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A benzene chain-based contribution method for prediction of physical properties of aromatic compounds

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ABSTRACT

The physical properties of aromatic and condensed ring especially polybenzene compounds are severely lacking and difficult to obtain from experiment, while the existing estimation methods are hard to be applied to this system. A new benzene chain-based contribution (BC–C) method is proposed on the basis of the three order group contribution method of Marrero and Gani method in this study, several new groups are defined by considering their benzene chain structure. The boiling point and critical properties are estimated using the BC–C and Joback–Reid methods and their average relative deviation are compared. Through the critical properties estimated by the BC–C method, the liquid densities can be calculated using the Riedel and Yamada–Gunn equations. The calculated data agreed well with the literature data with an overall average absolute relative deviation of less than 10%. The BC–C method provides a new and easy approach for prediction of the physical properties of aromatic compounds through defining of the new groups and receives precise predicted results.

1. Introduction

The physical properties of pure compounds and mixtures play an important role in the process synthesis and simulation as well as product design [1,2]. However, obtaining all the properties by experimental methods is difficult. Thus, the generally reliable predictive method of estimating the missing properties based on experiment data is very significant.

The practicality and versatility of group contribution methods make them the preferred way to predict a variety of physical and thermodynamic properties. With the development of groups and models, group contribution methods fall into five main types: (i) multi-level group contribution method, (ii) group-interaction contribution method, (iii) position group contribution method, (iv) neural network group contribution method, (v) and the combination of these methods.

The simple first-level group contribution methods such as Joback and Reid [3], Ambrose [4], Lydersen [5], and so on are the most widely used. Constantinou et al. [6] proposed a complex estimation technique based on conjugated forms. Their work was followed by a less complex method proposed by Constantinou and Gani [2], wherein the estimation of the compounds can be performed at two levels. Dalmazzone et al. put forward a new method using Benson's second order group to predict the critical temperature and enthalpies of vaporization of covalent compounds [7]. To some extent, these two-level group contribution methods are applicable to isomers except for the complex and polyfunctional compounds. Marrero and Gani [8] then proposed an estimation method that could be performed at three levels and used for the prediction of the physical properties for the majority of the compounds [9]. Fontdevila and Rubio [10] proposed the group interaction contribution method that considered molecules as aggregates of the group interaction instead of the structural groups. Morejon and Fontdevila [11] extended this method to the estimation of boiling point and critical properties. Wang et al. proposed the position group contribution method that used the contribution of groups as well as the position correction that could distinguish isomers to estimate the boiling point, melting point, and critical properties [12–16]. Gharagheizi [17] proposed a new method called the neural network group contribution method, which applied neural networks to develop the group contribution correlations. This method was then used to predict physical properties such as the flash point, critical properties, surface tension, acentric factor, and so on [18–22]. Some researchers combined two or more different group contribution methods to obtain a satisfactory result. For example, Nannoolal [23–25] proposed a method to predict the boiling point, critical properties, and vapor pressure via group contribution and group interaction methods, which were also utilized by Moller [26] to estimate vapor pressure. Lazzus [27] used a hybrid

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Notations

List of symbols

M	molar mass (g mol^{-1})
N_p	total number of data points
P_b	normal boiling pressure (1.01325 bar)
P_c	critical pressure (bar)
T_b	normal boiling temperature (K)
T_c	critical temperature (K)
T_r	reduced temperature
V_c	critical volume (cm^3 mol^{-1})

Abbreviations

AARD	average absolute relative deviation
RD	relative deviation
BC–C	the method developed in this work
YG	Yamada and Gunn equation
J–R	Joback and Reid method

Greek letters

ρ	density (g cm^{-3})
ω	acentric factor

Subscripts

cal	calculated data
lit	literature data

method combining group contribution and neural network as well as particle swarm optimization to predict flash temperature.

Aromatic compounds occupy a significant position in the chemical industry, and predicting their physical properties accurately through reliable methods is imperative. Through literature research, we found that Simamora [28,29] predicted the melting points and boiling points of aromatic compounds, Tabernero [30] estimated the sublimation enthalpies of solids constituted by aromatic and/or polycyclic aliphatic rings, Karasek [31] predicted the solubilities of aromatic heterocycles and hydrocarbons in pressurized hot water, and Godinho [32] estimated the boiling point and flash point of alkyl benzenes. The afore-mentioned methods are all based on the group contribution method and thus far, no special method is available for the description of aromatic compounds as well as the estimation of their boiling point and critical properties.

Among the methods described above, the M–G method is the most applicable in distinguishing isomers. However, aromatic compounds, especially polybenzene, possess a highly complex molecular structure, making it difficult to describe. With the need to describe aromatic compounds in a clearer and more convenient manner, the BC–C method is developed.

In this method, benzene and pyridine, a long chain consisting mainly of benzene, describe polybenzene compounds parallel to the manner by which C and carbon chain represent aliphatic compounds. Especially for polybenzene, the longest benzene chain is chosen as the main chain while other groups are considered substituents. Thus, the aromatic compounds are further divided into new fragments, and their critical properties, including the boiling point, are estimated using the BC–C method. Liquid density is then calculated through the Riedel [33] and YG [34] equations using the critical properties estimated by the BC–C method. Comparing the estimated value with the literature value of the critical properties, including the liquid density and boiling point, we can find that the BC–C method provides the satisfactory results in a simple manner.

2. Method proposed in this work

2.1. Database

The BC–C method proposed in this paper is aimed at estimating the physical properties of aromatic compounds especially polybenzene. To verify the applicability of the proposed method, literature data were collected from the NIST Database [35], Scientific Database from the Institute of Process Engineering, Chinese Academic Of Science [36], Chemical Properties Handbook: Physical Thermodynamic, Environmental, Transport, Safety and Health-Related Properties For Organic and Inorganic Chemicals (a book) [37], and the Yaws Critical Property Data for Chemical Engineering and Chemists (a book) [38]. Data with significantly different search values were screened. The screening principle involved discarding the data that deviated sharply from others [39]. For example, the boiling point of acenaphthene in the NIST database had three different literature values: 552.2 K, 552 K, and 502.65 K; in the Yaws Critical Property Data, the value was 550.54 K. Following the screening principle, this paper rejected the value of 502.65 K, and took the average of the three literature values which is 521.65 K as the boiling point of acenaphthene. We collected the physical properties of different aromatic compounds, including boiling points (66), critical properties (51), and density values (93).

2.2. Definition of new groups

In the description of aromatic compounds using the existing group contribution methods, the benzene is always broken up into the C—C single bond and double bond or aCH. The C—C bond is essentially longer than a double band but shorter than a single bond. The six bonds with the same length constitute the big benzene ring bond. Therefore considering benzene ring as an independent group is sensible. For polybenzene compounds, we try to describe them as chain hydrocarbons and divide into a main chain and several substituents. To some extent, the polybenzene chain differs from that of hydrocarbons because the chain itself is composed of benzene ring and not of C. Based on the different substituent groups, patterns, and the amount of benzene ring in the chain, the new groups are created (Table 1).

2.3. Description of the method

The BC–C method still uses the three-level theory of Marrero and Gani [8]. The new group created in the present study can be regarded as the first level of this method that can describe the basic structure of the polybenzene. The equations used to calculate the boiling points and critical properties are as follows [8]:

$$\exp\left(\frac{T_b}{222.543}\right) = \sum_i N_i T_{b1i} + \sum_j M_j T_{b2j} + \sum_k O_k T_{b3k} \quad (1)$$

$$\exp\left(\frac{T_c}{231.239}\right) = \sum_i N_i T_{c1i} + \sum_j M_j T_{c2j} + \sum_k O_k T_{c3k} \quad (2)$$

$$(P_c - 5.9827)^{-0.5} - 0.108998 = \sum_i N_i P_{c1i} + \sum_j M_j P_{c2j} + \sum_k O_k P_{c3k} \quad (3)$$

$$V_c - 7.95 = \sum_i N_i V_{c1i} + \sum_j M_j V_{c2j} + \sum_k O_k V_{c3k} \quad (4)$$