



## Fast estimation of sorption of organic compounds in polymeric packaging materials



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### ABSTRACT

Partition coefficient of organic flavor compounds between polymers and food/beverage is essential to the development of packaging materials. A fast and reliable prediction tool is highly desired. A prediction approach based on well known Flory-Huggins theory is explored. Via incorporating group contribution methods, the Flory-Huggins theory gains the ability of describing molecular structures. Therefore, it is able to describe the effects of crystallization, branching, copolymer, mixture of polymer with additives, polymer blend, composition variations and coexisting solutes. The predicted solubilities in parenteral and aqueous NVPS solutions are in close agreement with experimental results, indicating that FH-GCM can be used for prediction of partition coefficient in dilute solution.

### 1. Introduction

Partition of organic compounds between polymeric materials and coexisting solvents is fundamental to a variety of applications in environmental treatment, separation, bioprocessing and food industries (Mackay, Celsie, & Parnis, 2016). Copolymer of *N*-vinylpyrrolidone and styrene was reported long ago to effectively remove the organic contaminants at a low but still toxic concentration (ppm and below) by concentrating these dilute contaminants onto the polymeric phase (Haulbrook, Feerer, Hatton, & Tester, 1993). Polyoxymethylene (POM), polydimethylsiloxane (PDMS) and low-density polyethylene (LDPE) are often used in single-phase polymeric passive samplers for measuring the concentration of hydrophobic organic compounds in water (Adams, Lohmann, Fernandez, Macfarlane, & Gschwend, 2007; Endo, Hale, Goss, & Arp, 2011; Lohmann & Muir, 2010; Thompson, Hsieh, & Luthy, 2015). Solid inert polymers have been explored as non-aqueous phase in two-phase partitioning bioreactors to eliminate organic pollution (Munoz, Daugulis, Hernandez, & Quijano, 2012).

In food/beverage industry, polymers are widely used as packaging materials. Sorption of aroma molecules from liquor and drink into polymeric packaging materials during storage is an important cause of aroma loss. The scalping of aroma compounds in typical polymers such as LDPE, polylactate (PLA) (Charara, Williams, Schmidt, & Marshall, 1992; Fukamachi, Matsui, Hwang, Shimoda, & Osajima, 1996;

Weerasinghe & Pettitt, 1994) as well as can coatings were investigated (Matsui & Osajima, 1993; Wietstock, Glattfelder, Garbe, & Methnert, 2016). On the other hand, the additives or polymer residues migrating from the polymeric materials to the solvent phase raises issues related to safety and aging of the packaging polymers (Bhunja, Sablani, Tang, & Rasco, 2013). These phenomena are closely related to the solubility of organic compounds in both liquid (solvent) and solid (polymers) phases, i.e. partition of organic compounds between polymeric and coexisting solvents. Therefore, understanding the partitioning behavior of chemicals is essential. However, experimental measurement of partition coefficient is difficult when the total concentration of the chemicals or the solubility on one phase is very low or the molecular weight of the chemicals is large (Lee, Shim, & Kwon, 2014). It is thus highly desired that a simple and fast prediction approach is available to calculate the partition coefficient of organic compounds between polymeric materials and coexisting solvents, which is very helpful to develop safe polymeric packaging.

Quantitative structure-activity relationships (QSARs) has been reported to calculate the partition coefficient through building up a correlation of molecular structural properties with the partition coefficient from available experimental data and the correlation is then used for prediction (Mamy et al., 2015; Vega, Shing, & Rull, 1994). However, the accuracy of QSARs is largely depending on the size of available experimental dataset. Obviously, it is not suitable to those cases that

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experimental data is not available or there is only limit experimental data.

Atomistic simulation is also used to calculate the solubility and partition coefficient through calculating the chemical potentials of organic compounds in both liquid and solid phases. It is well known that the chemical potentials of an organic compound in both liquid solvent and solid polymer phases must be equal when reaching thermodynamic equilibrium. As will be illustrated in the next section, the equilibrium

$$V_s c_i^s(x_1^s, \dots, x_i^s, \dots, x_{n-2}^s) + V_p(x_1^p, \dots, x_i^p, \dots, x_{n-2}^p) c_i^p(x_1^p, \dots, x_i^p, \dots, x_{n-2}^p) = V_s c_{i,0} \quad (i = 1, \dots, n - 2) \quad (2)$$

concentration of organic compound in both liquid solvent and solid polymer phases is related to the chemical potentials. Therefore, these equilibrium concentrations can be obtained and then the corresponding partition coefficient can be calculated. Atomistic molecular dynamics (MD) or Monte Carlo (MC) simulations coupled with either Widom insertion or thermodynamic integration sampling techniques (Bhatnagar, Kamath, Chelst, & Potoff, 2012; Ghobadi, Taghikhani, & Elliott, 2011; Gillet, Vitrac, & Desobry, 2009; Gillet, Vitrac, & Desobry, 2010; Hess, Peter, Ozal, & van der Vegt, 2008; Lundsgaard, Kontogeorgis, & Economou, 2011; Nguyen, Guiga, Dkhissi, & Vitrac, 2017; Nguyen, Guiga, & Vitrac, 2016; Ozal, Peter, Hess, & van der Vegt, 2008; Papadopoulou, Becker, Lupkowski, & Vanswol, 1993; Xiang & Anderson, 2013; Yang, Ahmed, & Sandler, 2013) are able to give the chemical potentials for chemicals in liquid solvent as well as polymer phases but they are very time consuming especially when rigid polymers or crosslinked networks involved. Thus, it is not suitable for fast screening of a large batch of chemicals.

Flory-Huggins theory (FH) is widely used to calculate the Gibbs free energy change of polymer solution (Flory, 1942; Huggins, 1941) and therefore the chemical potentials. The details of FH theory are documented in many literatures as well as in textbooks. Here we just give a brief summary. It uses a rigid lattice to represent polymer-solvent system and assumes polymer to be a chain of connected segments, each of which occupies one site of a lattice. The arrangement of segments in the lattice is through random walking. Each solvent molecule occupies a lattice site too. Flory-Huggins interaction parameter ( $\chi$ ) is an important parameter and can be obtained either experimentally or through Hansom solubility parameter estimated by group contribution method (GCM) (Lindvig, Michelsen, & Kontogeorgis, 2002).

Herein, we explore the applicability of Flory-Huggins theory to calculate the partition coefficient of organic compound between polymeric materials and coexisting solvents, aiming to find a simple, fast and effective approach to help the formulation of proper polymer packaging. The concentration of organic solute to be studied is at ppm scale, i.e. very dilute. It is the concentration scale that aroma molecules in beverages usually exist in and quite often, very few experiments are available. We also apply our approach to the systems containing a mixture of organic solutes at ppm scale and in contact with various polymeric materials, which corresponds to the cases that beverage packed in polymeric container or polymer coated aluminium can. The polymers selected are common packaging materials such as polyethylene (LDPE and HDPE), ethylene vinyl alcohol (EVOH) and polyethylene terephthalate (PET). As can be seen in the main text, our approach is simple and fast with acceptable accuracy. Thus, it can be used for fast screening of a large batch of organic compounds and also polymer components for packaging.

## 2. Approach

For a system containing liquid solvent, solid polymer and organic solutes, assuming polymers are not dissolved into the solvent phase, the following thermodynamic conditions (Eq. (1)) need to be satisfied at equilibrium for each solute component,  $i$ , partitioning between the solvent and polymer phases.

$$\mu_i^s(x_1^s, \dots, x_i^s, \dots, x_{n-2}^s) = \mu_i^p(x_1^p, \dots, x_i^p, \dots, x_{n-2}^p) \quad (i = 1, \dots, n - 2) \quad (1)$$

where the numbers from 1 to  $n - 2$  denote different types of solutes. The superscripts,  $s$  and  $p$ , on the chemical potential ( $\mu$ ) and mole fraction ( $x$ ), represent solvent and polymer phases, respectively.

In addition, for each solute component, the summation of the amounts distributed in both phases is constant (Eq. (2)), i.e. equals to the initial amount.

Eqs. (1)–(2) are two boundary conditions for an organic solute compound partitioning between polymer and solvent phases and are the basis to calculate the partition coefficient. The chemical potentials involved are then obtained by Flory-Huggins theory.

Flory (Flory, 1942) and Huggins (Huggins, 1941) derived free energy of mixing based on an incompressible lattice model. Applying the theory to a system with multiple solutes in polymer and assuming all components are treated in the same way, each of which has  $n_i$  molecules of  $s_i$  segments disregarding whether it is a solute or polymer, the free energy change is written as

$$\Delta G = kT \left[ \sum_i (n_i \ln \phi_i) + \sum_{i,j(i < j)} (n_i s_i \chi_{ij} \phi_i \phi_j) \right] \quad (3)$$

Here,  $\phi$  is the volume fraction. In the second summation, the interaction  $\Delta H_{ij} = n_i s_i \chi_{ij} \phi_i \phi_j$  is mutual between any pairs of components  $i$  and  $j$ , hence satisfying  $n_i s_i \chi_{ij} \phi_i = n_j s_j \chi_{ji} \phi_j$ .  $\chi_{ij}$  is defined as interaction parameters, related to solubility parameters ( $\delta$ ) through  $\chi_{ij} = \frac{V_{i,seg}}{k_B T} f(\delta_{i,\alpha}, \delta_{j,\alpha})$ ; it can then be found that  $\chi_{ij}/V_{i,seg} = \chi_{ji}/V_{j,seg}$  where  $V_{i,seg}$  and  $V_{j,seg}$  are segmental volumes. From all these relations, we derive the chemical potential change for component  $i$ ,

$$\begin{aligned} (\mu_i - \mu_i^0)/k_B T = & \ln \phi_i + 1 - \phi_i/x_i + s_i \left\{ \sum_{p(p \neq i)} [\chi_{ip} (1 - \phi_i) \phi_p] \right. \\ & \left. - \sum_{p,q(p < q, p \neq i, q \neq i)} \left( \left( \frac{V_{i,seg}}{V_{p,seg}} \right) \chi_{pq} \phi_p \phi_q \right) \right\} \quad (4) \end{aligned}$$

where  $\mu_i^0$  is the chemical potential of pure component  $i$  and  $x_i$  is the mole fraction of component  $i$  in the mixture. If applied to binary systems, Eqs. (3)–(4) are reduced to the widely-used two-component FH equations (Lindvig et al., 2002; Mansoori, 2005).

The excess chemical potential of solute in solvent phase is calculated using standard expression for regular liquid solution.

As shown in Eq. (4), the segmental volume and binary interaction parameter between any pairs of components are the key inputs for Flory-Huggins chemical potential. The estimation of interaction parameters can be converted to the calculation of Hansen solubility parameters for pure components (Lindvig et al., 2002),

$$\chi_{ij} = \alpha V_{i,seg} [(\delta_{d,i} - \delta_{d,j})^2 + 0.25(\delta_{p,i} - \delta_{p,j})^2 + 0.25(\delta_{h,i} - \delta_{h,j})^2]/k_B T \quad (5)$$

Here solubility parameters are represented by three components – dispersion ( $\delta_{d,i}$ ), polar ( $\delta_{p,i}$ ) and hydrogen-bonding ( $\delta_{h,i}$ ) components.

We use group contribution methods (GCM), which assumes the property of a substance is an addition of contributions from all constituent chemical groups, to estimate the segmental volume (Constantinou, Gani, & O'Connell, 1995) and solubility parameters (Van Krevelen & Te Nijenhuis, 2009a). These methods are capable to capture molecular structure information while still remaining efficient. The properties will then be calculated as the summation of group contributions weighted by the mole fraction of each group or the probability of the state the group is in,  $x_i$ ,

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