Estimation of pure component properties
Part 2. Estimation of critical property data by group contribution

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Abstract

A new group contribution method for the estimation of critical property data has been developed. The method is based on structural group definitions, with minor modifications, of a method recently published for the estimation of the normal boiling point by Nannoolal et al. [Y. Nannoolal, J. Rarey, D. Ramjugernath, W. Cordes, Fluid Phase Equilib. 226 (2004) 45–63]. Special care was taken to ensure physically meaningful extrapolation to large and multifunctional compounds, as it could be shown that such extrapolation may lead to very improbable or unrealistic results in the case of some methods published earlier. Regression of group increments was not performed simultaneously but with great care one group at a time. With all other group increments fixed, all data for components with a specific group led to approximately the same group increment. This allowed one to determine group increments for cases where only one reliable experimental value was available. For the case of more than one strongly associating group, a group interaction contribution was required as these groups do not observe simple additivity. The estimation of the critical temperature requires knowledge of the normal boiling point. Critical pressure and volume can be estimated from chemical structure alone. The performance of the new model has been compared with 10 well-known estimation methods from literature and the results indicate that the new model is significantly more reliable. To enable comparison, chemical family definitions have been developed that allow one to automatically classify new components and thus, inform the user about the expected reliability of the different methods for a component of interest. Chemical family definitions are based on the kind and frequency of the different structural groups in the molecule. In addition to these advantages, the range of applicability of the new method is larger than that of comparable methods.
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1. Introduction

Critical property data are of great practical importance as they are the basis for the estimation of a large variety of thermodynamic properties using the corresponding states principle. In addition, critical temperature and pressure data provide valuable information for the regression and prediction of vapor pressures at high temperature and are required by equations of state for the description of pure component and mixture behavior.

At the critical point, all components show the same striking anomalies like infinite heat capacity and compressibility. Fluid properties in this state are completely dominated by long range fluctuations and density correlation. The critical temperature and

pressure are extremely well defined. Due to the infinite compressibility, experimental critical densities are usually of lower reliability.

Unfortunately, most components are not sufficiently stable at or near the critical temperature, and as a result experimental measurements of their critical properties are extremely difficult, if not impossible. It is therefore vital that prediction methods be developed which are capable of not only reasonably accurate predictions, but which are also reliable with a low probability of failure when applied to extrapolation. Unluckily, the critical point is difficult to capture by molecular simulation due to the very large autocorrelation length at and near this state.

Since the first developments of group contribution methods by Riedel [1] in 1949 and Lydersen [2] in 1955, a large number of methods has been developed for the estimation of critical property data. While various different approaches can be found

in literature, the use of the group contribution concept still seems to provide the most reliable and easy to obtain results.

The objective of this work was to develop a new estimation method for the critical temperature, pressure and volume of organic compounds with a wide range of applicability and to give a detailed analysis of its performance compared to ten well-known previously published methods.

Reliability analysis of such estimation methods is of significant practical importance as a tool to assess process model reliability in chemical process design and optimization. Different authors have reported extensive tests of critical property estimation methods in the past based on a smaller set of data, fewer methods and less differentiation with respect to classes of chemically similar compounds. A very detailed comparative study of four different estimation methods was recently published by Yan et al. [3].

2. Overview on available methods and motivation

A variety of estimation methods for critical property data are available in the open literature. A broad overview of these methods together with a detailed discussion of their reliability was given by Poling et al. [4]. In addition, several authors evaluated the performance of models utilizing a large common set of experimental data [3]. In this paper the comparison to other generally applicable methods is restricted to those which are based on the group contribution concept and are applicable over a wide range of components. Table 1 gives an overview on the timeline of major previous developments in group contribution methods for critical properties. Due to their practical and theoretical importance, estimation of critical properties has attracted much interest of researchers from all over the world. Critical property estimation methods restricted to individual classes of components (alkanes, alkenes, etc.) were excluded from Table 1.

Table 1
Important group contribution methods for the estimation of critical property data

Year	Reference	Additional information (T_c estimation)	Abbreviation
1949	Riedel [1]	–	RI
1955	Lydersen [2]	T_b	LD
1978	Ambrose [5]	T_b	–
1979	Ambrose [6]	T_b	AB
1980	Daubert [7]	T_b	DB
1982	Fedors [8]	–	–
1984	Joback [9]	T_b	–
1984	Klincewicz and Reid [10]	T_b	KR
1986	Somayajulu [11]	T_b	SJ
1987	Joback and Reid [12]	T_b	JR
1994	Constantinou and Gani [13]	–	CG
1995	Tu [14]	–	CT
1996	Wilson and Jasperson [15]	T_b	WJ
1999	Marrero-Morejon and Pardillo-Fontdevila [16]	T_b	MP
2001	Marrero-Morejon and Gani [17]	T_b	–
2001	Wen and Quiang [18]	T_b	WQ

In addition to the methods given in Table 1, numerous publications cover the use of QSPR (quantitative structure property relation) correlations and popular mathematical methods like neural networks for critical property estimation. While the correlative power of these approaches has been demonstrated in many cases, the extrapolative ability of these methods is not convincing, especially to conditions well outside their correlative range.

Classical estimation techniques can be divided into those which require only the molecular structure and others which require further relevant properties. For typical organic compounds of interest, the ratio of T_c/T_b is often within the range of 1.4 ± 0.3. Thus, knowledge of the normal boiling temperature greatly simplifies critical temperature estimation. If experimental normal boiling point or vapor pressure information is not available, group contribution estimation for this auxiliary property can be employed. These are usually of better quality and have a greater range of applicability due to the much larger set of experimental data available for these properties e.g., reliable critical temperatures can be found for approximately only 600 components, whilst experimental normal boiling point data in the open literature cover more than 18 000 substances.

Besides the simple group additivity schemes, a number of more complex estimation routes using topological indices [5,6] or bond interactions [16] have also been employed in this comparative study. Most of the available methods have been implemented in the software package Artist [19]. Estimation results were compared with a critically evaluated database in order to develop an expert system for the selection of the best model for a specific type of component. Model implementations were carefully verified, partly in cooperation with the authors.

The new estimation method developed is based on our experience with previous work on normal boiling temperatures [20,21] and vapor pressures [22]. As our preliminary work [23] showed significant improvements with respect to the published methods, it was decided to also invest further effort into the development of a new group contribution method for critical property data. In addition to a detailed description of the new method, this paper contains extensive comparative test results for 10 literature methods (The RI and WJ methods have not been included due to historical reasons for the RI method and the fact that the WJ method requires additional information apart from structure and boiling point, viz. density and is outside the scope of this work). These should be of great value for users who rely on critical property estimation for process simulation, risk assessment or environmental models.

3. Development of the new method and results

The new method employs a slightly improved fragmentation scheme compared to the method for the estimation of normal boiling temperature published earlier [21]. The list of structural groups for the new method, second order corrections and interacting groups are given in Tables 2–4, respectively. All modified groups and corrections from the previous work are listed in