Prediction of true critical temperature of multi-component mixtures: Extending fast estimation methods

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ABSTRACT

Various fast estimation methods such as Chueh–Prausnitz, Grieves–Thodos, modified Wilson, and Redlich–Kister are available for predicting vapor–liquid critical temperature of fluid mixtures. In order to use these methods for a multi-component mixture, interaction parameters are required for each binary set of components. In the present work, 4524 experimental data on true critical temperature of 571 binary mixtures were collected through comprehensive literature search. Based on this data set, the available fast estimation methods were extended and new interaction parameters for each binary set were introduced. In order to extend the applicability of these methods, new correlations were developed to estimate interaction parameters. Finally, the capability of different methods was evaluated for predicting true critical temperature of 68 different multi-component mixtures with 427 data points.

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1. Introduction

Accurate prediction of critical points for multi-component mixtures is a key point in understanding the phase behavior of mixtures at high temperatures and pressures [1–3]. As a common engineering application, many processes like supercritical extraction are designed to take advantage of the special phase behavior in the critical region [4]. Another practical example in designing separation processes is understanding the probability of retrograde condensation or evaporation, which is dependent on the critical behavior of fluid mixtures [5]. Chemical and process engineers face various wide range multi-component mixtures with different chemical families, which must be analyzed and examined for vapor–liquid critical behavior. One solution is to rely on the published experimental data or conduct new experimental measurements. Since these measurements are often time-consuming and expensive, such practices are usually replaced by different alternatives such as theoretical models or empirical methods for predicting critical behavior of fluid mixtures. Methods for predicting true critical properties of multi-component mixtures can be categorized as follows [6]: (a) fast estimation methods (known as empirical methods) and (b) rigorous methods, which are based on the complex thermo-dynamic conditions of the critical state. Hicks and Young [1],
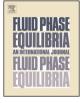
Sadus [2,7], Deiters and Kraska [8], and Reid et al. [9] extensively discussed and compared these methods.

Rigorous methods are usually preferred to fast estimation techniques. With the aid of rigorous methods, not only vapor–liquid, but also global critical behavior of fluid mixtures can be predicted. Besides, building complex phase envelops is possible by using rigorous methods. Despite the advantages of rigorous methods, these methods have some disadvantages and limitations [2,6,7]. Some of these limitations are: complexity of the methods, lack of analytical translations of criticality as a function of measurable thermodynamic variables [2], influence of the mixing rules, combining rules and adjustable parameters on the accuracy of predictions, and the necessity of a "priori" knowledge of the number and approximate location of critical points. As for the last item, Stradi et al. [10] and Henderson and co-workers [11–13] have proposed innovative solutions to overcome this deficiency.

Fast estimation methods can predict vapor–liquid critical behavior of mixtures. Although, these methods cannot be considered as a solution to rigorous methods drawbacks [6,14]; but one should not ignore their important advantages like low computational cost, and simplicity of application. These methods can be used for preliminary checking of experimental measurements and can be applied to provide proper initial guesses for rigorous methods like the one proposed by Heidemann and Khalil [15].

Fast estimation methods are empirical techniques and their accuracy is dependent on the availability of experimental data [4,14]. Measurements of vapor–liquid critical temperature has

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Nomenclature

a, b, c, d, e	Correlation constants
A_{ij}	Grieves–Thodos or modified Wilson binary interaction parameter of component i and j
C	Correlation constant
E	Mixture effect term, K
k	Number of Redlich–Kister expansion term
m	Number of expansion term
n	Number of components in the mixture
T_{ci}	Pure component critical temperature of component i, K
T_{cm}	Mixture critical temperature, K
T_{ref}	Reference temperature, 1 K
V_{ci}	Pure component critical volume of component i, cm^3/mol
x_i	Molar composition of component i
θ_i	Surface fraction parameter of component i
Φ_i	Volume fraction parameter of component i
τ_{ij}	Chueh–Prausnitz equation binary interaction parameter of component i and j
ϕ_{ij}	Arbitrary parameter defined by Eq. (22)
ζ_{ij}	Arbitrary parameter defined by Eq. (23)

been performed on many binary mixtures (e.g., experimental data presented in Hicks and Young [1]). Recent attempts like the one performed by Najafi et al. [6] have extended fast estimation methods to a larger number of binary and multi-component mixtures. They were mainly focused on extending Chueh–Prausnitz method. Other classes of the fast estimation methods were not studied recently and the only comprehensive researches were done on a limited number of binary mixtures by Spencer et al. [14] and Elliot and Daubert [4] (i.e., a data set with 1700 points). In the current study, wide range of experimental data for 571 binary mixtures with 4524 points have been used to revisit and extend the available true critical temperature fast estimation methods. It will be demonstrated the extended methods are accurate in calculating the true critical temperature of common fluid mixtures (i.e., containing hydrocarbons and non-hydrocarbons).

2. Fast estimation methods of true critical temperature for fluid mixtures

The methods proposed for fast estimation of vapor–liquid critical temperature can be classified into four categories according to their approach: (a) methods without interaction parameters, (b) methods based on fitted interaction parameters, (c) methods based on excess properties, and (d) methods based on group-contribution technique.

2.1. Methods without interaction parameters

Li method belongs to current category. The results of this method show the critical temperature of a mixture can be calculated directly from the critical properties of the components without adjustable parameters [16]. The resulted expression of Li method is:

$$T_{cm} = \sum_{i=1}^{n} \Phi_i T_{ci} \qquad (1)$$

where,

$$\Phi_i = \frac{x_i V_{c_i}}{\sum_{j=1}^{n} x_j V_{c_j}} \qquad (2)$$

2.2. Methods based on fitted interaction parameters

The important methods in this category are Grieves and Thodos [17] and Chueh and Prausnitz [18].

2.2.1. Chueh–Prausnitz method
The equations of Chueh–Prausnitz method are as follows:

$$T_{cm} = \sum_{i=1}^{n} \theta_i T_{ci} + \sum_{i=1}^{n} \sum_{\substack{j=1 \\ j \neq i}}^{n} (\theta_i \theta_j \tau_{ij}) T_{ref} \qquad (3)$$

where,

$$\theta_i = \frac{x_i V_{c_i}^{(2/3)}}{\sum_{j=1}^{n} x_j V_{c_j}^{(2/3)}} \qquad (4)$$

and T_{ref} is the reference temperature. In this paper, we assume that $T_{ref} = 1$ K. This method is based on two assumptions: $\tau_{ij} = \tau_{ji}$, and $\tau_{ii} = 0$. For a binary mixture, the simplified form of Eq. (3) is:

$$T_{cm} = \theta_1 T_{c1} + \theta_2 T_{c2} + 2\theta_1 \theta_2 \tau_{12} \qquad (5)$$

The τ_{ij} in Chueh–Prausnitz equation represents an empirical binary interaction parameter that should be determined by fitting binary experimental data. Chueh and Prausnitz [18] and Schick and Prausnitz [19] provided τ_{ij} values for 87 binary mixtures. Later, based on data set provided by Spencer et al. [14], Reid et al. [9] presented correlations to generalize the technique known as modified Chueh–Prausnitz (MCP) method. Najafi et al. [6] extended Chueh–Prausnitz method for 529 binary mixtures. Their extended method is addressed in this paper as first extended Chueh–Prausnitz or FECP method. They also modified correlations proposed in MCP method and introduced modified extended Chueh–Prausnitz or MECP method.

2.2.2. Grieves–Thodos method
The Grieves–Thodos method is represented by:

$$T_{cm} = \sum_{i=1}^{n} \frac{T_{ci}}{1 + (1/x_i) \sum_{\substack{j=1 \\ j \neq i}}^{n} A_{ij} x_j} \qquad (6)$$

For binary mixtures, the simplified form of Eq. (6) is:

$$T_{cm} = \frac{T_{c1}}{1 + (x_2/x_1) A_{12}} + \frac{T_{c2}}{1 + (x_1/x_2) A_{21}} \qquad (7)$$

where A_{ij} is the binary interaction parameter. Grieves and Thodos [17] gained A_{ij} values for 41 binary mixtures composed of hydrocarbons. They also proposed a simple correlation based on the normal boiling point of pure hydrocarbons for estimating proper A_{ij} values. Because the needed values for a comprehensive review of this method were unavailable or out of range, the proposed equations were not further evaluated by researchers [14].

2.3. Methods based on excess properties

The theory of methods based on excess properties was discussed extensively, elsewhere [20]. The important methods in this category are Redlich–Kister (RK) [21,22] and modified Wilson (MW) [23,24].

2.3.1. Redlich–Kister method
The equation used in Redlich–Kister method is:

$$T_{cm} = \sum_{i=1}^{n} x_i T_{ci} + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} x_i x_j \sum_{k=1}^{n+1} \left(C_{ij_{(k)}} (x_i - x_j)^{k-1} \right) T_{ref} + E_{(m)} \qquad (8)$$