The group contribution method (GC) versus the critical point-based approach (CP): Predicting thermodynamic properties of weakly- and non-associated oxygenated compounds by GC-PPC-SAFT and CP-PC-SAFT

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ABSTRACT

In this study GC-PPC-SAFT and the CP-PC-SAFT Equations of State have been implemented for estimating thermodynamic properties of weakly-associated and non-associated oxygenated compounds, while the primarily attention has been paid to the elevated pressure data. The analysis indicates that the polar contribution of GC-PPC-SAFT has a negligibly small impact on predicting the high pressure data. Apparently, in the cases of the weakly- and non-associating compounds a major factor responsible for accuracy of the models at elevated pressures is the curvature of the dispersion contribution. At the same pressures CP-PC-SAFT tends to predict the lower values of densities and higher values of sound velocities. These predictions of CP-PC-SAFT are particularly accurate in the cases of slightly polar compounds with reliable values of the critical constants. Both models are capable of yielding only raw estimations of C_P. Although CP-PC-SAFT has a clear advantage in predicting the available compressibility data, GC-PPC-SAFT is superior in qualitative estimating the isobaric thermal expansion coefficients. However the major advantage of GC-PPC-SAFT is the more accurate estimation of the vapor pressures away from the critical points.

1. Introduction

Development of a universal Equation of State (EoS) model capable of reliable predicting the entire set of properties for large variety of compounds and their mixtures in whole thermodynamic phase space is a challenging problem of modern thermodynamics, which has not been satisfactorily solved yet. As demonstrated elsewhere [1–26], the theoretically-based models belonging to the rapidly developing family of the Statistical Association Fluid Theory (SAFT) equations are characterized by advanced universality since they can be applied for simultaneous estimating of phase equilibria and various auxiliary thermodynamic properties in the particularly wide range of conditions. At the same time, one of the problems hindering wide industrial implementation of many versions of SAFT is a lacking of standardization in evaluating their substance-specific parameters [27]. Moreover, most of these approaches directly refer to the considered data, which

diminishes their predictive values. The widely adopted methods of addressing these problems imply evaluation of the specific parameters for large number of substances belonging to different chemical families with their further generalization according to contribution of various molecular groups [28–48]. These group-contribution (GC) methods substantially enhance the predictive value of SAFT approaches, allowing their implementation to the compounds that have not been previously considered in the fitting procedures. The recently proposed critical point-based modified version of PC-SAFT (CP-PC-SAFT) can be considered as an alternative to the GC-methods. This model implements a standardized numerical solution of the substance-dependent parameters at the characteristic states, namely the pure compound critical and triple points. Thus far CP-PC-SAFT has been implemented for predicting various thermodynamic properties of light compounds, *n*-alkanes, 1-alkenes [49], 1-alkanols [50], aromatic and haloaromatic compounds [51], some haloalkanes [52,53] and their mixtures in wide range of conditions. In this respect it should be pointed out that with some exceptions [34], the GC versions of SAFT have been predominantly implemented for predicting various kinds of phase equilibria rather the single phase thermodynamic properties of liquids at elevated pressures.

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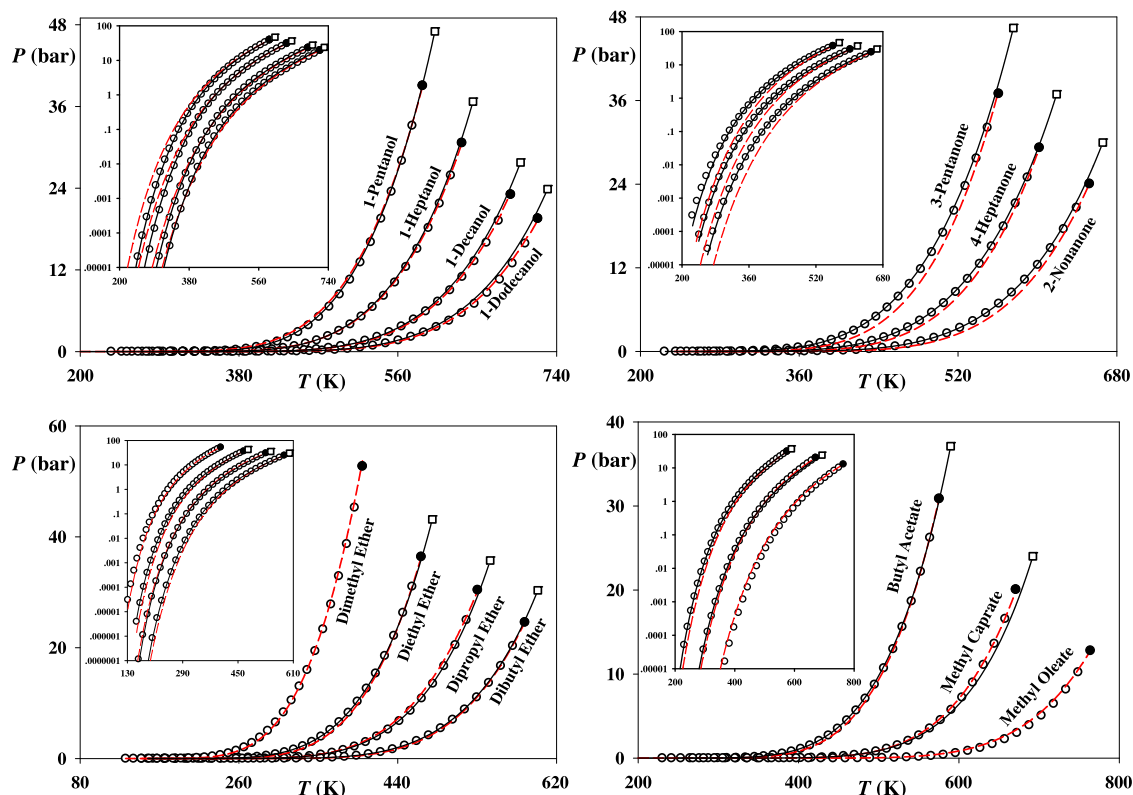
Fig. 1. Examples of the results for the vapor pressures. Literature vapor pressure data—empty circle points [97]. Literature critical points—filled circle points [97]. Predictions: black solid lines—GC-PPC-SAFT, red dashed lines—CP-PC-SAFT. Empty square points—critical points predicted by GC-PPC-SAFT. The critical points predicted by CP-PC-SAFT are identical to the literature data. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
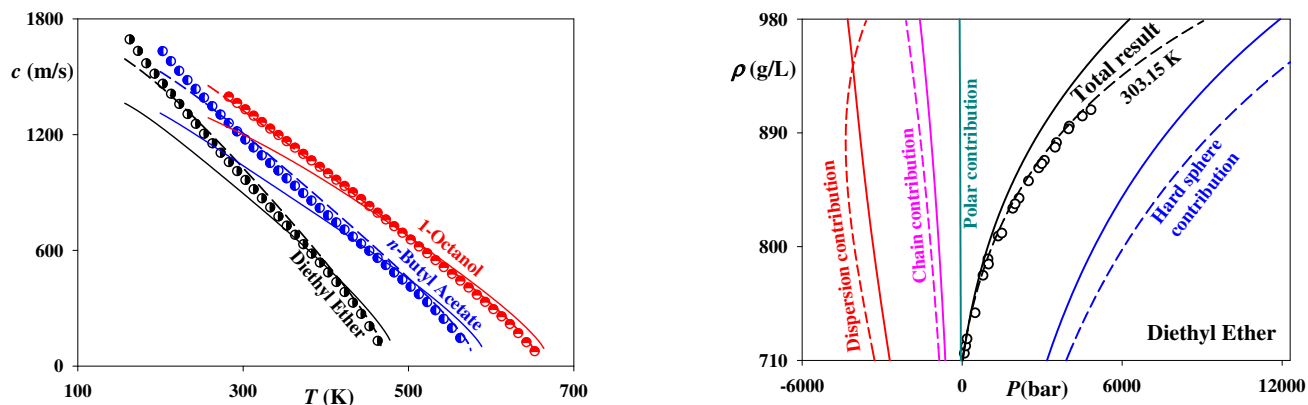

Fig. 2. Examples of the results for the sound velocities in saturated liquids. Experimental data—points [98,99]. Predictions: solid lines—GC-PPC-SAFT, dashed lines—CP-PC-SAFT.

This study compares the accuracies of two predictive approaches, namely CP-PC-SAFT and GC-PPC-SAFT [36–48] in estimating the thermodynamic properties of weakly-associated and non-associated linear oxygenated compounds. This selection is explained by the limitations of the model under consideration. In particular, the strongly associated compounds have not been considered yet since the current version of CP-PC-SAFT has not been adopted for their treatment. At the same time, the current group matrix of GC-PPC-SAFT does not cover the branched oxygenated compounds.

The experimental data on the 1-alkanols heavier than 1-Propanol [54–69] have been discussed in the previous study [50]. Since its publication, another important Ref. [70] reporting various data of 1-Butanol has become available. Unfortunately, the
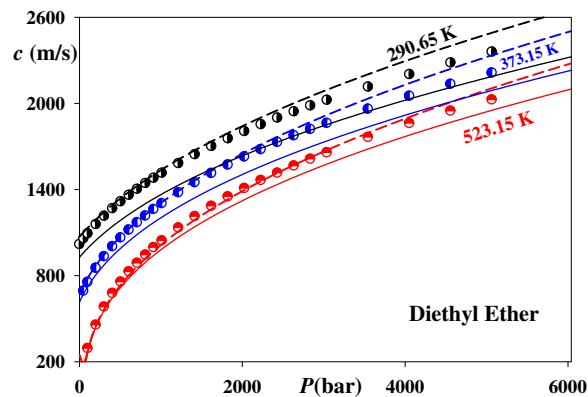

Fig. 3. Density contributions of SAFT terms and sound velocity in Diethyl Ether. Experimental data—points [56,100,101]. Predictions: solid lines—GC-PPC-SAFT, dashed lines—CP-PC-SAFT.