Position Group Contribution Method for the Prediction of Critical Properties of Organic Compounds Containing Nitrogen

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Introduction

Knowledge of physicochemical properties of organic compounds is essential for predicting their behavior [1-6]. Critical properties are the most widely used of physical properties in chemical engineering design and experimental. Although many hundreds amount of experimental data are available in literature, but most components are not sufficiently stable at or near the critical temperature, and as a result experimental measurements of their critical properties, Tc and Pc, are extremely difficult. In such conditions, mathematical models could be used to provide a reasonable estimation of the properties. Some of the significant group contribution methods for estimation of melting points were developed by Joback-Reid, [2] Constantinou-Gani. [5] and Marrero-Gani. [6-7] Joback -Reid developed a first-order group contribution method with 40 groups for organic compounds containing halogens, oxygen, nitrogen and sulfur. Constantinou-Gani introduced a two-level group contribution scheme consisting of 63 first-order groups and 40 second-order groups. Marrero-Gani modified this model further using the third-order groups that could account for more complex heterocyclic and large polyfunctional alicyclic compounds. Quantitative Structure-Property Relationships (QSPR) methods also could be used to estimating of properties. [8-10] This method is based on specific families of compounds, such as alkanes (Charton et al [11]), aldehydes, amines, ketones [12], benzenes[10] and Pyridinium Bromides[13] are some of these families

for which QSPR models have been developed. Katritzky [14] reviewed the QSPR methods range in accuracy from very well to similar accuracy as group contributions However, most of group contribution methods have a serious problem that they cannot distinguish among structural isomers, and QSPR method take an extremely complex calculation in its processing. To overcome this problem, a position group contribution method has been proposed and applied for the prediction of critical properties such as critical temperature or critical pressure of pure organic compounds [15-16].

The position group contributions method for the critical temperature and critical pressure

The first step consisted in testing correlations to represent the properties. Only one-parameter contribution was considered for each group. The critical pressure function is constructed by all groups' contribution as well as position correction. The position corrections were used to take into account longer distance interactions, which could distinguish most isomer include cis- and trans- or Z- and E- structure of organic compounds for their thermodynamics properties.

Here, the critical temperature and critical pressure can be expressed as:

$$T_c / K = T_0 + \sum_i A_i N_i + \sum_j A_j \tan\left(N_i / N\right) + \sum_k A_k P_k + a_1 \exp\left(1/M\right) + a_2 \exp\left(1/N\right) \quad (1)$$

$$P_c / MPa = P_0 + \sum_i A_i N_i + \sum_j A_j \tan\left(N_i / N\right) + \sum_k A_k P_k + a_1 \exp\left(1/M\right) + a_2 \exp\left(1/N\right) \quad (2)$$

$$N = \sum_i N_i + \sum_j N_j \quad (3)$$

The estimation methods for critical temperature and critical pressure have the same distribution function of position group contribution totally[15-16].

Parameter A_i or A_j stands for i or j group contributions, N_i for the number of each group that carbon element forms the centre of the group in the molecular formula, N_j for the number of each group that non-carbon element forms the centre, N for total number of groups, P_k for the position correlation factor, and a_1, a_2 for parameters of the model. The set of contributions that allowed to minimize the

residual estimation difference was then computed by regression. M is molecular weight. According to the IUPAC nominating method, we draw the structures and assign the P_k values for the relevant positional correction. Table 1 reports the values computed for the group contributions A_i. And our method developed is applicable only to comparatively low-molar-mass compounds involving carbon chain from C2 to C18

The sources of experiment data were from: a series of critical compilation reviews by the critical properties group of the IUPAC Ⅰ.2 on thermodynamics, the works were published in J Chem Eng Data by Ambrose,17-19 Tsonopoulous,18,19,23,24 Daubert,21 Gude,20 Kudchadker,23 and Marsh K.N. et al..25,26 Critical data was also obtained from a compilation of organic property data by Ma 27.

Conclusion

In this work, based on position group contribution method, a new method recently proposed for the estimation of the critical temperature is extended to the prediction of critical pressure. Contributions for compounds containing carbon, hydrogen, oxygen, nitrogen, sulphur, chlorine and bromine were reported, especially for 89 different organics containing nitrogen, and that position compensation factor has been developed which could distinguish between the thermodynamic properties of most isomers of organic compounds including cis- and trans- or Z- and E- structures. It is shown that it is possible to use a similar framework to predict the two properties of organic compounds. The predicted results of organic compounds containing nitrogen for critical temperature and critical pressure showed that the position group contribution method performs significantly better than other methods used for comparison

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