Heterosegmental Modeling of Long-Chain Molecules and Related Mixtures using PC-SAFT

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Fatty-acid-based, long-chain molecules like fatty-acid methyl esters are progressively used as renewable feedstock for the chemical industry. However, experimental pure-component and mixture data are scarce. Thus, a predictive thermodynamic modeling is desirable. For this purpose, a heterosegmental approach was developed based on the thermodynamic model PC-SAFT, which allows for a predictive description of pure-component and mixture properties of long-chain molecules within a homologous series.

The different species of the homologous series, e.g. long-chain esters, are composed of an identical head domain (e.g., -$COOCH_3$) which is connected to an *n*-alkylic residue that only varies in chain length. In this work, this fact was taken into account for modeling of thermodynamic properties using a new heterosegmental approach of PC-SAFT. Here, a long-chain molecule is modeled as a coarse-grained chain comprising a tail and a head domain representing the *n*-alkylic residue and the functional head moiety, respectively.

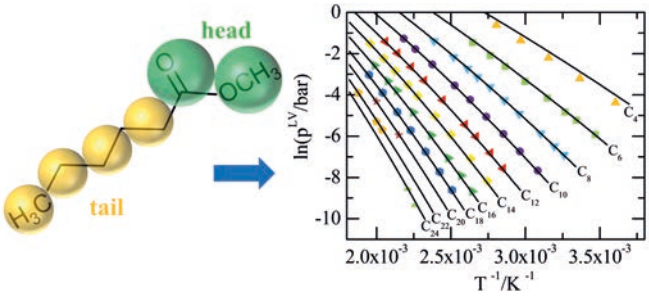

Figure 1: Schematic representation of the heterosegmental approach of PC-SAFT along with the vapor pressures of some methyl alkanoates (methyl butanoate to methyl tetracosanoate). Lines: modeling results with PC-SAFT. Symbols: experimental data taken from literature.

In Figure 1, this modeling concept is illustrated for methyl hexanoate as an example. Due to its similarity, the *n*-alkylic residue is modeled as an *n*-alkane applying the PC-SAFT pure-component parameters of the *n*-alkanes, which were obtained beforehand from independent experimental data of the pure *n*-alkanes. The head domain was modeled as a polar group and its PC-SAFT parameters were determined universally for the entire homologous series. Hence, the proposed approach allows for a predictive description of pure-component properties of long-chain compounds like fatty-acid methyl esters. Applying the new approach, the vapor pressures (Figure 1) and liquid densities of the pure methyl alkanoates could be modeled in remarkable agreement with the available experimental data. Moreover, the excess enthalpies and excess volumes of the binary methyl alkanoate + *n*-alkane mixtures were investigated in this work. Again, the methyl alkanoates were modeled using the heterosegmental approach. It should be emphasized that no experimental data of any binary mixture was used to obtain any model parameter. Hence, the modeling results are full predictions of PC-SAFT. Using this approach, the molar excess enthalpies and molar excess volumes of the binary methyl alkanoate + *n*-alkane mixtures were predicted in very good agreement with the available experimental data as can exemplarily be seen in Figure 2 for the molar excess enthalpies of some binary methyl alkanoate + *n*-tridecane mixtures. Besides the methyl alkanoates, the proposed heterosegmental approach of PC-SAFT was also successfully applied to describe pure-component and mixture properties of long-chain ethyl alkanoates, *n*-aldehydes, *n*-alcohols, *n*-amines, and *n*-alkyl carboxylic acids.

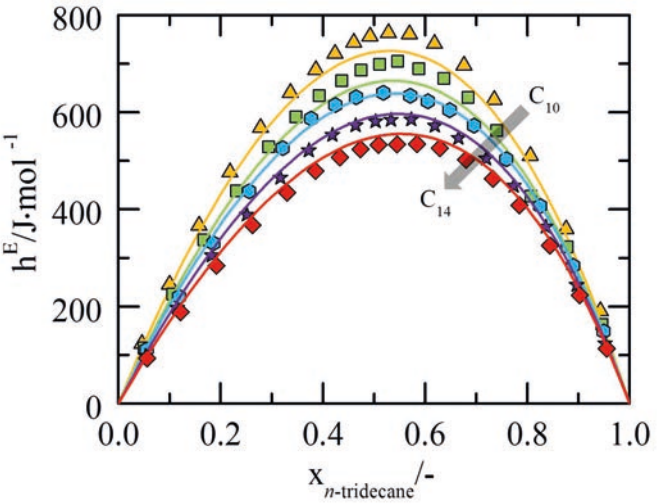

Figure 2: Molar excess enthalpies of the binary methyl alkanoate (methyl decanoate (C_{10}) to methyl tetradecanoate (C_{14})) + *n*-tridecane mixtures. Lines: predictions with PC-SAFT. Symbols: experimental data taken from literature.

Publications:
N. Haarmann, S. Enders, G. Sadowski; Heterosegmental Modeling of Long-Chain Molecules and Related Mixtures using PC-SAFT: 1. Polar Compounds, Ind. Eng. Chem. Res. 2019, 58(7), 2254-2574.

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