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Flash point prediction of the binary and ternary systems using the different local composition activity coefficient models

Ali Haghtalab*, Jaber Yousefi Seyf, Yousef Mansouri

Department of Chemical Engineering, Tarbiat Modares University, P.O. Box 14115-143, Tehran, Iran

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ABSTRACT

The flash point is an important physical property which is used to estimate the fire hazard of a flammable liquid. The prediction of this property for single and multi-components systems allows one to avoid the occurrence of fire or explosion. The several models have been developed for prediction of the flash point of the multi-component mixtures so far. In the present work, the activity coefficient models of Wilson, NRTL, UNIQUAC, and NRTL-NRF are used through general flash-point model of Liaw et al. to predict the flash point of the binary and ternary systems. In most cases due to lack of experimental binary vapor–liquid equilibrium data, the experimental closed cup flash point data are used to predict the binary interaction parameters in the activity coefficient functions. Moreover, the binary interaction parameters are used to predict the flash point of the ternary systems. Finally, one can conclude the results of NRTL model is superior respect to the other local composition models.

1. Introduction

When a flammable liquid is transported, used, or stored, safe handling is particularly important, which requires knowledge of the liquid's fire and explosion hazard. The flash point is an important physical property which can be used to estimate the risk of fire and explosion of a flammable liquid. The flash point of a flammable liquid is the temperature at which the vapor pressure of the liquid is such as to emit sufficient vapor to form a combustible mixture with air that corresponds to the lower flammable limit (LFL) [1]. Flash point is one of the important safety items which is considered in the typical material safety data sheet (MSDS), and can be experimentally determined using the flash point analyzer. To determine the flash point, the ASTM D93-90 and ASTM 92-90 standard test methods are applied through Pensky-Martens closed cup and Cleveland Open Cup, respectively [1]. The Cleveland Open Cup flash point method gives usually a few degrees greater than the Pensky-Martens closed cup flash point method [1]. Recently, due to the importance of the usage, storage, and handling of flammable organic waste solvents, which have been led to serious problems in Taiwan [2], determination of the flash point is critical. Flash point of pure substance can be predicted by its LFL and Antoine equation [3]. If the LFL of the pure components is known, then the LFL of a mixture (LFL_{mix}) can be evaluated using the Le Chatelier mixing rule [4]. Affens and McLaren have developed a model based on the Raoult's law which makes it possible to predict the overall flammability properties of n-alkanes mixtures using the properties of individual components [5]. White et al. used the method of Affens and McLaren to estimate the flash point of two aviation fuel mixtures (JP-4/JP-8 and JP-5/JP-8), and they correlate flame spread induction time and flame spread rates through the estimated mixture flash point [6]. Although the model of Affens and McLaren can be used to predict the flash point of ideal mixtures, but it cannot be successfully used to predict flash point of non-ideal solution. Liaw et al. developed a mathematical model for the prediction of the flash point of both ideal and non-ideal mixtures that seems to be very promising [7,8]. Based on the Liaw model for prediction of mixture flash point, composition of vapor phase is necessary to be estimated. But prior to estimating vapor phase composition, it is necessary to evaluate liquid-phase activity coefficient based on an excess Gibbs energy function. The models such as Margules and Van Laar activity coefficient functions can be used for moderately non-ideal solutions. The known local composition models such as Wilson [9], NRTL [10], UNIQUAC [11], and NRTL-NRF [12] have been frequently applied in phase equilibrium computations such as vapor–liquid and liquid–liquid equilibrium calculations. Moreover,

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* Corresponding author.
E-mail addresses: haghtala@modares.ac.ir, ahaghtalab@hotmail.com (A. Haghtalab).

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these local composition models have been known as molecular activity coefficient models that are used to correlate the flash point of mixtures [7,8,13]. On the other hand, the UNIFAC type models (Original UNIFAC and Modified UNIFAC (Dortmund)) have been successfully used to estimate the flash point of miscible or partially miscible mixtures [14,15] and tailor-made green diesel blends [16]. Although Quantitative Structure-Property Relationships (QSPRs) have been used to predict the flash point of pure compounds, but recently a few works have been dedicated to the flash point of mixtures [17–20].

To our best knowledge, the data of flash point of multicomponent solutions appears to be scarce in the literature. Thus, the prediction of the flash point of multicomponent mixtures is still under investigation and can be an active research area. In the present work, the experimental data have been given by the literature [21,22] so that in most cases the binary interaction parameters of Wilson, NRTL, UNIQUAC, and NRTL-NRF models have been optimized through the experimental flash point data due to the lack of experimental VLE data. These optimized interaction parameters are used to predict the flash point of the ternary systems and their results are compared with the experiment. It should be noted the UNIFAC and ASOG models are known as the group contribution models that are used to estimation of activity coefficients that can be used to estimate the flash point of the pure and multicomponent mixtures. In this work, our objectives are to compare the results of the molecular models through correlation and prediction of the flash point of the pure and multicomponent mixture.

2. Flash point-prediction model

The Liaw model [7], which is the modification of Le Chatelier's rule [4], is most frequently used for prediction of the flammable (or combustible) flash point of the multicomponent mixtures as

$$\sum_{i=1}^{n} \frac{y_i}{LFL_i} = 1 \tag{1}$$

where y_i is the vapor phase composition of a flammable component i, and LFL_i is the lower flammable limit of a pure component “i” that can be defined as

$$LFL_i = \frac{P_{i,fp}^{sat}}{P} \tag{2}$$

where P denotes the atmospheric pressure and $P_{i,fp}^{sat}$ stands for the vapor pressure of component i at the flash point of pure component i. The vapor phase composition of component “*i*” can be obtained through VLE calculations. In the VLE condition, for each component the isofugacity rule is applied at the given pressure and temperature as

$$f_i^v = f_i^l \tag{3}$$

$$y_i \phi_i P = x_i \gamma_i f_i^\circ \quad ; \quad y_i P \cong x_i \gamma_i p_i^{sat} \ (\text{ideal vapor phase})$$

where ϕ is the fugacity coefficient which is assumed to be unity where the vapor phase is ideal gas at low pressure and γ_i denotes the activity coefficient. By combining Eqs. (1)–(3), one can write as

$$1 = \sum_{i=1}^{n} \frac{x_i \gamma_i p_i^{sat}}{p_{i,fp}^{sat}} \tag{4}$$

where p_i^{sat} is the vapor pressure of pure component *i* at the mixture flash point temperature that is calculated as

$$\ln p_i^{sat} = A + \frac{B}{T} + C \ln T + DT^E \tag{5}$$

where pressure is in pa and T in Kelvin. The constants of this equation for the different components are given in Table 1. The activity coefficient of component *i* can be calculated by the different activity coefficient models such as Wilson, NRTL, UNIQUAC and NRTL-NRF.

3. Results and discussion

3.1. The flash point of a binary solution

The experimental data of the acetic acid-pentanol, pentanol-hexanol, acetic acid-cyclohexanone, hexanol-cyclohexanone, pentanol-cyclohexanone, and acetic acid-hexanol systems were given in the literature [22]. To predict the flash point of a mixture it is necessary to specify the interaction parameters of the activity coefficient models using the isothermal or isobar VLE data. To our best knowledge, there are not any VLE data for the acetic acid-pentanol, acetic acid-cyclohexanone, and hexanol-cyclohexanone systems. In addition for the pentanol-hexanol system there is no data at or near atmospheric pressure. For the first four binary systems, the activity coefficient interaction parameters were determined using the experimental flash point data. For the last two binary mixtures, the interaction parameters were determined by both the isobar VLE data and the experimental flash point data so that their results were compared. The binary interaction parameters were used for prediction of the flash point of the hexane-acetic acid-cyclohexanone ternary system. The flash point calculations are carried out through satisfying the following objective function, which is obtained by rearranging Eq. (4) as

$$\sum_{i=1}^{n} \frac{x_i \gamma_i p_i^{sat}}{p_{i,fp}^{sat}} - 1 = 0 \tag{6}$$

Table 2 presents the experimental flash point data and the structural parameters of the several compounds that are used in the UNIQUAC model. Using the flash point data of the binary mixtures, the binary interaction parameters are optimized through the local composition activity coefficient models as presented in Table 3. Also this table shows the deviations for the acetic acid-pentanol, pentanol-hexanol, acetic acid-hexanol, acetic acid-cyclohexanone, pentanol-cyclohexanone and hexanol-cyclohexanone systems using NRTL and UNIQUAC functions. Similarly, Table 4 demonstrates the results using Wilson and NRTL-NRF models. Moreover, Fig. 1 presents the calculated flash point of these mixtures and their comparison with the experiment. As shown in this figure, the NRTL model presents the most accurate results for the acetic acid-pentanol, pentanol-hexanol, acetic acid-cyclohexanone and pentanol-cyclohexanone systems. On the other hand, the NRTL-NRF model presents the minimum deviation for the acetic acid-hexanol and hexanol-cyclohexanone systems. Also Fig. 1 shows that most of the present systems demonstrate a negative deviation from Raoult's law which is corresponded to the positive deviation in the flash point. In the case of the pentanol-cyclohexanone system which presents a positive deviation from Raoult's law (negative deviation in flash point), the NRTL-NRF model presents a large deviation so that one may conclude that this model is not suitable for those mixtures which present positive deviation from Raoult's law.