



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



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ABSTRACT

Various fast estimation methods such as Chueh–Prausnitz, modified Wilson, and Redlich–Kister were proposed for the prediction of vapor–liquid critical volume of fluid mixtures. In order to calculate true critical volume by these methods, some binary interaction parameters are required for each binary set of compounds in the mixture. Experimental data on true critical volume of mixtures is scarce. Therefore, methods like Chueh–Prausnitz were developed to some extent, while other methods such as modified Wilson, and Redlich–Kister have limited applications. In the present work, 630 experimental data on true critical volume for 116 different binary mixtures has been collected by comprehensive literature search. Then by introducing new interaction parameters for each binary set based on using all available experimental data, previous methods have been revisited and new methods have been introduced, as well. Besides, new correlations have been developed to estimate different interaction parameters in order to extend the applicability of these methods. Finally, the capability of different methods has been tested by predicting true critical volume of 8 different multi-component mixtures containing 54 experimental data points.

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1. Introduction

Accurate prediction of critical points for multi-component mixtures is a key step in understanding the overall phase behavior of mixtures [1–3]. As a common engineering application, the probability of retrograde condensation or evaporation is highly dependent on the understanding of the critical behavior of multi-component mixtures [4]. The best practical examples are designing super critical–fluid extraction processes, compression and refrigeration units [5]. There is no doubt that experimental measurement is the best way to find the critical points of a multi-component mixture. But these measurements are often time-consuming and expensive; therefore, different alternatives such as theoretical models and empirical methods become valuable. There are different methods available for prediction of true critical properties for multi-component mixtures [6]. These methods can be categorized as: (a) fast estimation methods, and (b) rigorous methods. These different approaches were widely discussed and compared in details by Hicks and Young [1], Sadus [2], Deiters and Kraska [7], and also Reid et al. [8].

There are numerous reasons that rigorous methods are preferable to the first approach because of their basis in thermodynamics, their

capability in predicting global critical behavior and also building complex phase envelopes. As it has been discussed before [6], these methods have also some disadvantages such as inaccuracies related to the mixing rules or binary interaction coefficients of the equations of state. Besides, simple equations of state used in rigorous methods such as the famous one proposed by Heidemann and Khalil [9] do not predict all critical points, precisely. For prediction of critical volume, the largest deviations are observed in comparison with the other critical properties [10]. In later studies, Abu-Eishah [5] replaced the simple equations of state with the advanced ones and improved the results of critical volume prediction for binary mixtures. But the deviations for some mixtures were still notable. It is true that fast estimation methods cannot be considered as a solution to these drawbacks, however, low computational cost, and simplicity of application are the main advantages of these methods. As the fast estimation methods are generally empirical techniques based on binary interaction parameters, their prediction accuracy is mainly dependent on the availability of experimental data [11,12]. Since, measuring vapor–liquid critical volume of a mixture is usually an expensive and difficult task, available data in literature is rare and hard to find. Naturally fast estimation methods for predicting critical volume are few and have a limited range of applicability [11,12].

In the present study by using a wide range of experimental data for 116 defined binary mixtures, we will revisit and extend the available fast estimation methods of predicting true critical volume for multi-component mixtures. It will be demonstrated that these

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Nomenclature

a, b, c, d, e	correlation constants
k	number of Redlich–Kister expansion term
n	number of components in the mixture
m	number of expansion term
A_{ij}	Wilson based equation binary interaction parameter of component i and j
B_{ij}	Extended T–K Wilson binary interaction parameter of component i and j
C	correlation constant
$C_{ij(k)}$	Redlich–Kister and Extended Redlich–Kister binary interaction parameter of component i and j
E	mixture effect term, cm^3/mol
T_{ci}	pure component critical temperature of component i , K
T_{ref}	reference temperature, 1 K
V_{ci}	pure component critical volume of component i , cm^3/mol
V_{cm}	mixture critical volume, cm^3/mol
V_{ref}	reference volume, $1 \text{ cm}^3/\text{mol}$
x_i	molar composition of component i
θ_i	surface fraction parameter of component i
Φ_i	volume fraction parameter of component i
ν_{ij}	binary interaction parameter of component i and j
ψ_{ij}	arbitrary parameter defined by Eq. (24)
δ_{ij}	arbitrary parameter defined by Eq. (25)
ϕ_{ij}	arbitrary parameter defined by Eq. (27)
ζ_{ij}	arbitrary parameter defined by Eq. (28)
φ_{ij}	arbitrary parameter defined by Eq. (30)
γ_{ij}	arbitrary parameter defined by Eq. (31)

methods can handle common industrial mixtures (i.e., mixtures containing hydrocarbons and non-hydrocarbons) with acceptable prediction accuracy by proper modifications based on a good experimental data set. Also, these methods can be applied to predict best initial estimates for rigorous methods such as Heidemann and Khalil [9] which needs critical volume as an initial guess for predicting true critical temperature and pressure of a multi-component mixture.

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

Few methods are proposed for fast estimation of vapor–liquid critical volume of mixtures. These methods can be categorized into three categories according to their approach: (a) methods based on fitted interaction parameters (such as Chueh and Prausnitz method [13]); (b) methods based on excess properties (such as modified Wilson method [10]); (c) methods based on group-contribution technique (e.g., Li and Kiran method [14]).

The important methods in the first category are Grieves and Thodos approximate graphical approach [15] and Chueh and Prausnitz analytical method [13]. Grieves and Thodos method was not further considered by researchers because of its limited range of experimental benchmark data [11]. Chueh and Prausnitz method was modified by Schick and Prausnitz [16] and correlations were presented by Reid et al. [8] in order to generalize the technique as Modified Chueh and Prausnitz (MCP) method. This method is more accurate than former methods in this category [11,12]. Moreover, the Chueh–Prausnitz method can be easily

extended to multi-component mixtures using binary interaction parameter obtained for each binary set in the multi-component mixtures.

The true critical volume of a mixture is usually not a linear mole fraction average of the pure component critical volumes. Therefore, Chueh and Prausnitz defined an arbitrary parameter called surface fraction θ , instead of mole fraction:

$$\theta_i = \frac{x_i V_{ci}^{(2/3)}}{\sum_{j=1}^n x_j V_{cj}^{(2/3)}} \quad (1)$$

Also, they introduced a new binary parameter, ν_{ij} , into their critical volume mixing rule. For binary mixture, the simplified form of Chueh and Prausnitz equation is as follows:

$$V_{cm} = \theta_1 V_{c1} + \theta_2 V_{c2} + 2\theta_1 \theta_2 \nu_{12} \quad (2)$$

As for multi-component mixtures, here we use the following modified form of the main equation:

$$V_{cm} = \sum_{i=1}^n \theta_i V_{ci} + \sum_{i=1}^n \sum_{\substack{j=1 \\ j \neq i}}^n (\theta_i \theta_j \nu_{ij}) V_{ref} \quad (3)$$

In this equation it is assumed that: $\nu_{ij} = \nu_{ji}$, $\nu_{ii} = 0$, and $V_{ref} = 1 \text{ cm}^3/\text{mol}$.

Chueh and Prausnitz have provided ν_{ij} values for only 25 binary mixtures in their main paper [13]. These data were obtained by fitting experimental critical volumes of binary mixtures with Eq. (2). Also, a curve for correlating ν_{ij} was presented that could be used to estimate this parameter for paraffin–paraffin, paraffin–aromatic, and paraffin–carbon dioxide binary systems. This curve is called Chueh’s curve. Later, Schick and Prausnitz [16] slightly modified and extended the method. As an example, for mixtures containing one aromatic and one paraffin they instructed to use 83% of the ν_{ij} values obtained using Chueh’s curve for paraffin–aromatic systems. Later the MCP method was presented for estimating ν_{ij} . The proposed correlations and their related coefficients are extensively discussed in Section 6. Elliott and Daubert [12] improved the estimations of MCP method and introduced a new set of correlations known as Revised Chueh–Prausnitz (RCP) method. Their proposed correlations were limited to the systems containing paraffins or aromatics and non-hydrocarbon components were considered as a single group regardless of different chemical sub-families in this large group [6].

As the second category of fast estimation methods, methods based on excess properties were first considered by Partington et al. [17] for predicting critical temperature of various classes of mixtures. Etter and Kay [18] proposed correlations for prediction of vapor–liquid critical temperature and pressure of normal paraffin hydrocarbons. Based on excess properties concept, a general equation for predicting the critical volume of binary mixtures could be formulated as follows:

$$V_{cm} = x_1 V_{c1} + x_2 V_{c2} + V_c^{ex} \quad (4)$$

where V_c^{ex} values can be positive or negative based on the nature of mixture. The scarcity of the experimental values of critical volume resulted in non-availability of a general fast method for estimating either the sign or the magnitude of V_c^{ex} values [8,11]. One of the famous models proposed for estimation of excess thermodynamic properties is Redlich–Kister (RK) equation [19]. The Redlich–Kister expansion provides a flexible algebraic expression for representing excess properties of mixtures [20]. When excess critical volume of binary mixtures is considered, Eq. (4) is changed as follows by limiting Redlich–Kister expansion to three terms:

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