



Polymer–polymer miscibility and partial solvation parameters

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ABSTRACT

The novel predictive approach of Partial Solvation Parameters (PSP) is extended and applied to polymer mixtures. Quantum mechanics and statistical thermodynamics are used in order to extract information on the molecular descriptors of each compound and develop simple analytical expressions for all basic thermodynamic quantities of mixtures. Emphasis is given on hydrogen-bonded polymer mixtures. Apart from polymer–polymer miscibility, the PSP approach is used for the prediction of melting point depression, fraction of hydrogen-bonded groups, critical composition of a copolymer for miscibility with another polymer, and the Flory–Huggins $\chi_{1,23}$ interaction parameter of a solute–probe (1) at infinite dilution in a mixture of polymers (2,3) which is obtained from inverse gas chromatography (IGC) experiments. The predictions are compared with experimental data and the agreement is critically discussed. The predictions of polymer–polymer miscibility on the basis of spinodal lines are compared with the corresponding predictions on the basis of χ interaction parameters. The strength and weakness of the approach are also critically discussed in relation with its capacity and reliability to act as a designing tool of new compatible polymer blends. The perspectives of this unified approach to solution thermodynamics are discussed.

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1. Introduction

Polymer–polymer miscibility was, a couple of decades ago, one of the most popular subjects in the broader area of polymer science and engineering [1,2]. Still today, it remains a very important subject, since rational design of miscible polymer or copolymer systems may lead to high-value novel materials with specific sets of properties that respond to continuously emerging technological needs [1–3]. Although significant progress was made in the thermodynamic description of polymer mixtures, the prediction of polymer or copolymer miscibility still remains a rather underdeveloped subject, primarily, because of the very nature of these systems and the stringent requirements on their intermolecular interactions [1–7]. Very often they involve strong specific intermolecular forces such as hydrogen-bonding interactions leading to 3-D physically cross-linked networks whose handling is not a trivial issue [1,7–10]. Very often, also, the experimental data correspond to frozen in non-equilibrium states, especially when the system is found near or within its region of glassy state [1].

One of the early and most popular predictive approaches to polymer–polymer miscibility was the miscibility guide developed

by the group of Coleman and Painter [7,10]. In this guide, the Flory–Huggins χ_{12} interaction parameter [11] for a mixture of polymers 1 and 2 is calculated from the squared difference of their solubility parameters δ_1 and δ_2 , respectively [12,13]. Since this approach calculates only positive χ_{12} values, it was confined to polymers interacting with weak dispersive or van der Waals forces. Such a polymer blend should have a near zero χ_{12} interaction parameter in order to be miscible. The approach was extended to polymer pairs exhibiting polar or hydrogen-bonding interactions by tolerating more positive χ_{12} parameters depending on the strength of the favorable intermolecular interactions. A group-contribution scheme was used in order to calculate the non-hydrogen bonding solubility parameters and the associated molar volumes. In parallel, expressions for the hydrogen-bonding contributions to the mixing free-energy were developed [10], which require the knowledge of the equilibrium constants for each of the involved types of hydrogen bonds. In spite of its shortcomings, the contribution of the Coleman–Painter approach to understanding hydrogen bonding in polymer mixtures was significant.

The above approach [7,10], however, had not any direct connection with another popular approach, the Hansen Solubility Parameter method [14,15], which is widely used in characterizing polymers and polymer blends, especially, in inverse gas chromatography (IGC) experiments. Hansen's approach to miscibility resides on the *similarity* principle dictating that two components

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are miscible when each of the partial solubility parameters (dispersion, polar, and hydrogen-bonding) of one component have similar values with the corresponding partial solubility parameters of the other component. The Flory–Huggins χ_{12} interaction parameter is again calculated to be only positive, since it is defined as been proportional to the sum of the squared differences of partial or Hansen solubility parameters [14,15]. As a consequence, even polymer pairs interacting with strong specific forces are predicted to be immiscible ($\chi_{12} > 0$). In spite this, however, the Hansen's approach has been proved very useful in numerous studies and technological applications, especially, in IGC studies of polymers [14–16].

In the mean time, there was a remarkable advancement of predictive methods with sound foundations that can be applied to a variety of properties, especially, for non-polymeric substances. For space limitations, we will confine ourselves to two major directions, the Quantitative Structure–Property or Structure–Activity Relationships (QSPR/QSAR) and the quantum-mechanical Continuum Solvation Model (CSM) based predictive methods. From the first direction, one of the most successful and directly associated with our developments below is the QSPR/LSER (Linear Solvation Energy Relationships) approach [17,18] rooted in the solvatochromic approach [19–23] to solvation theory [24,25]. The COSMO-RS theory [26–28], one of the most successful recent developments in solution thermodynamics, is rooted in the conductor-like screening charge model (COSMO) [29] from the class of CSM models and is also used for our developments below.

In the QSPR/LSER approach [17,18], each solute compound is characterized by five molecular descriptors, V_x , S , E , A , and B , that stand for its McGowan volume [17], dipolarity/polarizability, excess molar refraction or electron polarizability, hydrogen-bonding acidity (electron acceptor/proton donor capacity), and hydrogen-bonding basicity, respectively. The methodology for obtaining LSER molecular descriptors, as finalized after a number of iterations, is now rather straightforward [17,18]. In the early development stages of LSER method [19–21] and the underlying scaled particle theory [24], the cohesive energy density (or the square of total solubility parameter, $ced = \delta^2$) of the solute was used to represent what was later represented by just its McGowan volume. In Hansen's method [14,15], however, the cohesive energy density of a compound is the sum of squares of the partial solubility parameters for the dispersive, polar, and hydrogen-bonding interactions, or

$$ced = \delta_d^2 + \delta_p^2 + \delta_{hb}^2 \quad (1)$$

Obviously, there is a drastic conceptual difference that separates the two methods and, thus, they were developed independently without any kind of interconnection.

On the other hand, COSMO-RS theory [26–28] combines in an eloquent manner quantum mechanics with statistical thermodynamics and handles interacting molecular surface charges computed by quantum chemical methods. The COSMO model is available in several quantum chemistry software suites, such as the Turbomole [30], the DMol3 [31], or the GAMESS-US [32]. Quantum chemically optimized geometries are provided for a number of computation DFT methods/basis sets. A cavity is created around a solute molecule, which is then solvated in infinite conducting medium, producing screening surface charges and giving the sigma charge density distribution profiles or sigma profiles. As a continuous distribution, the surface charge distribution or sigma profile has its statistical moments, known as COSMOments. Once the molecular surface charge distributions (COSMO files) are available, the COSMO-RS model calculates the system free-energy of mixing and other basic thermodynamic quantities in a Quasi-Chemical

surface group-contribution manner [33,34]. In contrast, however, to the classical group-contribution approaches, which require binary interaction parameters for the functional group pairs (binary interactions between groups), the COSMO-RS approach does not require any binary interaction parameters. As a result, a sigma-profile database is much smaller and easier to use than the classical group-contribution parameter databases. Sigma profiles require only the molecular structure and a density-functional theory calculation to incorporate new compounds into the database. A very large number of properties in a variety of systems have already been predicted successfully by the COSMO-RS model.

Based on QSPR/LSER and COSMO-RS models, in a series of recent papers [35–38], the concept of solubility parameter has been reconsidered and new molecular descriptors, the partial solvation parameters (PSPs), have been introduced. In direct analogy with LSER model [17,18], each compound is characterized by five PSPs, σ_W , σ_S , σ_E , σ_a , and σ_b corresponding to weak van der Waals, dipolarity/polarizability, electron polarizability, acidity, and basicity interactions, respectively. For all practical purposes, however, σ_S and σ_E may be combined into one polarity/refractivity PSP [36–38], σ_{pz} , without any significant loss in the predictive capacity of the new model. The solvation energy density (*sed*) is, then, defined as follows:

$$sed = \sigma_W^2 + \sigma_{pz}^2 + \sigma_a^2 + \sigma_b^2 \quad (2)$$

All compounds are divided into two major classes, the *homosolvated* and the *heterosolvated* ones. In *homosolvated* compounds the solvation energy density is identical with the cohesive energy density ($sed = ced$) while in *heterosolvated* compounds $sed \neq ced$. *Homosolvated* are the molecules which do not possess any hydrogen-bonding group (such as hydrocarbons) or possess, both, hydrogen-bonding donors and acceptors (such as alcohols, phenols, alcanoic acids, etc). Thus, these homosolvated compounds may self-associate and cross-associate. *Heterosolvated* are the molecules possessing hydrogen-bonding donors only (such as chloroform or acetylene) or acceptors only (such as ketones, ethers, esters, etc) and, thus, they may form hydrogen bonds only with another (heteron in Greek) compound and not with themselves (cross-associate only). The defining equations for PSPs and the method for their calculation are reviewed in the next section.

The introduction of PSPs led to a novel approach to solution thermodynamics, which was presented in ref. 37 and 38 for the case of binary mixtures. A simple method for obtaining PSPs of polymers, for which COSMO files are not available, was also proposed [38]. A variety of properties have been predicted successfully for both the concentrated and the infinite dilution case.

In this work, the PSP approach to solution thermodynamics will be generalized and analytical expressions will be derived for the basic thermodynamic quantities of mixtures. The infinite dilution case of a solute–probe (1) in a polymer mixture (2,3) solvent will be examined and consistent analytical expressions for the Flory–Huggins $\chi_{1,23}$ interaction parameter will be derived. The predictions of the PSP model will be compared with available experimental data on $\chi_{1,23}$ interaction parameter as well as on the χ_{23} interaction parameter of the binary polymer mixture. As will be shown, the latter are true Flory–Huggins interaction parameters compatible with spinodals and valid phase-separation thermodynamic considerations. In addition, the melting point depression in binary polymer mixtures will be predicted as well as the miscibility map in copolymer–homopolymer mixtures exhibiting competing intra-molecular and intermolecular hydrogen bonding. Before going, however, into solution thermodynamics, the defining equations for PSPs and the calculation methodologies will be reviewed in the next section.

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