Finitely limited group contribution correlations for boiling temperatures

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ARTICLE INFO

ABSTRACT

Group contribution correlations are presented for the boiling temperatures at (101.33 and 1.33) kPa and for critical temperature applicable to a broad range of organic compounds. The group contributions are based on UNIFAC groups to facilitate simultaneous group identification for estimation of activity coefficients. These correlations recognize a finite limit in boiling temperature and critical temperature as infinite molar mass is approached. The existence of this limit is suggested by: extrapolation of the experimentally measured boiling temperatures, by critical behavior polymer solutions, by engineering equations of state, and by molecular simulation results. The availability of two vapor pressures enables straightforward application of the Clausius–Clapeyron equation to estimate boiling temperatures at other points. In the presented approach, there are three parameters for the boiling temperature correlations and one parameter for the critical temperature plus 72 functional groups. The parameters are regressed through a database consisting of 336 hydrocarbons and 642 non-hydrocarbons. The database consists of various chemical families including aliphatics, olefinics, naphthenics, aromatics, alcohols, amines, nitriles, thiols, sulfides, aldehydes, ketones, esters, ethers, halocarbons, silicones, and acids. The average absolute percent deviations (AAD%) between the correlated and experimental temperatures are calculated in comparison with the Joback–Reid and Gani approaches. For the enthalpy of vaporization at $T = 298$ K, the Joback model makes calculations possible at 1.33 kPa by assuming that $Hvap$ is constant over this range. Also, Kolska and Gani have reported a correlation for heat of vaporization at the normal boiling point which is used in this study. We obtain (3.5, 4.7, and 4.1) AAD% in temperature for the present work using the Joback–Reid and Gani methods, respectively. Additionally, the accuracy of the present work is evaluated by calculating the vapor pressures from the DIPPR correlation at the predicted temperatures of each model. We obtained (33, 104, and 48) AAD% in pressure for the present work by means of the Joback–Reid, and Gani methods. The critical temperature correlation results in a 2.6 AAD% in critical temperature. Asher and Pankow have reported a UNIFAC-P_L° method to predict the vapor pressure of oxygen-containing compounds to model the behavior of organic aerosols over the temperature range of (290 to 320) K. The Asher et al. model is compared to this approach for 66 volatile species. For the vapor pressure at the 1.33 kPa boiling temperature, we obtain 37 AAD% for the present work and 95 AAD% using the Asher–Pankow method.

1. Introduction

Estimates of boiling temperatures can be extremely valuable in modeling many chemical processes. Boiling temperatures are direct measures of the (vapor + liquid) equilibria (VLE) of pure fluids, and accurate VLE for pure fluids is essential for accurate VLE of mixtures. Mixture VLE plays a crucial role in many processes. Examples might include compressor lubricants for ozone-friendly refrigerants, components in distillation of biofuels, or oxidation products of volatile organic compounds. In cases like these, the boiling temperatures are key indicators of volatility and solubility. Generally, one would like to know as much as possible about the boiling properties of a substance, including the vapor pressure from the triple point to the critical point. On the other hand, knowledge of the boiling temperatures at key pressures like (101.33 and 1.33) kPa can go a long way toward providing the necessary information when coupled with the Clausius–Clapeyron equation. While such data exist for many compounds, it is often the case that a new compound is being considered for which data are few or non-existent. Clearly, it would be desirable to have a reasonable prediction of the vapor pressure, even if the estimated error in the prediction were significant.

When considering boiling property predictions, the compounds of interest usually contain multiple functional groups and boil at high temperatures. High boiling temperatures generally preclude measurement of the entire vapor pressure curve because compounds tend to thermally decompose above $T = 670$ K [1]. In these

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cases, the critical properties must be estimated and properties defined in terms of the critical properties, like the acentric factor, must be treated with care. Then, the boiling properties play an even more important role. Functional group multiplicity also decreases the likelihood of reliable experimental measurements. Experimental studies tend to focus on homologous series. Hence, it is easy to understand how boiling point correlations based on nothing but molecular structure may often be necessary.

Reinhard and Drefahl [2] provide a review of many boiling point estimation methods. These methods can be classified as group contribution methods or more generically as "structure based" relationships. Generic structure based methods include correlations in terms of connectivity [3], graph theory, [4] or any number of descriptors that can be applied to a molecular structure. With this approach, the possibility exists to correlate the properties in terms of many subtle details of the molecular structure, thereby improving precision. On the other hand, the user interface for specifying these details becomes more complex. While graphical methods of specifying molecular structure are becoming more common, present "structure based" correlations are limited to homologous series and databases containing the properties of interest. Adapting the set of all possible structure based descriptors is relatively uncommon and lacking in physical interpretation. Group contribution methods, on the other hand, offer advantages of simple user input and wide applicability to a broad range of compounds and properties. Two group contribution methods provide particularly good examples of these advantages: the Joback and Reid [5] and the Constantinou and Gani [6] approaches. The Joback–Reid method is based on 41 simple first-order groups. Stein and Brown [7] extended the Joback–Reid method by increasing the number of groups to 85 and analyzing a database of 11,010 compounds. They retained the Joback–Reid model equation, however. The method of Constantinou and Gani [6] is based primarily on 78 UNIFAC groups [8], with the optional inclusion of second order groups when available. Also, Asher and Pankow [9] have suggested a new UNIFAC-based group contribution method to predict the behavior of organic aerosols over the temperature range of (290 to 320) K. Their correlation follows the methodology of Jensen *et al.* [10] and Yair and Fredenslund [11], which correlate the vapor pressure directly, instead of interpolating between boiling temperatures.

Recently, Sandler and coworkers [12–14] have reported the performance of the quantum mechanical COSMO-SAC-BP solvation model for predicting vapor pressure, enthalpy of vaporization, and normal boiling point temperature of a large database including environmentally significant substances. They report a 3.2 AAD% in normal boiling temperature for 369 compounds, comparable to 2.9% with the current method though their database was smaller.

The purpose of the present work is to report new correlations for the normal boiling temperature (101.33 kPa) and a similar correlation for the additional boiling temperature at 1.33 kPa. The new correlations are based on the assumption of a finite limit in the boiling temperature at infinite molar mass. The rationale for this assumption is explained in the Section 2. The advantage of having an additional boiling temperature available at, say, 1.33 kPa is that it enables interpolation through the Clausius–Clapeyron equation. Thus estimation of the boiling temperature is made possible at any pressure below roughly 0.2 MPa. We evaluate the relative accuracy of these correlations by comparing the Joback, Gani, and Asher–Pankow methods.

2. Background

The assumption of a finite limit in the boiling temperature is suggested on the basis of experimental results for pure n-alkanes [15,16], experimental results for polymer solutions [17–19], an

equation of state analysis [20–22], and molecular simulation results [23,24]. The result from the analyses of all of these data suggests that the reciprocal critical temperature should vary as $M^{-\frac{1}{2}}$, where M is the molar mass, and that the intercept at infinite molar mass should be non-zero. The critical temperature represents the terminus of the boiling temperature at the molar mass where the critical pressure approaches (101.33 or 1.33) kPa. Therefore, a finite limit for the critical temperature implies a finite intercept for the boiling temperature curve. In the 1.33 kPa case, analysis of variance shows the difference between its intercept and that of the critical temperature correlation to be negligible. Therefore, we have based our critical temperature correlation upon boiling temperature at 1.33 kPa and designed our correlations such that the critical temperature and T_b at 1.33 kPa curves converge at very high molar mass. Following Nikitin [16], the critical pressure approaches 101.33 kPa near a carbon number of C_{116} and it approaches 1.33 kPa when the carbon number approaches C_{2200}. These trends are illustrated in figures 1 and 2. These estimates are crude in the sense that they are far from the experimental results, but they serve to establish a rough estimate of the termini of the boiling curves. The termination of the 101.33 kPa curve obscures the fact that we assume a common intercept with the 1.33 kPa curve. Regression analysis on the two experimental data sets independently showed that the intercepts were within one estimated standard deviation of each other, making any distinction statistically insignificant.

Support for a finite limit in critical temperature can be found in several related analyses. The data for critical temperatures of polymer solutions like polystyrene in cyclohexane approach very high molar masses [17–19], and these clearly indicate a finite limit. On the other hand, these are not exactly the same as the critical temperatures of pure compounds. It is possible to study the pure compound critical temperature within the context of an assumed equation of state, as shown by Tsonopoulos and Tan [20] for the Flory EOS and Elliott and Lira [22] for the Elliott–Suresh–Donohue (ESD) model. The analysis for the ESD model is relatively simple but helps to illustrate several key points and limitations. The ESD model is described by:

$$Z \equiv \frac{P}{\rho RT} = 1 + \frac{4cb\rho}{1 - 1.9b\rho} - \frac{9.5qYb\rho}{1 - 1.7745Yb\rho} - \frac{Nd(1 - X^A)}{1 - 1.9b\rho}, \qquad (1)$$
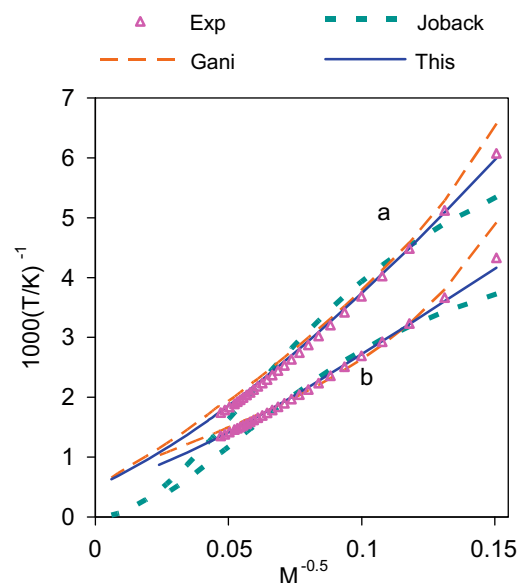

FIGURE 1. Plot of boiling temperatures of n-alkanes versus molar mass: (a) P = 1.33 kPa, (b) P = 101.33 kPa.