Group Contribution Estimation of SAFT and PC-SAFT Parameters

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Abstract:

The methodology of Elliott and Natarajan [J. R. Elliott, Jr., R. N. Natarajan, Ind. Eng. Chem. Res. 41 (2002) 1043] has been applied to statistical associating fluid theory (SAFT) [S. H. Huang, M. Radosz, Ind. Eng. Chem. Res. 22 (1990) 2284] and perturbed-chain statistical associating fluid theory (PC-SAFT) [J. Gross, G. Sadowski, Ind. Eng. Chem. Res. 40 (2001) 1244] equations of state to different families of compounds in order to describe their thermodynamic properties. Pure component parameters of each EOS are obtained through a regression method for a large number of compounds based on their boiling point temperatures at 10 and 760 mmHg, their estimated solubility parameter, liquid density, and standard hydrogen-bonding parameters. Then the group contribution (GC) to the SAFT and PC-SAFT shape factor parameters are obtained and presented for 88 functional groups. Hydrogen- bonding contributions based on a modified Wertheim theory [J. R. Elliott, Jr. Ind. Eng. Chem. Res. 35 (1996) 1624] are considered in this work. We have treated pure compounds of sixteen different families including: hydrocarbons, cyclic hydrocarbons, aromatic hydrocarbons, alcohols, amines, nitriles, thiols, aldehydes, ethers, ketones, esters, halocarbons, hydroxyls, multi-functional groups, acids, sulfides and silicones. The average absolute percent deviation (%AADP) of saturated vapor pressure is 35.28% for GC-SAFT and 25.69% for GC-PC-SAFT equations. The average absolute deviation (AADT) between experimental and calculated saturated temperature are 12.7 K and 8.49 K for GC-SAFT and GC-PC-SAFT equations, respectively. These results are quite outstanding for a group contribution approach.

KEYWORDS: Group contribution; SAFT; PC-SAFT; equation of state

1. Introduction

Polymeric materials, both as end products and intermediates, are an ever-increasing segment of chemical industry. Representation of polymer mixtures by equations of state especially developed for this task is a fairly mature area.[1] Recently the phase equilibria of mixtures of polymers in organic liquid solvents and in supercritical fluids have become very important.[2] The EOS-G^{ex} models[3] have the potential of describing such mixtures, and some work has been done on EOS-G^{ex} models that are applicable to polymer-solvent systems.[4-11] However, these methods do not generally include explicit treatment of hydrogen-bonding contributions. Also, the results so far indicate that there is a need for more work, especially in developing

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accurate predictive, rather than correlative, models. One point to stress is that the results of these early studies seem to indicate that the EOS parameters used for the pure polymers are not very critical success of these models, but how the solvent is described appears to be more important to the final results. [3] For this reason, in this research a group contribution method for solvents from several families were described that paves the way for analyzing polymer solution phase behavior. Finally, Benzaghou et al.[12] correlate equation of state parameters in terms of linear correlations for various functional groups and extrapolate them to polymer limit. One problem in applications of equations of state to pharmaceuticals or natural products is that the components may be poorly characterized from a thermodynamic perspective.[13] Experimental values for the melting temperature and the density may be all that is available. In these cases, the components must be characterized in terms of their chemical structure. These considerations motivated Elliott and Natarajan[14] to develop a predictive model for polymer solutions based on group contribution factors for the pure-component properties. Elliott and Natarajan[14] presented a group-contribution approach for the ESD equation, an equation similar to SAFT and PC-SAFT. They demonstrated accurate phase behavior correlations for a broad range of components and molecular weights. Extension of their method to SAFT would be straightforward. The basis of their method was the Elliott-Suresh-Donohue (ESD) equation of state.[15, 16] The ESD equation was generalized to polymers through a group contribution method to estimate the shape parameter, along with solubility parameters (heat of vaporization) and molar volumes that could also be estimated by group contribution methods. The method presented in Elliott and Natarajan[14] work could easily be adapted to similar equations of states like the statistical associating fluid theory (SAFT) equation[17, 18] and perturbed-chain statistical associating fluid theory (PC-SAFT) equation of state[19, 20] as have been performed in this research.

The purpose of the present study is twofold: (1) to adapt generalized form of three-parameter corresponding states to polymers, including hydrogen-bonding polymers, especially when the critical constants are unknown; (2) to get more accurate results in comparison with the polymer format of the ESD equation.[14]

2. Group Contribution form of SAFT and PC-SAFT Equations

Generally, each of the SAFT and PC-SAFT equations characterizes each pure component in terms of three parameters. The parameters for SAFT equation are: a temperature-independent segment volume, v^{oo}, a shape parameter, m, and a temperature-independent dispersion energy of interaction between segments, u^{o}/k. Also, nonassociating molecules are characterized in PC-SAFT equation by three pure-component parameters: the temperature-independent segment diameter, σ, the depth of the potential which is related to Barker-Henderson approach[27], ε, and the number of segments per chain, m. Meanwhile, hydrogen-bonding species require specification of three additional parameters: the number of hydrogen-bonding segments per molecule, N_d, the bonding volume, K^{AD}, and the hydrogen-bonding energy, ε^{HB}. All associating components are assigned two association sites (often referred to as the 2B model[16]). Although this is a reasonable assumption for some species (such as alcohols), it is a considerable simplification for other compounds-in particular for water. A study of Economou and Tsonopoulos[28] indicates that water is best represented with a four-site treatment, whereas Suresh and Elliott[16] found the two-site model to perform at least as well. For simplicity at this point, we follow the latter study as was justified by Gross and Sadowski[20]. However, the present work correlates the bonding volume in terms of b and m, and N_d is obvious from the molecular structure and general estimates of the hydrogen-bonding energy have been applied throughout the present work, as the previous one[14]. e^{HB}/k is

computed from the hydrogen-bonding group contribution method, effectively as an average over bonding sites. Using an average is crude, because different bonding sites should be treated differently, but the current SAFT and PC-SAFT models in this work are not that sophisticated. Elliott et al. are moving toward a more rigorous model in SPEAD[29]. So, only three parameters, v^{oo}, m, and $u^{°}/k$ for the SAFT EOS and σ, m, and ε for the PC-SAFT EOS, need to be characterized for each component.

The equations for bonding energy and bonding volume are based on understanding basic trends in the physical view of these parameters. The bonding volume is a value that remains relatively constant on a per segment basis. Since the molecular volume and shape parameter are both related to the effective number of segments in the molecule, it is assumed that $K^{AD} \sim b/m$. By correlating the bonding volume for a huge database, the generalized proportionality constant of 0.035 was obtained, giving $K^{AD} = 0.035\ b/m$ as a reliable general relation for both SAFT and PC-SAFT equations. For the hydrogen-bonding energy, we assumed 4 kcal/mol for hydroxyl groups and 1.5 kcal/mol for amine, amide, nitrile, and aldehyde groups as the previous work[14] on the ESD equation of state. These values were derived from previous studies of hydrogen-bonding energies for a wide range of components.[30]

Solubility parameter and liquid molar volume are two physical quantities that their benefit is known to every expert researcher in the polymer solution phase behavior. In this manner we use the best method of polymer characterization for parametrization of the SAFT and PC-SAFT equations. Expressions for the solubility parameter and the molar volume in terms of the equations of state are readily derived as shown below, providing two equations for the three unknown parameters. The task remaining is to develop a procedure for specifying the third parameter among v^{oo}, m, and $u^{°}/k$ for the SAFT equation and σ, m, and ε for the PC-SAFT equation. One approach is to apply a vapor-pressure datum, and that would be preferable if any vapor pressure were known. In the absence of vapor-pressure data, however, we propose a group contribution correlation for the shape parameter, m, as described below.

Group contribution factors for the shape parameter, m, were correlated in terms of functional groups from a database of 1034 pure components for SAFT EOS and PC-SAFT EOS.[31] The database consisted of shape parameters computed by first satisfying the solubility parameter (heat of vaporization) and molar volume constraints from the group contribution method and then solving for the shape parameter that matched the boiling temperature at 10 mmHg or 760 mmHg which is closer to 400K. Basically, we needed to compute the optimal SAFT and PC-SAFT shape factors (m) for a large number of components based on their boiling point temperature at 10 mmHg or 760 mmHg, and their estimated solubility parameter (heat of vaporization), liquid density, and standard hydrogen bonding parameters. This has required computing the solubility parameter from the energy departure function, which will require a computer routine for the energy and pressure of each equation of state. Then, the group contributions of the "m" parameter have been regressed. The basic idea of the shape parameter regression is to prepare a table of shape parameters that most closely match the way the shape parameters would be used when applying SAFT and PC-SAFT for polymers. Since application of SAFT and PC-SAFT would use the solubility parameter (heat of vaporization) and liquid molar volume, we needed to generate a set of pure-component parameters that are consistent with the experimental solubility parameter (heat of vaporization), liquid molar volume, and boiling temperature at 10 mmHg or 760 mmHg. Once we had a set of tabulated SAFT and PC-SAFT shape parameters for each molecule and a set of group descriptors for each molecule, we simply computed estimated

SAFT and PC-SAFT shape factors from the summation product of group contributions and group descriptors for each molecule. Then root mean square percent (%RMS*m* error) between the estimated SAFT and PC-SAFT shape factors were minimized by changing the group contributions and plays as an objective function role that defined in the following equation

$$\%RMSm = 100\sqrt{\frac{\left(\dfrac{m^{opt} - m^{calc}}{m^{opt}}\right)^2}{NDP}} \tag{1}$$

where *NDP* is the number of data points and m^{opt} and m^{calc} stand for the optimized and calculated shape factors as described above.

The boiling temperature at 10 mmHg or 760 mmHg was chosen as a standard vapor pressure because experimental data were available for a much larger number of high molecular weight compounds, especially for hydrocarbons from the API 42 compilation.[32] The boiling temperature at 10 mmHg or 760 mmHg was computed from the standard correlation for vapor pressure when available and from the tabulated data for compounds from the API 42 compilation. Table 1 demonstrates very interesting results that could be interested in many chemical applications including polymer related industries as discussed in the results section of this paper. These results show how polymer and pure component properties could be estimated based on group contribution estimation in a short computational time without the frustration and disappointment that so many researchers have experienced in experimental analysis.

UNIFAC groups were selected as the basis for the regression because the UNIFAC method is often used in evaluating mixture properties.[14] Note that there is no direct correspondence between the UNIFAC group definitions for a particular molecule and those from, say, Joback and Reid groups.[33] Thus, selecting Joback and Reid groups as the basis would necessitate two steps of group contribution definition before a new component could be used with UNIFAC as well as equations of state.[34] By using UNIFAC groups as the basis for all group contributions, all properties for new components can be specified in a single step.

There are several alternatives when selecting group contribution methods for estimating solubility parameters, δ [(cal/cm^3)$^{1/2}$] or heat of vaporization, H_{vap} (cal/mol), and liquid molar volumes at 298 K, V_L^{298}. We have focused on the method compiled by van Krevelen[35] for liquid molar volume and Constantinou and Gani[36] for heat of vaporization. Note that van Krevelen recommended that group contributions for polymers be independent of the contributions for solvents. Nevertheless, a comparison of van Krevelen's molar volume contributions to those of Hoy[37] (Table 7.10 of van Krevelen[35]) shows a small discrepancy of only 4%. By comparison, the method of Fedors[38] gives much larger discrepancies, especially for polystyrene and poly (vinyl alcohol). Hoy's contributions have an advantage of being characterized for many more groups than van Krevelen's. Furthermore, Hoy's correlation can be improved for small molecules by incorporating a small residual constant that has minimal impact on polymers. Hence, we adapt Hoy's correlation in the form $V_L^{298} = 12.1 + \sum v_i \Delta V_i$. We use Elliott and Natarajan[14] proposed values in cases of missing groups because their method has the less error in comparison with Fedors' approach. For completeness, we present in Table 2 the values[14] of UNIFAC group contributions for H_{vap}^{298} and V_L^{298} along with the group contributions for the shape parameter, *m*. Solubility parameters were computed from H_{vap}^{298} and V_L^{298} according to the definition $\delta = \left[(H_{vap}^{298} - 298R)/V_L^{298}\right]^{1/2}$.

The relationships for the solubility parameter from the SAFT and PC-SAFT equations are derived by expressing the heat of vaporization in terms the internal energy departure function, neglecting the departure function for the vapor. The internal energy departure function is given by the derivative of the free energy departure function. In the present work as the previous one[14], we consider the efficient form of Wertheim's theory treated by Elliott, [21] for which the energy and free energy of association can be written as

$$\frac{A^{ASSOC}}{RT} = 2N_d \ln(X^A) + N_d(1 - X^A) =$$
$$2N_d \ln(1 - F^2 / N_d) + F^2$$
(2)

$$\frac{U^{assoc}}{RT} = \frac{\beta \partial(A^{assoc} / RT)}{\partial \beta} = \left[1 - \frac{2Nd}{Nd - F^2}\right] 2F\beta \frac{\partial F}{\partial \beta}$$
(3)

$$\frac{\partial F}{\partial \beta} = \frac{\varepsilon^{HB} \sqrt{\alpha}}{2} \left[\frac{N_d - F^2}{1 + 2F\sqrt{\alpha}}\right] \frac{Y^{HB} + 1}{Y^{HB}}$$
(4)

$$\frac{U}{298R} = -\frac{\delta^2 V_L^{298}}{298R}$$
(5)

The expressions for the solubility parameter and the molar volume in terms of the SAFT equation of state is as follows

$$\frac{\delta^2 V_L^{298}}{RT} = \frac{9\eta m C \beta u^\circ \exp(-3\beta u^\circ)(2\eta - 4)}{(1-\eta)^3 [1 - C\exp(-3\beta u^\circ)]} -$$
$$\frac{m(1 + 2\beta e)}{1 + \beta e} \sum_i \sum_j i D_{ij} [\beta u]^i \left[\frac{\eta}{\tau}\right]^j -$$
$$\frac{9mC\beta u^\circ \exp(-3\beta u^\circ)}{1 - C\exp(-3\beta u^\circ)} \sum_i \sum_j j D_{ij} [\beta u]^i \left[\frac{\eta}{\tau}\right]^j +$$
$$\frac{9\eta C\beta u^\circ \left(\eta - \frac{5}{2}\right)(1 - m)\exp(-3\beta u^\circ)[1 - C\exp(-3\beta u^\circ)]}{(1-\eta)\left(1 - \frac{\eta}{2}\right)} +$$
$$\beta \varepsilon^{HB} \frac{F\sqrt{\alpha}(Y^{HB} + 1)}{Y^{HB}} \frac{N_d + F^2}{1 + 2F\sqrt{\alpha}}$$
(6)

where $\beta = 1/kT$ and $T = 298$ K.
A similar expression for PC-SAFT equation of state is

$$\frac{\delta^2 V_L^{298}}{RT} = T \left[(m-1)(g^{hs})^{-1} \left[\begin{array}{c} \frac{m}{\xi_0} \left(\begin{array}{c} \frac{3(\xi_{1,T}\xi_{2,T} + \xi_1\xi_{2,T})}{(1-\xi_3)} + \frac{3\xi_1\xi_2\xi_{3,T}}{(1-\xi_3)^2} + \frac{3\xi_2{}^2\xi_{2,T}}{\xi_3(1-\xi_3)} + \frac{\xi_2{}^3\xi_{3,T}(3\xi_3 - 1)}{\xi_3^2(1-\xi_3)} + \\ \left(\frac{3\xi_2{}^2\xi_{2,T}\xi_3 - 2\xi_2^3\xi_{3,T}}{\xi_3^3} \right) \ln(1-\xi_3) + \left(\xi_0 - \frac{\xi_2^3}{\xi_3^2} \right) \frac{\xi_{3,T}}{(1-\xi_3)} \end{array} \right) - \\ \left(\begin{array}{c} \frac{\xi_{3,T}}{(1-\xi_3)^2} + \left(\frac{d_T}{2} \right) \frac{3\xi_2}{(1-\xi_3)} + \\ \left(\frac{d}{2} \right) \left(\frac{3\xi_{2,T}}{(1-\xi_3)^2} + \frac{6\xi_2\xi_{3,T}}{(1-\xi_3)^3} \right) + \left(\frac{dd_T}{2} \right) \frac{2\xi_2^2}{(1-\xi_3)^3} + \\ \left(\frac{d}{2} \right) \left(\frac{4\xi_2\xi_{2,T}}{(1-\xi_3)^3} + \frac{6\xi_2{}^2\xi_{3,T}}{(1-\xi_3)^4} \right) \end{array} \right) - \\ 2\pi\rho \left(\frac{\partial I_1}{\partial T} - \frac{I_1}{T} \right) m^2 \beta\varepsilon\sigma^3 - \pi\rho m \left(\frac{\partial C_1}{\partial T} I_2 + C_1 \frac{\partial I_2}{\partial T} - 2C_1 \frac{I_2}{T} \right) (m\beta\varepsilon)^2 \sigma^3 \end{array} \right] + \right.$$

$$\beta\varepsilon^{HB} \frac{F\sqrt{\alpha}(Y^{HB} + 1)}{Y^{HB}} \frac{N_d + F^2}{1 + 2F\sqrt{\alpha}} \tag{7}$$

where δ is the solubility parameter, V_L^{298} is the liquid molar volume at 298 K, and R is the universal gas constant.

$$\xi_{n,T} = \frac{\partial \xi_n}{\partial T} = \frac{\pi}{6} \rho m n d_T d^{n-1} \tag{8}$$

$$n \in \{1,2,3\}$$

$$d_T = \frac{\partial d}{\partial T} = \sigma \left(3 \frac{\beta\varepsilon}{T} \right) [-0.12 \exp(-3\beta\varepsilon)]$$

where $T = 298$ K and the number density of molecules, ρ, is calculated from η through

$$\rho = \frac{6}{\pi} \eta (md^3)^{-1} \tag{9}$$

$$\frac{\partial I_1}{\partial T} = \sum_{i=0}^{6} a_i(m) i \xi_{3,T} \eta^{i-1} \tag{10}$$

$$\frac{\partial I_2}{\partial T} = \sum_{i=0}^{6} b_i(m) i \xi_{3,T} \eta^{i-1} \tag{11}$$

$$\frac{\partial C_1}{\partial T} = \xi_{3,T} C_2 \tag{12}$$

Equations 27 and 28 are used to match the solubility parameter (heat of vaporization) for SAFT and PC-SAFT respectively. The equations of state can be applied at $Z_L^{sat,298} = Z_L^{calc,298}$ to match the molar volume. $Z_L^{calc,298}$ is calculated from the equations of state and $Z_L^{sat,298}$ is obtained from eq 23 at 298 K. The value for m was assumed to follow a linear relationship with respect to the degree of polymerization in polymer solutions.

$$m = 1 + \sum_i \nu_i \Delta m_i \tag{13}$$

In summary, when no vapor-pressure data are available, we have three unknown quantities for each equation of state (v^∞, m, and u°/k for the SAFT and σ, m, and ε for the PC-SAFT) and three equations to determine them: in the case of SAFT, $Z_L^{sat,298} = Z_L^{calc,298}$ and eqs 27 and 34; in the case of PC-SAFT $Z_L^{sat,298} = Z_L^{calc,298}$ and eqs 28 and 34.

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If vapor-pressure data are available, it is extremely valuable to apply the data in the determination of the equation of state parameters. In those cases, eq 14 is replaced by the isofugacity criterion. Typically, the vapor-pressure data for heavy compounds are available at low pressures, because higher saturation pressures lead to temperatures that cause the compounds to degrade thermally. Under these conditions, the vapor phase may be treated as an ideal gas. These observations lead to a simplification of the isofugacity criterion

$$\ln \varphi^{L} = \ln \varphi^{V} \tag{14}$$

$$\beta \mu^{res}(T,K) = \widetilde{A}^{res} + (Z-1) \tag{15}$$

$$\ln \varphi + \ln Z = \beta \mu^{res}(T,K) \tag{16}$$

$$\widetilde{A}^{res} = \frac{\beta A^{res}}{N} \tag{17}$$

where $\widetilde{A}^{res}$ is the reduced Helmholtz free energy. For the SAFT EOS, we have

$$\widetilde{A}^{res} = m\left[\frac{4\eta - 3\eta^2}{(1-\eta)^2} + \sum_i \sum_j D_{ij}(\beta u)^i \left(\frac{\eta}{\tau}\right)^j\right] +$$

$$(1-m)\ln\frac{1-\frac{\eta}{2}}{(1-\eta)^3} + 2N_d \ln(1 - F^2/N_d) + F^2 \tag{18}$$

and for the PC-SAFT EOS the following relation could be obtained

$$\widetilde{A}^{res} = \frac{m}{\xi_0}\left[\frac{3\xi_1\xi_2}{(1-\xi_3)} + \frac{\xi_2^3}{\xi_3(1-\xi_3)^2} + \left(\frac{\xi_2^3}{\xi_3^2} - \xi_0\right)\ln(1-\xi_3)\right] -$$

$$(m-1)\ln g^{hs}(\sigma) - 2\pi\rho I_1(\eta,m)m^2\beta\varepsilon\sigma^3 - \pi\rho I_2(\eta,m)(\beta\varepsilon)^2(m\sigma)^3 \tag{19}$$

$$I_1(\eta,m) = \sum_{i=0}^{6} a_i(m)\eta^i \tag{20}$$

$$I_2(\eta,m) = \sum_{i=0}^{6} b_i(m)\eta^i \tag{21}$$

Note that the values of η^{sat} in eqs 35-42 must be computed at the saturation condition. This introduces a new unknown parameter into the set of equations. Fortunately, the availability of the vapor pressure indicates a fourth constraint equation.

$$Z_L^{sat} = P^{sat} b / \eta^{sat} RT \tag{22}$$

where Z_L^{sat} is calculated from the SAFT and the PC-SAFT equations of state. Hence, we have four equations and four unknowns in cases where P^{sat} is available. To facilitate understanding of how these equations are applied, examples are given in the appendix.

In the calculations of vapor phase, a truncated virial expansion after its second coefficient is used as follows

$$Z_V^{sat} = P^{sat} b / \eta^V RT = 1 + B_2\eta^v \tag{23}$$

if $B = \frac{Pb}{RT}$ then from eq 23:

$$B = \eta^V + B_2\eta^{\frac{2}{V}} \tag{24}$$

or

$$\eta^V = \frac{-1+\sqrt{1+4BB_2}}{2B_2}$$ (25)

The relation between η^V and the Helmholtz free energy that concluded from isofugacity criteria is as follows

$$2B_2\eta^V - \ln(\frac{Pb}{\eta^V RT}) = \tilde{A}^{res} + Z_L - 1 - \ln(Z_L)$$ (26)

or

$$\eta^v = \eta^L \exp[\tilde{\mu}_L^{res} - \tilde{\mu}_V^{res}]$$ (27)

where $\tilde{\mu}^{res} = \beta\mu^{res}/N$ is the reduced chemical potential and the residual chemical potential, μ^{res}, is obtained from eq 15. In order to calculate the second virial coefficient, we have

$$B_2 = \lim_{\eta\to 0}\left(\frac{Z-1}{\eta}\right) = (\frac{dZ}{d\eta})_{\eta=0}$$ (28)

With considering compressibility factor for SAFT and PC-SAFT and noting that $Z = 1 + B_2\eta$, we can define B_2 for each EOS as presented below
for the SAFT EOS,

$$B_2 = B_2^{seg} + B_2^{chain} + B_2^{assoc}$$ (29)

and for the PC-SAFT EOS,

$$B_2 = B_2^{hc} + B_2^{disp} + B_2^{assoc}$$ (30)

where B_2^{assoc} is the same for both SAFT and PC-SAFT equations of state and is derived as follows

$$B_2^{assoc} = -N_d^2\left[\frac{0.035}{m}\mathbf{Y}^{HB}\right] = -N_d^2\left[\frac{K^{AD}\mathbf{Y}^{HB}}{b}\right]$$ (31)

We have the following relations for the SAFT EOS

$$B_2^{seg} = 4m$$ (32)
$$B_2^{chain} = 2.5$$ (33)

and for the PC-SAFT,

$$B_2^{hc} = \frac{3}{2}m + \frac{5}{2}$$ (34)

$$B_2^{disp} = \frac{-12a_0}{md^3}m^2\beta\varepsilon\sigma^3 - \frac{6b_0}{d^3}(m\beta\varepsilon)^2\sigma^3$$ (35)

3. Results and discussions

The coverage of families of compounds is given in Table 1. The deviations in Table 1 correspond to the percent of average absolute deviation (%AADP) for vapor pressure of pure compounds from several different families at their saturation temperature of 10 mmHg, 100 mmHg and 760 mmHg along with the average absolute deviations (AADT) in saturated temperature. Note that as mentioned in section 2, our objective function that had to be minimized was %RMSm not %AADP or AADT. The average absolute percent deviation (%AADP) of saturated vapor pressure is 35.28% for GC-SAFT and 25.69% for GC-PC-SAFT equations. The average absolute deviation (AAD) between experimental and calculated saturated temperature are 12.7 K and 8.49 K for GC-SAFT and GC-PC-SAFT equations,

respectively. These results are quite interesting and prove that this method is reliable where no experimental data is available.

The root mean square percent (%RMSm) correlation errors shape parameters from the values that exactly matched the 10 mmHg or 760 mmHg boiling point temperature are generally around 10% for the PC-SAFT equation and around 5% for the SAFT equation, a fairly large amount of error for PC-SAFT EOS. On the other hand, the values of the shape parameters are very sensitive to the estimates of the solubility parameter as analyzed by Elliott and Natarajan.[14] Nevertheless; we recommend that the shape parameter correlation should only be applied when vapor pressures data are not available. Table 1 demonstrates that SAFT and PC-SAFT equations provide better results for hydrocarbons as expected and the results for acids are not so interesting. Therefore, a special hydrogen-bond should be considered for acids and the associated models should be revised for them. Note that polymer solution phase equilibria is more sensitive to the vapor pressure of solvent and since we have presented a predictive method for low molecular weight compounds from various families, application of this model to polymer solutions is straight forward. Hence, in the next research we would have an interesting predictive method for describing phase behavior of polymer solutions based on associated models and Wertheim's theory.

Table 2 shows the optimized amount of shape parameter for each group that could be used for obtaining other thermodynamic properties. Note that low molecular compounds and polymers could be generated from the groups that have been presented in Table 2.

4. Conclusions

We have proposed a generalized group contribution approach of the principle of three-parameter corresponding states for 16 different families of compounds that paves the way for treating polymer solutions in the same manner as regular ones. In this method SAFT and PC-SAFT equations of state were used to demonstrate the group contribution manner. The results are more accurate than the previous group contribution ESD EOS. In the future research the shortcoming of this approach would be obviated with considering the detailed analysis of mixtures and mixing rules and by extension to heavy compounds and polymer solutions. For such small molecules that have been considered here, finding an experimental vapor pressure data point to improve the accuracy along with the solubility parameter and the liquid molar volume is highly recommended.

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Table 1. Different Families of Compounds and Percent of Absolute Average Deviation (%AAD) in the Pure Component Vapor Pressure along with the Absolute Deviation in Saturation Temperature

group	no. in database	% AADP error in P^{vap1}		AADT error in T^{sat} (K)^2	
Equation of state		SAFT	PC-SAFT	SAFT	PC-SAFT
hydrocarbons	75	41.25	24.09	7.83	5.93
cyclic hydrocarbons	45	20.12	15.25	3.03	4.19
aromatic hydrocarbons	225	22.52	20.07	33.55	6.54
alcohols	90	54.95	23.96	15.14	6.16
amines	61	32.42	30.23	12.37	12.02
nitriles	27	42.49	22.15	21.01	8.32
sulfides, thiols	61	26.92	19.41	6.74	5.67
aldehydes	21	24.11	14.27	3.28	4.17
ethers	53	33.17	20.72	6.22	6.4
ketones	84	29.74	21.00	4.73	4.58
esters	44	30.02	19.56	5.54	6.24
halocarbons	104	40.51	30.13	9.81	8.99
hydroxyls	27	38.89	30.53	13.85	6.26
Multi-functional groups	50	44.27	46.67	14.54	15.05
acides	51	50.91	40.36	24.7	23.26
silicones	16	32.24	32.64	10.85	12.09
Overall	**1034**	**35.28**	**25.69**	**12.07**	**8.49**

$$^1 \%\text{AADP} = \frac{100}{3NDP}\left(\sum_{i=1}^{NDP}\frac{\left|P^{sat}(760)-760\right|}{760} + \sum_{i=1}^{NDP}\frac{\left|P^{sat}(100)-100\right|}{100} + \sum_{i=1}^{NDP}\frac{\left|P^{sat}(10)-10\right|}{10} \right)$$

$$^2\ \text{AADT} = \frac{1}{3NDP}\left(\sum_{i=1}^{NDP}\left|T^{sat}(760)-T^{calc}(760)\right| + \sum_{i=1}^{NDP}\left|T^{sat}(100)-T^{calc}(100)\right| + \sum_{i=1}^{NDP}\left|T^{sat}(10)-T^{calc}(10)\right| \right)$$

Table 2. Group Contribution for Estimating the Shape Parameter, *m*, the Liquid Molar Volume, and the Heat of Vaporization

group	Δm SAFT	Δm PC-SAFT	ΔV	ΔH_{vap}	group	Δm SAFT	Δm PC-SAFT	ΔV	ΔH_{vap}	group	Δm SAFT	Δm PC-SAFT	ΔV	ΔH_{vap}
CH_3	1.075	0.415	21.6	4.116	FCH_2O	0.797	-0.206	33.2	11.227	ACF	0.035	0.442	18.6	4.877
$CH_2<$	0.636	0.386	15.6	4.65	CH_2NH_2	0.370	0.037	32.6	14.599	CF_3	5.503	3.651	37.2	8.901
$>CH-$	-0.332	0.083	9.6	2.771	$CHNH_2$	-1.332	0.129	26.6	11.876	CF_2	4.863	1.814	26.0	1.86
$>C<$	-1.013	-0.276	3.6	1.284	CH_3NH	1.062	0.517	32.6	14.452	CF	6.565	1.887	14.8	8.901
$RCH_2<$	0.589	0.310	15.6	4.65	CH_2NH	0.955	0.164	26.6	14.481	COO	1.339	0.630	25.7	13.4
$>RCH-$	-0.417	-0.106	9.6	2.771	CHNH	2.392	2.378	20.6	14	SiH_3	-0.470	6.254	*21.6*	3.4
$>RC<$	-0.031	0.277	3.6	1.284	CH_3-RN	-0.444	-1.238	34.2	6.947	SiH_2	-0.371	0.247	*58.4*	3.4
$CH_2=CH$	0.624	0.255	32.4	6.714	CH_2-RN	4.121	0.230	28.2	6.918	SiH	1.691	0.645	*53.7*	3.4
$CH=CH$	-0.005	0.013	26.4	7.37	$ACNH_2$	3.799	1.995	24.4	28.453	Si	-0.470	1.344	*50.3*	3.4
$CH_2=C$	-0.021	0.216	26.4	6.797	C_5H_4N	2.367	1.279	*75.7*	31.523	SiH_2O	2.537	1.735	*33.8*	6.8
$CH=C$	-0.066	0.087	20.4	8.178	C_5H_3N	2.367	1.279	*69.7*	31.005	SIHO	2.537	1.735	*33.8*	6.8
$C=C$	-1.281	-0.548	14.4	9.342	CH_2CN	-0.496	0.186	38.7	23.34	SiO	2.537	1.735	*33.8*	6.8
$CH_2=C=CH$	0.576	0.493	*39.5*	12.9	COOH	5.998	2.874	26.1	43.046	tert-N	4.301	-0.912	12.6	4.19
ACH	0.422	0.142	13.4	4.098	CH_2Cl	0.800	0.570	35.1	13.78	CCl_2F	0.978	0.658	53.8	13.322
AC-	2.206	1.842	7.4	12.552	CHCl	0.883	0.545	29.1	11.985	HCClF	8.461	2.708	40.3	16.6
$ACCH_3$	1.317	0.665	29.0	9.776	CCl	0.580	0.448	23.1	9.818	$CClF_2$	2.080	0.829	45.5	8.301
$ACCH_2$	0.081	0.727	23.0	10.185	$CHCl_2$	2.493	0.991	48.6	19.208	$CONH_2$	1.409	0.356	34.3	41.9
ACCH	-0.157	0.613	17.0	8.834	CCl_2	3.092	1.616	42.6	17.574	$CONHCH_3$	14.293	8.860	49.9	38.5
OH	4.282	0.176	12.5	24.529	CCl_3	9.563	5.830	62.1	33.4	$CONHCH_2$	13.854	8.832	43.9	51.787
ACOH	10.522	3.081	19.9	40.246	ACCl	0.256	0.537	26.9	11.883	$CON(CH_3)_2$	15.368	9.275	*78.9*	38.9
CH_3CO	2.495	1.193	38.9	18.999	CH_2NO_2	3.236	1.979	*50.2*	30.644	$CONCH_3CH_2$	14.929	9.246	*72.9*	39.1
CH_2CO	1.904	1.47	32.9	20.041	$CHNO_2$	1.502	1.335	*46.3*	26.277	$CON(CH_2)_2$	14.490	9.218	*66.9*	39.3
CHO	0.815	0.054	23.3	12.909	$ACNO_2$	-0.032	0.046	*31.4*	19.7	$C_2H_5O_2$	5.054	0.649	50.0	36.657
CH_3COO	3.519	2.426	43.0	22.709	CH_2SH	0.359	0.193	*46.7*	14.931	$C_2H_4O_2$	0.273	0.173	44.0	14.956
CH_2COO	1.940	0.903	37.0	17.759	I	-0.308	-0.037	*42.6*	14.364	CH_3S	1.380	0.684	39.6	16.921
HCOO	1.462	0.960	*43.3*	14.5	Br	0.203	0.251	25.3	11.423	CH_2S	1.562	1.121	33.6	17.117
CH_3O	2.331	1.138	28.0	10.919	$CH\equiv C$	1.882	0.247	*40.2*	7.751	CHS	-0.027	0.353	27.6	13.265
CH_2O	0.136	0.087	22.0	7.478	$C\equiv C$	0.239	0.328	*28.8*	11.549	C_4H_3S	-0.063	0.643	65.7	27.966
CH-O	-0.084	-0.089	16.0	5.708	Cl(C=C)	1.620	0.731	19.5	7	C_4H_2S	-0.124	0.717	59.7	28