Prediction of Vapor–Liquid Equilibrium for Polymer Solutions Based on the COSMO-SAC Model

Li Yang, Xiaochun Xu, Changjun Peng, Honglai Liu, and Ying Hu
State Key Laboratory of Chemical Engineering and Dept. of Chemistry, East China University of Science and Technology, Shanghai 200237, China

DOI 10.1002/aic.12178

To extend the application of the COSMO-SAC model to phase-equilibrium calculations of polymer solutions, a new strategy for estimating the charge-density profile, the cavity volume and the cavity surface area of polymer molecules is proposed by finding reasonable parameters for the corresponding repeating structure units. The molecular parameters for polymers are obtained by summing up the corresponding COSMO calculated values of the repeating units calculated by the algorithms of DMol3 (a density functional theory) or MOPAC (a semi-empirical method). Combining with the COSMO-SAC model, the activities and equilibrium pressures for several typical polymer solutions are satisfactorily predicted indicating that the proposed method can be used for the prediction of vapor–liquid equilibrium of polymer solutions. It was also found that both DMol3 and MOPAC can be used though the results obtained from them are slightly different. The results in this paper show that the method proposed has the potential to predict other phase-equilibrium properties of polymer systems. © 2010 American Institute of Chemical Engineers *AIChE J,* 56: 2687–2698, 2010

Keywords: polymer solutions, vapor–liquid equilibrium, COSMO-SAC

Introduction

The thermodynamic properties of polymer solutions have a central role in the process of development of advanced polymer material. For instance, the knowledge of phase behavior is indispensable to the design and optimization of separation and purification processes. To save the experimental efforts, it is very important to develop appropriate methods to estimate phase equilibria of polymer solutions. Traditionally, there are two types of thermodynamic models: One is the group contribution activity coefficient model[1–4] and the other is the group contribution equation of state model.[5–12] Although the prediction methods can give many effective guide of phase behavior of polymer solutions; however, the interaction parameters between functional groups in these models must be obtained by fitting a large set of experimental phase equilibrium data. What is more, they also suffer from the inability to distinguish between the molecular isomers and to predict the parameters of new functional groups which are not included in their existing database. So it is desirable to develop a priori method for predicting phase behavior of polymer solution without using any experimental data.

Recently, a new method of ‘‘conductor-like screening model for real solvent’’ (COSMO-RS) started from the quantum chemical solvation calculations to predict macroscopic thermodynamics properties was first proposed by Klamt and co-workers.[13–16] In principle, this method can be used to estimate directly the activities of any species in any mixture by quantum mechanical calculations and then to predict the phase equilibrium of a mixture without any experimental data. Later, Lin and Sandler[17–19] developed a COSMO segment activity coefficient model (COSMO-SAC) based on the

---

Additional Supporting Information may be found in the online version of this article.

Correspondence concerning this article should be addressed to H. Liu at hlliu@ecust.edu.cn.

COSMO-RS method. In this model, the authors combined COSMO calculations with the Staverman–Guggenheim equation to calculate the segment activity coefficient. Later, a new model of COSMO-RS(ol) derived from COSMO-RS and UNIFAC(Do) was given by Gmehling et al.[20,21] These methods have been applied for the calculation of phase equilibrium of various mixtures of normal fluids and extended to the calculation of phase behavior at elevated pressure. For example, the approaches of COSMO-RS combined with SRK[22] and MSRK[23] equations of state (EoS) were used to predict vapor–liquid equilibrium (VLE) of hydrocarbons, water and alcohol mixtures at high pressure. Lee and Lin[24] employed COSMO-SAC and PR EoS to predict VLE of some systems at elevated pressure. The COSMO-RS and COSMO-SAC methods have also been extended to predict thermodynamic properties of systems containing ionic liquids.[25,26] These applications suggest that the COSMO-type models can provide promising description of thermodynamic properties of small molecule solutions. However, to our knowledge, there is only a little report on the application of COSMO methods in polymer systems in references reported currently and we would try to perform this extension in this work.

In COSMO method, the key is the quantum mechanical calculation of the COSMO data for different molecules. With the development of software of quantum chemical calculations and computer hardware, it could be possible to make calculations for more complex molecules. However, it is a difficult and even impossible task at present to make quantum mechanical calculations for a complete polymer molecule composed of thousands of monomers. In this work, we suppose that the polymer molecule is formed by a large amount of the repeating unit. We then attempt to extend COSMO-SAC model proposed by Sandler and coworkers[17–19] to predict VLE of polymer solutions. Two procedures have been made. First, an assumption is made that each polymer molecule is composed of a series of the representative repeating structure units and the quantum chemical data of polymer chain can be obtained by summing up that of the repeating units. Second, we select DMol3[27] and MOPAC2009[28] packages for the quantum chemical calculations of the repeating unit and test the effects of the two different quantum mechanics algorithm on the results of VLE of polymer solutions.

The rest of the article is organized as follows: in COSMO-SAC model section, model is briefly reviewed. The computational details of polymer COSMO data,[29] especially the procedure for obtaining the repeating unit COSMO data are discussed in Application of COSMO-SAC to polymer solutions section. In Results and discussion section, we present the predicted results and the comparison with experimental results for several examples of typical polymer solutions including the linear polymer, the polymer with side alkyl group, the polymer with aromatic group, and the polymer containing other elements besides carbon atoms in main chain. Finally, the conclusion is made.

COSMO-SAC Model

The COSMO-SAC model[17–19] was developed based on the COSMO-RS model[13–15] and the group contribution solvation model.[17,30] In the later model, the segment activity coefficients are calculated via the molecular solvation free energy in solution, which is obtained from ab initio solvation calculations.[13,14,17,30] In the COSMO-SAC model, Lin and Sandler employed a two-step process[17] to calculate the solvation free energy. They assumed that the charges on the solute are first turned off, and then the charges are turn on. The latter step is equivalent to the path proposed in COSMO-RS in which the charges are first screened in a perfect conductor, and then the conductor is restored to the real solvent. In the calculation for the restoring free energy, similar to COSMO-RS, the molecule is treated as surface segment muster and the restoring free energy is calculated by summing interaction energies between surface segments.

The activity coefficient of a solute i in the COSMO-SAC model is expressed by two terms contributed from the restoring free energy of solute and the turning off free energy (forming a hard sphere or cavity), respectively, as follows:

$$\ln\gamma_{i/S} = n_i \sum_{\sigma_m} P_i(\sigma_m)[\ln\Gamma_S(\sigma_m) - \ln\Gamma_i(\sigma_m)] + \ln\gamma_{i/S}^{SG} \tag{1}$$

where the first term on the right is the contribution of the restoring free energy of solute, it is a summation over all possible charge density σ_m in a molecule i. In condensed phase, each segment is assumed to pair with another segment. Therefore, for each σ_m, the surface segment activity coefficients in pure liquid i, $\Gamma_i(\sigma_m)$, and in solution, $\Gamma_S(\sigma_m)$, are calculated by the following equations,

$$\ln\,\Gamma_i(\sigma_m) = -\ln\left\{\sum_{\sigma_n} p_i(\sigma_n)\Gamma_i(\sigma_n)\exp\left[\frac{-\Delta W(\sigma_m,\sigma_n)}{RT}\right]\right\} \tag{2}$$

$$\ln\,\Gamma_S(\sigma_m) = -\ln\left\{\sum_{\sigma_n} p_S(\sigma_n)\Gamma_S(\sigma_n)\exp\left[\frac{-\Delta W(\sigma_m,\sigma_n)}{RT}\right]\right\} \tag{3}$$

where $p_i(\sigma_n)$ and $p_S(\sigma_n)$ are the probability of finding a segment with a surface charge density σ_n in pure liquid i and in solution, respectively. The summation is over all possible charge density σ_n, in other word, over all possible segment pairs between σ_m of a molecule i and all other σ_n.

In the above equations, as the charge property of a molecule, the σ profile, $p(\sigma)$, of each component is the most important property in COSMO methods which is obtained through the COSMO quantum chemical calculations.

For the pure liquid i, $p_i(\sigma)$ can be expressed as

$$p_i(\sigma) = \frac{n_i(\sigma)}{n_i} = \frac{A_i(\sigma)}{A_i} \tag{4}$$

where $n_i(\sigma)$ is the number of segments with surface charge density σ, $A_i(\sigma)$ is the surface area of segment with surface charge density σ, $A_i = \sum_\sigma A_i(\sigma)$ is the total cavity surface area, $n_i = \sum_\sigma n_i(\sigma)$ is the contribution of surface segments of each molecule i to the mixture. An adjustable parameter[17] a_{eff} defined as a standard segment surface area is needed in this method, and $n_i = A_i/a_{\mathrm{eff}}$, $n_i(\sigma) = A_i(\sigma)/a_{\mathrm{eff}}$, $a_{\mathrm{eff}} = 7.5(\text{Å}^2)$.

Table 1. Parameters Used in the COSMO-SAC Model

Symbol	Value	Description
r_{av}	0.81764 Å	σ averaging radius
a_{eff}	7.5 Å	Effective surface segment surface area
c_{hb}	85580.0 (kcal/Å^4)/(mol e^2)	Hydrogen-bonding constant
σ_{hb}	0.0084 e/Å^2	σ cutoff for hydrogen bonding
α'	9034.97 (kcal/Å^4)/(mol e^2)	Misfit energy constant
z	10	Coordination number
q	79.53 Å^2	Standard area parameter
r	66.69 Å^3	Standard volume parameter

For a solution, the σ profile is the weighted sum of the σ profile of all of the components and can be calculated by

$$p_S(\sigma) = \frac{\sum_i x_i n_i p_i(\sigma)}{\sum_i x_i n_i} = \frac{\sum_i x_i A_i p_i(\sigma)}{\sum_i x_i A_i} \tag{5}$$

where x_i is mole fraction of component i.

The screening charge density σ^* from the COSMO output is averaged to give the apparent charge σ on a standard surface segment using the following equation[31]:

$$\sigma_v = \frac{\sum_u \sigma_u^* \frac{r_u^2 r_{\mathrm{av}}^2}{r_u^2 + r_{\mathrm{av}}^2} \exp\left(-\frac{d_{uv}^2}{r_u^2 + r_{\mathrm{av}}^2}\right)}{\sum_u \frac{r_u^2 r_{\mathrm{av}}^2}{r_u^2 + r_{\mathrm{av}}^2} \exp\left(-\frac{d_{uv}^2}{r_u^2 + r_{\mathrm{av}}^2}\right)} \tag{6}$$

where σ_v is the average surface charge density on segment v, r_{av} is the averaging radius (an adjustable parameter $r_{\mathrm{av}} = 0.81764$ Å). d_{uv} is the distance between segments u and v, and r_u is the radius of segment u.

$\Delta W(\sigma_m, \sigma_n)$[17] in Eqs. 2 and 3 is called the exchange energy, which is the energy required to form one pair of (σ_m, σ_n) from a neutral pair. In COSMO-SAC model, the exchange energy is calculated by

$$\Delta W(\sigma_m, \sigma_n) = \left(\frac{\alpha'}{2}\right)(\sigma_m + \sigma_n)^2 + c_{\mathrm{hb}} \max[0, \sigma_{\mathrm{acc}} - \sigma_{\mathrm{hb}}] \min[0, \sigma_{\mathrm{don}} + \sigma_{\mathrm{hb}}] \tag{7}$$

where α' is the misfit energy constant, c_{hb} is the hydrogen-bonding interaction energy, σ_{hb} represents a cutoff value for hydrogen-bonding interaction. These parameters have been given in COSMO-SAC model as shown in Table 1. σ_{acc} and σ_{don} are the larger and smaller values of σ_m and σ_n, respectively. The contribution of the nonelectrostatic interaction coming mainly from the dispersion interaction disappears because it is assumed as a constant and can be cancelled out.

The second term on the right of Eq. 1, $\ln\gamma_{i/S}^{SG}$, is the contribution of the turning off or cavity free energy, which comes from the combinatorial entropy of the arrangement of molecules and is calculated by the Staverman–Guggenheim expression[17]:

$$\ln\gamma_{i/S}^{SG} = \ln\left(\frac{\phi_i}{x_i}\right) + \frac{z}{2} q_i \ln\left(\frac{\theta_i}{\phi_i}\right) + l_i - \frac{\phi_i}{x_i}\sum_j x_j l_j \tag{8}$$

where z is the coordination number, usually set to be 10, θ_i and ϕ_i denote surface area fraction and the volume fraction for component i, they can be calculated by:

$$\theta_i = \frac{x_i q_i}{\sum_j x_j q_j}; \;\; \phi_i \frac{x_i r_i}{\sum_j x_j r_j} \tag{9}$$

r_i and q_i are the normalized molecular volume and surface area parameters for component i and can be calculated by COSMO output cavity volume V_i^{COSMO} and cavity surface area A_i^{COSMO}

$$r_i = \frac{V_i^{\mathrm{COSMO}}}{r}; \;\; q_i = \frac{A_i^{\mathrm{COSMO}}}{q} \tag{10}$$

Both $r = 66.69$ (Å^3) and $q = 79.53$ (Å^2)[17] in Eq. 10 are universal parameters in the COSMO-SAC. The parameter l_i in Eq. 8 is defined as

$$l_i = \frac{z}{2}[(r_i - q_i) - (r_i - 1)] \tag{11}$$

The equations of activity coefficient are now completely given. The COSMO calculations containing charge density profile, cavity volume, and cavity surface area are performed through quantum chemistry packages. The detailed information about COSMO-SAC model can be found in original paper.[17]

Application of COSMO-SAC to Polymer Solutions

There are many references concerning the applications of COSMO-SAC in normal small molecule systems. As the calculation of COSMO, different quantum chemistry software can be conveniently used for these systems.[17–19,31,32] In COSMO-SAC model, the most time-consuming processes are the optimization of molecular geometry. Currently, there are 1432 kinds of compounds that COSMO files have been provided.[18,31,33] However, there is only a few of literature reported about the application of COSMO-types model in polymer systems.[34,35] The reason may be attributed to the fact that the polymer molecule is composed of thousands of monomers and the quantum mechanical calculation could not afford the arduous task using the existing computer equipment. In this work, only the linear polymers were considered. We suppose that each polymer molecule in system is composed of a series of repeating units and the molecular parameters of polymer can be calculated by summing up the values of the repeating units. The detailed calculation procedure is given as following:

(1) An appropriate smallest repeating structure unit of polymer was set. Because the repeating unit is generally unsaturated, in the COSMO calculations for the segment charge density of repeating structure unit, head groups should be added to the repeating unit to complement the unsaturated chemical bonds. The most common one used is the hydrogen atom. In some cases, when the repeating unit has side groups or has atoms other than carbon, they might notably influence on the electronic configuration of the head group in the unit, therefore, a bigger one, such as the methyl group —CH_3, is used to replace the hydrogen atom as a head

Table 2. Atomic Radii for Creating the COSMO Molecular Cavity

Element	Cavity Radius (Å)	Element	Cavity Radius (Å)
H	1.30	S	2.16
Li	1.57	Cl	2.05
B	2.048	K	2.223
C	2.00	Zn	1.626
N	1.83	Ge	2.70
O	1.72	As	2.35
F	1.72	Se	2.20
Na	1.80	Br	2.16
Si	2.20	Sn	2.55
P	2.12	I	2.32

group. However, adding head groups inevitably leads to the distortion of the structure of the true repeating unit. To eliminate this distortion by the head groups, considering the fact that the longer is the chain the weaker is the influence of the head groups, following strategy was adopted: several multimers containing 1, 2, 3 to 10 smallest repeating units were constructed, respectively. Each multimer contains two head groups to complement its unsaturated chemical bonds.

(2) The geometry optimization and COSMO calculation of the above multimers containing 1, 2, 3 to 10 smallest repeating units in ideal gas state are performed by the VWN-BP functional at the DNP basis set level[35–37] in DMol3 package.[27] The specific parameters are cited from references[18,31] and the algorithm is the same as one in VT2005.[18,31,36] It is worthy to point out that the geometry optimization and COSMO calculation can also be calculated by using other quantum chemistry computation method such as PM6 semi-empirical methods[38] in MOPAC2009.[28] As a consequence, the COSMO files can be obtained to provide the optimized molecular geometry. In calculations, the needed atomic radii are listed in Table 2.[13–15,17–19,31]

(3) According to the results of the COSMO calculation, the average segment charge density and the σ-profiles of the above multimers with different number of smallest repeating units within the range of –0.025 to 0.025 e/Å^2 are calculated by using Eqs. 4 and 5, respectively. In evidence, the difference between the multimers of a neighboring pair of them is just the true repeating unit. So the difference of the σ-profiles of the neighboring two multimers can be regarded as an approximation for the σ-profile of the true repeating unit. The same is that the differences of the cavity surface area $A_{\text{unit}}^{\text{COSMO}}$ and the cavity volume $V_{\text{unit}}^{\text{COSMO}}$ of neighboring two multimers can then be obtained which are regarded as the approximation for $A_{\text{unit}}^{\text{COSMO}}$ and $V_{\text{unit}}^{\text{COSMO}}$ of the true repeating unit. Because there are 10 multimers containing 1, 2, 3 to 10 smallest repeating units were constructed, respectively, nine samples data of approximated σ-profile, $A_{\text{unit}}^{\text{COSMO}}$ and $V_{\text{unit}}^{\text{COSMO}}$ of repeating unit should be got when this difference method for the neighboring two multimers was carried out. The σ-profile $p_i(\sigma)$ of the true repeating unit are obtained by taking the ensemble average of selected samples of these nine approximated σ-profiles. The cavity surface area $A_{\text{unit}}^{\text{COSMO}}$ and the cavity volume of the repeating unit $V_{\text{unit}}^{\text{COSMO}}$ are also given by similar average method. To eliminate the fluctuation in σ-profile calculation due to the influence of head groups, generally, last four samples, viz. 7-6, 8-7, 9-8 and 10-9, were selected as an ensemble.

(4) The number of the smallest repeating structure unit in a polymer molecule is calculated by $N_{\text{unit}} = M_{\text{polymer}}/M_{\text{unit}}$ where M_{polymer} and M_{unit} represent the molecular masses of the polymer and the repeating unit, respectively. The parameters of cavity volume and cavity surface area for a polymer molecule are then obtained

$$V_{\text{polymer}}^{\text{COSMO}} = N_{\text{unit}} \times V_{\text{unit}}^{\text{COSMO}} \tag{12}$$

$$A_{\text{polymer}}^{\text{COSMO}} = N_{\text{unit}} \times A_{\text{unit}}^{\text{COSMO}} \tag{13}$$

Although the approach proposed here is similar to the group contribution method of Mu et al.[21] and the group contribution solvation model of Lin et al.,[32] the strategy is different from them in principle. The polymer molecule is assumed to be composed of the repeating structure unit in this work instead of the group pieces. The assumption of this model can better characterize the properties of the real polymer molecule. The feasibility of this model can be tested through the phase equilibrium calculations. In calculations, the COSMO files of DMol3 package for solvent molecule are directly adopted from the VT2005 Database,[18,31,33] and the COSMO files of MOPAC package are calculated by using the MOPAC2009 package.

After the polymer molecular COSMO data are obtained, the segment activity coefficients can be calculated by Eqs. 2 and 3 for pure liquid and mixture and the solute activity coefficients are given via Eq. 1. During this process, the σ-profile of polymer molecule is obtained through Eq. 5. The activity coefficient from the cavity free energy contribution is calculated by Eq. 8 after obtaining r_i and q_i via Eqs. 10, 12, and 13.

Once COSMO data of the repeating unit of the polymer were obtained, the phase equilibrium of different polymer solutions can be predicted by using COSMO-SAC model due to there are many of compounds that COSMO files have been provided.[18,31,33] Therefore, the COSMO data of the repeating units can be as a part of the database, which provides advantage for application of COSMO-SAC model.

Results and Discussion

To test the feasibility of this model, several examples of typical polymers are selected and the comparison between predicted and experimental results of VLE is presented. The selected polymers contain a linear polymer [polyethylene (PE)], two polymers with alkyl side group [polypropylene (PP) and polyisobutylene (PIB)], a polymer with aromatic side group [polystyrene (PS)] and a polymer including other atoms besides carbon in main chain [polydimethylsiloxane (PDMS)].

In general, the polymer has very low volatility and the solubility of molten polymer in gas phase can be ignored. The equilibrium equation for binary mixtures containing polymer at a fixed temperature can be written as

$$p_i\varphi_i = p_i^{\text{sat}}\varphi_i^{\text{sat}}a_i = p_i^{\text{sat}}\varphi_i^{\text{sat}}\gamma_i x_i \tag{14}$$

where p_i is the gas phase pressure of component i, p_i^{sat} is the saturated vapor pressure, γ_i a_i and x_i are the activity factor,

Table 3. The Margin Values and Average Value of the Charge Density Profile of PE Repeating Units

Charge Density	$\Delta p(\sigma)$ Distribution Profile				Average Profile
	7-6	8-7	9-8	10-9	
−0.025	0	0	0	0	0
↕	0	0	0	0	0
−0.004	0	0	0	0	0
−0.003	0.021677941	0.045886265	0.033309528	0.021265172	0.022513553
−0.002	0.201753836	0.128518735	0.210505119	0.159375613	0.176372095
−0.001	0.206869881	0.248517862	0.181401528	0.250897443	0.240626865
0	0.172087537	0.192724673	0.194457659	0.191964924	0.201774967
0.001	0.207760755	0.178305215	0.172062644	0.209754983	0.175570006
0.002	0.145999799	0.172890079	0.139091937	0.13208531	0.104455674
0.003	0.038104891	0.035144769	0.064931212	0.031008343	0.075759204
0.004	0.005377893	−0.00128091	0.004727493	0.004614488	0.002927635
0.005	0	0	0	0	0
↕	0	0	0	0	0
0.025	0	0	0	0	0

There are negative profile values due to difference of the neighboring repeating units for certain polymer molecules, but the influence would be eliminated during samples' averaged processes. The other polymers average profile and volumes can be found in the supporting information.

activity, and mole fraction, respectively. φ_i is the fugacity coefficient of component i in gas phase and φ_i^{sat} is the fugacity factor of saturated vapor of component i obtained from the equation of state truncated at second virial coefficient.[39] The predicted results and the comparison between theoretical and experimental values[40,41] are discussed as follows.

As mentioned earlier, we construct samples from one smallest repeating unit to 10 smallest repeating units for every polymer and obtain the corresponding differences of the neighboring pairs. To eliminate the distortion by the head groups, the neighboring pairs of 7-6, 8-7, 9-8, 10-9 are selected for PE, PP, PIB as an ensemble. Good prediction results are obtained compared with experimental values. However, for PDMS and PS, unsatisfied results were obtained. The reason might lie in the fact that they contain aromatic side group and silicon for main chain of polymer, the influence of head groups are not as important as that for PE, PP, and PIB. On the other hand, as shown in Figures 1d, e, the fluctuations of the differences of the neighboring pairs are quite notable indicating the inadequacy inherited in the quantum chemistry method. When the method is applied to real system containing the PS and PDMS, we tried to select all the nine differences of the neighboring pairs as an ensemble and calculate the ensemble average. Fortunately, the prediction results are greatly improved. The results of PDMS systems are almost consistent with experimental values and that of PS are also improved.

Linear polymer—polyethylene (PE)

As mentioned earlier, the first step is to set the appropriate repeating structure unit of polymer molecule. As PE is a product of polymerization of ethylene, the group of $—CH_2—CH_2—$ should be considered as the smallest repeating unit. Because of the unsaturated bond contained in the group of $—CH_2—CH_2—$, the hydrogen atom must be added to the $—CH_2—CH_2—$ group to avoid the unsaturated bond in calculation. Thereby, the molecule calculated is ethane. Sequentially, the multimers of repeating unit of PE including 6–10 smallest repeating units are *n*-hexane to *n*-eicosane, and the difference between the multimers of the neighboring pair is the true repeating unit of $—CH_2—CH_2—$. Four neighboring pairs, 7-6, 8-7, 9-8, 10-9 are selected as an ensemble.

The charge density distribution of the smallest repeating unit of PE is obtained by taking the ensemble average of the difference between the multimers of a neighboring pair for the ensemble. Table 3 shows the differences of the σ-profiles of the multimers of 7-6, 8-7, 9-8, 10-9 and the averaged results. Based on our assumption, the averaged results are not only the σ-profiles of the repeating unit $—CH_2—CH_2—$ but also the σ-profiles of a PE molecule. It must be point out that a negative profile value could be appeared when this difference method for only one neighboring pair is adopted, but the influence would be eliminated by taking the ensemble average. Therefore, this average method for multisamples could avoid furthest the chanciness and randomicity from only one sample. As shown in Figure 1a, the charge density distribution of the repeating unit $—CH_2—CH_2—$ changes within a limited range. The average values can be considered as the most reasonable charge density distribution of the repeating unit and used to represent the PE profiles, $p_i(\sigma)$. The calculation of phase equilibrium can then be carried out by $p_i(\sigma)$ and others COSMO output data.

A comparison between experimental data[41] and COSMO-SAC predicted results for PE + cyclopentane mixture is showed in Figure 2. The COSMO calculation is performed in DMol3 package[27] and the fugacity coefficients are used to characterize the nonideality of gas phase. In the figure, w_1 is the weight fraction of solvent, the symbols are experimental data and the solid lines represent theoretical results. The predicted results are consistent with experiments. However, if the gas phase is treated as an ideal gas, as shown by the dotted line, a little deviation occurs. The same procedure is also applied to calculate VLE of PE + 3-pentanone and PE + *n*-propylacetate as shown in Figures 3 and 4, respectively.[41] In these systems, the average molecular weight of PE is 76 kg/mol.[41] From these figures, satisfactory results for PE + 3-pentanone at two different temperatures can be observed, and the predicted results at low temperature are slightly better than those at higher temperature for PE + *n*-propylacetate. In addition, the deviation between the predicted equilibrium pressure and experiments at elevated pressure enhances

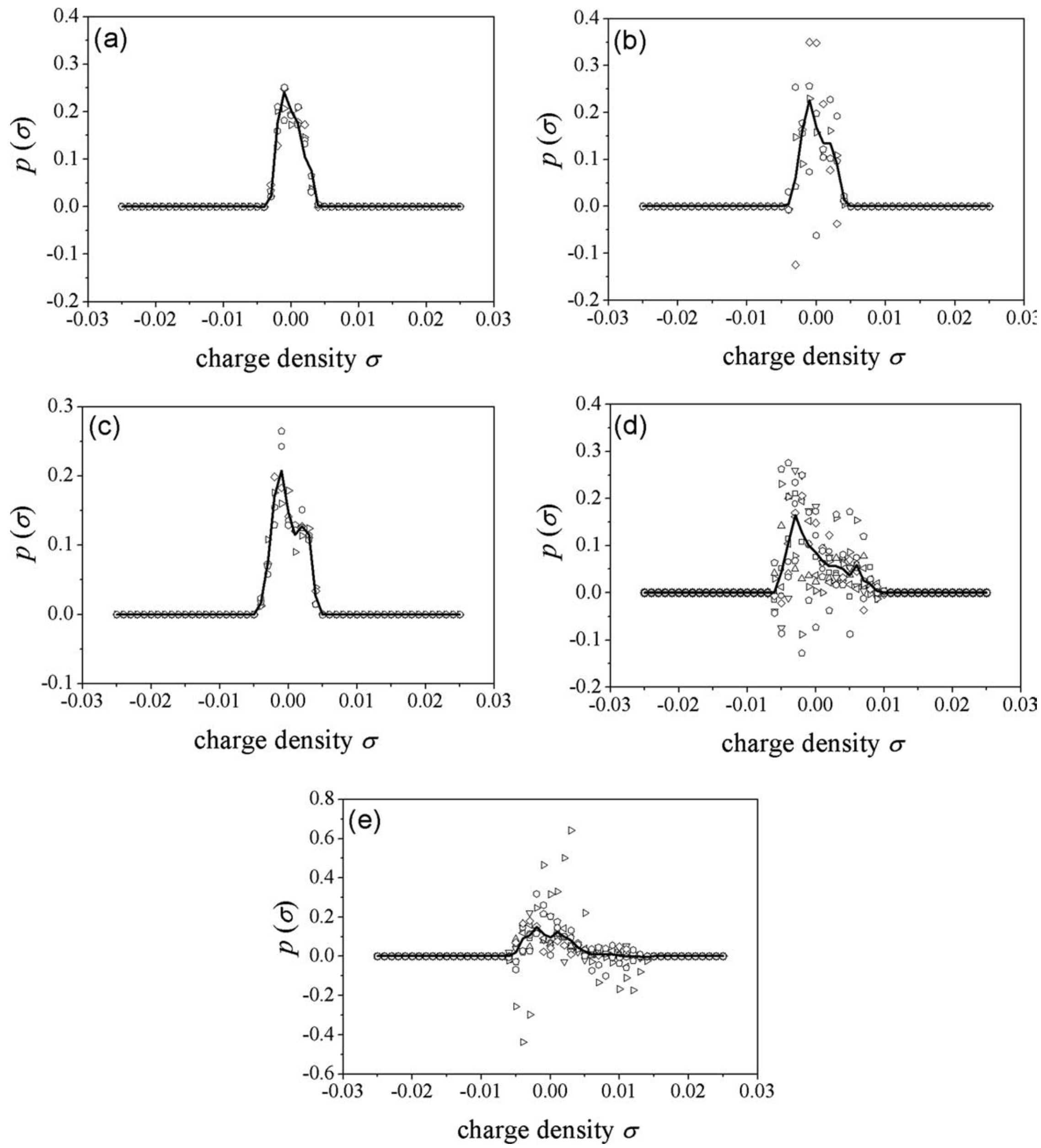

Figure 1. The average charge density profile of repeating units for (a) PE, (b) PP, (c) PIB, (d) PS, and (e) PDMS.

There are negative profile values due to difference of the neighboring repeating units for certain polymer molecules, but the influence would be eliminated during samples averaged processes. The line is average value and the points are samples value. The unit of charge density σ is e/Å^2.

with the increase of solvent concentration even using nonideality correction. In general, the predicted VLE for PE solutions using COSMO method are satisfactory without any experimental data adopted.

Polymer with alkyl side group—polypropylene (PP) and polyisobutylene (PIB)

In PP molecule, the group of $\text{—CH(CH}_3\text{)—CH}_2\text{—}$ is set as the smallest repeating unit. These repeating units connect orderly together as $\text{—CH(CH}_3\text{)—CH}_2\text{—CH(CH}_3\text{) —CH}_2\text{—}$ to construct a PP molecule, the deviant group such as $\text{—CH(CH}_3\text{)—CH}_2\text{—CH}_2\text{—CH(CH}_3\text{)—}$ would not exist. For $\text{—CH(CH}_3\text{)—CH}_2\text{—}$, a hydrogen atom is added the group of $\text{—CH}_2\text{—}$ and a methyl group is added the other head of $\text{—CH(CH}_3\text{)—}$ to form a saturated molecule. For PIB, the smallest repeating unit is $\text{—C(CH}_3\text{)}_2\text{—CH}_2\text{—}$ and a hydrogen atom is added the group of $\text{—CH}_2\text{—}$ and a methyl group is added the group of $\text{—C(CH}_3\text{)}_2$ to eliminate the unsaturated bonds. The profiles $p_i(\sigma)$ for PP and PIB were shown in Figures 1b and c, respectively. Four neighboring pairs, 7-6, 8-7, 9-8, 10-9 are selected as an ensemble.

The comparison between the predicted activities and the experimental data at 298.15 K for PP solutions in three solvents including 3-pentanone, 2,4-dimethyl,3-pentanone, and

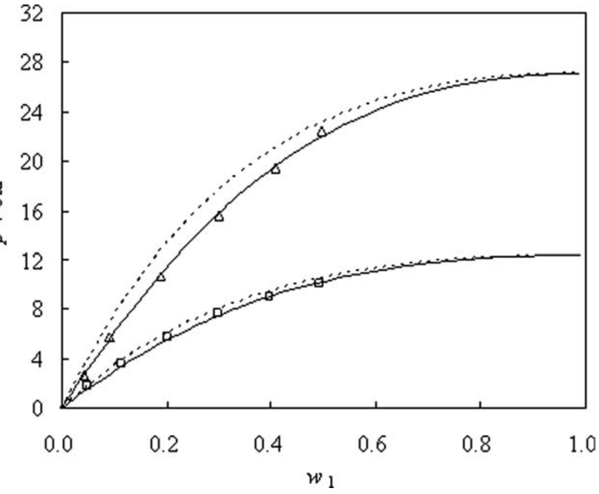

Figure 2. VLE for cyclopentane (1) + PE (2) at 425.65 K (square) and 474.15 K (triangle).

Solid line: the predicted results from COSMO-SAC-DMol3 + non-ideality correction; dash line: the predicted results from COSMO-SAC-DMol3 + ideal gas

tetrachloromethane[40] are shown in Figure 5–7. The corresponding average molecular masses of PP are 20, 20, and 15 kg/mol,[40] respectively. To test the effect of different quantum chemistry calculation method on VLE, DMol3, and MOPAC2009 package are applied to perform the quantum mechanical calculation of the repeating unit of polymer. In Figures 5–7, the solid line denotes the results from COSMO-SAC-DMol3 and the dash line represents ones from COSMO-SAC-MOPAC. Good predicted activities compared with experimental data are obtained by using different QM software, although there is a little deviation observed between the two approaches. For 3-pentanone + PP mixture, the results from COSMO-SAC-MOPAC are better than that from COSMO-SAC-DMol3 at low concentration region of solvent, while the opposite phenomena is observed at high concentration region, as shown in Figure 5. For 2,4-dimethyl-3-pentanone + PP and tetrachloromethane + PP systems, the predicted results by both DMol3 and MOPAC are given in Figures 6 and 7, respectively. The predicted results are in good agreement with experimental data.

The calculated results for three systems containing PIB are shown in Figures 8–10. These systems include *n*-pentane + PIB, cyclohenxane + PIB, and benzene + PIB[40] and the corresponding average molecular masses of PIB are 2250, 100, and 45 kg/mol,[40] respectively. Both DMol3 and MOPAC2009 package are used to perform quantum chemistry calculation and the results are denoted by the solid line and dash line in the figures, respectively. For *n*-pentane + PIB and cyclohenxane + PIB, both DMol3 and MOPAC can well reproduce the experimental data. For *n*-pentane + PIB,

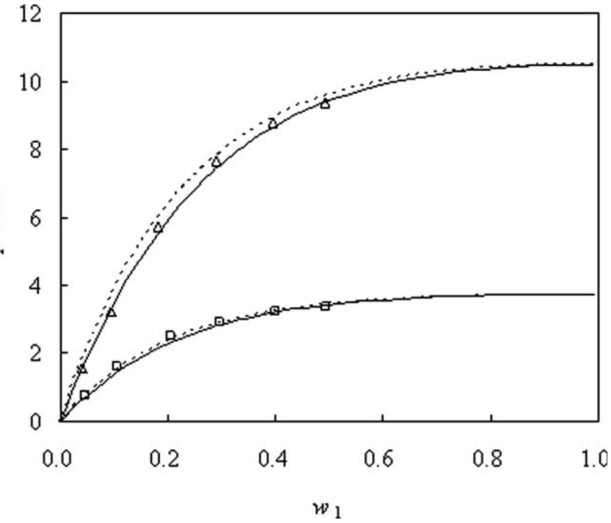

Figure 3. VLE for 3-pentanone (1) + PE (2) at 425.15 K (square) and 477.15 K (triangle).

The lines have same means as Figure 2.

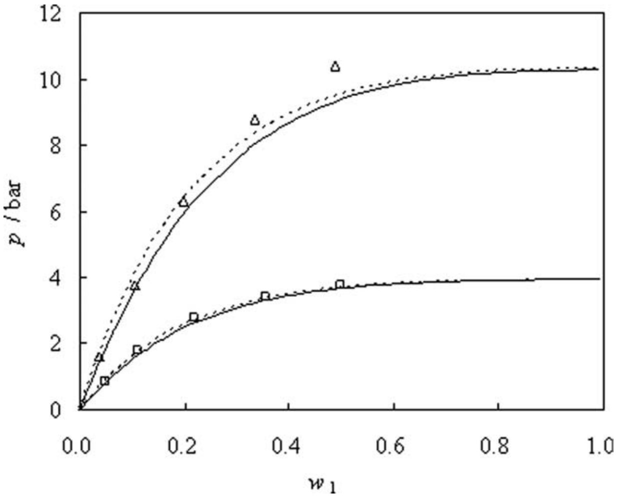

Figure 4. VLE for n-propylacetate (1) + PE (2) at 426.15 K (square) and 474.15 K (triangle).

The lines have same means as Figure 2.

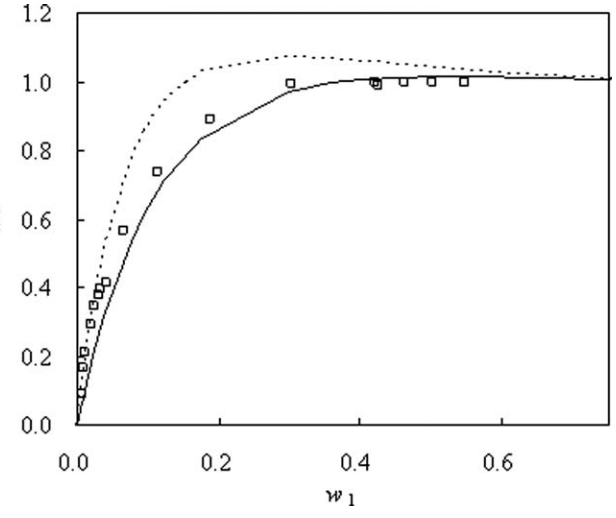

Figure 5. The activity of solvent in 3-pentanone (1) + PP (2) at 298.15 K.

Solid line: the predicted results from COSMO-SAC-DMol3, dash line: the predicted results from COSMO-SAC-MOPAC.

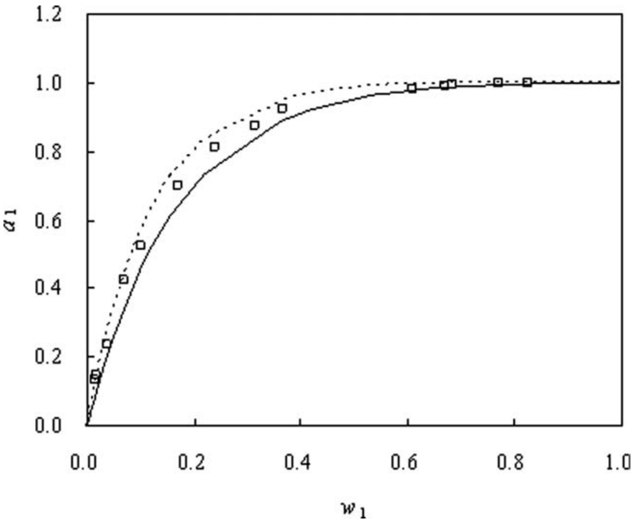

Figure 6. The activity of solvent in 2,4-dimethyl,3-pentanone (1) + PP (2) at 298.15 K.

The lines have same means as Figure 5.

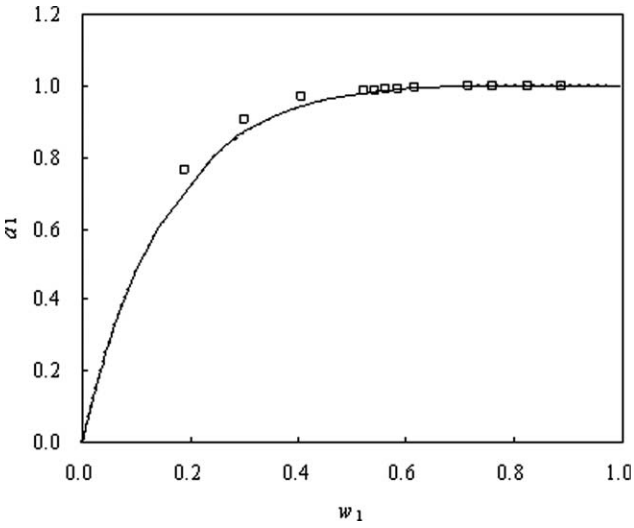

Figure 8. The activity of solvent in n-pentane (1) + PIB (2) at 298.15 K.

The lines have same means as Figure 5.

the predicted results are lower than the experiments at low concentration region of *n*-pentane. However, for benzene + PIB system, the obtained results from MOPAC are obviously better than ones from DMol3.

The predicted results for different average molar mass of PP systems and PIB systems show that when the $p_i(\sigma)$, $A_{\text{unit}}^{\text{COSMO}}$, and $V_{\text{unit}}^{\text{COSMO}}$ of the repeating units were obtained and average molar mass of the polymer were known, the $p_i(\sigma)$, $V_{\text{polymer}}^{\text{COSMO}}$, and $A_{\text{polymer}}^{\text{COSMO}}$ of the polymer can be also obtained and these information is one and only for a given polymer. So the average molar mass of the polymer is also one of the input data. The good prediction results show again that the appropriate COSMO data of the repeating units of the polymer can be completely served as a part of the database.

Polymer with aromatic side group—polystyrene (PS)

The PS molecule contains aromatic side group. The smallest repeating unit is a group of $-\text{CH}(\text{C}_6\text{H}_5)-\text{CH}_2-$. Similarly, a hydrogen atom is added the group of $-\text{CH}_2-$ and a methyl group is added the other group of $-\text{CH}(\text{C}_6\text{H}_5)-$ to make the unit saturated. All neighboring pairs are selected as an ensemble. The $p_i(\sigma)$ for PS is shown in Figure 1d. Both DMol3 and MOPAC2009 package are used to perform quantum chemistry calculation to test the effects of the two different quantum-mechanics algorithm on the results of VLE of polymer solutions, and the results are showed by the solid line and dash line in the succeeding figures, respectively.

Figure 11 shows the comparison between experiments and COSMO-SAC predicted results for PS + cyclopentane system at 318.15 K and the average molecular mass of PS is 154 kg/

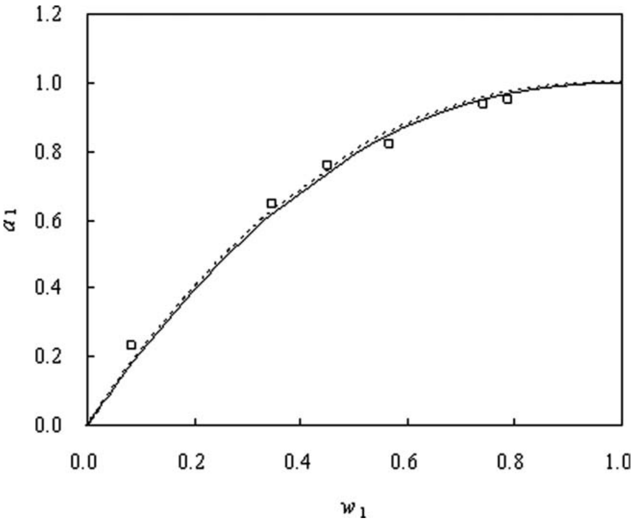

Figure 7. The activity of solvent in tetrachloromethane (1) + PP (2) at 298.15 K.

The lines have same means as Figure 5.

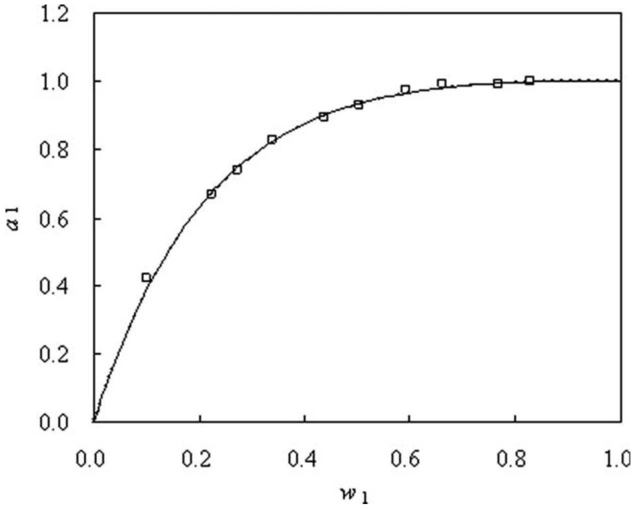

Figure 9. The activity of solvent in cyclohenxane (1) + PIB (2) at 298.15 K.

The lines have same means as Figure 5.

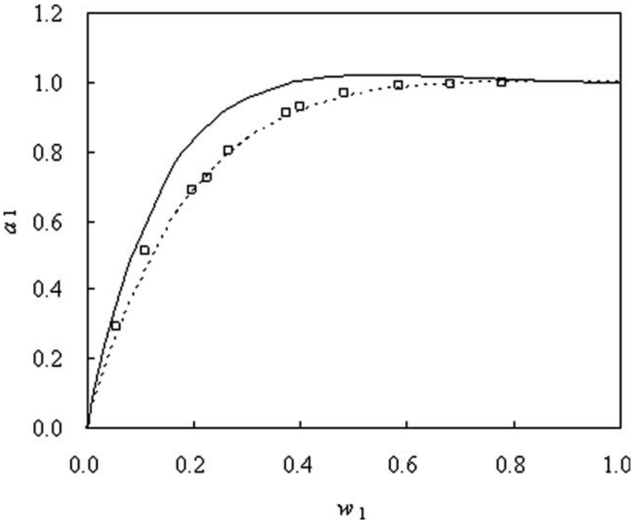

Figure 10. The activity of solvent in benzene (1) + PIB (2) at 338.15 K.

The lines have same means as Figure 5.

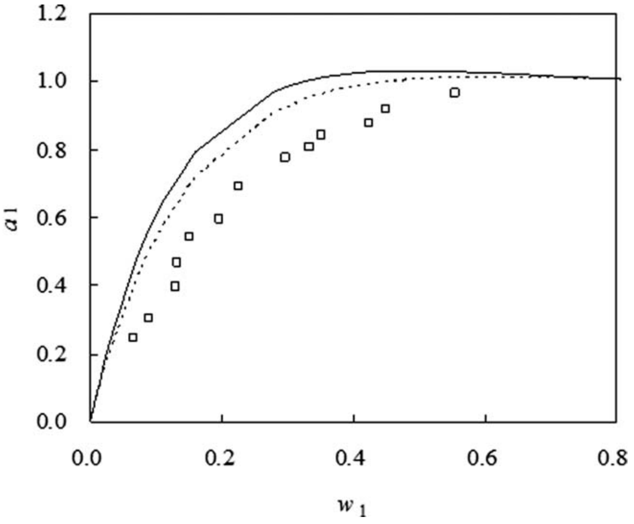

Figure 12. The activity of solvent in benzene (1) + PS (2) at 293.15K.

The lines have same means as Figure 5.

mol.[40] The predicted results from MOPAC are consistent with experiments; whereas, the predictions from DMol3 are slightly higher than experiments. The predicted and experimental results for the mixture of benzene and PS (the average molecular weights of PS is 20 kg/mol[40]) at 293.15 K are given in Figure 12. The results from both MOPAC and DMol3 are greater than the experiments, although the former algorithm can give comparable good results. The similar phenomena for PS (290 kg/mol[40]) + trichloromethane is also given in Figure 13. The inaccuracy may be attributed to the reason that the used repeating structure unit of PS is not the optimized structure. From Figure 1d, the differences of charge density profile between the neighboring multimers for PS fluctuate larger than that of other polymers indicating that the selection of the repeating unit plays an important role in calculation of phase equilibrium.

Polymer containing silicon and oxygen atoms—polydimethylsiloxane (PDMS)

The PDMS is a linear polymer molecule with the silicon and oxygen atoms included in the main chain. The smallest repeating unit is $—Si(CH_3)_2—O—$. Two methyl groups are necessary to eliminate the unsaturated bond. One of them is used to keep the geometry configuration of the repeating unit and the other is used to keep the electron cloud density distribution uniform. If only adding a hydrogen atom to the oxygen group, the electron cloud density might be attracted by oxygen atom and the profile of electron density could not follow the fact of a symmetric electron cloud density distribution of polymer. All neighboring pairs are selected as an ensemble. The charge density profile $p_i(\sigma)$ for PDMS repeating unit is shown in Figure 1e. Similarly, both DMol3 and

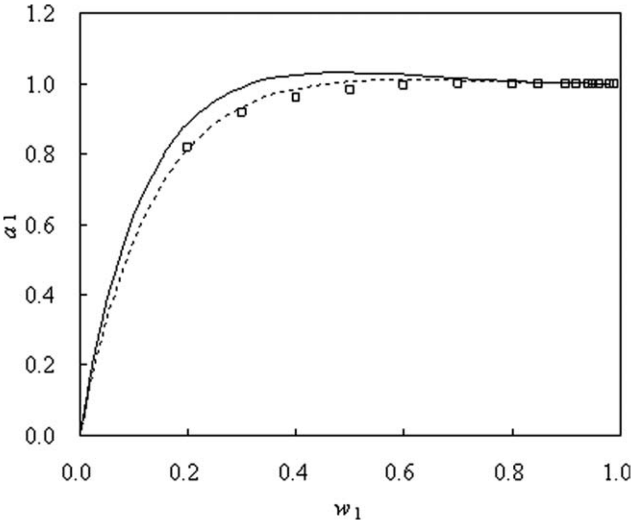

Figure 11. The activity of solvent in cyclohenxane (1) + PS (2) at 318.15 K.

The lines have same means as Figure 5.

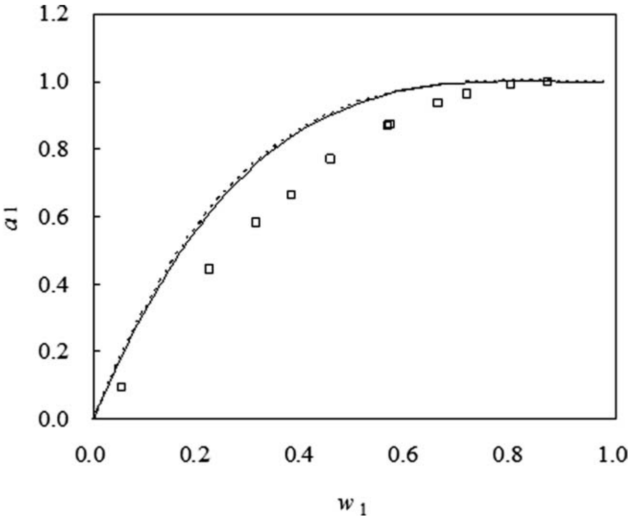

Figure 13. The activity of solvent in trichloromethane (1) + PS (2) at 298.15 K.

The lines have same means as Figure 5.

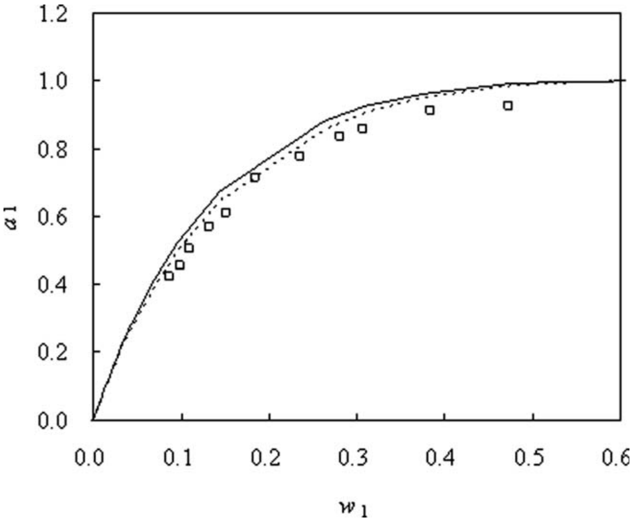

Figure 14. The activity of solvent in benzene (1) + PDMS (2) at 298.15 K.

The lines have same means as Figure 5.

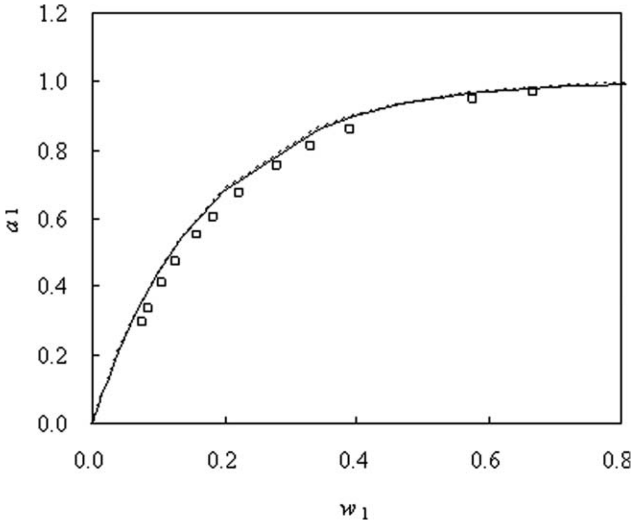

Figure 16. The activity of solvent in 2,2,4-trimethylpentane (1) + PDMS (2) at 298.15 K.

The lines have same means as Figure 5.

MOPAC are used to perform the quantum chemistry calculations and the results are denoted by the solid line and dash line in the following figures, respectively.

The relations of the mass fraction and activity for mixtures of PDMS with benzene, toluene, or 2,2,4-trimethylpentane[40] are illustrated in Figures 14, 15, or 16, respectively. The average molecular mass of PDMS is 4170 g/mol[40] for all systems. Figure 14 shows the comparison between theoretical values and experiments for benzene + PDMS system. The predicted and experimental results for toluene+ PDMS system is given in Figure 15. Figure 16 compares the predicted results and experiments for 2,2,4-trimethylpentane + PDMS system. In general, the quantum chemistry calculation from both DMol3 and MOPAC package can well reproduce the experimental data, although the predicted activity values from both methods are slightly higher than experiments.

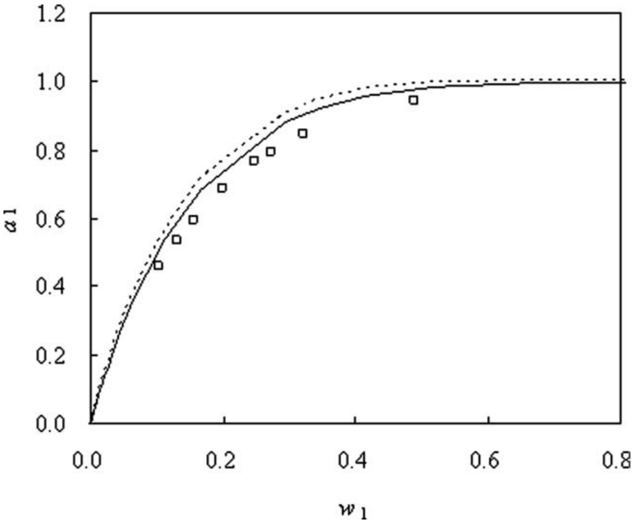

Figure 15. The activity of solvent in toluene (1) + PDMS (2) at 298.15 K.

The lines have same means as Figure 5.

Conclusion

To extend the COSMO-SAC model to phase equilibrium calculations of polymer solutions, a new method for calculating the charge density distribution, cavity volume, and cavity surface area of polymer was proposed. In this method, each polymer molecule is assumed to be composed of a series of repeating structure unit, and the quantum chemistry data of polymer can be obtained by summing up the corresponding values of the repeating unit. The parameters of the repeating unit are obtained by taking average of an ensemble composed of several neighboring multimer pairs. This work shows that the VLE of polymer solutions can be satisfactorily predicted by COSMO-SAC model without using any experimental information.

Several examples for typical polymer solution have been given and the predicted results are in good agreement with the experimental data for the investigated mixtures indicating that the proposed approach for polymer quantum mechanical calculation based on different quantum chemistry algorithms can give reasonable prediction in practice for polymer solutions. Besides the different calculated results can be reproduced by using VWN-BP function at the DNP basis set level[35–37] in DMol3 package and by using PM6 semiempirical methods[38] in MOPAC2009 package, the quantum chemistry calculations in MOPAC2009 software are faster on PC computer. However, if the computer hardware could not be upgraded quickly with the increase of the atom number in a molecule, the calculated jobs would not be performed in MOPAC2009. The DMol3 package needs less hardware resource in comparison with MOPAC2009 package and it can complete any calculation jobs only with enough time. Therefore, any quantum chemistry software can be chosen when the COSMO-SAC model is used to the phase equilibrium calculation of polymer solution.

In COSMO-SAC model,[17] two universal parameters, namely the effective surface segment surface area a_{eff} and the hydrogen-bonding constant c_{hb}, obtained by fitting the experimental data of small molecular are needed and their values are affected by the selected samples. Lin et al.[17] show that the predicted results from COSMO-SAC are worse than that of UNIFAC model for some special systems in which some new segments (samples) were not contained in the database of COSMO-SAC. However, the COSMO-SAC model still has an extensive range of practical application in comparison with the UNIFAC model because the interaction parameters between groups in UNIFAC model obtained by regressed the experimental data must be given in advance, while no new parameter is needed in the COSMO-SAC model. In this work, we assume that the generalized parameters obtained from the small molecule samples in COSMO-SAC model can be used for polymers. On the other hand, polymer is considered as monodispersed chains composed of an identical number of repeating structure unit and the charge density distribution, cavity volume, and cavity surface area of polymer molecule are calculated by summing up the corresponding parameter values of the repeating unit. In addition, it is a question that whether the nonelectrostatic mostly dispersion interactions between segments could be ignored in calculating the exchange energy $\Delta W(\sigma_m, \sigma_n)$ for some special substances such as PS. Thus it is not surprising that some deviations between the theoretical and experimental values have been observed for some polymer solutions. However, our work, as a preliminary and exploratory guide, show that the COSMO-SAC model can be satisfactorily extended to predict the phase behavior of polymer solutions once the appropriate repeating structure unit of polymer is found.

This work is an attempt that the VLE of polymer solutions is predicted by quantum chemistry calculations. However, the present work only focuses on the simply homopolymer and the copolymer and nonlinear polymer are not taken into account. The comparison of the results between the group contribution activity coefficient model or the group contribution equation of state model and this model has not been made as well. Furthermore, there are many other important works, such as the prediction of liquid–liquid equilibrium of polymer solution using COSMO-SAC model, finding more quickly quantum chemistry estimation method for polymers and so on, also needs to be performed in the future.

Acknowledgments

Financial support for this work was provided by the National Natural Science Foundation of China (No. 20776040, 20876041, 20736002), National Basic Research Program of China (2009CB219902), Program for Changjiang Scholars and Innovative Research Team in University of China (Grant IRT0721) and the 111 Project (Grant B08021) of China.

Supporting Information Available: The supporting materials contain surface area, volumes and profile of charge density for the repeating unit of PE, PP, PIB, PS and PDMS. These materials are available free of charge via the Internet.

Notation

a_{eff} = effective contact surface area of a segment
$A^{\text{COSMO}}_{\text{polymer}}$ = cavity surface area of polymer
$A^{\text{COSMO}}_{\text{unit}}$ = cavity surface area of the repeat unit
c_{hb} = hydrogen-bonding coefficient
d_{uv} = distance between the uth and vth segment
k = Boltzmann constant
M_{polymer} = polymer molecular weight
M_{unit} = the repeat unit molecular weight
N_{unit} = the numbers of the repeat unit
n_i = contribution of molecule i to the surface segments in the solution
$p_i(\sigma)$ = probabilistic surface charge distribution for pure component i
$p_s(\sigma)$ = probabilistic surface charge distribution for mixture s
q = normalized area parameter
r = normalized volume parameter
r_{av} = averaging radius
R = universal gas constant
T = temperature
$V^{\text{COSMO}}_{\text{polymer}}$ = cavity volume of polymer
$V^{\text{COSMO}}_{\text{unit}}$ = cavity volume of the repeat unit
ΔW = exchange energy
x = mole fraction in the liquid phase
w = the weight fraction of solvent
σ = screeing charge density
α' = misfit constant
σ_{hb} = cutoff screening charge density for hydrogen bonding
σ_{don} = screening charge density for hydrogen-bond donor
σ_{acc} = screening charge density for hydrogen-bond acceptor
$\Gamma_i(\sigma)$ = segment activity coefficient for pure component i
$\Gamma_S(\sigma)$ = segment activity coefficient for mixture S
$\gamma^i{}_S$ = component activity coefficient in the mixture S

Literature Cited

1. Oishi T, Prausnitz JM. Estimation of solvent activities in polymer solutions using a group-contribution method. *Ind Eng Chem Process Des Dev*. 1978;17:333–339.
2. Iwai Y, Arai Y. Measurement and prediction of solubilities of hydrocarbon vapors in molten polymers. *J Chem Eng Jpn*. 1989;22:155–161.
3. Elbro HS, Fredenslund A, Rasmussen P. A new simple equation for the prediction of solvent activities in polymer solutions. *Macromolecules*. 1990;23:4707–4714.
4. Hu Y, Zhou H, Liu HL, Wu DT, Prausnitz JM. Estimation of vapor-liquid equilibria for polymer solutions by a group-contribution method. *Fluid Phase Equilibria*. 1997;134:43–54.
5. Holten-Andersen J, Fredenslund A, Rasmussen P, Carvoli G. Phase equilibria in polymer solutions by group contribution. Fluid Phase Equilibria. *Fluid Phase Equilibria*. 1986;29:357–364.
6. Holten-Andersen J, Rasmussen P, Fredenslund A. Phase equilibria of polymer solutions by group contribution, 1: vapor-liquid equilibria. *Ind Eng Chem Res*. 1987;26:1382–1390.
7. High MS, Danner RP. A group contribution equation of state for polymer solutions. *Fluid Phase Equilibria*. 1989;36:1625–1632.
8. Chen F, Fredenslund A, Rasmussen P. Group-contribution Flory equation of state for vapor-liquid equilibria in mixtures with polymer. *Ind Eng Chem Res*. 1990;29:875–882.
9. Bogdanic B, Fredenslund A. Revision of the group-contribution flory equation of state for phase equilibria calculations in mixtures with polymers. *Ind Eng Chem Res*. 1994;33:1331–1340.
10. Lee B-C, Danner RP. Prediction of polymer solvent phase equilibria by a modified group-contribution EOS. *AIChE J*. 1996;42:837–849.
11. Boudouris D, Constantinou L, Panayiotou C. A group contribution estimation of the thermodynamic properties of polymers. *Ind Eng Chem Res*. 1997;36:3968–3973.
12. High MS, Danner RP. Application of the group contribution lattice-fluid EOS to polymer solutions. *AIChE J*. 1990;36:1625–1632.
13. Klamt A. Conductor-like screening model for real solvents: a new approach to the quantitative calculation of solvation phenomena. *J Phys Chem*. 1995;99:2224–2235.
14. Klamt A, Jonas V, Burger T, Lohrenz JCW. Refinement and parametrization of COSMO-RS. *J Phys Chem A*. 1998;102:5074–5085.
15. Klamt A, Eckert F. COSMO-RS: a novel and efficient method for the a priori prediction of thermophysical data of liquids. *Fluid Phase Equilibria*. 2000;172:43–72.

16. Klamt A, Krooshof GJP, Taylor R. COSMOSPACE: alternative to conventional activity-coefficient models. *AIChE J*. 2002;48:2332–2349.
17. Lin ST, Sandler SI. A priori phase equilibrium prediction from a segment contribution solvation model. *Ind Eng Chem Res*. 2002; 41:899–913.
18. Wang S, Lin ST, Chang J, Goddard WA, Sandler SI. Application of the COSMO-SAC-BP solvation model to predictions of normal boiling temperatures for environmentally significant substances. *Ind Eng Chem Res*. 2006;45:5426–5434.
19. Wang S, Sandler SI, Chen CC. Refinement of COSMO-SAC and the applications. *Ind Eng Chem Res*. 2007;46:7275–7288.
20. Grensemann H, Gmehling J. Performance of a conductor-like screening model for real solvents model in comparison to classical group contribution methods. *Ind Eng Chem Res*. 2005;44:1610–1624.
21. Mu TC, Rarey J, Gmehling J. Group contribution prediction of surface charge density profiles for COSMO-RS(ol). *AIChE J*. 2007; 53:3231–3240.
22. Constantinescu D, Klamt A, Geana D. Vapor-liquid equilibrium prediction at high pressures using activity coefficients at infinite dilution from COSMO-type methods. *Fluid Phase Equilibria*. 2005; 231:231–238.
23. Shimoyama Y, Iwai Y, Takada S, Arai Y, Tsuji T, Hiaki T. Prediction of phase equilibria for mixtures containing water, hydrocarbons, and alcohols at high temperatures and pressures by cubic equation of state with G(E) type mixing rule based on COSMO-RS (vol 243, pg 183, 2006). *Fluid Phase Equilibria*. 2006;247:205–207.
24. Lee MT, Lin ST. Prediction of mixture vapor-liquid equilibrium from the combined use of Peng-Robinson equation of state and COSMO-SAC activity coefficient model through the Wong-Sandler mixing rule. *Fluid Phase Equilibria*. 2007;254:28–34.
25. Banerjee T, Singh MK, Khanna A. Prediction of binary VLE of imidazolium-based ionic liquids by COSMO-RS (vol 45, pg 3207, 2006). *Ind Eng Chem Res*. 2006;45:6876–6876.
26. Freire MG, Santos L, Marrucho IM, Coutinho JAP. Evaluation of COSMO-RS for the prediction of LLE and VLE of alcohols plus ionic liquids. *Fluid Phase Equilibria*. 2007;255:167–178.
27. DMol3,4.9, San Diego: Accelrys Inc., 2003.
28. MOPAC2009 software. http://openmopac.net/MOPAC2009.html.
29. Klamt A, Schüürmann G. COSMO: a new approach to dielectric screening in solvents with explicit expressions for the screening energy and its gradient. *J Chem Soc Perkin Trans 2*. 1993;(5):799–805.
30. Tomasi J, Mennucci B, Cammi R. Quantum mechanical continuum solvation models. *Chem Rev*. 2005;105:2999–3093.
31. Mullins E, Oldland R, Liu YA, Wang S, Sandler SI, Chen CC, Zwolak M, Seavey KC. Sigma-profile database for using COSMO-based thermodynamic methods. *Ind Eng Chem Res*. 2006;45(12): 4389–4415.
32. Hsieh CM, Lin ST. Determination of cubic equation of state parameters for pure fluids from first principle solvation calculations. *AIChE J*. 2008;54:2174–2181.
33. VT-2006 sigma profile database. http://www.design.che.vt.edu/VT-Databases.html.
34. Klamt A. *COSMO-RS From Quantum Chemistry to Fluid Phase Thermodynamics and Drug Design*. Elsevier, 2005.
35. Delley B. The conductor-like screening model for polymers and surfaces. *Mol Simul*. 2006;32:117–123.
36. Delley B. An all-electron numerical method for solving the local density functional for polyatomic molecules. *J Chem Phys*. 1990; 92:508–517.
37. Delley B. From molecules to solids with the DMol(3) approach. *J Chem Phys*. 2000;113:7756–7764.
38. Stewart JJP. Optimization of parameters for semiempirical methods V: Modification of NDDO approximations and application to 70 elements. *J Mol Model*. 2007;13:1173–1213.
39. Walas SM. *Phase Equilibria in Chemical Engineering*. Butterworth Publishers, 1985.
40. Wen H, Elbro HS, Alessi P. *Polymer Solution Data Collection*. Frankfurt: DECHEMA, 1992.
41. Wohlfarth C. *CRC Handbook of Thermodynamics Data of Polymer Solutions at Elevated Pressures*. Boca Raton: CRC Press, 2005.

Manuscript received July 27, 2009, and revision received Dec. 31, 2009.