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A model for predicting flash point of alkane-alkane and water-alcohol mixtures by the Cubic-Plus-Association Equation of State

Hossein Jalaei Salmani [a], Mohammad Nader Lotfollahi [a,*], Seyed Hossein Mazloumi [b]

[a] Faculty of Chemical, Petroleum and Gas Engineering, Semnan University, Semnan 35131-19111, Iran
[b] Chemical Engineering Department, Faculty of Engineering, Ferdowsi University of Mashhad, Mashhad, Iran

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ABSTRACT

A vapor-pressure-based model has been constructed to predict the closed-cup flash points of binary miscible mixtures. The model utilizes a cubic-plus-association (CPA) equation of state (EoS) to thermodynamically describe the behavior of both liquid and vapor phases. The alkane-alkane and water-alcohol mixtures were selected to examine the predictive potential of the model. Compared to known models, which use the activity coefficient models, the proposed flash point calculation procedure has fewer binary interaction parameters (BIPs) and does not need the Antoine equation to calculate the vapor pressure of pure components. Moreover, another advantage is that by utilizing the published experimental flash point data, no binary vapor-liquid equilibrium (VLE) data are required to obtain the BIPs.

1. Introduction

The flash point is one of the most important properties of flammable liquids to evaluate process safety, and it is of great significance to safely handle, transport, and store such chemicals (Vidal et al., 2004). The flash point temperature is defined as the lowest temperature at which a flammable liquid emits enough vapor to make an ignitable mixture with air (Valenzuela et al., 2011). At the flash point, the produced vapor is insufficient for maintaining combustion and it can only burn temporarily (Alibakhshi et al., 2017; Cheng et al., 2015; Keshavarz et al., 2016). Experimental flash point data can be determined by heating an ignitable liquid in a vessel and then inserting an ignition source above the liquid surface. The temperature, at which the produced vapor flashes or ignites, is designated as the flash point. There are two general flash point measurement procedures for pure substances and mixtures, which are called closed-cup and open-cup (ASTM Standard D56, 2010; ASTM Standard D1310, 2007). The flash points determined with the closed-cup method are usually lower than the open-cup method values (Moghaddam et al., 2012) because in the open-cup method, the volatile components in the sample are able to be vaporized into the surrounding atmosphere before applying the ignition source. The closed-cup method produces reliable and consistent results, especially for multicomponent mixtures (Hristova and Damgaliev, 2013; Liaw et al., 2008; White et al., 1997). The experimental determination of the flash point is always preferred, but it can be time-consuming and expensive for mixtures. Therefore, it is especially necessary to establish techniques for estimating the flash point of mixtures by correlative and/or predictive models (Moghaddam et al., 2012). There are numerous studies for estimating the flash point of pure compounds and mixtures, but they cannot be easily classified in a sharp manner. Three distinct groups of prediction models can be considered in which the closed-cup procedure is implemented to estimate the flash point of flammable liquid mixtures: a) empirical correlations, b) prediction models based on molecular structure, and c) prediction models based on vapor pressure. Torabian and Sobati (2017) presented new empirical model to predict the flash point of mixtures containing different alcohols. Their model predicted the flash point of mixtures as a function of molar composition and the flash point of pure compounds. Albahri (2015) employed a structural group contribution method to obtain the flash point temperature by two techniques: artificial neural networks and multivariable nonlinear regression. Among the various types of methods applied for the flash point estimation, vapor-pressure based models are theoretically more reliable than empirical models since each parameter in the model has a physical meaning. They are usually established by combining Le Chatelier's rule (Le Chatelier, 1891) with a vapor-liquid equilibrium (VLE) model (Phoon et al., 2014).

Affens and McLaren (1972) established a model by combining Raoult's law, Dalton's law, and Le Chatelier's rule in which the flash point of alkane mixtures was predicted by the flash point and proportions of the individual components. The prediction efficiency of their model was limited to the ideal liquid solution. In the sim-

* Corresponding author.
E-mail address: mnlotfollahi@semnan.ac.ir (M.N. Lotfollahi).

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Nomenclature

List of symbols

a	Temperature dependent attractive term parameter (Pa. m^6. mol^{-2})
b	Co-volume independent-temperature parameter (m^3. mol^{-1})
f	fugacity of a pure compound
f_i	fugacity of component*i* in the mixture
k_{ij}	Binary interaction parameter
n_i	The moles number of component*i*
P	Pressure (Pa)
$P^{fp}_{i,sat}$	Saturated vapor pressure of component *i* at its flash point (Pa)
R	Universal gas constant (J. mol^{-1}. K^{-1})
T	Temperature (K)
T_c	Critical temperature (K)
V	Total volume (m^3)
v	Molar volume (m^3. mol^{-1})
X^{A_i}	Mole fraction of the molecule *i* which does not form bonds at site A
x_i	Mole fraction of component *i* in the liquid mixture
y_i	Mole fraction of component *i* in the vapor mixture
Z	Compressibility factor

Abbreviations

BIP	Binary interaction parameter
CPA	Cubic-Plus-Association
EoS	Equation of state
LFL	Lower flammability limit
n_p	number of points
SRK	Soave-Redlich-Kwong
VLE	Vapor-liquid equilibrium

Superscripts

cal	Calculated
exp	Experimental
fp	Flash point
l	Liquid
v	Vapor

Subscripts

i,j	Component index
fp	Flash point

Greekletters

β	Association energy
ε	Association volume (Pa. m^3. mol^{-1})
Δ	Association strength
ρ	Molar density (mol. m^{-3})
φ	Fugacity coefficient
γ	Activity coefficient

plified form of Affens model proposed by White et al. (1997), the lower flammability limit (LFL) was considered to be a temperature-independent parameter which was only valid for ideal solutions. The Hanley model (Hanley, 1998) was constructed to predict the flash point of a multicomponent mixture by combining the VLE calculation with the LFL and the net heat of combustion. Lee and Ha (2003) presented a model suitable for binary aqueous mixtures by taking into account the VLE and the Clausius-Clapeyron equation. Liaw et al. (2002) proposed a vapor-pressure-based model for ideal and non-ideal binary miscible solutions and extended their model to aqueous-organic (Liaw and Chiu, 2003) and partially miscible mixtures (Liaw et al., 2008). Today, their model, which is widely used, considers the LFL as a temperature-independent parameter and considers an ideal vapor phase above the liquid mixture.

The activity coefficient models such as Margules, Wilson (1964), NRTL (Non-Random Two Liquid) (Renon and Prausnitz, 1968), UNIQUAC (universal quasi-chemical) (Abrams and Prausnitz, 1975), and UNIFAC (universal functional activity coefficient) (Fredenslund et al., 1975, 1977) can be utilized in the Liaw model to take into account liquid phase non-ideality. Although the general model of Liaw provides a highly accurate prediction, this accuracy is strongly dependent on the designated activity coefficient model. Furthermore, most of these models include two or more binary interaction parameters (BIPs) which need binary VLE data as input.

In this study, a vapor-pressure-based model has been constructed to predict the closed-cup flash point of binary miscible mixtures in which the thermodynamic behavior of both liquid and vapor phases are investigated by an equation of state (EoS). In recent years, the cubic-plus-association (CPA) EoS has been able to predict the phase equilibria of many non-ideal systems such as alcohol-hydrocarbon, alcohol-water, glycols-hydrocarbon, glycols-water, amines-hydrocarbon, amines-alcohols/water, alcohols-acid, acids–hydrocarbon and many others (Kontogeorgis and Folas, 2010). Therefore, the CPA EoS was implemented in this study. Furthermore, to increase the accuracy and convenience, the BIP has been calculated by utilizing the experimental flash points data instead of the binary VLE data. The great advantage of this approach is that the binary VLE data are not needed anymore. The proposed model was evaluated in predicting flash point of alkane mixtures because they are abundantly used in most industries. The proposed model was also compared with highly effective models. Accordingly, the binary alkane mixtures utilized by Li et al (Li et al., 2014) were considered. Moreover, non-ideal water-alcohol mixtures due to their own complexity were selected as another practical category to examine the predictive potential of the model.

2. Theory

2.1. Model description

In the closed-cup method, it is assumed that a thermodynamic equilibrium occurs between the liquid and the vapor generated above it. There are two general approaches to investigate the vapor-liquid equilibrium, the γ-φ and the φ-φ approaches. In the γ-φ approach, the thermodynamic behavior of liquid and vapor phases are studied by calculating the activity coefficient of component *i* in the liquid phase (γ_i) to represent the liquid phase non-idiality and by calculating the fugacity coefficient of component *i* in the vapor phase (φ_i) to represent the vapor phase non-ideality, respectively. On the other hand, in the φ-φ approach, an EoS describes the non-idealities of both liquid and vapor phases. As a matter of fact, the γ-φ approach has been used to predict the flash points with the Liaw and similar models (In, 2015; Liaw et al., 2002; Moghaddam et al., 2012). In this research, the φ-φ approach has been applied to predict the flash points.

The CPA EoS is a combination of a simple EoS such as Soave-Redlich-Kwong (SRK) EoS (Soave, 1972) and an association term to account for hydrogen bonding effects in associating compounds (those compounds that can form hydrogen bonds) such as water and alcohols as follows (Kontogeorgis and Folas, 2010):

$$P = P^{SRK} + P^{Association} = \left(\frac{RT}{v-b} - \frac{a}{v(v+b)}\right) + \left(-\frac{1}{2}\frac{RT}{v}\left(1+\rho\frac{\partial \ln g}{\partial \rho}\right)\sum_i x_i \sum_{A_i}\left(1-X_{A_i}\right)\right) \quad (1)$$