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# Application of the modified Group-Contribution Perturbed-Chain SAFT to branched alkanes, n-olefins and their mixtures

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ABSTRACT

A new empirical approach has been developed to estimate parameters of the modified Group Contribution Perturbed-Chain statistical associating fluid theory (mg-SAFT) for alkane and alkene isomers. A key advantage of this approach is that the molecular parameter of isomer components is distinguished simply through the chain length parameter. New group parameters for 1-alkenes, cis- and trans-alkenes, methyl-alkanes and dimethyl-alkanes are determined. Several pure compound properties such as the vapor pressure, liquid density, enthalpy of vaporization, heat capacities are predicted. It has been found that the use of two adjustable parameters in determining the chain length parameters of different isomer groups in the fitting procedure for alkane or alkene isomers is enough to provide a good description of PVT and some derivative properties. Test and comparison with other existing SAFT-based group-contribution approaches were performed in calculating the vapor pressure and saturated liquid density of heavy compounds. The results show that, mg-SAFT describes the fluid phase behavior for light compounds with a comparable accuracy compared to other group contribution approaches and much better for heavier compounds (prediction results).



## 1. Introduction

The precise knowledge of phase equilibrium property is vital for the design of chemical and petrochemical processes. Even the data of n-alkanes are available up to n-hexatriacontane, the limited data are mainly accessible to isomers of nonane [1]. The experimental data of heavy and branched alkanes/alkenes are important to chemical and petrochemical industries. However, the experimental PVT and phase equilibrium data of these molecules are still scarce. For instance, many kinds of heavy and branched alkanes, n-alkenes are found in synthetic oils derived from the Fischer-Tropsch synthesis, it is also widely agreed that the $C_8$-$C_{14}$ olefin fractions, such as 1-tetradecene meet viscosity and pour points specifications for formulation into oil based muds, which is particularly useful for offshore drilling. Further process development of this process requires properties of these fluids to be known or estimated with reasonable accuracy.

Alkane and alkene isomers provide a very good example of how molecular structure affects its physical properties. Within the framework of the Statistical Associating Fluid Theory (SAFT) the modeling of chain molecules is carried out by application of Wertheim's first-order thermodynamic perturbation theory (TPT1) where isomers of the same chain length cannot be distinguished [2]. Over the last decade, Group Contribution based SAFT approaches have been proposed in an effort to develop predictive approaches. In this concept, the EoS parameters can be estimated based on functional groups that appear in the molecular structure, rather than molecular parameters. Importantly, the contribution of each chemical group is supposed to be transferable and allows to predict of the thermodynamic properties of new compounds. One of the first real group-contribution based SAFT approach is probably that proposed by Tamouza et al. [3], in which the molecular parameters are calculated from their group contributions by applying the Lorentz-Berthelot combining rules. Further examples of this type of methodologies are GC versions based on a *homonuclear* adaptation of the SAFT-VR [3], PC-SAFT [3,4] or simplified PC-SAFT [5] EoS. Another class of approach involves the direct description of the parameters of an EoS within a GC formalism have been implemented within the framework of SAFT incorporating *heteronuclear* molecular model. Examples the work of McCabe et al. [6–8], they implemented a square-well potential to describe the

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group-group interactions; or Lymperiadis et al. [9,10] suggested GC approach based on the SAFT-VR model. In similar work, the Group Contribution SAFT-γ Mie approach has also been proposed by Dufal et al. [11–13], or a group-contribution version based on the PC-SAFT EoS [14,15]. Various chemical families were regarded, including n-alkanes [3,7,9,10,16], branched alkanes [7,9–11,13,17], n-alkenes [7,9,10]. Alongside the aforementioned SAFT-based group contribution methods, other techniques have been developed where the molecular properties are not calculated as functions of the occurrences of chemical groups alone, but also account for their positioning within the molecule by defining superstructures. The aim of such approach is to account for proximity effects and to distinguish the representation of isomers [5,17,18].

The aim of this work is to apply a modified group-contribution approach based on the PC-SAFT EoS (called mg-SAFT) [16] in calculating PVT and phase equilibrium data of alkane, alkene isomers and their mixtures with a reliable, comprehensive and efficient parameter-estimating method. Different isomers were supposed to be distinguished via its chain length parameter or more precisely through the chain parameter of the isomer group. For this purpose, we proposed in this work a new and simple correlation, which requires a minimum adjusted parameter, allows to estimate the chain length of "isomer group". This new empirical approach will be shown to allow for an effective treatment of the different molecular structure of alkane and alkene isomers. Then, the PVT and phase equilibrium data of heavy and branched alkane, n-alkene and their mixtures were predicted by using the mg-SAFT with the new GC parameters. Simultaneously, comparisons were carried out between the mg-SAFT and other similar GC-SAFT models in the literature.

## 2. mg-SAFT model

mg-SAFT is a modification of GC-PC-SAFT proposed by Tamouza et al. [3] allowing to compute the EoS parameters. In previous work [16], mg-SAFT was successfully used for the correlation and prediction of VLE data of n-alkanes, alkyl-cyclopentanes, alkyl-cyclohexanes and alkyl-benzenes. The equation of state combined with the modified group contribution in this work is the original PC-SAFT [19], is expressed as a sum of hard chain and dispersion contributions to the residual Helmholtz energy:

$$a^{res} = a^{hc} + a^{disp} \tag{1}$$

For non-associating compounds, the PC-SAFT EoS requires three specific parameters: segment number (m), segment diameter (σ), and the segment dispersion energy parameter (ε/k). The expression of PC-SAFT EoS is not recalled here, and the interested reader is referred directly to the original paper for more details [19].

PC-SAFT applies to mixtures using the van der Waals one-fluid model [20], as well as modified Lorentz–Berthelot mixing rules that relate the potential parameters $\varepsilon_{ij}$ and $\sigma_{ij}$ between molecules, *i* and *j*.

$$\varepsilon_{ij} = (1 - k_{ij})\sqrt{\varepsilon_{ii}\varepsilon_{jj}} \tag{2}$$

$$\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2} \tag{3}$$

In mg-SAFT, the EoS parameters: segment energy, segment diameter and chain length parameter of the molecule are calculated through a modified group contribution relations [16]:

$$\varepsilon = \sum_{i=1}^{n_{groups}} n_i \sqrt{\left(\prod_{i=1}^{n_{groups}} \varepsilon_i^{n_i}\right)} - n_{groups}\ \alpha \tag{4}$$

$$\sigma = \sum_{i=1}^{n_{groups}} n_i\sigma_i \Big/ \sum_{i=1}^{n_{groups}} n_i \tag{5}$$

$$m = \sum_{i=1}^{n_{groups}} n_i R_i \tag{6}$$

Where $n_i$ is the number of groups *i* in the molecule made of $n_{groups}$ different groups, $\alpha$ is the group's dispersive energy correction factor ($\alpha$ = 0.223 K), which was obtained by regressing simultaneously with the $CH_2$ and $CH_3$ group's parameters from the vapor pressure and liquid density of n-alkanes [16]. Note that these equations generally apply to compounds belonging to well defined chemical families (1-alkene, n-alkanes, …) with exception of the two first members (ethane, 1-propene, …) that should be treated specifically.

## 3. Results and discussion

In this paper, we determined the group parameters for six new functional groups by regressing to the corresponding experimental data of some members of different chemical families (1-alkenes, n-alkenes, and methyl-alkanes, dimethyl-alkanes). Due to the inability of PC-SAFT EoS to represent the critical and sub-critical regions satisfactorily with a single set of parameters [21,22], in all cases, the group parameters were regressed simultaneously on vapor pressures and saturated liquid density from 0.4 *Tc* to 0.95 *Tc* (Tc, experimental value of the critical temperature of each component) [16]. The regression function that was used is written as:

$$F_{obj} = \frac{1}{N_{Psat}}\sum_{1}^{N_{psat}}\left(\frac{P_{cal}^{sat} - P_{exp}^{sat}}{P_{exp}^{sat}}\right) + \frac{1}{N_{\rho liq}}\sum_{1}^{N_{\rho liq}}\left(\frac{\rho_{cal}^{liq} - \rho_{exp}^{liq}}{\rho_{exp}^{liq}}\right) \tag{7}$$

$N_{Psat}$ and $N_{\rho liq}$ are the number of the experimental vapor pressures and saturated liquid density data, respectively.

The choice of pure compounds used in the regression database for each system is dictated by the availability of experimental data from DIPPR [1]. For each chemical series studied, we have chosen some representative compounds with a carbon number up to 10 to be included in the regression database. As already noticed by different authors, the group contribution techniques are generally not well suited to study small molecules (the two first members of the series) as proximity effects are neglected. This strategy has been followed within the context of different authors [6,7,12,16,23,24] where the two first molecules are generally excluded from the regression database. All other available data for heavier compounds will be used to compare predictions from the model.

In order to simplify the mg-SAFT model and minimize the number of adjusted parameters, we attempted to transfer the group's dispersive energy correction factor (α) that was obtained in the previous work for ($CH_2$) and ($CH_3$) groups to all other groups considered in this work without any further regression.

When study different isomer molecules such as methyl-alkanes or n-alkenes, the molecule's parameters are determined via the relations (4) to (6), at this level, mg-SAFT cannot distinguish between two different isomers since only the numbers of groups are