Predicting Solubilities in Polymer Systems Using COSMO-RS

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Abstract

COSMO-RS is an advanced method for calculating the thermodynamic properties of chemical compounds and their mixtures. Unlike other approaches which use group contribution or limited to chemical structures for which empirical data exists, COSMO-RS is based on quantum mechanical calculations. By a unique combination of electron Density Functional Theory (DFT) with continuum solvation theory and efficient statistical thermodynamics procedures, COSMO-RS extends the broad applicability of DFT to thermophysical property predictions. Thus COSMO-RS is able to predict the free energies of almost any chemical compound in almost any solvent and mixture. A number of applications of COSMO-RS to VLE and LLE of small molecules have already been reported. The ability to predict the solubilities of gases, plasticizers and other additives in polymers is of practical importance. Since the permeability of polymer films depends on the solubility of a fluid compound in the polymer, this capability is very useful in the development of selective membranes. Similarly, predicting the solubilities of polymers in a given solvent has many industrial applications. Using COSMO-RS to predict polymer solution properties requires special treatment. In this presentation, the procedure for calculating solubilities in systems containing polymers and polymer blends will be described, the limitations of the approach will be pointed out, and then comparisons between experimental results and COSMO predictions will be given.

Introduction

The solubility of gaseous and liquid substances in polymers is a subject that has continued to receive wide attention due to its tremendous industrial relevance. It is important for the development and design of polymerization reactions and its associated downstream processes such as stripping and solvent recovery. A notable example is gas-phase polymerization of ethylene where knowledge of the solubility of the monomer in the polymer is vital to the design and operation of the process. In addition, the ability to predict solubility of substances in polymers is important in accounting for residual monomer and solvents in polymer products and for development of selective membranes.

While some simpler hydrocarbons can nowadays be reasonably well described by molecular simulations (molecular dynamics and Monte Carlo simulations), polymers and polymer blends still are a challenge for such simulation techniques despite 30 years of active parameterization of appropriate force-fields. Computations of solubility of solutes in polymers are usually carried out using either molecular models or group contribution models. The molecular modeling approach is a correlative method in the sense that it is based upon regression of experimental data of the system to obtain interaction parameters. Models that fall

into this category include, among others, equation of state models (such as SAFT, polymer-SRK, and Sanchez-Lacombe) and activity coefficient models (such as Flory-Huggins, polymer-NRTL and UNIQUAC).

The second approach is based upon group contribution models. This modeling approach is predictive when the group parameters are known; the structure of the mixture components is the only required input. Examples of models belonging to this category are UNIFAC-FV, GCLF, and GC-Flory. Perhaps, UNIFAC is the most widely used model amongst the group contribution models. Oishi and Praustnitz (1978) have extended UNIFAC to treat polymer solutions by adding a term that accounts for the free-volume (FV) difference between polymer and solvent molecules. While this difference is usually insignificant for liquid mixtures of small molecules, it is important for polymer/solvent systems. Another extension of UNIFAC to polymer solutions is given by Holten-Andersen et al. (1987) who obtained the free volume contribution form an equation of state based on perturbed-hard-chain theory. High and Danner (1990) have compared predictions of the UNIFAC free-volume model of Oishi and the Holten-Andersen equation of state activities in a variety of polymer solutions. They found that both models predict solvent activities reasonably well.

Klamt and coworkers (Klamt, 1995; Klamt and Eckert, 2000; Klamt *et al*, 2001; Eckert and Klamt, 2002) have proposed a new model called COSMO-RS. COSMO-RS is a novel a priori prediction method for thermodynamic properties of chemical compounds and their mixtures. The name is composed of "conductor-like screening model" (COSMO), which is an efficient variant of dielectric continuum salvation methods in quantum chemical programs, and its extension to "real solvents" (RS), which is a statistical thermodynamics approach based on the results of quantum chemical COSMO calculations.

It is a novel approach for calculating the activity coefficients of a solute dissolved in a continuous polarizable medium. COSMO-RS is based on self-consistent and exact solution of statistical thermodynamic relationship which is very fast. This is in contrast to the use of mean field approximations in most group contribution models. Thus, COSMO-RS allows for the efficient and consistent calculation of all thermodynamic quantities in mixtures. Unlike UNIFAC, the method does not use functional groups but uses surface charges for atoms that depend not only on particular atom, but also on the identity of other atoms in the same molecule. Thus, Klamt's method overcomes one of the serious limitations of UNIFAC. COSMO-RS have been successfully applied to predict solubility in mixtures of small molecules. Recently, Diedenhofen et. al., (2003) reported the calculation of activity coefficients at infinite dilution for 38 organic compounds in three different ionic liquids using the COSMO-RS method.

This work presents the application of the quantum chemically based thermodynamic prediction model COSMO-RS to polymer/solvent systems. The procedure for calculating solubilities in systems containing polymers and polymer blends will be described, the limitations of the approach will be pointed out, and then comparisons between experimental results and COSMO predictions will be given.

Theory

General COSMO-RS Theory

The theory of COSMO-RS has been described in detail in several articles [Klamt, 1995; Klamt and Eckert, 2000; Klamt *et al*, 2001; Eckert and Klamt, 2002]. Therefore, only a short survey of the basic concept will be presented here. The starting point of COSMO-RS is the state of a molecule X in its ideally (electrostatically) screened state, i.e., the state of X embedded in a perfect conductor. This state can be calculated with reasonable effort with dielectric continuum solvation models (CSMs). Apparently, the conductor-like screening model COSMO is optimally suited for this task, because it is derived from the limiting case of a molecule in a conductor. Density functional theory (DFT), combined with COSMO, allows for good accuracy of the relevant electrostatics. As a result of a DFT/COSMO calculation we do not only yield the total energy of X in its self-consistent state in the conductor, but we also gain the polarization charge density σ, which the conductor places on the cavity to screen the electric field of the molecule. This polarization charge density is a very good local descriptor of the polarity on the molecular surface. The σ profile of a component needs to be calculated only once. Because this is a time-consuming step, σ profiles are stored in a database. Figure 1 shows some σ-profiles of some compounds [Ecket and Klamt, 2004].
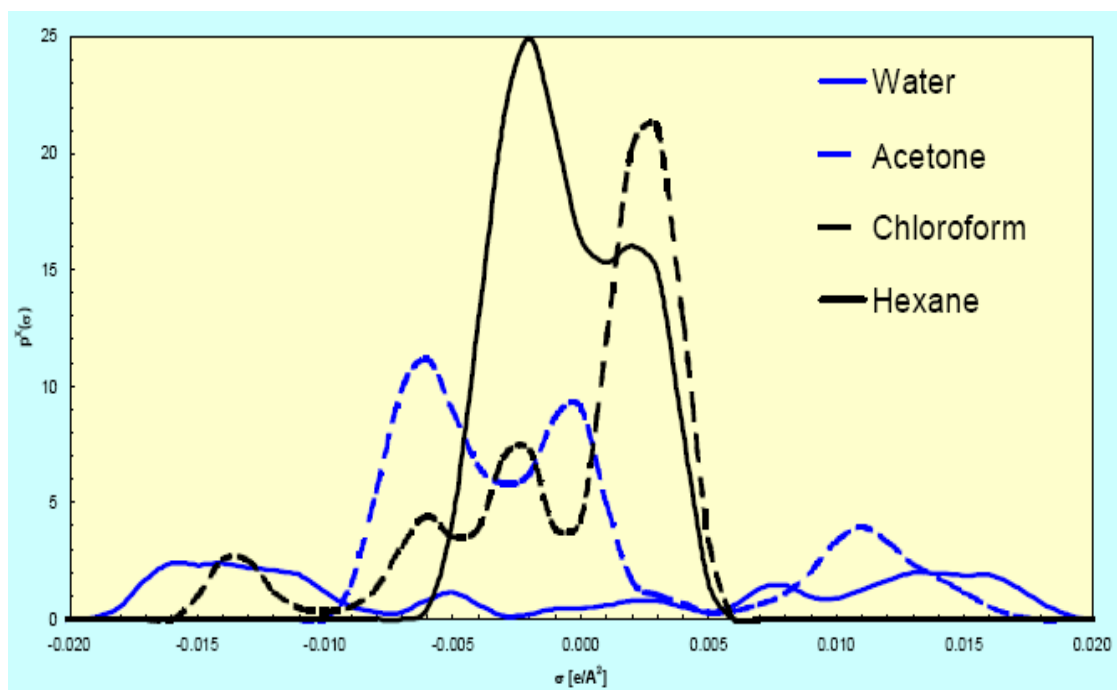

Figure 1: σ-profiles of some compounds.

In the second step, the polarization charge density of the COSMO calculation is used to extend the model toward the "Real Solvents" (COSMO-RS). The 3D polarization density distribution on the surface of each molecule X is converted into a distribution function, the so-called σ-profile $P^{Xi}(\sigma)$, which gives the relative amount of surface with polarity σ on the surface of the molecule. The σ-profile for the entire solvent of interest S, which might be a mixture of

several compounds, $p_S(\sigma)$, can be built by adding the $P^{X_i}(\sigma)$ values of the components weighted by their mole fractions x_i in the mixture.

$$p_S(\sigma) = \sum_{i \in S} x_i p^{X_i}(\sigma)$$

The most important molecular interaction energy modes, that is, electrostatics (E_{misfit}) and hydrogen bonding (E_{HB}), are described as functions of the polarization charges of two interacting surface segments σ and σ' or $\sigma_{acceptor}$ and σ_{donor}, if the segments are located on a hydrogen bond donor or acceptor atom. The less specific van der Waals (E_{vdW}) interactions are taken into account in a slightly more approximate way.

$$E_{misfit}(\sigma,\sigma') = a_{eff}\frac{\alpha'}{2}(\sigma + \sigma')^2$$

where a_{eff} is the effective contact area between two surface segments and α' is an adjustable parameter.

$$E_{HB} = a_{eff}c_{HB}\min\left(0; \min\left(0; \sigma_{donor} + \sigma_{HB}\right)\max\left(0; \sigma_{acceptor} - \sigma_{HB}\right)\right)$$

wherein c_{HB} and σ_{HB} are adjustable parameters.

$$E_{vdW} = a_{eff}(\tau_{vdW} + \tau'_{vdW})$$

In the above equations, there are five adjustable parameters, an interaction parameter $\acute{\alpha}$, the effective contact area a_{eff}, the hydrogen bond strength c_{HB}, the threshold for hydrogen bonding σ_{HB}, and the element-specific vdW interaction parameter τ_{vdW}. To take into account the temperature dependence of E_{HB} and E_{vdW}, temperature-dependent factors are applied, each with one adjustable parameter as defined in Klamt and Eckert, (2000).

The chemical potential of a surface segment with screen charge density (SCD) σ in an ensemble described by normalized distribution function $p_S(\sigma)$ is give as:

$$\mu_S(\sigma) = -\frac{RT}{a_{eff}}\ln\left[\int p_S(\sigma')\exp\left(\frac{a_{eff}}{RT}\left(\mu_S(\sigma') - E_{misfit}(\sigma,\sigma') - E_{HB}(\sigma,\sigma')\right)\right)d\sigma'\right]$$

The distribution function $\mu_S(\sigma)$ is a measure for the affinity of the system S to a surface of polarity σ. The vdW energy, which does not appear the chemical potential equation, is added to the reference energy in solution (energy of the COSMO calculation). The chemical potential of compound X in the system S (the solvent) can now be calculated by integration of $\mu_S(\sigma)$ over the surface of the compound.

$$\mu_S^X = \mu_{res\,S}^X + \mu_{comb\,S}^X = \int p^X(\sigma)\mu_S(\sigma)d\sigma + \mu_{comb\,S}^X,$$

where the residual part, i.e. the part resulting from the interactions of the surfaces in the liquid, is given by the surface integral of function $\mu_S(\sigma)$ over the solute surface, which is expressed using the σ-profile of the solute, and a combinatorial contribution, which arises from the different shapes and sizes of the solute and solvent molecules.

The activity coefficient of a solute X in a liquid S is given by:

$$\gamma_S^X = \exp\left\{\frac{\mu_S^X - \mu_X^X}{RT}\right\}.$$

where μ_S^X is the potential in the solvent S and μ_X^X is the potential of the pure compound X.

Solubility in Polymers and Polymer Blends

In most of its typical applications, COSMOtherm is intended to treat complete molecules as one entity. In such a case, obviously all atoms of the compound have to be taken into account in the calculation of the sigma profile. This corresponds to a weight of 1 for all atoms.

However, if we consider very large molecules like polymer chains, it may be impossible to do a single quantum chemical calculation for the entire molecule. Instead, it is useful to compose the large molecule out of molecular fragments which are calculated independently, but which have to be sufficiently saturated by e.g. one or more monomeric units at all sites where the fragment is cut. Hence, the COSMO-file of such a compound will contain atoms of the saturation region, which should not be taken into account in the COSMOtherm calculation. (Figure 2)This can be achieved by setting the weight of these atoms to zero, while the weights of the atoms of the fragment itself are kept one. The weighting can be done directly in the compound section of the input file with the w={ } keyword, as described in the COSMO*therm* User's Manual [Eckert and Klamt, 2004]. Alternatively, it is possible to use the so-called COSMO-metafiles (extension .mcos) provided in the COSMO*therm* database.
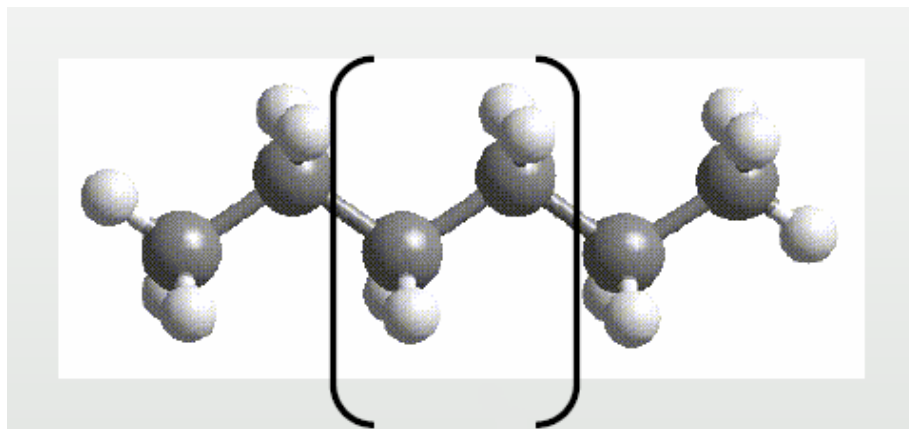

Figure 2: σ-profile from monomeric repeat unit (PE)

The chemical potential of the polymer is calculated from a monomer (or larger) repeat unit, and hence the corresponding solvent area and volume do not reflect the real surface area and volume of the polymer. It is therefore necessary to switch off the combinatorial contribution term. However, the combinatorial portion will have to be calculated later to add to the residual contribution to obtain the true chemical potential. In this work, the Staverman-Guggenheim form of combinatorial contribution is used, plus the free volume contribution as suggested by Oishi and Prausnitz (1978).

In the framework of the standard COSMO-RS theory, a polymer can be described as a "pseudo liquid" that consists of polymer repeat units. This simple approach leads to the following limitations:
- Crystalline polymers can not be computed.
- The approach is valid for low solute load only. Polymer swelling and structural effects cannot be taken into account.

The solubility of a gaseous compound in a polymer can be calculated from its partial vapor pressure and activity coefficient:

$$p_i = p_{0i} x_S^X \gamma_S^X$$

$$x_S^X = \frac{p_X}{p_{0X}} \frac{1}{\gamma_S^X}$$

Where

P_{0X} : vapor pressure of the pure compound.

P_X : partial pressure of the solute (X) in the gas phase.

x_S^X : mole fraction of the solute (X) in the polymer (S).

γ_S^X : activity coefficient of the solute (x) in the polymer (S)

For a liquid compound, the mole fraction of the solute in the polymer is the reciprocal of the activity coefficient:

$$x_S^X = \frac{1}{\gamma_S^X}$$

Thus, the polymer solubilities of gaseous and liquid compounds are obtained from an activity coefficient or Henry Law coefficient calculation ($k_H = p_i^0 \gamma_i$) rather than a solubility calculation. However, the iterative procedure for the calculation of γ_i should not be used with polymers, since this procedure treats the polymer like a liquid. Instead, the activity coefficient at infinite dilution can be used as a reasonable approximation for polymers at low solute load.

$$\gamma_S^X \approx \gamma_S^{X,\inf}$$

Methodology

The calculations of solubilities were performed roughly in four steps.

- In the first step, the geometry and polarization charge density on the molecular surface were calculated for polymer and solvent molecules. The TURBOMOLE program based on the density functional theory (DFT) was used for these calculations and the high quality COSMO (conductor-like screening model) parameterization with full geometry optimization at the TZVP (triple-ζ valence polarized) basis set was applied.

- In the second step, the solvent activity coefficient for each polymer–solvent system was obtained using the charge densities of the polymer and solvent molecules by the COSMO-RS method. COSMO-RS implemented in the COSMOtherm [Eckert and Klamt, 2004] was used in the present study. Only the residual portion is obtained in this step. The combinatorial part is switched off as discussed earlier.

- In the third step, the Staverman-Guggenheim (SG) form of combinatorial contribution plus the free volume contribution as suggested by Oishi and Prausnitz (1978) are then added to the residual activity coefficient.

- Reciprocal of the activity coefficient gives the solubility.

It took about 4 hrs on average to calculate charge density of PS monomer by TURBOMOLE with Pentium 4 3.0GHz. On the other hand, it takes seconds to do a typical calculation of solubility of polymer solution by COSMOtherm. A flow chart for COSMO-RS calculation is represented in Figure 3 [Eckert and Klamt, 2004].
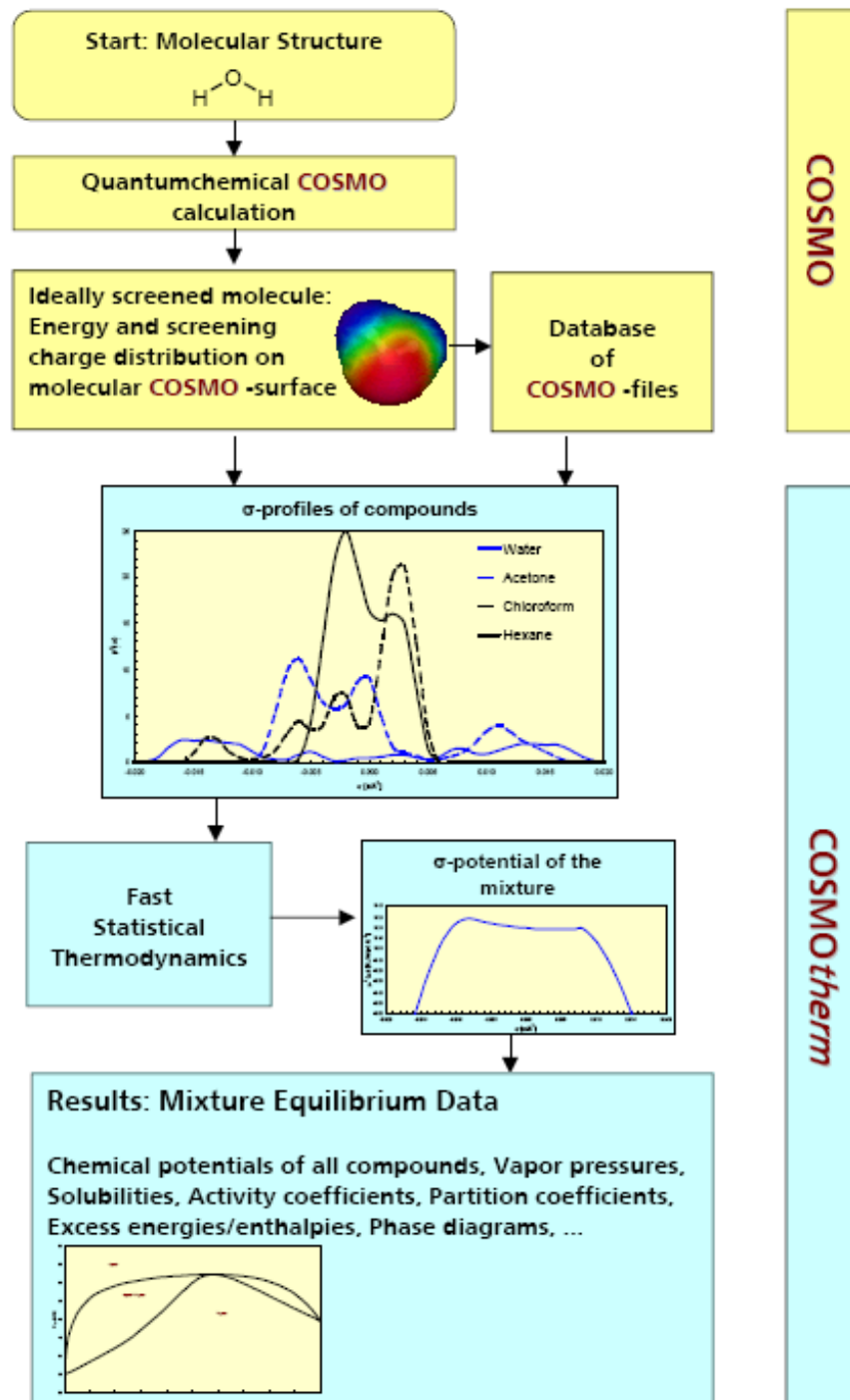
Flow chart of a COSMO*therm* calculation:

Figure 3: COSMO-RS calculation procedure

Results and Discussion

Solubilities of polymer solutions are usually reported as solvent activity coefficients. Reciprocal of the activity coefficient of solute in polymer gives the solubility for low solute load. The job then reduces to predicting experimental activity coefficients using COSMO-RS. The database assembled by Danner and High (1993) was chosen as basis for comparison. The following systems were selected for the purpose of this study; PS-acetone, PS-cyclohexane, PS-toluene, and PVC-toluene.

PS-Acetone

Figure 4 gives the graphical comparison between the activity coefficients of acetone in PS-acetone system at (a) 298.15K and (b) 323.15 K. SG-COSMO predicts the activity coefficients reasonably well. However, the FV-COSMO predicted the experimental values with much higher deviations at both temperatures.
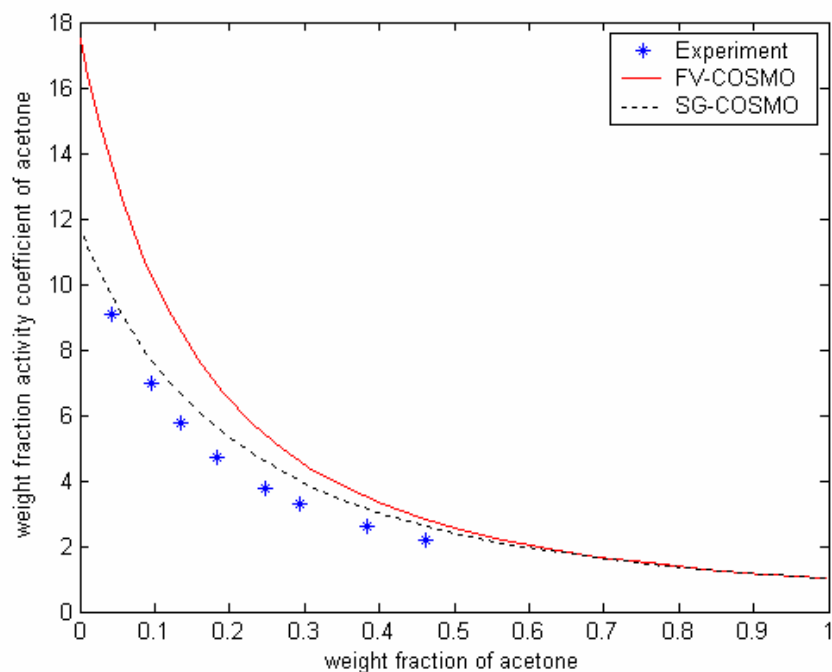
(a) 298.15 K (PS-Acetone)
Bawn, C. E. H.; Wajid, M. A. "High Polymer Solutions. Part 7. Vapour Pressure of Polystyrene Solutions in Acetone, Chloroform and Propyl Acetate", Trans. Faraday Soc. 52, 1658 (1956).
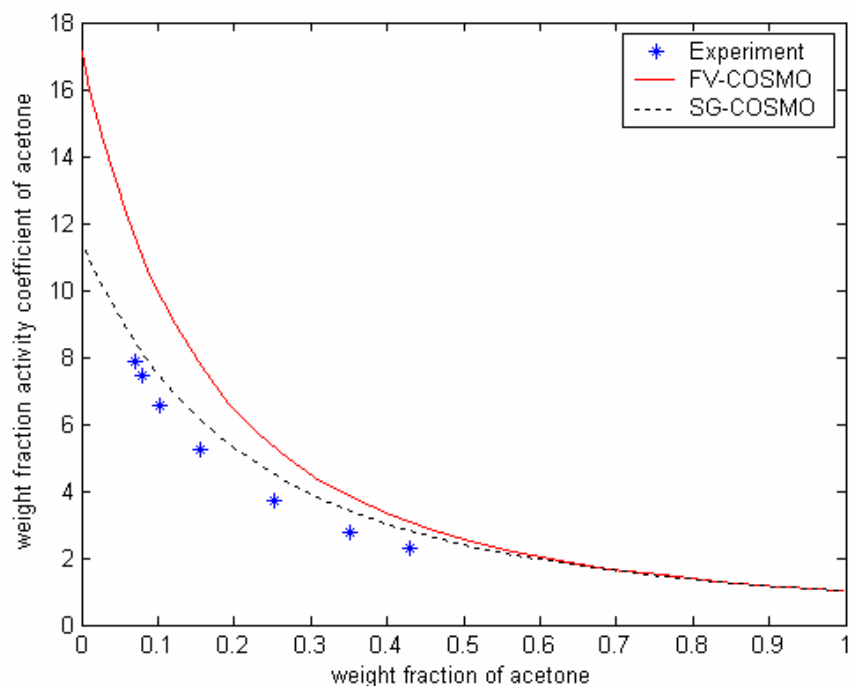
(b) 323.15 K (PS-Acetone)

Bawn, C. E. H.; Wajid, M. A. "High Polymer Solutions. Part 7. Vapour Pressure of Polystyrene Solutions in Acetone, Chloroform and Propyl Acetate", Trans. Faraday Soc. 52, 1658 (1956).

Figure 4: Comparison between Predicted and Experimental weight fraction activity coefficient of acetone in polystyrene-acetone (PS-acetone) systems
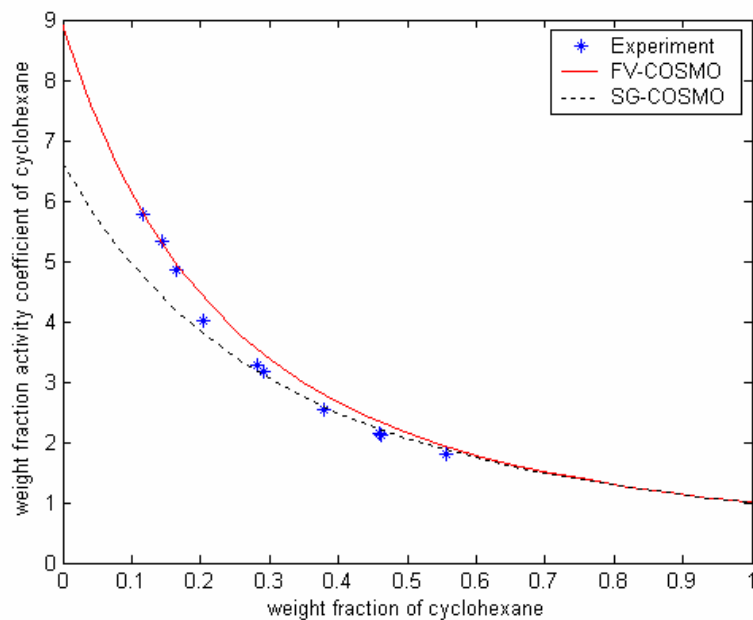
PS-cyclohexane

Figure 5 gives the graphical comparison between the activity coefficients of cyclohexane in PS-cyclohexane system at **(a) 297.15K; (b) 307.15 K**; **(c) 317.15 K**; and **(d) 338.15 K**. For this system, the FV-COSMO provided excellent predictions of the experimental values than SG-COSMO at all temperatures. The added accuracy of the FV-COSMO over SG-COSMO is most likely due to the free-volume contribution. However, the predictions are not very good at much lower compositions of cyclohexane.
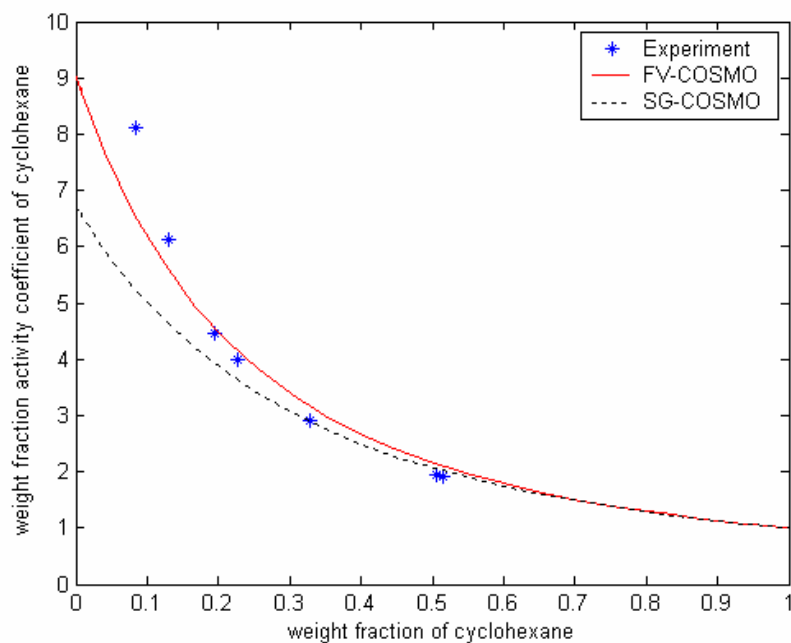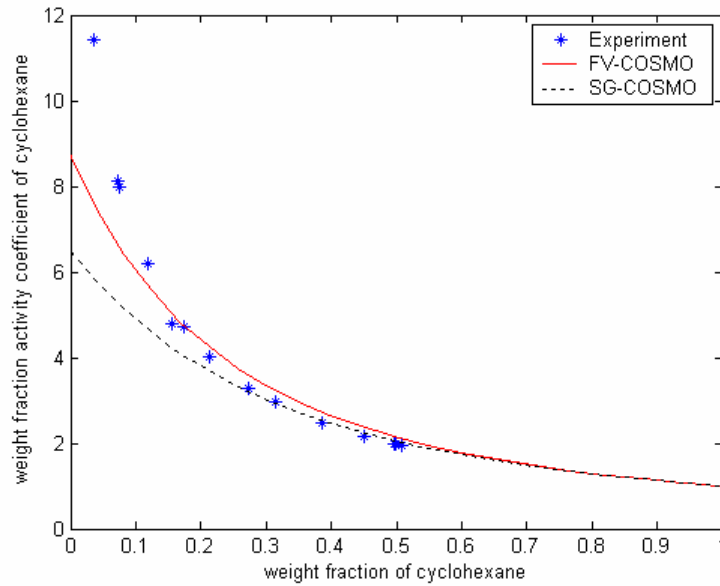
(a) 297.15 K (PS-cyclohexane)

*Krigbaum, W. R.; Geymer, D. O. "Thermodynamics of Polymer Solutions. The Polystyrene-Cyclohexane System Near the Flory Theta Temperature", J. Am. Chem. Soc. 81, 1859 (1959).
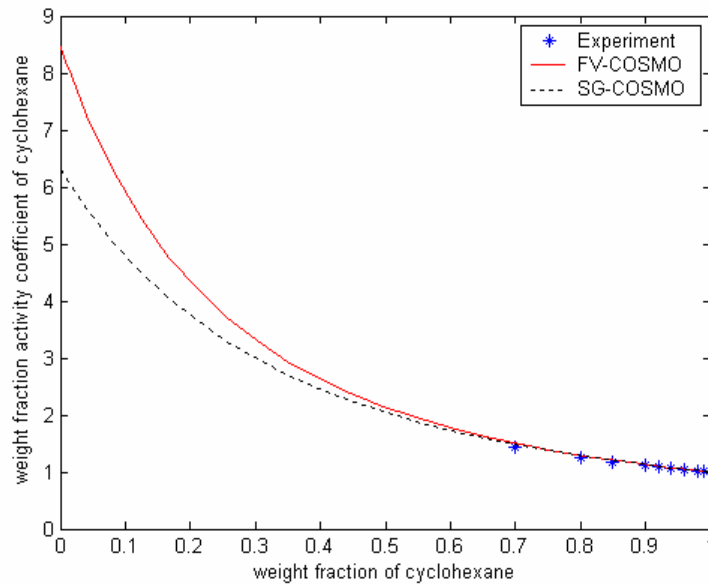

(b) 307.15 K (PS-cyclohexane)

*Krigbaum, W. R.; Geymer, D. O. "Thermodynamics of Polymer Solutions. The Polystyrene-Cyclohexane System Near the Flory Theta Temperature", J. Am. Chem. Soc. 81, 1859 (1959).

(c) 317.15 K (PS-cyclohexane)

*Krigbaum, W. R.; Geymer, D. O. "Thermodynamics of Polymer Solutions. The Polystyrene-Cyclohexane System Near the Flory Theta Temperature", J. Am. Chem. Soc. 81, 1859 (1959).

(d) 338.15 K (PS-cyclohexane)

*Agathonos, P.; Karaiskakis, G. "Thermodynamic Study of Polymer-Solvent Systems by Reversed-Flow Gas Chromatography", J. Appl. Polym. Sci. 37, 2237 (1989).

Figure 5: Comparison between Predicted and Experimental weight fraction activity coefficient for cyclohexane in polystyrene-cyclohexane (PS-cyclohexane) systems
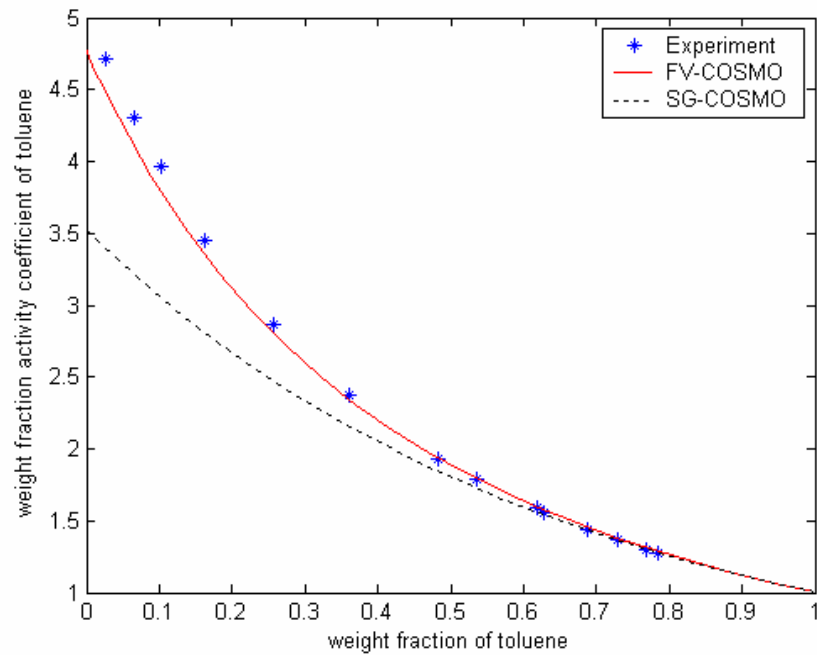
PS-toluene

Figure 6 gives the graphical comparison between the activity coefficients of toluene in PS-toluene system at **(a) 294.5 K; (b) 383.15 K**; **(c) 413.15 K**; and **(d) 443.15 K**. The FV-COSMO consistently provided better predictions of the experimental values than SG-COSMO at all temperatures. However, deviations between the experimental and predicted values begin to increase as the temperature goes up. Generally, there is very good agreement between the two. Figure **(e)** shows toluene solubility, reciprocal of the low solute loading activity coefficient of Figure **(d)**.
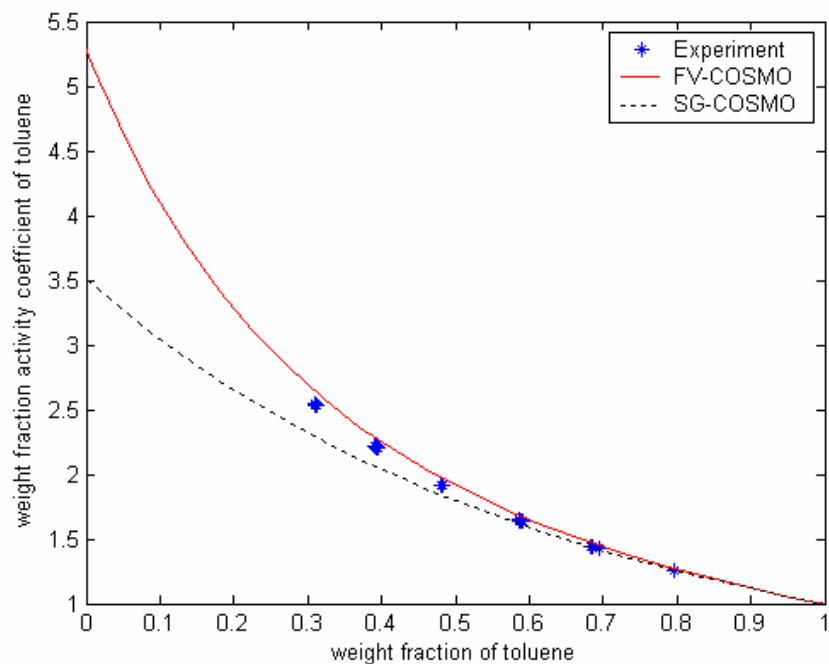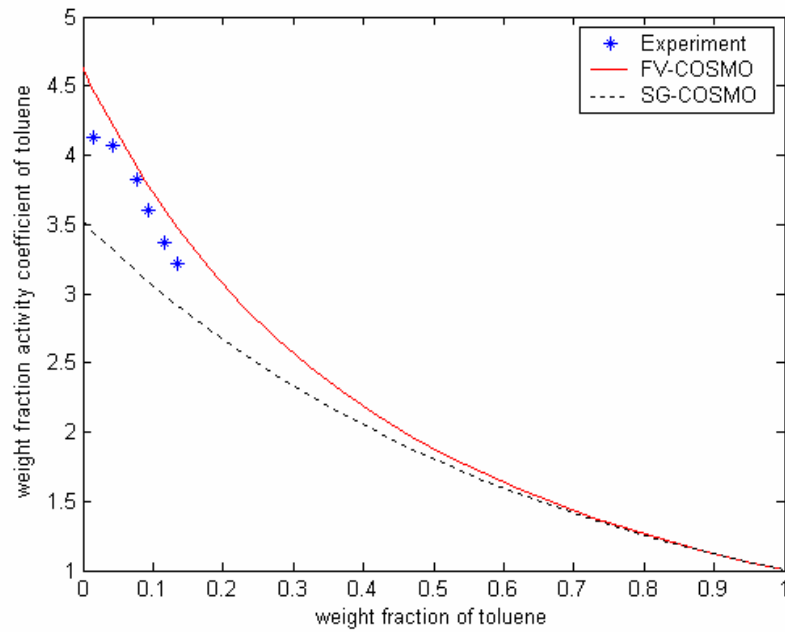

(a) 294.5 K (PS-toluene)

*Corneliussen, R.; Rice, S. A.; Yamakawa, H. On the Thermodynamic Properties of Solutions of Polar Polymers. A comparison of Experiment and Theory",   J. Chem. Phys. 38, 1768 (1963).
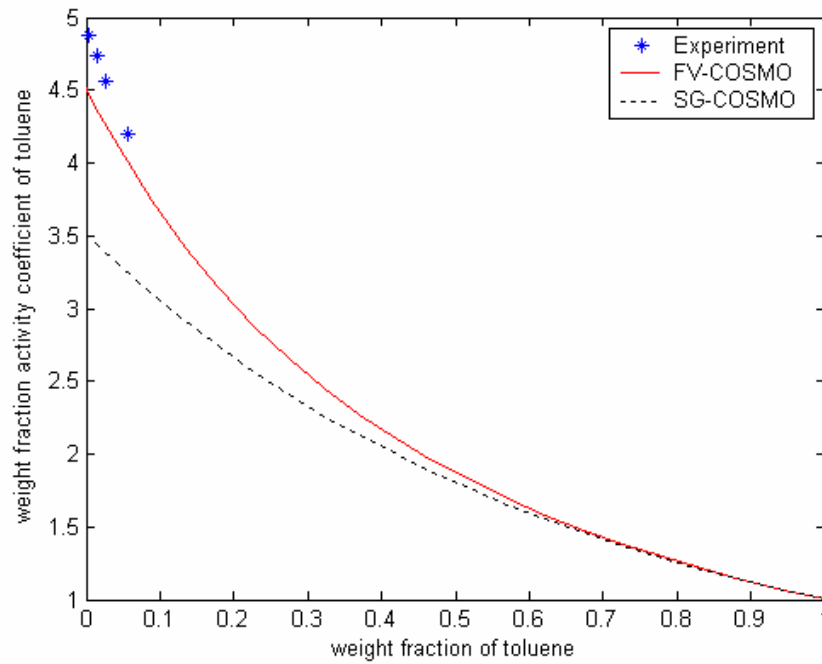
(b) 383.15 K (PS-toluene)

*Vrentas, J. S.; Duda, J. L.; Hsieh, S. T. Thermodynamic Properties of Some Amorphous Polymer-Solvent Systems", Ind. Eng. Chem. Prod. Res. Dev. 22, 326 (1983)
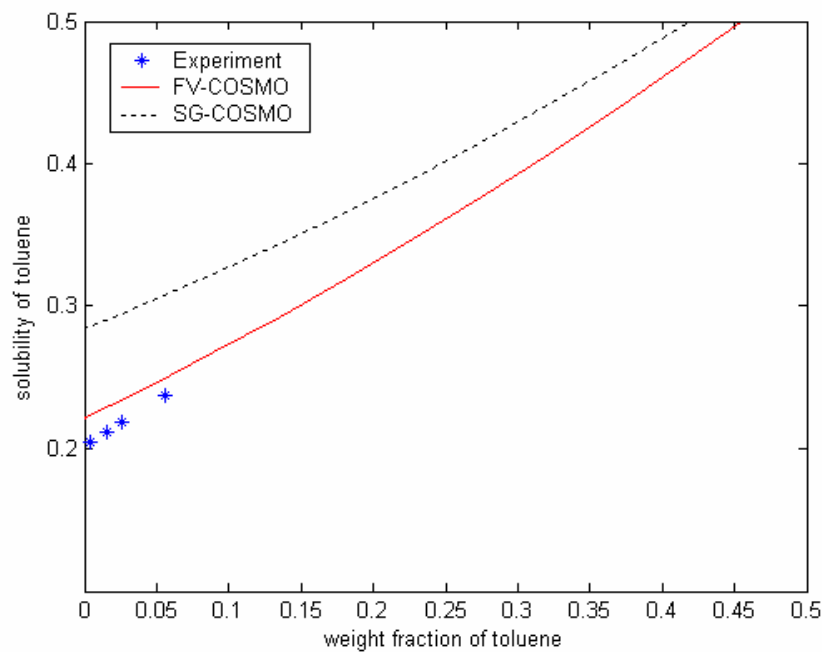

(c) 413.15 K (PS-toluene)

*Vrentas, J. S.; Duda, J. L.; Hsieh, S. T. Thermodynamic Properties of Some Amorphous Polymer-Solvent Systems", Ind. Eng. Chem. Prod. Res. Dev. 22, 326 (1983)

(d) 443.15 K (PS-toluene)

*Vrentas, J. S.; Duda, J. L.; Hsieh, S. T. Thermodynamic Properties of Some Amorphous Polymer-Solvent Systems", Ind. Eng. Chem. Prod. Res. Dev. 22, 326 (1983)

(e) 443.15 K (PS-toluene)

Figure 6: Comparison between Predicted and Experimental weight fraction activity coefficient for toluene [(a) to (d)], (e) toluene solubility; in polystyrene-toluene (PS-toluene) systems

PVC-toluene

Figure 7 gives the graphical comparison between the activity coefficients of toluene in PVC-toluene system at **316.35 K**. Similarly, the FV-COSMO provided better predictions of the experimental values than SG-COSMO. However, there is room for improvement in the predictions of the FV-COSMO.
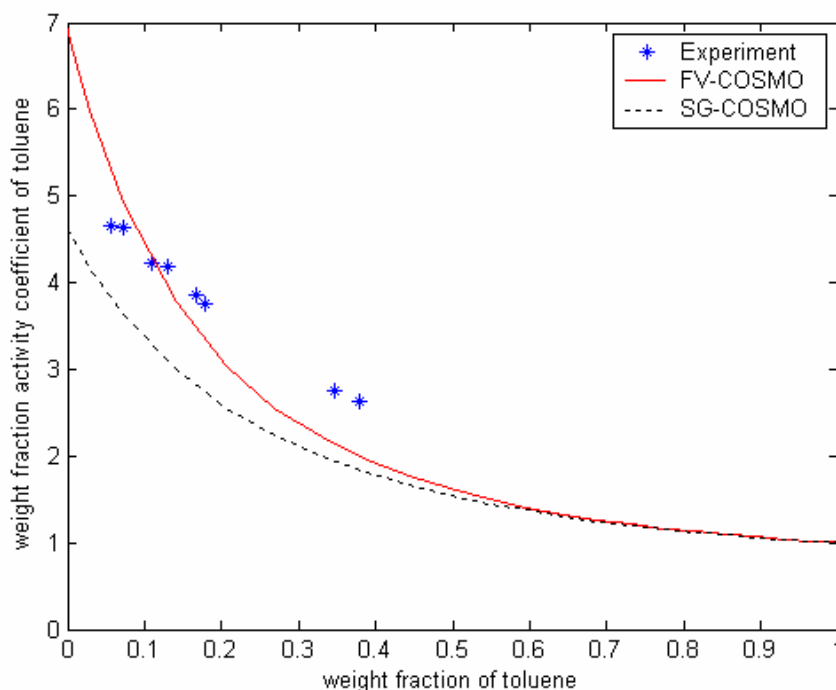

Figure 7: Comparison between Predicted and Experimental weight fraction activity coefficient for toluene in poly vinyl chloride-toluene (PVC-toluene) systems (316.35K)

Conclusions

The present results demonstrated that COSMO-RS has reasonably reproduced the selected experimental data and have proved that this method is generally applicable in predicting the solvent activities (in effect solubility) in polymer solutions. Even though the approach is only valid for low solute load, it was able to predict higher solute loading with high degree of accuracy for some systems. However, there is still room for improvements in the COSMO-RS predictions.

The major drawback of the method of this sort has been the computation time. As far as the problems treated in the present study are concerned, the computation barrier has been practically overcome and the method is entirely feasible. In the present COSMOtherm implementation, the COSMO-RS method treats polymer as a liquid solvent of monomer repeat units, its validity is therefore limited to non-crystalline polymers only (Klamt and Eckert, 2004).

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