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A new method for the prediction of flash points for ternary miscible mixtures

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ABSTRACT

The flash point is one of the most important physicochemical parameters used to characterize the fire and explosion hazard for flammable liquids. The flash points of ternary miscible mixtures with different components and compositions were measured in this study. Four model input parameters, being normal boiling point, the standard enthalpy of vaporization, the average number of carbon atoms and the stoichiometric concentration of the gas phase for mixtures, were employed and calculated based on the theory of vapor–liquid equilibrium. Both multiple linear regression (MLR) and multiple nonlinear regression (MNR) methods were applied to develop prediction models for the flash points of ternary miscible mixtures. The developed predictive models were validated using data measured experimentally as well as taking data on flash points of ternairy mixtures from the literature. Results showed that the obtained average absolute error of both the MLR and the MNR model for all the datasets were within the range of experimental error of flash point measurements. It is shown that the presented models can be effectively used to predict the flash points of ternary mixtures with only some common physicochemical parameters.

1. Introduction

The flash point (FP) of a pure liquid or mixtures of liquids is defined as the lowest temperature at which sufficient material is vaporized to form an ignitable mixture in air under the specified test conditions (AIChE/CCPS, 1993). It is one of the major properties used to assess the fire and explosion hazards of a flammable liquid. This parameter is of importance in the practice of safety considerations in storing, processing, and handling given compounds.

The flash point of a substance can be obtained from the chemical manufacturer's Material Safety Data Sheets (MSDSs) (MSDS, 2014), Lange's Handbook of Chemistry (Dean, 1999) or from the Design Institute of Physical Properties (DIPPR) database of the American Institute of Chemical Engineers (DIPPR, 2006). The flash points of mixed liquids are less commonly reported. Experimental measurement is the most effective and reliable way to obtain flash point data of mixtures. However, it is also considered to be very dependent on the test apparatus and test methods (Gmehling and Rasmussen, 1982; Lance et al., 1979). Furthermore, the measuring process is resource- and time-consuming. For toxic and radioactive compounds, the process is more difficult or even impossible. Therefore, the development of theoretical prediction methods that are convenient and reliable in predicting the flash points of mixtures is desirably required and is an ongoing research field.

Many researchers have developed prediction models to estimate the FP of binary liquid mixtures (Affens and McLaren, 1972; Gmehling and Rasmussen, 1982; Hanley, 1998; Liaw and Chiu, 2003, 2006; Liaw et al., 2002, 2008a, 2008b; Vidal et al., 2006; White et al., 1997), but little for ternary mixtures.

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Recently, Liaw et al. (2004, 2009, 2010, 2011), Liaw and Chen (2013), Liaw and Tsai (2013) successfully proposed a series of mathematical models to predict the flash points of ternary mixtures for both non-ideal and ideal solutions. Furthermore, they found that the minimum flash point behavior (i.e., the flash points lower than those of the pure components) for a binary highly non-ideal solution may disappear on addition of a specific third component, such as the minimum flash point for methanol + methyl acrylate becomes less pronounced when a third component, methyl acetate, is added. If the mole fraction of methyl acetate is increased to 0.3, the minimum flash point increases, while when the mole fraction is increased to more than 0.4, the minimum flash point disappears (Liaw et al., 2004), e.g., the minimum flash point of the ternary mixture should be higher than the lower flash point of one of the three components to make it disappear, higher than two out of three flash points, etc.

Meanwhile, empirical methods have also been developed for predicting the FP of mixtures. Garland and Malcolm (2002) developed a statistical model to predict the flash point of an organic acid–water solution. Kim and Lee (2010) proposed a predictive model based on the partial least squares (PLS) method, and the results were compared with those from the calculated methods using physicochemical laws such as Raoult's law and the Van Laar equation. Catoire et al. developed an equation based on pure compound predictions involving vaporization enthalpy, boiling point, and the number of carbon atoms (Catoire and Naudet, 2005) and later extended this equation to mixtures (Catoire et al., 2005, 2006).

The objective of this study is to provide a new empirical method to estimate the FP of ternary miscible mixtures as applied in hazard assessment and process design.

2. Materials and methods

2.1. Data sets

The data set for this study consists of 182 data points, all of which were determined experimentally. Based on the ASTM7094 standard, the flash points of five sets of common and frequently used mixtures (2-propanol + methanol + butanone; 1-amyl alcohol + methanol + n-heptane; n-octane + methanol + n-heptane; ethylene glycol monobutyl ether + methanol + n-heptane, and alcohol + toluene +butanone) with different compositions were measured using a Grabner FLPH Miniflash Tester (Grabner, Austria).

2.2. Determination and calculation of input parameters

There are many physicochemical properties associated with the flash point of mixed liquids. Most of the existing prediction models of flash points have employed some particular properties as input parameters, such as normal boiling point and lower flammable limit (LFL). Hshieh (1997) proposed a prediction model of flash points for silicone and general organic compounds using boiling points as input parameters. Jones (1998) developed a prediction model based on three correlated parameters, being enthalpy of vaporization, vapor pressure, and lower flammable limit to calculate the flash points of hydrocarbons, and this model worked well. Similarly, Catoire et al. (2005, 2006) developed equations to predict the flash points of both binary and ternary mixtures based on three correlated parameters, being the normal boiling point, the number of carbon atoms in the vapor phase, and the standard enthalpy of vaporization.

The flash point of a liquid mixture is the temperature at which the vapor pressure curve crosses the lower flammable limit (LFL) (Mashuga and Crowl, 1998; Vidal et al., 2004). Kim and Lee (2010) employed the LFL, saturated vapor pressure and mixed mole ratio as input parameters to establish the flash point for mixed liquids. However, the lower flammable limit of a combustible vapor reduces slightly as the temperature increases, which will cause a small but certain error in the prediction of the flash point. In addition, not all lower flammable limit values of chemicals are available from the literature or databases. (Mashuga and Crowl, 2000).

In this study, the normal boiling point (T_b), the standard enthalpy of vaporization ($\Delta_{vap}H_m$), the average number of carbon atoms (n), and stoichiometric concentration (C) in the gas phase were selected as input parameters to characterize flash points of ternary mixed liquids.

For liquid mixtures, the normal boiling point is the temperature at which $\sum_i P_i = 1$ atm, where P_i denotes the partial pressure of the pure component i in the gas phase at the temperature T_b. $P_i = x_i\gamma_i P_i^{sat}$, where x_i denotes the mole fraction of the pure component i in the liquid phase ($\sum_i x_i = 1$), γ_i denotes the activity coefficient of the pure component i in the liquid phase at temperature T_b. P_i^{sat} denotes the saturated vapor pressure of the pure component i at temperature T_b, which can be calculated according to the Antoine equation or obtained from literature. The UNIFAC method was employed to calculate the gas–liquid balance parameters of mixed liquids, and subsequently the normal boiling points of the mixed liquids were calculated by the VLECalc 1.3 program (http://vle-calc.com/index.html).

Within the range of 293.15–308.15 K, the evaporation enthalpy can be considered as a constant. The vapor pressures at three temperatures near 298.15 K (293.15 K, 303.15 K and 308.15 K) were calculated based on the Clausius-Clapeyron equation, the plot of $\ln P \sim 1/T$ was drawn and hence, the standard evaporation enthalpy at 298.15 K was obtained from the slope of this straight line.

The average number of carbon atoms and the stoichiometric concentration in the gas phase for mixtures can be calculated by $n = \sum_i y_i n_i$ and $C = \sum_i y_i C_i$, where n_i is the number of carbon atoms for pure substance i, C_i is the stoichiometric concentration of the flammable component i and y_i is the mole fraction of combustible component i in the vapor phase at the flash point. Because the flash point is unknown, y_i is approximately defined as the mole fraction of component i in the vapor phase at its boiling point (Catoire et al., 2006).

2.3. Modeling methods

In this paper, both the multiple linear regression (MLR) and multiple nonlinear regression (MNR) methods are applied for the prediction models of the flash point. In order to find the relationship between physicochemical properties and the flash points, four parameters of the mixtures were employed as input variables.

For the statistical analysis, the software package SPSS 19 (Pallant, 2010) was used and the linear fit was carried out with 95% confidence interval. Moreover, the data processing system (DPS) available in this software package was employed to perform nonlinear fitting of the relationship between flash points and input parameters, and the corresponding nonlinear prediction model was established. The nonlinear relationship