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Thermodynamic property prediction for high molecular weight molecules based on their constituent family

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ABSTRACT

A method for predicting the critical temperature of high molecular weight molecules is proposed. The method is based on a modification of the functional form of the Joback method and the use of constituent functional group trends. To demonstrate the predictive capability of the method several pure fluids and their binary mixtures with CO_2 are studied. In particular, diglyme, triglyme and tetraglyme whose molecular weights range from 134 to 222, are shown to reveal excellent predictions between 3 and 9% deviation for saturated liquid densities. Application to vapor–liquid phase equilibria for CO_2-glyme systems exhibit 4–8% deviation in saturated liquid densities and 1% for vapor densities. For the system of oleic acid + CO_2, pure component parameters from the method allow the correlation of the vapor pressure of oleic acid and the solubility of H_2 in oleic acid with a BWR type of equation of state and temperature dependent interaction parameters. Solubility of CO_2 in triolein is also well correlated. The critical temperature of a polyalkylene glycol with a molecular weight of 1100 is predicted to be 842 K, whereas the prediction by of the Joback method predicts 8541 K, and so cannot be used in equation of state calculations. The pure component properties predicted with the new functional form of the Joback method also allow reliable correlation of CO_2-polyalkylene glycol vapor–liquid equilibria.

1. Introduction

When the critical properties of a pure substance are known, it is possible to predict thermodynamic properties using corresponding state theories such as equations of state (EoS). For the substances in which the critical properties are unknown, simple predictive methods based on molecular group contributions such as those of Joback and Reid [1], Constantinou and Gani [2], Marrero and Gani [3] or Valderrama and Robles [4] methods are effective. However, in all of these group contribution methods, the uncertainty of the predictions becomes higher as the molecular weight (M_w) increases and at values of $M_w = 1000$ or more, the relationships may not give physically realistic results. Moreover, for big molecules such as polyalkylene glycols (PAGs), glymes or other molecules for which data are unavailable and are generally not included in databases for group contribution methods, the applicability of the method may be doubtful even though data exist for small molecules having the same constituent families (e.g., ether, di-ol).

To predict the thermodynamic properties of higher molecular weight molecules, the method of Joback and Reid [1] is taken as an example and two observations are made. First, the Joback method [1] becomes unsuitable for predicting the properties of high molecular weight molecules because it uses a quadratic function that has a maximum at some value of molecular weight. Second, the Joback method has linear contribution increments for the critical temperature (T_c), critical pressure (P_c), critical volume (V_c) and boiling point (T_b) that combines all constituent families and does not take advantage of specific trends of constituent families. To address these limitations, the following approach was developed:

(i) First, a monotonically increasing functional ratio T_b/T_c is introduced with the sum of contribution increments for the molecule being obtained from the Joback correlation.
(ii) Second, the correlation is based on constituent family trends (hydrocarbons, ethers, esters).

A 15-constant BWR EoS [8–12] with predicted parameters is used as an equation of state and the properties of pure substances or mixture properties [8–12,14–18] are predicted and compared with experimental data. Large molecules and molecules that are

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generally unfamiliar to property databases (glymes, PAG, etc.) are considered. The prediction of the properties of high molecular weight molecules from their relationships with their constituent families of small molecules is considered along with the appropriate functional forms and a methodology for group contribution methods that can predict the properties of large molecules thus demonstrated.

2. Prediction of critical temperature developing Joback method

2.1. Relationship between $\sum\Delta_T$ of Joback correlation and T_b/T_c

According to the Joback correlation [1], the critical temperature T_c is obtained from the following relation:

$$T_c[\mathrm{K}] = T_b\left[0.584 + 0.965\sum\Delta_T - \left(\sum\Delta_T\right)^2\right]^{-1} \tag{1}$$

$$T_b[\mathrm{K}] = 198 + \sum\Delta_b \tag{2}$$

where T_b is the boiling point, Δ_T and Δ_b are contribution increments for the critical temperature and boiling point, respectively. Since Eq. (1) has a linear relationship, T_c approaches a very large value at high molecular weights according to Eq. (2). For example, T_c of triolein is 4019 K and that of PAG-1 (a polyalkylene glycol) is 8581 K. From these values, predictions cannot be reliably made with an equation of state.

To avoid the direct T_b calculation, the value of T_b/T_c from Eq. (1) is written as follows,

$$\frac{T_b}{T_c} = 0.584 + 0.965\sum\Delta_T - \left(\sum\Delta_T\right)^2 \tag{3}$$

For about 400 substances [5], the experimental values of T_b/T_c were plotted against $\sum\Delta_T$ from the Joback correlation as shown in Fig. 1. Except for higher alcohols, the trends are similar for all constituent families and excellent correlations can be made.

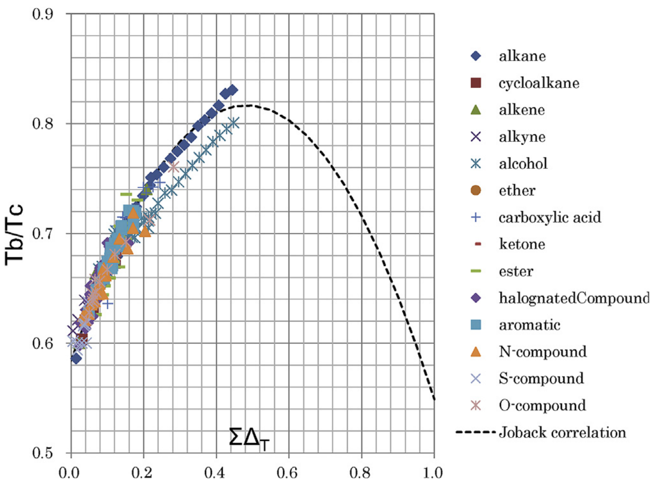

Fig. 1. Relation between T_b/T_c and $\sum\Delta_T$ obtained by Joback [1].

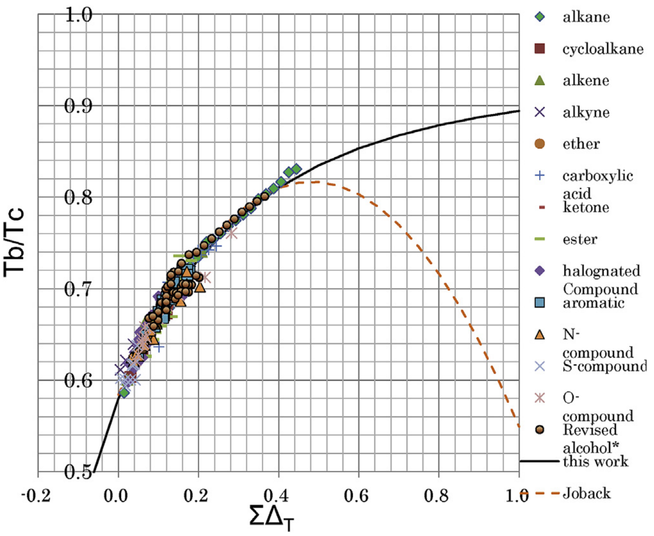

Fig. 2. Correlation between T_b/T_c and $\sum\Delta_T$ applicable to high molecular weight molecules considered in this work. Revised alcohol: contribution of OH increment is neglected for higher alcohols.

For a large molecules, however, the value of T_b/T_c decreases with molecular weight when using eq. (3), which is undesirable. As the molecular weight increases, the value of T_b/T_c should increase monotonically and have a maximum value of unity at best. For higher alcohols, the effect of hydrogen bonding (effect of OH-increment) can probably be neglected. To address these issues, the following function form is employed (Fig. 2)

$$\frac{T_b}{T_c} = -\frac{1}{\left(1.3 + \sum\Delta_T\right)^4} + 0.93 \tag{4}$$

The above expression shows that a maximum value of T_b/T_c is 0.93.

2.2. Method of calculating T_c that avoids direct calculation of T_b

The next step in the proposed method is to obtain a relationship between T_c and T_b/T_c. For about 400 substances [5], the experimental values of T_b/T_c are plotted against T_c as shown in Fig. 3. Although there appears to be no clear trends in the data, excellent correlations for the constituent families can be obtained. For example, chain hydrocarbons (alkane, alkene and alkyne) and esters can be correlated by the same function,

$$T_b/T_c = 4.639 \times 10^{-7}\,T_c^2 - 6.783 \times 10^{-5}\,T_c + 0.5840 \tag{5}$$

While chain alcohols and carboxylic acids can be expressed by

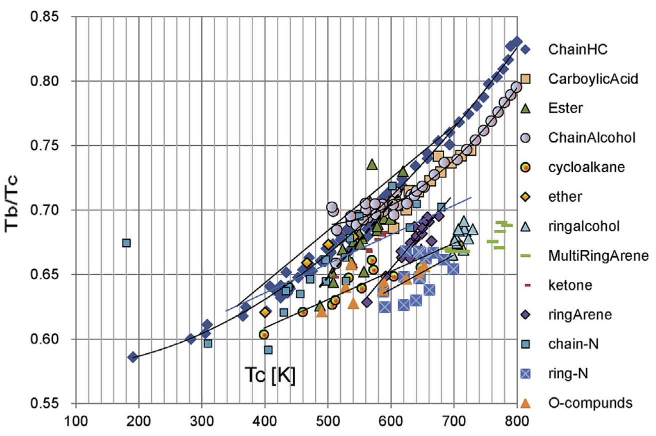

Fig. 3. Relationship between T_c and T_b/T_c depending for constituent families.