An off-lattice Flory-Huggins approach of the partitioning of bulky solutes between polymers and interacting liquids

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An off-lattice Flory-Huggins approach of the partitioning of bulky solutes between polymers and interacting liquids

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Abstract

The desorption of additives and polymer residues from materials (P) is of significant concern for a wide range applications, including polymer ageing, off-odors, safety of materials in contact with food or water... With diffusion coefficients, partition coefficients between P and hydrogen-bonding liquids (L), denoted $K_{i,L/P}$ for a solute i, are fundamental quantities to assess the loss of plastics constituents. For a polymer with a crystallinity c, they are defined as $\ln(K_{i,L/P}) - \ln(1-c) = (\mu_{exi,P} - \mu_{exi,L})/(kBT)$, where $\{\mu_{exi,k}\}k=L,P$ are the excess chemical potentials and where $kB$ is the Boltzmann constant. Our ambition was to relate calculations of $\{\mu_{exi,k}\}k=L,P$ at atomistic scale to measurable partition coefficients obtained for bulky solutes with different stiffness and shape, such as hindered phenolic antioxidants, $n$-alkanes and $n$-alcohols. For large solutes in dense and cohesive phases (P or L), promising computation techniques involve free energy perturbation and non-equilibrium methods, thermodynamic integration, extended ensembles (Gibbs or osmotic ensembles). Because the free energy landscape of the coupled i+k system contains several minima and highly heterogeneous barriers, a low convergence is generally achieved. To overcome such complications, we calculated $\{\mu_{exi,k}\}k=L,P$ at atomistic scale in the framework of the Flory-Huggins approximation. The main advantage is that the mixing energy for a wide range of conformers was derived from pairwise interactions and a continuous approximation of the packing of molecules without representing explicitly large molecular systems. The translational entropy in L was inferred from a mesoscopic representation of the liquid medium matching the radial distributions calculated by isothermal and isobaric molecular dynamics simulations. The corresponding predictions were satisfactory compared with 38 experimental $K_{i,L/P}$ values between polyethylenes, polystyrene and different alcohols (isopropanol, ethanol).
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Abstract

The desorption of additives and polymer residues from materials (P) is of significant concern for a wide range of applications, including polymer ageing, off-odors, safety of materials in contact with food or water, etc. With diffusion coefficients, partition coefficients between P and hydrogen-bonding liquids (L), denoted $K_{i,L/P}$ for a solute $i$, are fundamental quantities to assess the loss of plastics constituents. For a polymer with a crystallinity $c$, they are defined as

$$\ln(K_{i,L/P}) - \ln(1-c) = \left( \mu_{i,P}^{\text{excess}} - \mu_{i,L}^{\text{excess}} \right)/(k_B T),$$

where $\{\mu_{i,k}^{\text{excess}}\}_{k=L,P}$ are the excess chemical potentials and where $k_B$ is the Boltzmann constant. Our ambition was to relate calculations of $\{\mu_{i,k}^{\text{excess}}\}_{k=L,P}$ at atomistic scale to measurable partition coefficients obtained for bulky solutes with different stiffness and shape, such as hindered phenolic antioxidants, n-alkanes and n-alcohols. For large solutes in dense and cohesive phases (P or L), promising computation techniques involve free energy perturbation and non-equilibrium methods, thermodynamic integration, extended ensembles (Gibbs or osmotic ensembles). Because the free energy landscape of the coupled $i+k$ system contains several minima and highly heterogeneous barriers, a low convergence is generally achieved. To overcome such complications, we calculated $\{\mu_{i,k}^{\text{excess}}\}_{k=L,P}$ at atomistic scale in the framework of the Flory-Huggins approximation. The main advantage is that the mixing energy for a wide range of conformers was derived from pairwise interactions and a continuous approximation of the packing of molecules without representing explicitly large molecular systems. The translational entropy in L was inferred from a mesoscopic representation of the liquid medium matching the radial distributions calculated by isothermal and isobaric molecular dynamics simulations. The corresponding predictions were satisfactory compared with 38 experimental $K_{i,L/P}$ values between polyethylenes, polystyrene and different alcohols (isopropanol, ethanol).
1. Introduction

The increasing concern for environmental and health issues raises the need of predictive approaches to assess chemical risks along the food and feed chain. To stimulate the innovation of products with enhanced safety, models are particularly required in areas covered by new or reinforced regulations, including the new EU chemicals legislation REACH (European Community (2006)). Our contribution is focused on the development of a combination of decision tools and predictive approaches of the contamination of food products and drinking water by synthetic materials in contact. This effort follows the recently-enforced EU general framework regulation 1935/2004/EC (European Community (2004)), which imposes risk assessment and risk management decisions for any new substance not belonging to a previous positive list. The current picture is becoming all the more complex than new practices, including the misuse of recycled materials (Begley et al. (2002)) for food contact applications or possible interactions with the process (Grob et al. (2006), Franz et al., (2004)), may lead to the migration of non-intentionally added substances. A general modeling framework based on probabilistic modeling (Vitrac and Hayert (2005)) or intervals (Vitrac and Hayert (2007)) has been proposed by us for monolayer and multilayer materials respectively. It has been applied to assess the contamination of food products ready on the market (Gillet et al. (2009a)) and to estimate consumer exposure (Vitrac et al. (2007a)). Reducing uncertainty in predicted contamination values and ingested amounts require accurate estimate of diffusion coefficients in polymers and partition coefficients, denoted $K_{i,L/P}$, between polymers, denoted $P$, and main food constituents or food simulants, denoted $L$. Whereas a significant amount of diffusion coefficients have been collected (Begley et al. (2005)) and modeled (Vitrac et al. (2006)), a much less effort has been done to assess and predict partitioning for bulky plastics additives, such as polymeric antioxidants, light stabilizers, photoinitiators and pigments. In particular, no solubility value for these large substances in either $P$ or liquids have been reported in publicly available databases, which are mainly focused on smaller solutes and waste waters, such as the IUPAC-NIST Solubility Database (NIST (2009)).

A first significant attempt for predicting partitioning between alcohols and polyethylene for volatile compounds and linear alkanes, based on solubility coefficients in $P$ and on regular solution theory in $L$, was described in (Baner and Piringer (1991)) but it required an adjustable parameter, which was shown to vary with the size and shape of the considered solute. Besides, the effect of crystallinity between different polyethylenes was neglected. Recently, we proposed a tailored method combining a generic ab-initio atomistic forcefield and a Flory-Huggins (FH) approximation of interactions to predict excess chemical
potentials in amorphous regions of polyethylene and in $L$ for a wide range of solutes and food simulants including several alcohols and water (Gillet et al. (2009b and 2009c)). The starting point was to notice that a large asymmetric discrepancy, on one hand, between the sizes of solute $i$ and $P$ molecules and, on the other hand, between the sizes of solute $i$ and $L$ molecules, occurred. As a result, the positional entropy was guessed to spread significantly potential energies when solute $i$ was inserted among $P$ or $L$ molecules. The direct sampling of highly dispersed potential energies of solutes much larger than voids among many other molecules by particle insertion (Widom (1963)) or deletion (Boulougouris et al. (2001)) methods is currently not tractable with tailored methods (Hess et al. (2008), Özal et al. (2008)). To avoid cumbersome explicit calculations of many-molecules interactions, excess chemical potentials were derived from pair contact energies within the framework of an off-lattice FH approximation (Bawendi et al. (1986, 1987 and 1988)). Contact energies were calculated at atomistic scale by putting in contact van-der-Waals surfaces for all combinations of pair molecules for a representative set of conformers in $P$ and in $L$. The number of neighbors was determined independently from a random sampling of molecules packing. Limitations to describe cooperative hydrogen bonding in water, inherent to the original FH approximation involving only interactions between pairs, have been surmounted naturally by incorporating a geometrical model of long-lived hydrogen bonds (Gillet et al. (2009c)). As a first guess, translational entropies in both $P$ and $L$ were derived assuming that all species pervade space respectively to their size while mutually excluding one another (Gillet et al. (2009b)). Two deviations were however identified in $L$ from molecular dynamics (MD) simulations performed at constant temperature and pressure (Gillet et al. (2009c)): i) a mainly positive excess volume in mixtures with polar simulants due to a local modification of hydrogen bonding network around each solute and ii) a partial overlap between $L$ molecules and large alkyl-chains, which reduces their dispersion in $L$. Neglecting previous effects reduce causes a loss of accuracy for large molecules.

The objective of this work is to provide a general framework to predict $K_{iL/P}$ with tailored computational methods for bulky plastics additives, combining one or many hindered rigid patterns with possibly flexible regions. Hence such appealing analyses should be directly applicable to predict the lifetime of formulated industrial materials and to predict the contamination of food products by ubiquitous antioxidants. The complication in developing a multiscale methodology, from atoms to solute scale, arises from the absence of resemblance between rigid patterns and $L$ molecules or with $P$ monomers. Due to a lack of general theory, the optimal length scale of polymer segments to calculate optimally the pair interactions with $P$ remains in particular unknown as well as the contribution of excluded volumes on positional entropy. These effects were
specifically studied by comparing experimentally and calculated $K_{i,L/P}$ for two linear polymers, a rubber semi-crystalline polymer (high density polyethylene) and a glassy amorphous polymer (atactic polystyrene), and by calculating explicitly the radial distributions of alcohols around typical plastics additives from isobaric MD simulations.

2. Theory

This section deals with the most important assumptions to predict excess chemical potentials in binary mixtures, $i+P$ and $i+L$, consisting in species with dissimilar sizes and subsequently partitioning between a polymer and a liquid. The interested reader can find additional details in (Gillet et al. (2009b and 2009c)).

2.1 A scalable representation of $i+P$ and $i+L$ interactions

The central idea is to obtain a scalable off-lattice representation of molecular interactions, which preserves the most relevant features of quantities, namely enthalpic and entropic contributions, involved in mixture thermodynamics while pursuing computational efficiency. It is worth to notice that several refinements and sophistications at atomistic scale were motivated by the general discussion initiated by Hansen (2007) on the limitations of common semi-empirical techniques, based on group contributions, to derive excess mixing enthalpies. This choice is illustrated in Fig. 1.
Figure 1. Mapping of $i-L$ molecule interactions from atomistic scale, as calculated from molecular dynamics simulation, up to solute scale. The main view is oriented along the principal solute axes. Only $L$ molecules belonging to the slice containing the solute are represented.

The depicted approach differs from concurrent techniques reviewed in (Letcher (2007)) including Gibbs ensemble Monte Carlo (Panagiotopoulos (1992)), Thermodynamic Integration (Kirkwood (1935), van der Vegt et al.
(1998)) and Free Energy Perturbation techniques (Hess et al. (2008), Özal et al. (2008)), which involve an explicit representation of many molecules at atomistic scale. Indeed, only interactions between pair were described at atomistic scale. Hence the number of atoms increases linearly as the size of considered molecules and calculations can be performed without applying any cutoff to intramolecular and intermolecular potentials. An additional advantage arises from the ability to calculate configuration-dependent quantities and to average them over all spatial configurations and conformations of each molecule. Appropriate statistical weighting of intermolecular energies with temperature keeps the overall consistency of the sampling procedure even if individual configurations are derived from an arbitrary process free of constraints, e.g., independent of the considered condensed phase. Though the complexity is drastically reduced, this stage applied to all possible pairs accounts appropriately for the dispersion of short and long range atomistic interactions. Following the analogies to dilute solutions and gases, the distances between molecules do not need to be defined explicitly as soon as molecules are being put in contact. Hindrances between van-der-Waals surfaces were shown (Gillet et al. (2009c)) to be sufficient to reproduce the short-range effects of volume exclusion and attrition. For flexible solutes with sizes close or greater than their persistence length, conditions of poor solvent, in which solute fragments prefer self contacts over contacts with the solvent, are circumvented when solute conformers are derived from MD in the corresponding solvent.  

In our systems of interest, mixtures $i+L$ or $i+P$, are not constituted of equal-sized spherical molecules so that the excess entropy for each mixture is not zero at infinite solute dilution. This contribution can significantly counterbalance endothermic molecular interactions by increasing the number of accessible configurations to $L$ molecules or $P$ segments. As shown in the original Flory-Huggins theory (Flory, 1941 and 1942; Huggins, 1942$^a$ and 1942$^b$) from statistical mechanics grounds, the number of system micro-configurations per solute insertion does not depend on solute size in $P$, while the solute remains much smaller than polymer chains. By contrast, it is expected to be proportional to solute size when the continuous phase consists of smaller molecules. The proportionality coefficient may depend on the solute shape and flexibility (Gillet et al. (2009b)). Since the translational entropy in mixtures depends only on the arrangements of the positions of all center-of-masses, it can be calculated efficiently using a smoothed density or a mean field model involving lumped beads of size compatible with the solute volume, irrespectively to its true shape. Hence generalized Flory approximation treats molecules as equivalent fused hard spheres or beads (Honnell and Hall (1989)) comprising either an isometric portion, e.g. a polymer consists of connected spheres, or a collection of molecules. As local chemical details are lost for most of molecules, segments
overlap may be supposed rare and a given position is considered to be occupied by a single bead at a time. In liquids consisting of molecules much smaller than the solute, the previous idealization can be complicated by a modification of the local structure of the host medium close to the solute. It was thus demonstrated that hydrocarbon molecules are hydrated by energy-low and entropy-low bulky water structures (Mikheev et al. (2007)). When the density of liquid molecules fluctuates significantly close to the solute, the previous criterion of volume filling must be relaxed by envisioning soft solute beads, which can be partially overlapped by \( L \) molecules as if solute bead-\( L \) bead interactions were attractive at short distance. Such a coarse graining process can be consistently derived by mapping \( i-L \) pair distribution, i.e. spatial correlations, calculated at atomistic scale onto solute beads. The possible deviations between hard spheres and soft beads can be routinely corrected if they were assessed for homologous series of solutes and \( L \) molecules.

### 2.2 Excess chemical potentials

Excess chemical potential at infinite dilution for solute \( i \) in phase \( k \) was calculated according to the Flory-Huggins mean-field approximation, as detailed in Klenin (1999):

\[
\left\{ \frac{\mu_{i,k}^{\text{excess}}}{k_B T} \right\}_{k=P,L} = \left( 1 - \frac{1}{r_{i,k}} - n_{i,k}^{\text{overlapping}} \right) \cdot \phi_k + \chi_{i,k}^{(T)} \cdot \phi_k^2
\]

(1)

where \( k=P \) for the polymer amorphous region and \( k=L \) for the liquid food simulant. \( \phi_k \) denotes the volume fraction in beads of type \( k \) and was assumed to be close to unity at infinite dilution. \( \chi_{i,k} \) is the Flory-Huggins interaction coefficient, which value depends on absolute temperature \( T \). Physically, \( k_B T \chi_{i,k} \) presents the excess enthalpy of mixing, where \( k_B \) is the Boltzmann constant. In our approach depicted in Fig. 1, it includes also a non-positional entropic contribution, which arises from the dispersion of pair contact energies and fluctuation of packing. The mixture \( i+k \) is expected to be significantly endothermic (\( \chi_{i,k} > 0 \)) when the cavity for solute \( i \) absorbs energy to be created.

The term \( 1 - r_{i,k}^{-1} - n_{i,k}^{\text{overlapping}} \) represents the positional entropic contribution associated to the placement of molecules enclosed within volume commensurable to the solute volume. \( r_{i,k}^{-1} \) is the number of molecules \( k \) filling an isometric volume equal to the solute volume. Due to the high molecular mass of polymer chains, \( r_{i,k}^{-1} \) is consistently assumed close to 0 for \( k=P \). Our determinations (Gillet et al. (2009c)) of partial molar volumes from MD simulations in NPT ensemble showed
that the volume of the solute cavity in polar simulants could be reliably and efficiently estimated from the volume enclosed within the solute surface accessible to hydrogen atoms, regardless of the considered alcohol. The last term, $n_{k}^{overlapping}$, is zero for $k=P$ and is only significant in $L$ for bulky solutes, whose shape deviates from the sphere. It corrects the estimation of the entropic contribution by accounting for the average number of $L$ molecules overlapping the solute cavity due to a modification of the local structure of $L$. A typical configuration of $L$ molecules overlapping the solute cavity is reproduced in Fig. 1 from atomistic scale, where the particular configuration was calculated, up to the mesoscopic scale, where positional entropy is calculated. Since the positional entropy is calculated assuming isotropic exclusion-volume interactions (i.e. molecular shape details are lost), an intermediate scale depicts similar interactions, when ellipsoid-like particles are used instead. It is worth to notice that overlapping between $F$ and $i$ is not an artifact due to the coarse-graining process but an intrinsic property of $i$-$F$ arrangements at atomistic scale, which is lost at mesoscopic scale by the idealization of molecules as hard spheres.

2.3 Estimation of the Flory-Huggins coefficient

According to the Flory-Huggins theory (Flory (1941 and 1942), Huggins (1942a and 1942b)), the enthalpy of a mixture containing molecular species $A$ and $B$ is approximated as the product of the ensemble-averaged pair contact energies, denoted $\langle \varepsilon_{A+B} \rangle_T$, with the average number of $B$ molecules surrounding $A$, denoted $\langle z_{A+B} \rangle$, (or $A$ molecules surrounding $B$ denoted $\langle z_{B+A} \rangle$). Such a description leads to the following expression of the excess enthalpy of mixing:

$$
\frac{k_B T \chi_{ik}^{(2)}}{2} = \frac{\langle \varepsilon_{i+k} \rangle_T \langle z_{i+k} \rangle + \langle \varepsilon_{k+i} \rangle_T \langle z_{k+i} \rangle - \langle \varepsilon_{i+i} \rangle_T \langle z_{i+i} \rangle - \langle \varepsilon_{k+k} \rangle_T \langle z_{k+k} \rangle}{2}
$$

(2)

$\langle \rangle_T$ is the temperature ensemble average operator and is defined as:

$$
\langle \varepsilon_{A+B} \rangle_T = \frac{\int p_{A+B}(\varepsilon) e^{-\varepsilon/k_B T} \cdot \varepsilon \cdot d\varepsilon}{\int p_{A+B}(\varepsilon) e^{-\varepsilon/k_B T} \cdot d\varepsilon}
$$

(3)

where $p_{A+B}(\varepsilon)$ is the distribution of contact energies and $\exp(-\varepsilon/k_B T)$ is the corresponding Boltzmann factor.

2.4 Solute partitioning between two polymers

From previous considerations, the positional entropic contribution on excess chemical potential is not specific of the chemical nature of the polymer and consequently does not affect the macroscopic solute partitioning between two
polymers. By contrast, as the translation of large solute requires the relaxation of polymer segments (Mauritz (1990)), it is reasonable to assume that crystalline regions remain free of any solute. The macroscopic partition coefficient, \( K_{i;P_1/P_2}^{app} \), between two polymers \( P_1 \) and \( P_2 \) depends therefore on their volume fraction of crystalline phase, denoted \( c_1 \) and \( c_2 \), as:

\[
K_{i;P_1/P_2}^{app} = \frac{1 - c_1}{1 - c_2} \exp \left( \frac{\mu_{i,P_2}^{\text{excess}} - \mu_{i,P_1}^{\text{excess}}}{k_B T} \right) = \frac{1 - c_1}{1 - c_2} \exp \left( \chi_{i,P_2} - \chi_{i,P_1} \right) = \frac{1 - c_1}{1 - c_2} K_{i;P_1/P_2} \tag{4}
\]

Where \( K_{i;P_1/P_2} \) is the partition coefficient between amorphous regions of \( P_1 \) and \( P_2 \). It is worth to notice that \( K_{i;P_1/P_2}^{app} \) values can be experimentally determined without exchanging matter between \( P_1 \) and \( P_2 \) from two independent equilibriums between \( L \) and \( P_1 \) and between \( L \) and \( P_2 \):

\[
K_{i;P_1/P_2}^{app} = K_{i;L/P_1}^{app} / K_{i;L/P_2}^{app} \tag{5}
\]

### 2.5 Partitioning between \( L \) and \( P \)

Similarly partitioning between \( L \) and \( P \) is expressed as:

\[
K_{i;L/P}^{app} = \frac{1}{1 - c} \exp \left( \frac{\mu_{i,P}^{\text{excess}} - \mu_{i,L}^{\text{excess}}}{k_B T} \right)
= \frac{1}{1 - c} \exp \left( \chi_{i,P} - \chi_{i,L} + \nu_{i,L}^{-1} - \nu_{i,L} \right) = \frac{1}{1 - c} K_{i;L/P} \tag{6}
\]

### 3. Materials and Methods

#### 3.1 Partitioning data

Most of experimental \( K_{i;L/P} \) values between polyethylenes and ethanol 95% for bulk molecules were collected at 313 K from literature (Baner and Piringer (1991), Vitrac et al. (2007b)). The values are detailed in Gillet et al. (2009b). Additional partition coefficients for bulky molecules were experimentally assessed between high density polyethylene (HDPE) and ethanol, between polyethylene and isopropanol and between amorphous polystyrene (PS) and ethanol.

Virgin HDPE and atactic PS flakes, supplied from ATOCHEM (Paris, France), were formulated by additives during a first extrusion step according to specifications detailed in Table 1. Films were subsequently processed as 0.14 m wide, 0.3 mm thick ribbons. Both extrusions were performed at semi-industrial
scale at 200°C in a bi-screw extruder (model BC-21 Clextral, France). The density crystallinity of HDPE was determined by differential scanning calorimetry at 72.5%. The glass transition temperature of PS was assessed similarly at 90°C.

\( K_{L/P} \) values were derived by contacting at 313 K 100 cm³ of liquid with 10 cm³ of polymer cut in small pieces. Triethylphospite (Sigma-Aldrich, USA) was added to the liquid to prevent the oxidation of studied molecules. Contact times were up to 6 months for PS. Residual concentrations in \( P \) were determined after an extraction step in dichloromethane as described by Coulier et al. (2005). Residual polystyrene in dichloromethane was precipitated in isopropanol. All concentrations were assessed via High Performance Liquid Chromatography (Xterra C8 columnn Waters, USA) using an UV diode array detector or an evaporative light scattering detector. The protocol was similar to the one described by Garrido-López et al. (2005).

Partitioning of Chimassorb 81 between two incompatible polymers, polyethylene and polystyrene, was derived via Eq. (5) by putting in contact each formulated material with a series of liquid with increasing polarity: isopropanol, 95% ethanol, 75% ethanol, 50% ethanol. This protocol, well-suited for non-volatile solutes, led to different thermodynamical equilibriums with different residual concentration in \( P \) and made it possible therefore to check the linearity of the desorption isotherm in each polymer.
Table 1. Main characteristics of experimentally studied plastics additives

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Solute</th>
<th>CAS number</th>
<th>Chemical structure</th>
<th>Technological function</th>
<th>$V_{i}^{II}$ ($\text{Å}^3$)</th>
<th>Melting range ($^\circ$C)</th>
<th>Polymer</th>
<th>Concentration range (mg·kg$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A,D</td>
<td>Chimassorb</td>
<td>01843-05-6</td>
<td><img src="image" alt="Chemical structure" /></td>
<td>UV-stabilizer</td>
<td>$547 \pm 5$</td>
<td>48-49</td>
<td>HDPE/PS</td>
<td>3000-3500</td>
</tr>
<tr>
<td>B</td>
<td>Erucamide</td>
<td>00112-84-5</td>
<td><img src="image" alt="Chemical structure" /></td>
<td>Surface agent</td>
<td>$668 \pm 4$</td>
<td>79</td>
<td>HDPE</td>
<td>3000-3500</td>
</tr>
<tr>
<td>B</td>
<td>Irgafos 168</td>
<td>31570-04-4</td>
<td><img src="image" alt="Chemical structure" /></td>
<td>Hydroperoxide decomposer</td>
<td>$1074 \pm 9$</td>
<td>183-186</td>
<td>HDPE</td>
<td>2500-3000</td>
</tr>
<tr>
<td>I</td>
<td>Irganox 1035</td>
<td>41484-35-9</td>
<td><img src="image" alt="Chemical structure" /></td>
<td>Antioxidant</td>
<td>$1048 \pm 8$</td>
<td>63-78</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>B</td>
<td>Irganox 1076</td>
<td>2082-79-3</td>
<td><img src="image" alt="Chemical structure" /></td>
<td>Antioxidant</td>
<td>$984 \pm 7$</td>
<td>50-55$^e$</td>
<td>HDPE</td>
<td>500-1000</td>
</tr>
<tr>
<td>E</td>
<td>Irganox 245</td>
<td>36443-68-2</td>
<td><img src="image" alt="Chemical structure" /></td>
<td>Antioxidant</td>
<td>$958 \pm 5$</td>
<td>76-79</td>
<td>PS</td>
<td>300-500</td>
</tr>
<tr>
<td>C</td>
<td>Irganox 3114</td>
<td>27676-62-6</td>
<td><img src="image" alt="Chemical structure" /></td>
<td>Stabilizer</td>
<td>$1256 \pm 8$</td>
<td>218-223</td>
<td>/</td>
<td>300-500</td>
</tr>
<tr>
<td>C</td>
<td>Irganox PS802</td>
<td>00693-36-7</td>
<td><img src="image" alt="Chemical structure" /></td>
<td>Antioxidant</td>
<td>$1283 \pm 8$</td>
<td>64-67</td>
<td>HDPE</td>
<td>300-500</td>
</tr>
<tr>
<td>C</td>
<td>Tinuvin 326</td>
<td>03896-11-5</td>
<td><img src="image" alt="Chemical structure" /></td>
<td>UV-stabilizer</td>
<td>$457 \pm 6$</td>
<td>138-141</td>
<td>HDPE</td>
<td>500-1000</td>
</tr>
</tbody>
</table>

3.2 Monte Carlo sampling of contact energies

Pair contact energies and packing configurations were sampled at atomistic scale as depicted in Fig. 1b with specific algorithms (Gillet et al. (2009b)) designed by us for the Materials Studio environment (Accelrys, USA). Although our approach was conceptually similar, the commercial implementation of Eqs. (2) and (3) in the package Blends was not privileged as it was optimized for small spherical solutes. The sampling of $p_{A+B}(\varepsilon)$ relied on the random sampling of contact energies between a seed molecule, e.g. $A$, with a contact molecule, e.g. $B$, for a
large set of spatial configurations (up to \(10^{11}\)) with almost spherical probability and a large set of conformers (up to \(10^7\)) representative of their considered condensed state (e.g. solid, liquid). Random moves to sample pair interactions included rotations and translations until Van-der-Waals surfaces were put in contact. The number of neighbors, \(z_{A+B}\), was determined similarly by packing molecules until no more seed surface was accessible to any other contact molecules.

The sampling procedure has been specifically optimized to minimize biases between molecules with highly different sizes, shapes and flexibility. The different strategies are gathered in Table 2. Infinitely long polymer chains were simulated by preventing head and tail atoms from being in contact with any surface. Except for \(i+L\) interactions involving non-flexible solutes, conformers were efficiently extracted from isothermal long-term molecular dynamics simulation (up to 20 ns) in vacuum (i.e. configurations in gas phase).

<table>
<thead>
<tr>
<th>Biases</th>
<th>Description and implemented strategy</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Correlation between (\varepsilon_{A+B}) and (z_{A+B}) so that the approximation</strong> (\langle \varepsilon_{A+B} \cdot z_{A+B} \rangle_T \approx \langle \varepsilon_{A+B} \rangle_T \langle z_{A+B} \rangle_T) is no more accurate.</td>
<td>This bias can be controlled only for the pair (i+P) by updating the length of considered oligomers. The overall bias is minimum when (\chi_{i,P}) is minimum with the number of monomers.</td>
<td>Gillet et al. (2009b)</td>
</tr>
<tr>
<td><strong>Sampling of (\varepsilon_{A+B}) on non convex surfaces</strong></td>
<td>To avoid an oversampling of internal cavities with small seed molecules, contact sampling combines both an isotropic contraction and expansion method along the direction of centers-of-mass between (A) and (B).</td>
<td>Gillet et al. (2009b and 2009c)</td>
</tr>
<tr>
<td><strong>Sampling of (\varepsilon_{A+B}) for large and highly flexible solutes</strong></td>
<td>To avoid the oversampling of contact energies along the direction of centers-of-mass between (A) and (B), an anisotropic sampling is used. Very low energy configurations associated to stacked arrangements of aromatic solutes are weighted according to their geometric probability of occurrence rather than on their Boltzmann factor. This strategy corrects the fact that the pi-pi interactions are not spherically isotropic with neighbors.</td>
<td>Gillet et al. (2009b)</td>
</tr>
<tr>
<td><strong>Sampling of (\varepsilon_{i+i}) with aromatic interactions</strong></td>
<td>Since the conformations of flexible molecules in poor solvents differ from the ones observed in gas phase, conformers were generated from molecular dynamics in (L).</td>
<td>Gillet et al. (2009c)</td>
</tr>
<tr>
<td><strong>Sampling of (\varepsilon_{i+L}) for flexible solutes</strong></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

All potential energies were calculated using the ab-initio COMPASS forcefield (Accelrys, USA) without applying any cutoff.
3.3 Molecular dynamics simulation

Packing configurations around solute in L was assessed by isobaric and isothermal molecular dynamics (MD) simulations at 313 K. Initial periodic cells involving a solute molecule and $10^3$ L molecules were obtained with the Amorphous Cell commercial software (Accelrys, USA), using a compression box technique, as described by Rigby (2004). Each cell was subsequently submitted to a long term MD with an integration time step of 10-15 s. Temperature and pressure were kept constant by coupling the simulated cell with an infinite external heat bath (Andersen thermostat) and with an isotropic pressure bath (Berersen barostat). MD simulations were equilibrated during 2 ns and repeated on two configurations. Distance cutoffs of 15.5 Å were applied to Van-der-Waals interactions with a spline tail correction of 5 Å. A tridimensional Ewald summation technique with a lattice update of 5 Å was used to calculate Coulombic interactions.

The volume enclosed within the solute surface accessible to hydrogen atoms, denoted $V_i^H$ and tabulated in Table 1, was inferred by rolling a spherical probe with a radius commensurable to a hydrogen atom. The number of L molecules overlapping the previous volume was defined as the number of molecules enclosed between the solute center-of-mass and the inflexion point of the following criterion:

$$C(r) = \frac{4}{3} \pi r^3 - V_i^H \int_0^r g_{i,L}(r) 4\pi r^2 \, dr$$

where $g_{i,L}(r)$ is the pair radial distribution (i.e. probability to find a L molecule at the distance $r$ from the center-of-mass) of L molecules around the solute i. $V_i^H$ is the molar volume of L. Criterion (7) characterized the rate of filling a spherical volume centered on the solute center-of-mass with L molecules. Before the inflexion point, the exclusion-volume interaction with solute dominated, whereas it was the packing of L molecules beyond.
4. Results and discussion

4.1 Partitioning between polyethylene and polystyrene

According to the Flory-Huggins theory (Flory (1941 and 1942), Huggins (1941 and 1942)), $\chi_{i,P}$ does not depend on polymer length. In our approach, due to the approximation of infinitely long chains by oligomers without contacting head and tail atoms, the excess mixing energy derived from Eq. (2) depended on the number of monomers. The effect of the number of monomers is depicted in Figure 2 for three typical bulky hindered phenolic solutes with increasing size and flexibility (see Table 1).

For all tested conditions, a range of minimum $\chi_{i,P}$ values was obtained when the length of oligomers maximized the contact surface area and therefore London dispersion forces (attractive forces). For short oligomers, contact exclusion with head and tail atoms was overestimated, while poor convergence was achieved with long oligomers. Solute-polymer configurations of minimal contact energies and corresponding to optimal oligomer lengths (i.e. leading to a minimal $\chi_{i,P}$ value) are depicted in Figure 3. The numbers of two body contacts were maximized. The contacts were punctual in polyethylene whereas an exact structure match could be achieved via specific pi-pi interactions between aromatic rings of solutes and polystyrene. In the case of BHT, an aromatic ring of styrene monomer could be inserted between the two tertiobutyl substituents of the aromatic ring without interacting with head and tails atoms.
Figure 2. Effect of the number of monomers on the Flory Huggins coefficient, $\chi_{i,P}$, for: a-b) BHT, c-d) Chimassorb 81, e-f) Irganox 245 a,c,e) in amorphous polyethylene and b,d,f) in atactic polystyrene. 95% confidence intervals derived from continuous local polynomial approximation are plotted as dashed lines. The results were duplicated for chains shorter than 5 monomers and triplicated beyond. All polystyrene chains have random and independent distributions of aromatic rings along the backbone chain.

Globally, the optimal number of monomers increased with solute bulkiness in polyethylene and with the distance between solute aromatic rings in
polystyrene. In practice, the expectation of contact energies was derived from the averaging of thermalized contact energies distributions via the Boltzmann factor (see Eq. (3)).

Figure 3. Solute (ball and stick) – polymer (stick) configurations of minimal contact energies at 313 K and corresponding to the optimal oligomer length depicted in Figure 2. a-b) BHT, c-d) Chimassorb 81, e-f) Irganox 245 a,c,e) in amorphous polyethylene and b,d,f) in atactic polystyrene.

Distributions of contact energies corresponding to Figure 2 are depicted in Figure 4 for the optimal number of monomers. The importance of short-range attractive interactions at 313 K was assessed by almost symmetric weighted distributions.

The random distribution of aromatic rings along the chain of atactic polystyrene increased drastically the size of the configuration space along a virtual infinite polymer chain by introducing a huge number of possible diads,
triads, tetrads, pendads, etc. This effect appeared as a large discrepancy in $\chi_{i,P}$ estimates beyond five monomers (Figure 2).

The accuracy of predictions depicted in Figure 2 was tested for Chimassorb 81 by comparing our simulated results with the experimental value of the partition coefficient between high-density polyethylene (density 72.5 %) and polystyrene at 313 K, $K_{\text{app}}^{\text{PE/PS}}$. A highly reliable estimate of $K_{\text{app}}^{\text{PE/PS}}$ (value of 7.1 ± 0.1) was calculated from the total least squares approximate (via singular value decomposition) of the experimental linear desorption isotherm plotted in Figure 5a. A corresponding estimate of $\chi_{i,\text{PE}} - \chi_{i,\text{PS}}$ was inferred by means of Eq. (4) and
compared with values predicted from Figures 2c and 2d (Figure 5b). Predicted and calculated values were in remarkable agreement. This global validation confirmed the consistency of main assumptions used in our approach to assess excess chemical potentials of bulk solutes in polymers:
- crystalline regions are inaccessible to bulky solutes,
- the condition of minimal bias in $i+P$, $i+i$, $P+P$ interaction energies is fulfilled at the minimum of $\chi_{i,P}$ with the number of considered monomers,
- non-positional entropy plays a significant role and must be sampled accordingly at atomistic scale.

Figure 5. a) Linear sorption isotherm of Chimassorb 81 between a high density polyethylene (crystallinity 72.5%) and an amorphous atactic polystyrene by performing independent equilibriums with a 10 fold larger volume of liquid (from left to the right: ethanol 50%, ethanol 75%, ethanol 95%, isopropanol). The dashed and dot-dashed lines plot the reference curve $y=x$ and the 95% interval of the total least-squares regression line. b) Experimental estimate of $\chi_{i,PE} - \chi_{i,PS}$
(continuous line) and value derived from Figures 2b and 2e (dot-dashed line). Box-and-whisker diagram plots the uncertainty on experimental values as determined from a complete sensitivity analysis via Monte-Carlo on measurements errors.

3.2 Partitioning between polyethylene and alcohols

The concept of solute cavity in alcohols and the associated modification of the local structure were investigated by isothermal and isobaric MD simulation at 313 K and 10^5 Pa. The important information gained by molecular simulation is illustrated in Figure 6 for a BHT molecule in solution with 10^3 methanol molecules and with 10^3 ethanol molecules.

![Figure 6](image)

Figure 6. Local arrangement of a,c) methanol and b,d) ethanol molecules around a BHT: a-b) Pair and radial distributions averaged during a 2 ns MD simulation run, c-d) corresponding density map projected along the two principal axes of BHT. Only $L$ molecules belonging to BHT slice were included in the analysis. The dot-dashed line plots the experimental value of density at 313 K.

The local structure of each pure liquid was derived as reference from independent simulations containing only $L$ molecules. It was verified that MD simulation was able to predict the limiting density of each liquid with accuracy.
similar to the experiment. The two first overlapping peaks of the radial distribution of methanol molecules highlighted the prevalence of pairs involving, on one side, two upside-down hydrogen bonds (first peak) and, on the other side, interactions with methyl group (second peak). Similar packing between nearest neighbors was observed in ethanol, but with a higher peak separation due to the large hindering by the ethyl group. Next-nearest neighbors did not exhibit a specific orientation and a single peak was identified. Similar descriptions were obtained in the literature (Matsumoto and Gubbins (1990), Saiz et al. (1999)) for methanol and ethanol respectively.

The insertion of BHT perturbed the short range liquid order in two different ways combining a hard core, with a radius almost equal to the thickness of the aromatic ring, and a smooth exclusion shell related to the hindering by tertiobutyl groups. One peak was also identified as in the liquid structure due to the possible hydrogen bonding between \( L \) and the phenol group. The increase in \( L \) density close to phenol is particularly highlighted in projected cross-sections depicted in Figures 6c and 6d.

![Figure 7. a) Solute-\( L \) pair distributions of a homologous series of phenolic antioxidants in ethanol, b) corresponding potential mean force, c) first derivative of the criterion of space filling defined in Eq. (7), d) cumulated number of ethanol molecules included within a sphere of radius \( r \) and centered on the solute center-of-mass.](image-url)
Similar calculations in ethanol were performed for a homologous series of bulky molecules including up to 3 BHT patterns and a possible alkyl chains (see Table 1). The radial distributions were interpreted by calculating the effective potential, denoted \( U_{i,F}(r) \), to insert a \( L \) molecule at a distance \( r \) from the center-of-mass according to Eq. (8). The results are plotted in Figure 7 along with the cumulated number of ethanol molecules, which can fill a spherical volume centered on the solute center-of-mass.

\[
U_{i,F}(r) = -k_B \cdot T \cdot \log \frac{g_{i,L}(r)}{g_{F,L}(r)}
\]  

(8)

Stiff and hindered molecules such as BHT and Irganox 3114 did not exhibit a significantly negative potential mean force close to their center-of-mass and could be idealized as isometric hard spheres. On the opposite, solutes including a flexible chain, such as Irganox 1076 and Irganox 1035, had a center-of-mass which was not located along the molecule contour so that \( L \) molecules could overlap the internal region around the center-of-mass. The effect was exacerbated in Irganox 1076 due to the absence of symmetry of the molecule around the center-of-mass. The criterion of space filling defined in Eq. (7) assessed how fast an isometric sphere of radius \( r \) was filled with \( L \) molecules with a packing equivalent to the bulk. The distance, from which the rate of filling started to decrease (Figure 7c), highlighted the maximal length scale, beyond which solute ceased to modify significantly the local correlation between the arrangements of \( L \) molecules. The number of overlapping \( L \) molecules, \( n_{i,L}^{\text{overlapping}} \), was inferred by counting the average number within the limiting sphere.

The values of \( n_{i,L}^{\text{overlapping}} \) are tabulated in Table 3 for the thirty-five bulky solutes considered in the present study along with calculated Flory-Huggins coefficients in \( L \) and \( P \). The corresponding partition coefficients between \( F \) and \( P \), \( K_{i,F/P} \), are compared with experimental values in Figure 8 for \( F= \) ethanol and isopropanol and \( P= \) amorphous region of polyethylene and atactic polystyrene. Without any adjustment, the whole methodology was able to predict \( K_{i,F/P} \) values of bulky solutes with a deviation, which fitted in most cases within experimental errors. Since it is usually much more difficult to experimentally assess very low residual concentrations in \( P \), experimental errors tended to be larger for \( K_{i,F/P} \) values greater than one. Although its chemical affinity for polar liquids was low, partitioning of Irgafos 168 with ethanol could not be estimated accurately due to its high reactivity.
Table 3. Flory-Huggins interaction parameters calculated at 313 K and entropic contributions in L.

<table>
<thead>
<tr>
<th>Solute</th>
<th>(\chi_{i,\text{ethanol}})</th>
<th>(\chi_{i,\text{isopropanol}})</th>
<th>(\chi_{i,\text{PE}})</th>
<th>(\chi_{i,\text{PS}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Decane</td>
<td>4.40 ± 0.01</td>
<td>3.21 ± 0.09</td>
<td>3.28 ± 0.002</td>
<td>2.51 ± 0.07</td>
</tr>
<tr>
<td>Undecane</td>
<td>4.65 ± 0.003</td>
<td>3.50 ± 0.13</td>
<td>3.50 ± 0.001</td>
<td>2.75 ± 0.10</td>
</tr>
<tr>
<td>Dodecane</td>
<td>5.06 ± 0.003</td>
<td>3.80 ± 0.09</td>
<td>3.87 ± 0.001</td>
<td>2.98 ± 0.07</td>
</tr>
<tr>
<td>Tridecane</td>
<td>5.31 ± 0.003</td>
<td>4.06 ± 0.14</td>
<td>4.10 ± 0.01</td>
<td>3.19 ± 0.07</td>
</tr>
<tr>
<td>Tetradecane</td>
<td>5.64 ± 0.01</td>
<td>4.35 ± 0.01</td>
<td>4.38 ± 0.001</td>
<td>3.41 ± 0.07</td>
</tr>
<tr>
<td>Pentadecane</td>
<td>6.16 ± 0.01</td>
<td>4.62 ± 0.01</td>
<td>4.85 ± 0.001</td>
<td>3.63 ± 0.07</td>
</tr>
<tr>
<td>Hexadecane</td>
<td>6.35 ± 0.05</td>
<td>4.96 ± 0.01</td>
<td>5.03 ± 0.001</td>
<td>3.89 ± 0.07</td>
</tr>
<tr>
<td>Heptadecane</td>
<td>6.72 ± 0.05</td>
<td>5.20 ± 0.14</td>
<td>5.36 ± 0.01</td>
<td>4.08 ± 0.07</td>
</tr>
<tr>
<td>Octadecane</td>
<td>7.10 ± 0.05</td>
<td>5.52 ± 0.12</td>
<td>5.62 ± 0.01</td>
<td>4.33 ± 0.07</td>
</tr>
<tr>
<td>Nonadecane</td>
<td>7.08 ± 0.05</td>
<td>5.78 ± 0.01</td>
<td>5.86 ± 0.001</td>
<td>4.54 ± 0.07</td>
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<tr>
<td>Eicosane</td>
<td>7.38 ± 0.02</td>
<td>6.06 ± 0.12</td>
<td>6.12 ± 0.001</td>
<td>4.75 ± 0.07</td>
</tr>
<tr>
<td>Docosane</td>
<td>7.91 ± 0.06</td>
<td>6.66 ± 0.16</td>
<td>6.78 ± 0.001</td>
<td>4.97 ± 0.07</td>
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<tr>
<td>Tetracosane</td>
<td>8.21 ± 0.06</td>
<td>7.22 ± 0.01</td>
<td>7.36 ± 0.001</td>
<td>5.22 ± 0.07</td>
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<td>Octacosane</td>
<td>8.90 ± 0.06</td>
<td>8.31 ± 0.15</td>
<td>8.41 ± 0.001</td>
<td>5.52 ± 0.07</td>
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<tr>
<td>Decanol</td>
<td>4.92 ± 0.04</td>
<td>5.08 ± 0.12</td>
<td>5.16 ± 0.001</td>
<td>3.98 ± 0.07</td>
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<tr>
<td>Undecanol</td>
<td>3.71 ± 0.04</td>
<td>3.92 ± 0.12</td>
<td>4.01 ± 0.001</td>
<td>3.10 ± 0.07</td>
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<tr>
<td>Dodecanol</td>
<td>3.77 ± 0.04</td>
<td>4.19 ± 0.15</td>
<td>4.28 ± 0.001</td>
<td>3.29 ± 0.07</td>
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<td>Tridecanol</td>
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<td>4.48 ± 0.15</td>
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<tr>
<td>Tetradecanol</td>
<td>4.80 ± 0.03</td>
<td>4.77 ± 0.15</td>
<td>4.86 ± 0.001</td>
<td>3.57 ± 0.07</td>
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<tr>
<td>Pentadecanol</td>
<td>5.62 ± 0.06</td>
<td>5.38 ± 0.17</td>
<td>5.47 ± 0.001</td>
<td>4.22 ± 0.07</td>
</tr>
<tr>
<td>Hexadecanol</td>
<td>5.71 ± 0.03</td>
<td>5.64 ± 0.14</td>
<td>5.73 ± 0.001</td>
<td>4.42 ± 0.07</td>
</tr>
<tr>
<td>Heptadecanol</td>
<td>6.04 ± 0.06</td>
<td>5.96 ± 0.14</td>
<td>6.05 ± 0.001</td>
<td>4.67 ± 0.07</td>
</tr>
<tr>
<td>Octadecanol</td>
<td>6.68 ± 0.06</td>
<td>6.21 ± 0.14</td>
<td>6.30 ± 0.001</td>
<td>4.98 ± 0.07</td>
</tr>
<tr>
<td>Nonadecanol</td>
<td>3.12 ± 0.02</td>
<td>4.01 ± 0.08</td>
<td>4.10 ± 0.001</td>
<td>3.15 ± 0.07</td>
</tr>
<tr>
<td>Eicosanol</td>
<td>4.40 ± 0.02</td>
<td>5.52 ± 0.03</td>
<td>5.63 ± 0.001</td>
<td>4.34 ± 0.07</td>
</tr>
<tr>
<td>Solute</td>
<td>$\pm 0.15$</td>
<td>$\pm 0.14$</td>
<td>$\pm 0.15$</td>
<td>$\pm 0.11$</td>
</tr>
<tr>
<td>------------------------</td>
<td>------------</td>
<td>------------</td>
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<td>------------</td>
</tr>
<tr>
<td>Erucamide</td>
<td>5.38</td>
<td>6.74</td>
<td>4.81</td>
<td>5.29</td>
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<tr>
<td>Irgafos 168</td>
<td>$\pm 0.05$</td>
<td>$\pm 0.12$</td>
<td>$\pm 0.10$</td>
<td>$\pm 0.09$</td>
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<tr>
<td>Irganox 1035</td>
<td>9.49</td>
<td>10.58</td>
<td>8.75</td>
<td>8.30</td>
</tr>
<tr>
<td>Irganox 1076</td>
<td>$\pm 0.08$</td>
<td>$\pm 0.25$</td>
<td>$\pm 0.1$</td>
<td>$\pm 0.19$</td>
</tr>
<tr>
<td>Irganox 245</td>
<td>7.14</td>
<td>9.93</td>
<td>6.03</td>
<td>7.80</td>
</tr>
<tr>
<td>Irganox 3114</td>
<td>$\pm 0.48$</td>
<td>$\pm 0.21$</td>
<td>$\pm 0.10$</td>
<td>$\pm 0.17$</td>
</tr>
<tr>
<td>Irganox PS802</td>
<td>8.48</td>
<td>9.67</td>
<td>5.92</td>
<td>7.59</td>
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<td>Tinuvin 326</td>
<td>14.54</td>
<td>12.67</td>
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<td></td>
<td>$\pm 0.78$</td>
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<td>$\pm 0.10$</td>
<td>$\pm 0.11$</td>
</tr>
<tr>
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<td>14.15</td>
<td>12.95</td>
<td>12.33</td>
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<tr>
<td></td>
<td>$\pm 0.09$</td>
<td>$\pm 0.24$</td>
<td>$\pm 0.06$</td>
<td>$\pm 0.19$</td>
</tr>
<tr>
<td></td>
<td>14.15</td>
<td>12.95</td>
<td>12.33</td>
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<td></td>
<td>$\pm 0.14$</td>
<td>$\pm 0.26$</td>
<td>$\pm 0.10$</td>
<td>$\pm 0.20$</td>
</tr>
<tr>
<td></td>
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<td>4.61</td>
<td>4.63</td>
<td>3.62</td>
</tr>
<tr>
<td></td>
<td>$\pm 0.09$</td>
<td>$\pm 0.18$</td>
<td>$\pm 0.10$</td>
<td>$\pm 0.14$</td>
</tr>
</tbody>
</table>

Significant deviations between prediction and experimental values occurred only for solutes comprising a long aliphatic segment, e.g. octacosane and Irganox 245, regardless their polarity. This discrepancy was associated to an overestimation of the isometric volumes $r_{i,F}^{-1}$ for flexible molecules longer or equal to their persistence length. Since these configurations were extracted from MD simulations, the partition between collapsed and coil structures could not be incriminated. It was therefore argued that the calculation of positional entropy from an idealization of solutes as hard spheres, much larger than the volume of $L$ molecules, was no more appropriated. A representation at an intermediate scale should be envisioned to take into account explicitly the dispersion of interactions between solute monomers or blobs and isometric volumes of $L$. The threshold, from which, the representation should be updated should depend on the relative size of $L$ molecules. Indeed, our prediction for Irganox 245 were highly accurate in isopropanol.
Figure 8. Comparison of calculated partition coefficients from Eqs. (2-3) and (6) with experimental values at 313 K: a-b) \( L = \text{ethanol} \), c) \( L = \text{isopropanol} \).

1: decane\(^a,b\), 2: dodecanol\(^a,b\), 3: tetradecane\(^a,b\), 4: hexadecane\(^a,b\), 5: octadecane\(^a,b\), 6: cosane\(^b\), 7: docosane\(^b\); 8: tetracosane\(^b\), 9: octacosane\(^b\); \( a \): dodecanol\(^b\); \( \beta \): tetradecanol\(^b\); \( \gamma \): hexadecanol\(^b\); \( \delta \): octadecanol\(^b\); A: BHT\(^b\); B: Chimassorb 81\(^d\); C: erucamide\(^d\); D: Irgafos 168\(^d\); E: Irganox 1035\(^d\); F: Irganox 1076\(^d\); G: Irganox 245\(^d\); H: Irganox 3114\(^d\); J: Irganox PS802\(^d\); K: stearic acid\(^d\); L: Tinuvin 326\(^d\); a: BHT\(^d\); b: Chimassorb 81\(^d\); c: erucamide\(^d\); d: Irgafos 168\(^d\); e: Irganox 1035\(^d\); f: Irganox 1076\(^d\); g: Irganox 245\(^d\); h: Irganox 3114\(^d\); j: Irganox PS802\(^d\); k: stearic acid\(^d\); l: Tinuvin 326\(^d\). \(^a\) = amorphous regions of polyethylene, experimental values in methanol and ethanol from Baner and Piringer (1991); \(^b\) = amorphous regions of polyethylene, experimental values in methanol and ethanol from Vitrac \textit{et al.} (2007); \(^c\) = amorphous regions of polyethylene, experimental values (this study); \(^d\) = polystyrene, experimental values (this study).
3.3 Partitioning between alcohols

The choice of an appropriate food simulant is of significant concern to assess the migration of plastics additives into food. For risk assessment purposes, the issue consists in putting in contact the material to be tested with a liquid, which will overestimate the real migration, while maintaining analytical analysis tractable. Our results demonstrated that the chemical affinity of plastic additive or polymer residue for a given liquid involves a non-intuitive relationship with the relative size of the solute, its flexibility, its polarity. To help risk assessors in the design of migration experiments, excess chemical potentials calculated for three alcohols (methanol, ethanol, isopropanol) where gathered as partial chemical potentials and depicted as a ternary barycentric plot in Figure 9.

Figure 9. Ternary plot of relative excess chemical potentials between methanol, ethanol and isopropanol. The scale on the right plots the absolute scale of excess chemical potentials.

The main interest of such a diagram is its ability to predict either a relative or absolute chemical affinity for unknown molecules based on homology.
principles. It is worth to notice that hexadecane is a neutral solute with almost a similar chemical affinity for the three represented alcohols.

5. Conclusions

The current work completes a series of three papers (Gillet et al., 2009b and 2009c), where a general tailored methodology has been devised to predict excess chemical potentials in polymers and in liquids. An additional effort was devoted to generate reference partitioning data, which were missing for bulky solute in glassy polymers or in polar liquids. The main targeted application was the prediction of the contamination of food products by organic substances originating from materials in contact but the field of application remains broader, e.g. environment pollution, polymer recycling.

Free energy of mixing were calculated within the framework of an off-lattice Flory-Huggins approximation by combining two different scales of molecular interactions. Pair contact energies were calculated at atomistic scale with an ab-initio forcefield well-suited for most organic substances comprising polymer, additives and polar liquids. As contacts were sampled for large set of conformers and configurations, non-positional entropic effects due to the flexibility of tested molecules and variation in packing were naturally accounted. This work contributes to demonstrate that the proposed sampling was accurate for bulky solutes in both flexible and stiff polymers. The predictions of excess chemical potentials for a typical plastics additive, Chimassorb 81, were in very well agreement with an accurate estimate of the partitioning between amorphous region of polyethylene and atactic polystyrene.

Positional entropies in mixture involving large solutes and much smaller liquid molecules contributed significantly to the final value of the solute excess chemical potential. This effect was analyzed in this study by assuming that the volume of the cavity required to insert a bulky solute is commensurable to the volume enclosed within its surface accessible to hydrogen atoms, as demonstrated in Gillet et al. (2009c). Mixture excess entropy was accordingly calculated by introducing a mesoscopic description of the solute-liquid mixture involving hard spheres with a volume equivalent to the solute cavity. Possible deviations to this representation were analyzed by calculating systematically the radial distribution of a wide range of bulky solutes, flexible or not, hindered or not, symmetric or not. It was shown that only flexible solutes or asymmetric molecules exhibited spherical cavities, which were overlapped by liquid molecules. These corrections made it possible to predict satisfactory partition coefficients between polymer and alcohols for almost all tested bulky solutes. Significant discrepancies occurred only for solutes longer than their persistence length. In this case, the assumption
of flexible elastic rod or sphere ceased to be accurate and a statistical description of interaction between blocks of solute and liquid molecules should be envisioned.

Current extensions are focused on the validation of the method for polyethylene terephthalate.

Notations

\( A \): any molecule with a seed role.
\( B \): any molecule with a contact role.
\( C(r) \): criterion defined in Eq. 7.
\( K_{i,k;j} \): partition coefficient of solute \( i \) between \( k=L,P_1 \) and \( j=P,P_2 \).
\( K_{i,k;j}^{app} \): apparent partition coefficient of solute \( i \) between \( k=L,P_1,PE \) and \( j=P,P_1,P_2,PS \).
\( L \): liquid (food simulant).
\( P \): polymer.
\( T \): absolute temperature (K).
\( U_{i,F}(r) \): effective potential to insert a \( L \) molecule at a distance \( r \) from the center of mass of solute \( i \).
\( V_L^{MT} \): molar volume of \( L \) (m\(^3\)).
\( c_k \): crystallinity of polymer \( P_k \) (volume fraction of crystalline phase).
\( g_{k,L}(r) \): density in \( L \) molecules around \( k \) molecules (molécules·m\(^3\)).
\( h_k = \phi_k / (\phi_i + \phi_{F_1}) \).
\( k_B \): Boltzmann’s constant (1.38·10\(^{-23}\) J·K\(^{-1}\)).
\( i \): solute index.
\( n_{i,k}^{\text{overlapping}} \): fractional number of \( k=P,L \) molecules overlapping \( i \).
\( p_{A+B}(\varepsilon) \): distribution of contact energies between \( A \) and \( B \).
\( r \): distance from the center of mass of the solute (m\(^3\)).
\( r_{i,k}^{1} \): number of \( k=L,P \) molecules to be rearranged when the solute \( i \) was displaced.
\( z_{j+k} \): coordination number of the arrangement when \( j=A,i,F,P \) is surrounded by molecules \( k=B,i,F,P \).

Greek Letters
\( \varepsilon_{j+k} \): contact energy associated to the contact(s) between a molecule \( j=A,i,F,P \) and a molecule \( k=B,i,F,P \) (J·mol\(^{-1}\)).
\( \mu_{i,k}^{\text{excess}} \): excess chemical potential of molecules solute \( i \) in \( k=L,P,P_1,P_2 \).
$\phi_k$: volume fraction of $k=i,L$.

$\chi_{k,j}$: Flory-Huggins parameter between $k=i,L,P$ and $j=L,P_1,P_2,PE,PS$.

**Mathematical operators**

$\langle \rangle$: averaging on the sampled configurational space.

$\langle \rangle_T$: Boltzmann-weighted ensemble averaging on the sampled configurational space.

**References**


