

Applications of the Simplified Perturbed-Chain Saft Equation of State

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Introduction

The prediction or correlation of the thermodynamic properties and phase equilibria with equations of state remains an important goal in chemical and related industries. Simplified PC-SAFT [1] is a novel equation of state based on statistical mechanics that has been successfully applied to a number of complex systems over wide ranges of conditions.

Our work aims in developing a theoretically based engineering tool that can be used for complex mixtures of importance to polymer and pharmaceutical industries. Common characteristics of all of these applications are complexity of molecules involved, the presence of various types of intermolecular forces (polarity, hydrogen bonding, etc.) and the frequent coexistence of many phases at equilibrium e.g. vapour-liquid-liquid or solid-liquid-liquid. The thermodynamic model to be developed is a group-contribution version of the simplified PC-SAFT [1] equation of state where the parameters of the model are estimated via group contributions which are based on the so-called “conjugation principle” [2].

Most SAFT-type models require three parameters for each pure non-association compound involved: the segment number (m), the interaction energy (ε/k in K), and the hard-core segment radius (σ in Å) that are typically estimated from vapour pressure and liquid density data over extended temperature ranges. For many different families of compounds, the segment radius and interaction energy are found to be constant with increasing the molar mass, while the segment number is found to be in a linear relationship with molar mass.

We present here applications of simplified PC-SAFT model to binary systems that include a variety of non-associating compounds using recently estimated pure component parameters [3]. These applications include:

- Investigations of trends and physical significance of the model's parameters
- Vapour-Liquid Equilibria (VLE) of mixtures containing heavy alkanes
- VLE of binary mixtures of perfluoroalkanes with alkanes and light gasses
- Liquid-Liquid Equilibria (LLE) in binary alkanes and perfluoroalkanes systems

Results and Discussion

In our recently published paper [3], beside the complete PC-SAFT table with **200** newly estimated parameters for different families of nonassociating compounds, phase equilibrium calculations for ethers, ketones, aromatic compounds, nitroalkanes, fluorinated compounds, siloxanes, and plasticizers in order to investigate the reliability of the newly estimated parameters are presented.

It is earlier shown [4] that mixtures with carbon dioxide, which is a strong quadrupolar compound, can be well described with PC-SAFT, even when the specific quadrupolar interactions are not explicitly taken into account. Mixture data of carbon dioxide with two heavy alkanes, octacosane and hexatriacontane, presented in **Figure 1**, are well correlated using low values of k_{ij} , actually lower than those previously published [4].

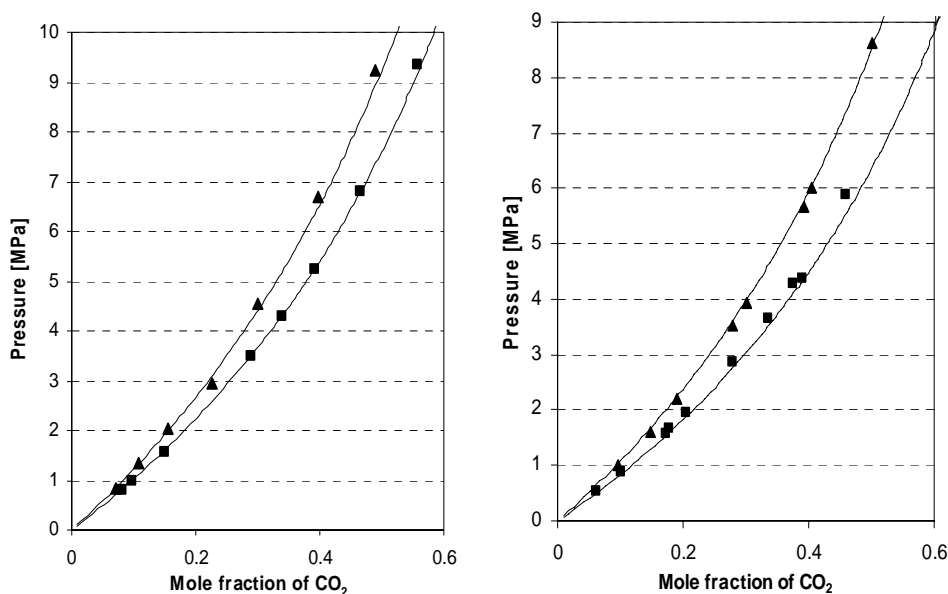


Figure 1. Vapor-liquid equilibrium for CO₂-octacosane and CO₂-hexatriacontane mixtures at 373.2 K and 423.2K, respectively. Comparison of simplified PC-SAFT correlation results with $k_{ij}=0.065$ to experimental data [5].

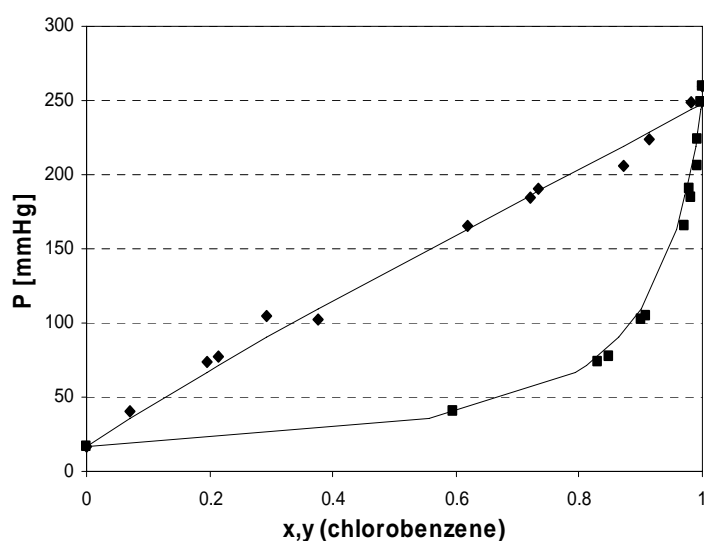


Figure 2. Binary phase diagram for the system of nitrobenzene and chlorobenzene at $T=368.15\text{K}$, where symbols represent experimental data [6], and lines correspond to the predictions ($k_{ij}=0$) from simplified PC-SAFT.

Another successfully modelled system is nitrobenzene-chlorobenzene shown in **Figure 2**. In this case, no interaction parameters are used.

Perfluoroalkanes are, due to their high intramolecular and low intermolecular forces that characterize them, a very important family of compounds and used in different fields such as biomedical applications. **Figure 3** shows the good agreement achieved between experimental data and simplified PC-SAFT estimations using new pure compound parameters for two perfluorohexane systems. The occurrence and location of the azeotrope are well captured by the model. These results show that the simplified PC-SAFT model allows the phase behaviour of alkanes and perfluoroalkanes to be quantitatively estimated with the use of a single binary interaction parameter.

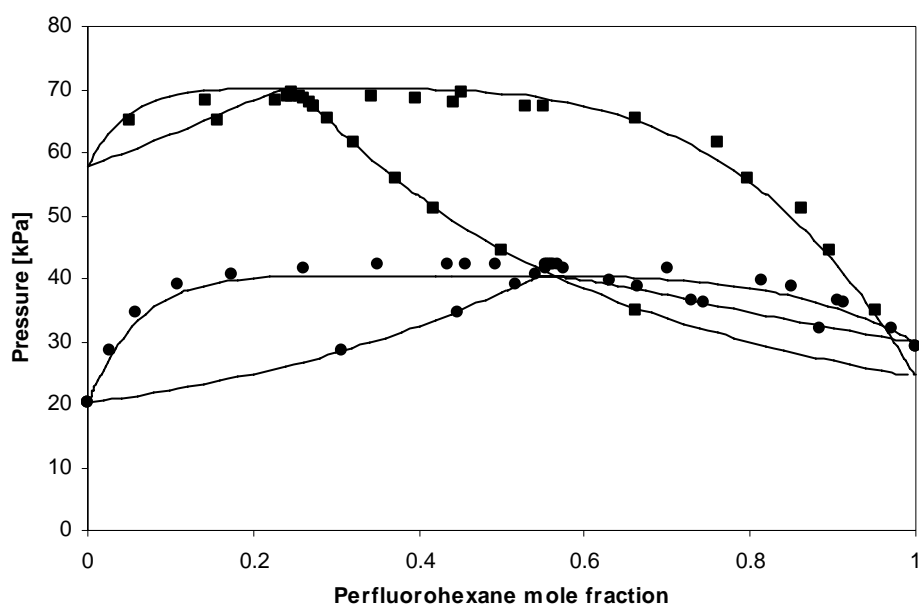


Figure 3. Vapour pressure of perfluorohexane + pentane (squares) at 293.15K and perfluorohexane + hexane (circles) at 298.65K, where symbols represent experimental data [7], and lines correspond to the correlations from simplified PC-SAFT with $k_{ij}=0.077$.

The linear relationship of simplified PC-SAFT parameters can be employed for various compounds as shown in **Figures 4-6** where group PC-SAFT parameters are plotted as function of molecular weight [3]. The success of this extrapolation further underlines the sound physical basis of the equation of state.

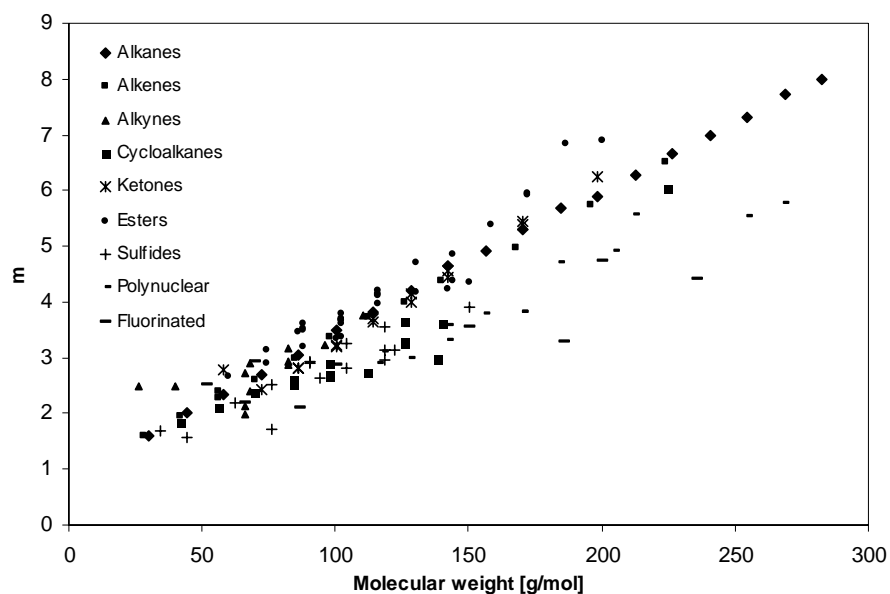


Figure 4. The segment number, m , versus molecular weight for different families of compounds.

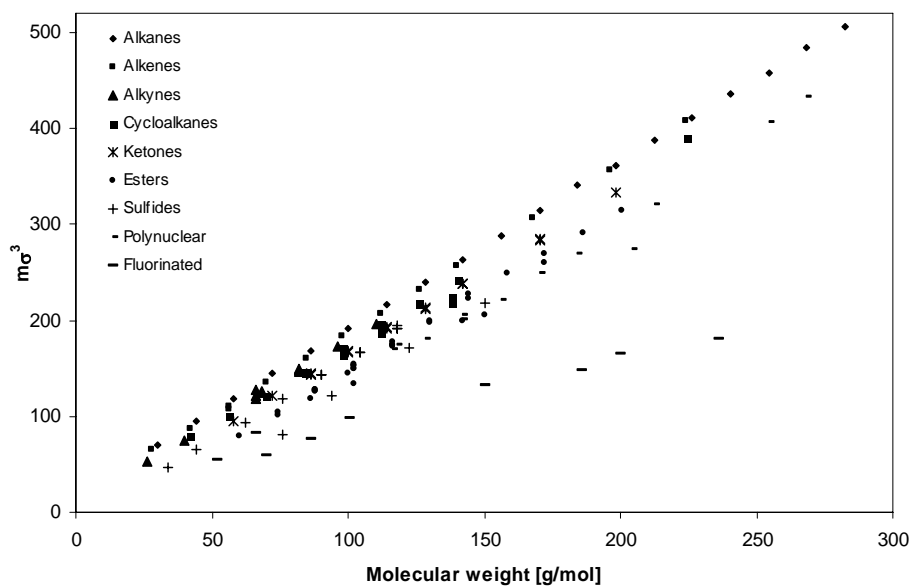


Figure 5. The parameter $m\delta^3$ versus molecular weight for different families of compounds.

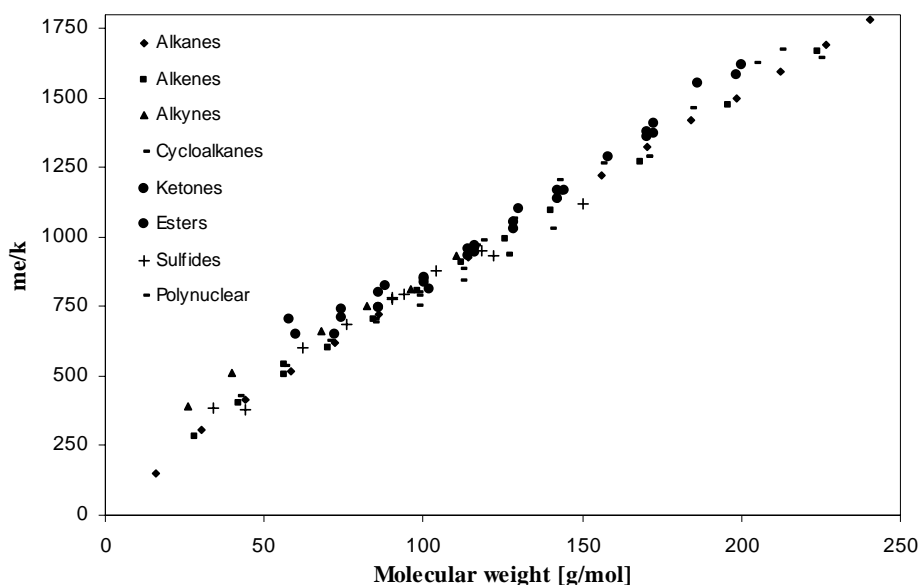


Figure 6. Group $m\epsilon/k$ versus molecular weight for different families of compounds.

Conclusions

We have tested the simplified PC-SAFT equation of state developed at IVC-SEP to predict and correlate VLE and LLE in systems containing a range of non-associating compounds. In general, simplified PC-SAFT is successful in predicting and correlating vapour-liquid and liquid-liquid equilibrium behaviour in a variety of different types of binary system. The three pure-compound PC-SAFT parameters are estimated for additional 200 substances.

Using newly estimated PC-SAFT parameters, the results justify the capability of simplified PC-SAFT in describing many asymmetric systems such as light alkanes-heavy alkanes and light gases-heavy alkanes. In a few cases, where predictions are not accurate, a small value of the binary interaction parameter is required to satisfactorily correlate experimental data.

References

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