

# Calculation of Solubility Parameter Using Perturbed-Chain SAFT and Cubic-Plus-Association Equations of State

Zhi-Yong Zeng,<sup>†,\*</sup> Yuan-Yuan Xu,<sup>†</sup> and Yong-Wang Li<sup>\*,†</sup>

State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, People's Republic of China and Graduate University of Chinese Academy of Sciences, Beijing 100049, People's Republic of China

Starting from the original definition of the solubility parameter, two models are developed to calculate the solubility parameter utilizing Perturbed-Chain SAFT and Cubic-Plus-Association equations of state, respectively. C<sub>3</sub>~C<sub>12</sub> *n*-alkanes and C<sub>1</sub>~C<sub>5</sub> 1-alcohols, which represent the nonassociative and associative compounds, respectively, were investigated mainly over wide ranges of temperature and pressure. Solubility parameters calculated by two models are in good agreement with Hansen solubility parameters (HSP) and the results of Monte Carlo simulation for all of these selected molecules. It is also found that the solubility parameter increases monotonically with increasing pressure, and decreases with increasing temperature for all of these studied molecules.

## Introduction

The concept of the solubility parameter was developed by Scatchard<sup>1</sup> and greatly extended by Hildebrand.<sup>2</sup> From then on, the universality of the solubility parameter was pointed out and its general applicability has been presented by means of numerical relations.<sup>3</sup> The solubility parameter can be particularly successful in describing, at least semiquantitatively, the thermodynamic properties of dilute solutions and especially so when the component liquids are nonpolar. On the one hand, the solubility parameter or the closely related cohesive energy density has been connected to other important thermodynamic properties,<sup>4</sup> such as surface tension, critical properties, wettability, the thermal expansion coefficient and the glass transition temperature of polymers. On the other hand, the concept has been applied widely in industry,<sup>5,6</sup> such as oil exploration, processing and transportation, storage of oil and natural gas, supercritical extraction, and polymer foaming and blending.

So far, several correlations for estimating solubility parameters have been developed.<sup>7–9</sup> Among them, Hansen developed a three-parameter model for the solubility parameter,<sup>10,11</sup> which is still widely applied. Those correlations are often useful and convenient at ambient conditions. Nevertheless, the ability to predict the solubility in organic liquids as functions of temperature and pressure is of greater practical and theoretical importance, and much attention has been paid to evaluate the effects of pressure and temperature on the solubility parameter. Verdier and Andersen concluded that the physical solubility parameter (excluding hydrogen bonding) agreed well with the internal pressure at low pressures, and carried out experiments to determine the physical solubility parameter of several pure compounds as a function of pressure.<sup>12</sup> Rai et al. calculated the Hildebrand solubility parameter of *n*-hexane, benzene, and ethanol with Monte Carlo (MC) simulations at  $T = 303.15$  K and for pressure ranging from 1 to 3000 bar.<sup>13</sup> Moreover, analytical equations of state (EOS) have been used to estimate the solubility parameter. Allada proposed to use Lee–Kelser

or modified Redlich–Kwong (SRK) EOS.<sup>14</sup> Panayiotou et al. adopted the lattice fluid theory and a lattice fluid hydrogen-bonding model, and divided the solubility parameter into two parts, physical and chemical.<sup>15,16</sup> Williams et al. used a fluid-specific equation of state to evaluate the solubility parameter of CO<sub>2</sub> over a wide range of temperature and pressure.<sup>17</sup> Generally, the internal pressure is taken as the interchangeable property of solubility parameter. In fact, the solubility parameter and the internal pressure are different concepts, and the differences are even greater for complex molecules and high-density fluids.<sup>18</sup> Besides, general cubic equations of state are often limited due to the problems of their accuracy for the application field. Other impressive progress has been made by the application of molecular simulations. Belmares et al.<sup>19</sup> reported that a Molecular Dynamics computer simulation procedure is a good tool for estimating Hildebrand and Hansen solubility parameters and could offer higher consistency in the estimation of Hildebrand and Hansen solubility parameters. Rai et al.<sup>20</sup> carried out the investigation with configurational-bias Monte Carlo simulations in the isothermal–isobaric and Gibbs ensembles using the transferable potentials for phase equilibria (TraPPE) force field, and demonstrated that the TraPPE force field is a significantly more accurate prediction approach. However, less computationally expensive models are more applicable.

Therefore, it is necessary to develop more reliable, convenient, and accurate models for calculating solubility parameter, which should be applicable for both associating and nonassociating substances over wide ranges of temperature and pressure.

In this work, the Perturbed-Chain SAFT (PC-SAFT) and Cubic-Plus-Association (CPA) EOS were used to develop the calculation models of the solubility parameter. Both equations of state account explicitly for the effect of hydrogen bonding on the thermodynamic properties of associating fluids using the perturbation theory, and they have successfully applied to a variety of complex phase equilibria, including hydrocarbons, alcohols, glycols, water, and organic acids, etc.<sup>21–23</sup>

The objective of this study is to obtain the solubility parameter models by using the PC-SAFT and CPA EOS and to investigate the performance of both models in calculating the solubility parameters of the C<sub>3</sub>~C<sub>12</sub> *n*-alkanes and C<sub>1</sub>~C<sub>5</sub> 1-alcohols at various conditions. The calculated results were compared with

\* To whom correspondence should be addressed. Tel.: +86-351-7560831. Fax: +86-351-7560668. E-mail address: ywl@sxicc.ac.cn.

<sup>†</sup> State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences.

<sup>‡</sup> Graduate University of Chinese Academy of Sciences.

the experimental data, Hansen Solubility Parameters (HSP), and the results of MC simulation.<sup>13</sup> Moreover, both models were applied to evaluate the pressure and temperature effects on the solubility parameter. The Peng–Robinson (PR) EOS is also given to calculate the solubility parameter of nonassociative compounds.

### Theory

On the basis of the original definition of the Hildebrand solubility parameter,<sup>2</sup> the concept of the solubility parameter is defined as the square root of cohesive energy density:

$$\delta = \left( \frac{-E}{V} \right)^{1/2} \quad (1)$$

where  $\delta$  denotes the solubility parameter,  $E$  and  $V$  represent the cohesive energy and the molar volume, respectively.

Several interpretations of the cohesive energy are available in literature,<sup>24,25</sup> one of widespread definitions, used by Hoy<sup>26</sup> for instance, is selected in this work, which is expressed as follows:

$$\delta = \left( -\frac{U_{\text{liq}}(T, P)}{V_{\text{liq}}(T, P)} \right)^{1/2} \quad (2)$$

In this definition, the cohesive energy is equal to the internal energy  $U$  of liquids. On the basis of the classic thermodynamic theory, the internal energy is given by the following:

$$U = U^{\text{ig}} + U^{\text{res}} \quad (3)$$

where  $U^{\text{ig}}$  is the internal energy of ideal gas, and  $U^{\text{res}}$  is the residual internal energy for real substances. In thermodynamics,  $U^{\text{ig}}$  is the total of the kinetic energy due to the motion of molecules (translational, rotational, vibrational) and the nuclear and electronic energy within molecules or crystals. The expression of  $U^{\text{ig}}$  could be given by the following:

$$U^{\text{ig}} = \frac{i}{2} RT \quad (4)$$

where  $i$  represent degrees of freedom, and  $R$  and  $T$  represent the gas constant and temperature, respectively. For polyatomic molecules, they possess three translational degrees of freedom and three rotational degrees of freedom, and all other degrees of freedom (e.g., vibrational) are treated as “frozen out” at room temperature. The freezing out of vibrational degrees of freedom becomes gradually less effective as molecules become heavier and more complex, and temperature increases higher. These contributions reduce the frequency of vibration of the molecular normal modes, and hence, the spacing between vibrational energy levels with translational and rotational energy. In this work, because the temperature is not high enough, and the studied molecules are  $n$ -alkanes and 1-alcohols, the vibrational energy is not considered in the model. Therefore,  $U^{\text{ig}}$  of  $n$ -alkanes and 1-alcohols, which are all taken as polyatomic molecules, is approximate to  $3RT$ .

Besides, the residual internal energy can be calculated from equations of state according to the following:

$$U^{\text{res}} = -RT \int_V^\infty \left[ T \left( \frac{\partial Z}{\partial T} \right)_V \right] \frac{dV}{V} \quad (5)$$

Perturbed-Chain SAFT was developed by Gross and Sadowski<sup>27</sup> on the basis of the perturbation theory of Barker and Henderson. In the original EOS, the ideal gas contribution (id), the hard-chain contribution (hc), and the dispersion contribution (disp) are included. Since the associative contribution was not considered in the original PC-SAFT paper,<sup>27</sup> the term given by

Michelsen and Hendriks<sup>28</sup> was adopted in this work. Then, Karakatsani et al.<sup>29</sup> further accounted for the dipole and dipole interactions and successfully extended the PC-SAFT model to dipolar fluids. For the purpose of focusing on the performance of the original PC-SAFT and keeping the simplicity of the model, the dipole and dipole interactions are not included in this work. So the complete PC-SAFT EOS, in terms of the compressibility factor, is expressed as follows:

$$Z = Z^{\text{id}} + Z^{\text{hc}} + Z^{\text{disp}} + Z^{\text{assoc}} \quad (6)$$

where  $Z$  is the compressibility factor.

On the basis of the original PC-SAFT model,<sup>27</sup>  $Z^{\text{hc}}$  is given by the following:

$$Z^{\text{hc}} = \bar{m} Z^{\text{hs}} - \sum_i x_i (m_i - 1) \rho \frac{\partial \ln g_{ii}^{\text{hs}}}{\partial \rho} \quad (7)$$

$$\bar{m} = \sum_i x_i m_i \quad (8)$$

where  $x_i$  is the mole fraction of chains of component  $i$ ,  $m_i$  is the number of segments in a chain of component  $i$ ,  $\bar{m}$  is the mean segment number in the mixture,  $\rho$  is the total number density of molecules, and  $g_{ii}^{\text{hs}}$  is the radial pair distribution function for segments of component  $i$  in the hard sphere system.

$Z^{\text{disp}}$  is given by the following:

$$Z^{\text{disp}} = -2\pi\rho \frac{\partial(\eta I_1)}{\partial \eta} \overline{m^2 \epsilon \sigma^3} - \pi\rho \bar{m} \left[ C_1 \frac{\partial(\eta I_2)}{\partial \eta} + C_2 \eta I_2 \right] \overline{m^2 \epsilon^2 \sigma^3} \quad (9)$$

where

$$\begin{aligned} \frac{\partial(\eta I_1)}{\partial \eta} &= \sum_{j=0}^6 a_j(\bar{m})(j+1)\eta^j \\ \frac{\partial(\eta I_2)}{\partial \eta} &= \sum_{j=0}^6 b_j(\bar{m})(j+1)\eta^j \end{aligned} \quad (10)$$

In the association term, the specific site–site interactions, due to hydrogen bonding, were taken into account in the equations. Both self-association and cross-association are considered for mixtures. Thus, it is able to calculate the hydrogen bonding component when there is intramolecular association or multiple cross-association. The term is given by the following:

$$Z^{\text{assoc}} = \frac{1}{2} \left( 1 + \frac{1}{V_m} \frac{\partial \ln g}{\partial (1/V_m)} \right) \sum_i x_i \sum_{A_i} (1 - X_{A_i}) \quad (11)$$

where  $V_m$  is the molar volume,  $X_{A_i}$  is the fraction of A-sites of molecule  $i$  that are not bonded with other active sites.

Then,  $X_{A_i}$ , which is the heart of the association term, is calculated by solving the following set of equations:

$$X_{A_i} = \frac{1}{1 + (1/V_m) \sum_j x_j \sum_{B_j} X_{B_j} \Delta^{A_i B_j}} \quad (12)$$

where  $B_j$  indicates summation over all sites.  $i$  and  $j$  are used to denote the molecules, whereas A and B indicate the bonding sites on a given molecule.

The term  $\Delta^{A_i B_j}$ , which is the association strength between site A on molecules  $i$  and site B on molecule  $j$ , is given by:

$$\Delta^{A_i B_j} = g(V_m)^{\text{ref}} \left[ \exp \left( \frac{\epsilon^{A_i B_j}}{RT} \right) - 1 \right] b_{ij} \beta^{A_i B_j} \quad (13)$$

where  $\epsilon^{A_i B_j}$  and  $\beta^{A_i B_j}$  are the association energy and volume of interaction between site A of molecule  $i$  and site B of molecule

$j$ , respectively, and  $g(V_m)^{\text{ref}}$  is the contact value of the radial distribution function for the reference fluid, which is given by

$$g(V_m)^{\text{ref}} = \frac{2 - \eta}{2(1 - \eta)^3} \quad (14)$$

$$\eta = \left( \frac{1}{V_m} \right) b \quad (15)$$

where  $\eta$  is the reduced fluid density and  $b$  is calculated by  $b = 0.08664RT_C/P_C$

CPA EOS is developed by the combination of the Soave–Redlich–Kwong (SRK) EOS with the association term of the Wertheim theory. Since it was first published by Kontogeorgis et al. in 1996,<sup>30</sup> this model has been applied in many complex systems.<sup>31,32</sup> In this work, the association term, given by Michelsen and Hendriks,<sup>28</sup> is still adopted. The complete expression is written as follows:

$$Z = \frac{V_m}{V_m - b} - \frac{\alpha(T)}{RT(V_m + b)} - \frac{1}{2} \left( 1 + \frac{1}{V_m} \frac{\partial \ln g}{\partial (1/V_m)} \right) \sum_i x_i \sum_{A_i} (1 - X_{A_i}) \quad (16)$$

$$\alpha(T) = a_0 [1 + c_1(1 - \sqrt{T_r})]^2 \quad (17)$$

where  $T_r$  is the reduced temperature,  $a_0$ ,  $b$ ,  $c_1$  are pure component parameters of CPA EOS.

For PR EOS,<sup>33</sup> it is given by the following:

$$Z = \frac{V_m}{V_m - b} - \frac{\alpha(T)/RT}{(V_m(V_m + b) + b(V_m - b))/V_m} \quad (18)$$

where

$$\alpha(T) = 0.45724R^2T_C^2/P_C[1 + \kappa(1 - T_r^{1/2})]^2 \quad (19)$$

$$\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2 \quad (20)$$

$$b = 0.0778RT_C/P_C \quad (21)$$

where  $T_C$ ,  $P_C$ , and  $\omega$  are the critical temperature, critical pressure, and acentric factor, respectively.

Using any one of above equations of state,  $U^{\text{res}}$  can be derived, the detailed expressions of the residual internal energy were shown in Appendix A.

The pure-component parameters of the PC-SAFT model include segment number ( $m$ ), segment diameter ( $\sigma$ ), and segment energy parameter ( $\epsilon/k$ ) for nonassociating substances, and two additional parameters are necessary for associating substances, namely the depth of square-well potential ( $\epsilon^A B_j$ ) and the bonding volume ( $\kappa^A B_j$ ). All of the parameters used in this work are provided by Gross and Sadowski.<sup>27,34</sup> Then, the CPA model contains five total parameters for pure component: three ( $a_0$ ,  $b$ ,  $c_1$ ) for nonassociating compounds and two ( $\epsilon^A B_j$ ,  $\kappa^A B_j$ ) additionally for associating compounds. These five parameters are provided by Kontogeorgis et al.<sup>31</sup> in this work. With regard to the PR model, its required parameters, including critical temperature ( $T_C$ ), critical pressure ( $P_C$ ) and acentric factor ( $\omega$ ), are all taken from Poilling's book.<sup>35</sup>

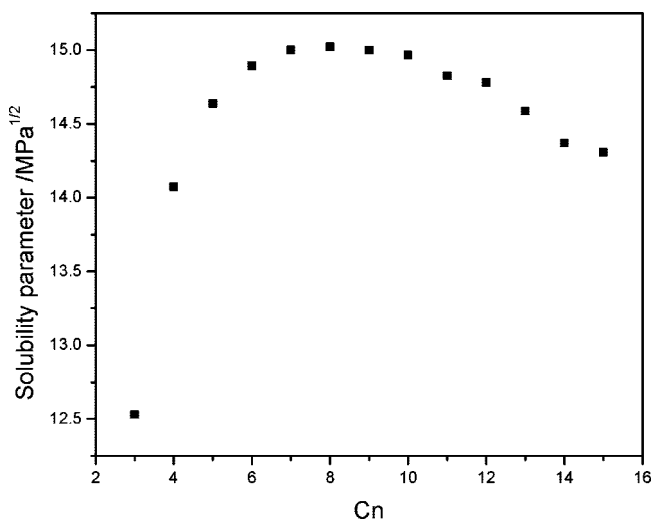
## Results and Discussion

**Solubility Parameters under Ambient Condition.** In this section, the solubility parameters of  $n$ -alkanes and 1-alcohols have been studied under ambient condition, which are the representatives of nonassociating and associating substances, respectively.

**Table 1. Comparisons Between Experimental and Calculated Solubility Parameters of  $n$ -Alkanes Under Ambient Condition**

$n$ -alkanes	solubility parameter/MPa <sup>1/2</sup>				
	experimental <sup>a</sup>	S–P <sup>b</sup>	PC-SAFT	CPA	PR
C <sub>3</sub> H <sub>8</sub>	13.10	12.85	13.53	12.21	12.53
C <sub>4</sub> H <sub>10</sub>	14.10	14.10	14.46	13.99	14.07
C <sub>5</sub> H <sub>12</sub>	14.40	14.34	14.74	14.49	14.64
C <sub>6</sub> H <sub>14</sub>	14.90	14.58	15.00	15.37	14.89
C <sub>7</sub> H <sub>16</sub>	15.20	15.12	15.08	15.03	15.00
C <sub>8</sub> H <sub>18</sub>	15.40	15.21	15.19	15.27	15.02
C <sub>9</sub> H <sub>20</sub>	15.60	15.25	15.27	15.41	15.00
C <sub>10</sub> H <sub>22</sub>	15.70	15.30	15.28	15.47	14.97
C <sub>11</sub> H <sub>24</sub>	15.80	15.40	15.30	15.32	14.83
C <sub>12</sub> H <sub>26</sub>	15.90	15.52	15.39	15.35	14.78
AAD%		1.59	2.27	2.25	3.17

<sup>a</sup> Ref 42. The ambient conditions:  $T = 298.15$  K,  $P = 1.00$  bar. <sup>b</sup> Ref 16.



**Figure 1.** The solubility parameters, calculated by PR model, as a function of carbon number of  $n$ -alkanes (Cn) at ambient condition.

First, PR, CPA, and PC-SAFT models were used to calculate the solubility parameters for C3 to C12  $n$ -alkanes. The results compared with experimental data are shown in Table 1. It is found that the average absolute deviations (AAD) are 2.27%, 2.25%, 3.17%, and 1.59% for PC-SAFT model, CPA model, PR model and the Stefanis–Panayiotou approach (S–P),<sup>16</sup> respectively.

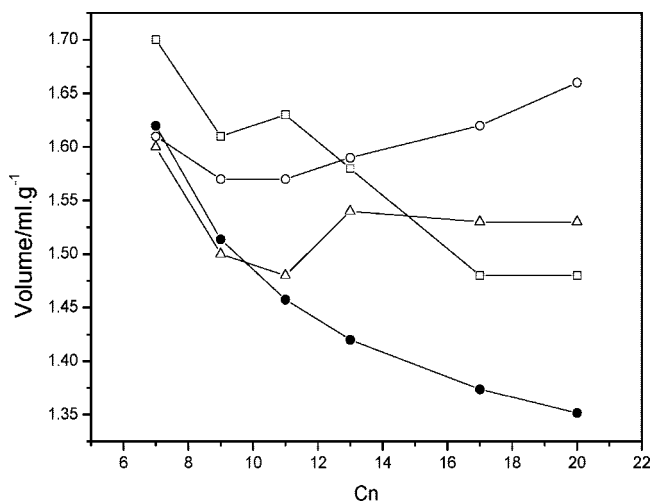
Moreover, according to the results of CPA and PC-SAFT models, the solubility parameters of  $n$ -alkanes increase monotonically with the increase of the carbon number (Cn), which is consistent with the experimental data. However, the PR model does not agree well. Figure 1 shows the solubility parameters calculated by PR model for C3–C24  $n$ -alkanes under the ambient condition, it is apparent that it does not monotonically increase but has a maximum in the  $n$ -octane. The main reason is that PR EOS causes volume deviations for  $n$ -alkanes. As the carbon number of  $n$ -alkane (Cn) increases, the solubility parameters should essentially increase. However, the values of volume deviations increase too, which leads to the decrease in solubility parameters. Therefore, the calculated solubility parameters increase initially, reach a maximum, and then fall off. The detailed information could be seen in Figure 2. In fact, the volume deviation has been found in the literature<sup>36,37</sup> too. The empirical concept of volume translation was thus proposed to improve the PR model.<sup>37,38</sup>

Second, the PC-SAFT and CPA models were used to estimate solubility parameters for methanol to 1-pentanol under the

**Table 2. Solubility Parameters (MPa<sup>1/2</sup>) of 1-Alcohols at Ambient Condition<sup>a</sup>**

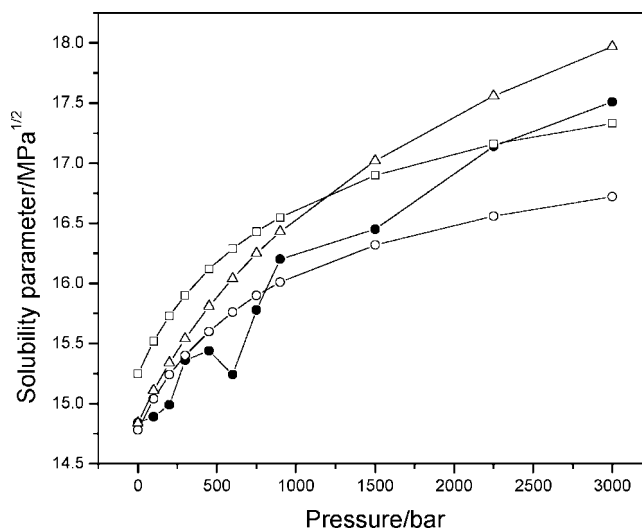
1-alcohol	$\delta_{\text{exp}}^{19}$	$\delta_{\text{S-P}}^{16}$	$\delta_{\text{MC}}^{20}$	$\delta_{\text{MD}}^{19}$	HSP <sup>35</sup>		PC-SAFT		CPA	
					$\delta_{\text{t}}$	$\delta_{\text{H}}$	$\delta_{\text{t}}$	$\delta_{\text{A}}$	$\delta_{\text{t}}$	$\delta_{\text{A}}$
CH <sub>4</sub> O	29.71	29.61	30.53	26.45	29.63	22.30	29.03	23.18	31.19	25.40
C <sub>2</sub> H <sub>6</sub> O	26.23	26.13	26.43	24.08	26.55	19.43	25.89	18.87	27.80	19.14
C <sub>3</sub> H <sub>8</sub> O	24.18	24.45	24.59	21.07	24.48	17.39	24.87	15.19	25.81	16.68
C <sub>4</sub> H <sub>10</sub> O	23.98	23.35	23.36	20.27	23.15	15.75	23.56	14.50	24.12	15.10
C <sub>5</sub> H <sub>12</sub> O	22.54	21.65	22.34	19.49	21.65	13.91	22.71	12.65	22.90	13.43
AAD%		1.68 <sup>b</sup>	1.75 <sup>b</sup>	12.21 <sup>b</sup>	2.03 <sup>b</sup>		1.79 <sup>b</sup>	7.3 <sup>c</sup>	3.98 <sup>b</sup>	5.41 <sup>c</sup>

<sup>a</sup> The ambient conditions:  $T = 298.15$  K,  $P = 1.00$  bar. <sup>b</sup> The average absolute deviation from the experimental data. <sup>c</sup> The average absolute deviation from the  $\delta_{\text{H}}$  of HSP.



**Figure 2.** The volumes of *n*-alkanes as a function of carbon number (Cn) at  $T = 373.15$  K,  $P = 50.00$  bar: (●) experimental data,<sup>41</sup> (Δ) calculated by CPA model, (○) calculated by PR model, and (□) calculated by PC-SAFT model.

ambient condition. The values of Hansen solubility parameters (HSP)<sup>36</sup> were cited to contrast with the results of both models. In HSP, the solubility parameter is divided into three parts,  $\delta_{\text{D}}$ ,  $\delta_{\text{P}}$ , and  $\delta_{\text{H}}$ , which describe atomic nonpolar interactions (D), molecular dipolar interactions (P), and molecular hydrogen bonding interactions (H), respectively. In the PC-SAFT model, the ideal gas contribution, the hard-chain contribution, and the dispersion contribution are together called the nonassociation term, and the hydrogen-bonding contribution is called the association term. For the CPA model, the part of SRK EOS is treated as the nonassociation term, and the association part is the same with PC-SAFT. Therefore, the solubility parameter is divided into two parts for PC-SAFT and CPA EOS:  $\delta_{\text{NA}}$  is contributed by the nonassociation term, and  $\delta_{\text{A}}$  is contributed by the association term. At the same time, the total solubility parameter is expressed as  $\delta_{\text{t}}$ . In both of the models, the association term takes the hydrogen bonding interaction between molecules. Thus, both  $\delta_{\text{A}}$  and  $\delta_{\text{H}}$  are contributed by the hydrogen bonding interactions, the comparisons are carried out between them. The results are shown in Table 2. It is found that the total solubility parameter calculated by the PC-SAFT and CPA models agrees well with the experimental data, the AAD are 1.79% and 3.98%, respectively, and the AAD between  $\delta_{\text{A}}$  and  $\delta_{\text{H}}$  are 7.30% and 5.41% for PC-SAFT and CPA models, respectively. Despite small deviations, it could be concluded that the association term of models are able to reproduce the molecular hydrogen-bonding part of HSP. Simultaneously, the results of other approaches are shown in Table 2. They are provided by Stefanis et al.,<sup>16</sup> Belmares et al.,<sup>19</sup> and Rai et al.,<sup>20</sup> and represent the Stefanis–Panayiotou approach, molecular dynamics (MD), and MC simulation, respectively. It is clear



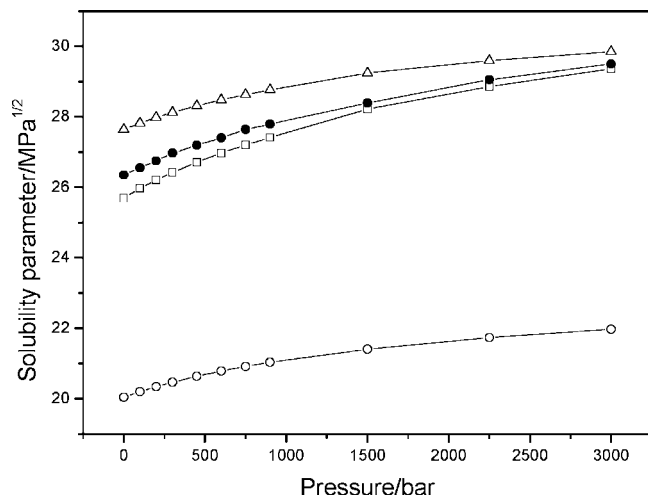
**Figure 3.** The solubility parameters of *n*-hexane as a function of pressure at 303.15 K: (●) calculated by MC simulation,<sup>13</sup> (Δ) calculated by CPA model, (○) calculated by PR model, and (□) calculated by PC-SAFT model.

that the MD approach has a larger average deviation and others obtain good results.

In this part, it is clear that the Stefanis–Panayiotou approach<sup>16</sup> has a higher accuracy than other approaches for both nonassociating and associating substances. However, the PC-SAFT and CPA models are also very accurate but less complicated approaches, thus they are suitable for engineering calculations. Then, they are applicable to any fluid over a wide range of temperature and pressure, and the parameters of pure substances could be acquired from the pressure–volume–temperature (PVT) data. In fact, group-contribution methods<sup>39</sup> have been developed to estimate the parameters of substances for PC-SAFT, thus, the present models could be applied widely in calculating solubility parameters. Especially, the PC-SAFT and CPA models are convenient for computing the solubility parameters of mixtures with one binary interaction parameters, which could be regressed from the experimental PVT data.

**Pressure Effects on Solubility Parameter.** Pressure effects on solubility parameter were investigated over the pressure range from 1 to 3000 bar, choosing *n*-hexane and ethanol as representatives. PR, CPA, and PC-SAFT models were used to calculate the solubility parameters at  $T = 303.15$  K. They were compared with the results of MC simulation,<sup>13</sup> and the typical results are shown in Figures 3 and 4 for *n*-hexane and ethanol, respectively. First, it reveals that the solubility parameter increases monotonically with the increase of pressure. Second, the results of these models are found to agree well with those of the MC simulations in calculating the solubility parameters. For *n*-hexane, the AAD of PC-SAFT, CPA, and PR models are 2.32%, 2.35%, and 1.67%, respectively. Moreover, it is noticed





**Figure 4.** The solubility parameters of ethanol as a function of pressure at 303.15 K: (●) calculated by MC simulation,<sup>13</sup> (Δ) calculated by CPA model, (○) calculated by PR model, and (□) calculated by PC-SAFT model.

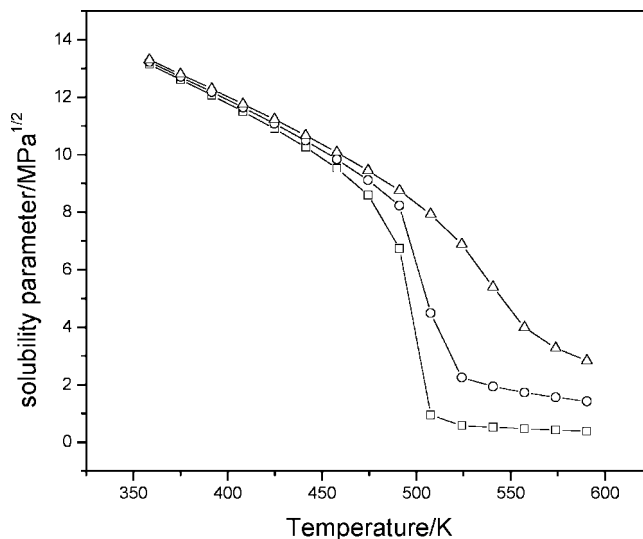
that CPA and PR models are better in the low pressure, but worse in the high pressure than PC-SAFT model. For ethanol, the AAD are 1.52%, 3.60%, and 24.37% for PC-SAFT, CPA models and PR model, respectively. Considering the average uncertainties of MC simulation<sup>13</sup> are 3.58% and 0.25% for *n*-hexane and ethanol, respectively, the results of PC-SAFT and CPA models coincide well with these of MC simulation.<sup>13</sup> PR model could calculate well for *n*-hexane, but the deviations are large for ethanol, the reason is that the PR model does not consider the contribution of the hydrogen bonding interaction, it does not hold true in calculating associating substances. Additionally, the solubility parameters calculated with the CPA model are larger than those calculated with PC-SAFT model for both of compounds.

**Temperature Effects on Solubility Parameter.** To study the temperature effects, the solubility parameters of *n*-hexane were studied with PC-SAFT model. On the basis of the Poling's book,<sup>35</sup> the critical pressure and temperature of *n*-hexane are 30.25 bar and 507.6 K, respectively. The typical results are shown in Figure 5. It can be seen that the solubility parameters decrease almost linearly as temperature increasing in the range from freezing point to boiling point. However, at the near and supercritical point, the trends are different at the different pressure conditions. At  $P = 10.00$  bar, there is a point where the solubility parameter falls down quickly with the increase of temperature, it could be explained that when the pressure is lower than the critical pressure, the liquid phase turns into vapor phase directly at boiling temperature. At critical pressure, it is found that the solubility parameter descends quickly around the critical point, where the liquid turns into critical fluid. At  $P = 50.00$  bar, the solubility parameter still decreases as the temperature increases, but the point is not apparent where the solubility parameter drops quickly.

## Conclusions

Starting from the definitions of cohesive energy density and the Hildebrand solubility parameter, a new approach utilizing PC-SAFT and CPA equations of state is provided to estimate the Hildebrand solubility parameter over wide ranges of temperature and pressure.

It is clarified that the PC-SAFT and CPA models are able to calculate the Hildebrand solubility parameter accurately for both the C3~C12 *n*-alkanes and C1~C5 1-alcohols. In addition, PR



**Figure 5.** The solubility parameters calculated with the PC-SAFT model as a function of temperature for *n*-hexane in near and super critical point. (□) at  $P = 10.00$  bar, (○) at  $P = 30.25$  bar, (Δ) at  $P = 50.00$  bar.

model has also been used to calculate the solubility parameters. It does not hold true for associating substances and C<sub>8+</sub> *n*-alkanes. Moreover, it is revealed that the solubility parameter calculated by the association term corresponds to the part of HSP contributed by hydrogen bonding interactions.

Alternatively, some conclusions have been drawn on pressure and temperature effects on the solubility parameter: it is found that the solubility parameter increases monotonically with the increase of pressures (from 1 to 3000 bar), and decreases with the increase of temperature between freezing point and boiling point. Good agreements were found between the results of MC simulation and the PC-SAFT, CPA models in calculating the solubility parameter of *n*-hexane and ethanol over the entire pressure range. PR model was also found to coincide essentially with the MC simulation for *n*-hexane.

Therefore, this work provides an accurate, reliable, and convenient approach to calculate the solubility parameter for both nonassociative and associative substances. The further development of these models would make for the applications in the polymeric fluids, water, organic acids, glycols, and their mixtures.

## Appendix A. Summary of Equations for Calculating the Solubility Parameter Using PC-SAFT, CPA, and PR Models

This section provides a summary of equations for calculating the solubility parameter. In the following, a tilde ( $\sim$ ) is used for reduced quantities. In the PC-SAFT model, the residual internal energy is given by the following:

$$\tilde{u}^{\text{res}} = \tilde{u}^{\text{na}} + \tilde{u}^{\text{assoc}} \quad (\text{A.1})$$

where

$$\tilde{u}^{\text{na}} = \tilde{a}^{\text{na}} + T\tilde{s}^{\text{na}} \quad (\text{A.2})$$

$$\tilde{u}^{\text{assoc}} = \tilde{a}^{\text{assoc}} + T\tilde{s}^{\text{assoc}} \quad (\text{A.3})$$

the expressions of  $\sim a^{\text{na}}$  and  $\sim s^{\text{na}}$  were provided clearly in the original PC-SAFT model,<sup>26</sup> and the  $\sim a^{\text{assoc}}$  of pure components, proposed by Chapman et al.,<sup>40</sup> is given by the following:

$$\bar{a}^{\text{assoc}} = \sum_A \left[ \ln X^A - \frac{X^A}{2} \right] + \frac{M}{2} \quad (\text{A.4})$$

$$\bar{s}^{\text{assoc}} = - \left( \frac{\partial(\bar{a}^{\text{assoc}})}{\partial T} \right)_V = - \sum_A \left( \frac{(\partial X_A / \partial T)_V}{X^A} - \frac{(\partial X_A / \partial T)_V}{2} \right) \quad (\text{A.5})$$

where  $M$  is the number of association sites of each molecule. In this work,  $M = 2$  for all studied 1-alcohols in the foundation of previous researches.<sup>30,31</sup> Then,  $X_A$  can be derived for 1-alcohols using its definition, it can be written as follows:

$$X_A = X_B = \frac{-1 + \sqrt{1 + 4\rho\Delta^{AB}}}{2\rho\Delta^{AB}} \quad (\text{A.6})$$

where  $\rho$  is the molar density. Together with eq A.6, the temperature derivative of  $X_A$  is given by the following:

$$\left( \frac{\partial X_A}{\partial T} \right)_V = \frac{2\rho(1 + 4\rho\Delta^{AB})^{-1/2}\Delta^{AB} - (-1 + \sqrt{1 + 4\rho\Delta^{AB}})(\partial\Delta^{AB}/\partial T)_V}{4\rho(\Delta^{AB})^2} \quad (\text{A.7})$$

$\Delta^{AB}$  can be calculated with eq 13, and its temperature derivative is given by the following:

$$\left( \frac{\partial(\Delta^{AB})}{\partial T} \right)_V = g(V_m)^{\text{ref}} \left[ \exp\left(\frac{\epsilon^{AB}}{RT}\right) \cdot \left(-\frac{\epsilon^{AB}}{RT^2}\right) \right] b\beta^{AB} \quad (\text{A.8})$$

In the CPA model, the internal energy of association term could be gotten as the same with PC-SAFT model. The nonassociation term is the SRK EOS, so  $\delta^{\text{SRK}}$  represents the solubility parameter of this part in this work. Combining with the expressions of SRK and PR EOS, the calculation equation of internal energy, eq 5, and the definition of the solubility parameter, eq 2, the expressions of the solubility parameter for two equations of state are given as follows: For the SRK model, it is given by the following:

$$\delta^{\text{SRK}} = \left( \frac{1}{b} \left( \alpha(T) - T \frac{d\alpha(T)}{dT} \right) \ln \left( 1 + \frac{b}{V} \right) \frac{1}{V} \right)^{1/2} \quad (\text{A.9})$$

For the PR model, it is given by the following:

$$\delta^{\text{PR}} = \left( \frac{\sqrt{2}}{4b} \left( \alpha(T) - T \frac{d\alpha(T)}{dT} \right) \left[ \ln \left( \frac{V + b(\sqrt{2} + 1)}{V - b(\sqrt{2} + 1)} \right) \right] \frac{1}{V} \right)^{1/2} \quad (\text{A.10})$$

## Acknowledgment

The authors gratefully acknowledge financial support from the Key Program of the National Outstanding Young Scientists Foundation of China under Grant No. 20625620 and the Knowledge Innovation Program of the Chinese Academy of Sciences. This work is also supported by Synfuels CHINA. Co., Ltd.

## Literature Cited

- (1) Scatchard, G. Equilibria in non-electrolyte solutions in relation to the vapor pressures and densities of the components. *Chem. Rev.* **1931**, *8* (2), 321.
- (2) Hildebrand, J. H.; Scott, R. L. *The Solubility of Nonelectrolytes*; Reinhold Publishing Corporation: New York, 1950.
- (3) Hansen, C. M. The universality of the solubility parameter. *Ind. Eng. Chem. Prod. Res. Dev.* **1969**, *8* (1), 2.
- (4) Miller, R. G.; Bowles, C. Q.; Chappelow, C. C.; Eick, J. D. Application of solubility parameter theory to dentin-bonding systems and adhesive strength correlations. *J. Biomed. Mater. Res.* **1998**, *41* (2), 237.

- (5) Yang, P.; Cong, Q.; Liao, K. J. Application of solubility parameter theory in evaluating the aging resistance of paving asphalts. *Pet. Sci. Technol.* **2003**, *21* (11–12), 1843.
- (6) Matsui, T.; Nagashima, K.; Fukamachi, M.; Shimoda, M.; Osajima, Y. Application of the solubility parameter in estimating the sorption behavior of flavor into packaging film. *J. Agric. Food Chem.* **1992**, *40* (10), 1902.
- (7) Fedors, R. F. A method for estimating both the solubility parameters and molar volumes of liquids. *Polym. Eng. Sci.* **1974**, *14*, 147.
- (8) Watson, K. M. Thermodynamics of the liquid state. *Ind. Eng. Chem.* **1943**, *35* (4), 398.
- (9) Blanks, R. F.; Prausnitz, J. M. Thermodynamics of polymer solubility in polar and nonpolar systems. *Ind. Eng. Chem. Fund.* **1964**, *3* (1), 1.
- (10) Hansen, C. M. the three dimensional solubility parameter key to paint component affinities: 1. solvents plasticizers, polymers, and resins. *J. Paint Technol.* **1967**, *39*, 505.
- (11) Hansen, C. M. The three dimensional solubility parameter—key to paint component affinities: 111. independent calculations of the parameter components. *J. Paint Technol.* **1967**, *9*, 511.
- (12) Verdier, S.; ersen, S. I. Internal pressure and solubility parameter as a function of pressure. *Fluid Phase Equilib.* **2005**, *231* (2), 125.
- (13) Rai, N.; Siepmann, J. I.; Schultz, N. E.; Ross, R. B. Pressure dependence of the hildebrand solubility parameter and the internal pressure: monte carlo simulations for external pressures up to 300 MPa. *J. Phys. Chem. C* **2007**, *111* (43), 15634.
- (14) Allada, S. R. Solubility parameters of supercritical fluids. *Ind. Eng. Chem. Proc. Des. Dev.* **1984**, *23* (2), 344.
- (15) Panayiotou, C. Solubility parameter revisited: an equation-of-state approach for its estimation. *Fluid Phase Equilib.* **1997**, *131* (1–2), 21.
- (16) Stefanis, E.; Tsivintzelis, I.; Panayiotou, C. The partial solubility parameters: An equation-of-state approach. *Fluid Phase Equilib.* **2006**, *240* (2), 144.
- (17) Williams, L. L.; Rubin, J. B.; Edwards, H. W. Calculation of hansen solubility parameter values for a range of pressure and temperature conditions, including the supercritical fluid region. *Ind. Eng. Chem. Res.* **2004**, *43* (16), 4967.
- (18) Barton, A. F. M. Solubility parameters. *Chem. Rev.* **1975**, *75* (6), 731–753.
- (19) Belmares, M.; Blanco, M.; Goddard, W. A.; Ross, R. B.; Caldwell, G.; Chou, S. H.; Pham, J.; Olafson, P. M.; Thomas, C. Hildebrand and hansen solubility parameters from molecular dynamics with applications to electronic nose polymer sensors. *J. Comput. Chem.* **2004**, *25*, 1814.
- (20) Rai, N.; Wagner, A. J.; Ross, R. B.; Siepmann, J. I. Application of the TraPPE force field for predicting the hildebrand solubility parameters of organic solvents and monomer units. *J. Chem. Theory Comput.* **2008**, *4*, 136.
- (21) Kouskoumvekaki, I. A.; Krooshof, G. J. P.; Michelsen, M. L.; Kontogeorgis, G. M. Application of the simplified PC-SAFT equation of state to the vapor-liquid equilibria of binary and ternary mixtures of polyamide 6 with several solvents. *Ind. Eng. Chem. Res.* **2004**, *43* (3), 826.
- (22) Gross, J.; Sadowski, G. Application of the perturbed-chain SAFT equation of state to associating systems. *Ind. Eng. Chem. Res.* **2002**, *41* (22), 5510.
- (23) Folas, G. K.; Kontogeorgis, G. M.; Michelsen, M. L.; Stenby, E. H. Application of the cubic-plus-association equation of state to mixtures with polar chemicals and high pressures. *Ind. Eng. Chem. Res.* **2006**, *45* (4), 1516.
- (24) Lyckman, E. W.; Eckert, C. A.; Prausnitz, J. M. Generalized liquid volumes and solubility parameters for Regular solution application. *Chem. Eng. Sci.* **1965**, *20* (7), 703.
- (25) Barton, A. F. M. *CRC Handbook of Solubility Parameters and Other Cohesion Parameters*; CRC Press Inc.: Boca Raton, 1983.
- (26) Hoy, K. L. New values of the solubility parameters from vapor pressure data. *J. Paint Tech.* **1970**, *42*, 76.
- (27) Gross, J.; Sadowski, G. Perturbed-chain SAFT: an equation of state based on a perturbation theory for chain molecules. *Ind. Eng. Chem. Res.* **2001**, *40* (4), 1244.
- (28) Michelsen, M. L.; Hendriks, E. M. Physical properties from association models. *Fluid Phase Equilib.* **2001**, *180* (1–2), 165.
- (29) Karakatsani, E. K.; Spyriouni, T.; Economou, I. G. Extended statistical associating fluid theory (SAFT) equation of state for dipolar fluids. *AIChE* **2005**, *51* (8), 2328–2342.
- (30) Kontogeorgis, G. M.; Voutsas, E. C.; Yakoumis, I. V.; Tassios, D. P. An equation of state for associating fluids. *Ind. Eng. Chem. Res.* **1996**, *35* (11), 4310.
- (31) Kontogeorgis, G. M.; Michelsen, M. L.; Folas, G. K.; Derawi, S.; von Solms, N.; Stenby, E. H. Ten years with the CPA (Cubic-Plus-Association) equation of state. Part I. Pure compounds and self-associating systems. *Ind. Eng. Chem. Res.* **2006**, *45* (14), 4855.

- (32) Kontogeorgis, G. M.; Michelsen, M. L.; Folas, G. K.; Derawi, S.; von Solms, N.; Stenby, E. H. Ten years with the CPA (Cubic-Plus-Association) equation of state. Part 2. Cross-associating and multicomponent systems. *Ind. Eng. Chem. Res.* **2006**, *45* (14), 4869.
- (33) Peng, D. Y.; Robinson, D. B. A new two-constant equation of state. *Ind. Eng. Chem. Fund.* **1976**, *15* (1), 59.
- (34) Gross, J.; Sadowski, G. Application of the perturbed-chain SAFT equation of state to associating systems. *Ind. Eng. Chem. Res.* **2002**, *41* (22), 5510.
- (35) Poling, B. E.; Prausnitz, J. M.; O'Connell, J. P. *The Properties of Gases and Liquids*, 5th ed.; McGraw-Hill: New York, 2000.
- (36) Hansen, C. M. *Hansen Solubility Parameters: A User's Handbook*; CRC Press: Boca Raton, FL, 2000.
- (37) P  neloux, A.; Rauzy, E.; Fr  ze, R. A consistent correction for Redlich-Kwong-Soave volumes. *Fluid Phase Equilib.* **1982**, *8* (1), 7.
- (38) Magoulas, K.; Tassios, D. Thermophysical properties of *n*-alkanes from C1 to C20 and their prediction for higher ones. *Fluid Phase Equilib.* **1990**, *56*, 119.
- (39) Tsai, J.-C.; Chen, Y.-P. Application of a volume-translated Peng-Robinson equation of state on vapor-liquid equilibrium calculations. *Fluid Phase Equilib.* **1998**, *145*, 193.
- (40) Doolittle, A. K. Specific volumes of *n*-alkanes. *J. Chem. Eng. Data* **1964**, *9*, 275–279.
- (41) Tihic, A.; Kontogeorgis, G. M.; Solms, N. v.; Michelsen, M. L. A Predictive group-contribution simplified PC-SAFT equation of state: application to polymer systems. *Ind. Eng. Chem. Res.* **2008**, *47* (15), 5092–5101.
- (42) Chapman, W. G.; Gubbins, K. E.; Jackson, G.; Radosz, M. New reference equation of state for associating liquids. *Ind. Eng. Chem. Res.* **1990**, *29* (8), 1709–1721.

Received for review May 21, 2008

Revised manuscript received August 28, 2008

Accepted September 04, 2008

IE800811F