circ = (-3.203 - 0.050 M_1) + (0.108 + 0.036 M_1) T_r^{-1} \quad (12)$$

$T_r$  being the reduced temperature ( $T/T_c$ ). When this expression is used to predict  $K_*^\circ$  for other hydrocarbons, the extrapolated results are in fair agreement with reported values [13] and [14]. Also, Eq. (12) can be used, as shown by Castro et al. [15], to estimate the solubility of liquid hydrocarbons in PP.

## 5. Comparison of experimental data with predictions

All experimental results obtained from data sorption in PE [10] and those presented here for PP were analyzed in the light of the novel models proposed by Doong and Ho [6]. Basically only two models will be used in this contribution. The first one is that deduced with UNIFAC and Michaels and Hausslein [9] approach and will be identified as UNIFAC-M-H (see Table 1). The second one as UNIFAC-F-R deduced following Flory–Rehner model. In Table 1 the main activity percentile error is presented for each penetrant both in PE and in PP experiments. Mean arithmetic values of  $f$  and  $M_c$  are reported.

As can be seen from our calculations none of the two models can be disregarded since the figures of main error are similar. However as reported by Doong and Ho [6] the UNIFAC-F-R is not able to reproduce the activity temperature dependence of penetrants in PE. From this point of view one is inclined to recommend

the UNIFAC-M-H model. However the situation is exactly the opposite when sorption data in PP are analyzed. In this case, again, mean errors are of the same order of magnitude but as UNIFAC-F-R model predicts a negligible temperature dependence on penetrant activity, in accordance with experimental observation, while the UNIFAC-M-H model predicts an endothermic heat of mixing.

At first sight, it is surprising a value of  $f=0.4915$  for PP and  $f=0.3354$  for PE since one would have expected exactly the opposite since, the crystalline fraction of PP is greater than that for PE. However it must be stressed that  $f$  does not solely depend on the crystalline fraction but also on the nature of the amorphous chain units. These, according to the model, are much more effective in PP than the corresponding chains in PE.

The discrepancy, between our numerical figures and those reported by Doong and Ho [6] with our previous results [10], is possibly because they had to read our experimental data from the graphics. On the other hand, the value of  $f=0.3354$  is now in the range proposed by Michaels and Hausslein [9].

## 6. Conclusions

New experimental sorption experiments of hydrocarbons in PP are reported. It is shown that penetrant–PP behavior is remarkably different from that of penetrant–PE. Solubility coefficient for hydrocarbon. PP are independent of pressure and only related to the reduced pressure and molecular weight of penetrant. Another remarkable difference is that the heat of mixing for penetrant–PP system is very small and negli-

gible in comparison with the heat of vaporization.

When previous (PE) and new (PP) experimental solubility and activity data are analyzed in the light of novel models it is shown that UNIFAC technique in conjunction with Flory–Rehner and Michael–Haus-slein model result in a powerful tool to predict solubilities of pure compounds and also their mixtures.

Although mean errors of the same order of magnitude are found with any of two models it is shown that UNIFAC-M-H model is best for PE and UNIFAC-F-R model is best for PP data behavior, respectively. The first model always predicts endothermic heat of mixing that are not negligible in comparison with heat of vaporization while the second predicts almost no temperature dependence on activity and very small exothermic heat of mixing estimates.

## 7. List of symbols

$a_1$	penetrant activity
$a_{1c}$	penetrant activity from combinatorial contribution
$a_{1fv}$	penetrant activity from free-volume contribution
$a_{1intc}$	penetrant activity from interactional contribution
$a_{1el}$	penetrant activity from elastic contribution
$f$	fraction of elastically effective chains in the amorphous region
$\Delta H_2$	specific heat of fusion for crystalline polymer (cal/g)
$\Delta H_s$	apparent heat of solution (cal/mol)
$\Delta H_{cond}$	heat of condensation (cal/mol)
$M_1$	molecular weight of penetrant (g/mol)
$M_n$	nominal average molecular weight of polymer (g/mol)
$p/p^0$	relative pressure of penetrant
$R$	gas constant
$T$	absolute temperature (K)
$T_M$	melting point of crystalline polymer (K)
$T_r$	reduced temperature
$V_1$	specific volume of penetrant (cm <sup>3</sup> /g)
$V_2$	specific volume of polymer (cm <sup>3</sup> /g)
$V_m$	specific volume of penetrant–polymer mixture (cm <sup>3</sup> /g)

$V_1^*$	specific hard-core volume of penetrant (cm <sup>3</sup> /g)
$V_2^*$	specific hard-core volume of polymer (cm <sup>3</sup> /g)
$V_m^*$	specific hard-core volume of penetrant–polymer mixture (m <sup>3</sup> /g)
$\bar{V}$	reduced specific volume, $V/V^*$ [see Eqs. (4) and (5)]
$w_2$	weight fraction of polymer
$w_1$	weight fraction of penetrant
$B$ and $S'$	constants in Eq. (10)
$S$	solubility (g penetrant/100 g polymer)
$S^0$	molar solubility per gram of polymer (mol/g)
$K^0$	solubility coefficient (mol/g amorphous polymer atm)

### 7.1. Greek symbols

$\alpha$	volume fraction of amorphous polymer
$\Gamma_k$	interactional activity of functional group k in penetrant–polymer mixture
$\Gamma_{1k}$	interactional activity of functional group k in penetrant
$\nu_{1k}$	number of functional group k in penetrant
$\rho$	density (g/cm <sup>3</sup> )
$\chi$	Flory–Huggins interaction parameter
$\phi_i$	volume fraction of component i in mixture
$\phi_i'$	segment weight fraction of component i in mixture

### 7.2. Subscripts

1	penetrant
2	polymer
i	component
a	amorphous
m	penetrant–polymer mixture
k	functional group

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