The Lower Flash Points of the Flammable and Non-flammable Liquid Mixture

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1. INTRODUCTION

The flash point are used to classify combustible liquids according to their relative flammability. The regulations for the safe handling, transportation, and storage of such substances are dependent on this classification, and the flash points are therefore of great important in the chemical industry.[1]

Experimental flash point data for most single component flammable liquids are readily available in the literature. Most published flash point data was for pure components. However, the flash points of mixtures that have a non-flammable component, such as water, have seen little study and the data that did exist was inconsistent. The non-flammable components add to flammable liquids to inhibit the flash. Therefore, the purpose of this study was to measure and predict the lower flash points for these systems to aid in evaluating the safety of flammable and non-flammable liquid mixtures.

Ha et al.[2] performed that experimental lower and upper flash points for binary system were compared with the calculated values by using Raoult's law and Van Laar equation.

The flash points for the system, water+propionic acid, were measured by Pensky-Martens closed cup tester, and compared with the values based on Van Laar equation[3] and Wilson equation[4].

The flash points of the closed cup tester were measured rather than the flash points of the open cup tester, because the open cup tester of multicomponent systems cannot be readily made, due to distillation of the mixture during heating. Further, the flash points of the closed cup tester are most widely used to characterize flammable substance hazards in practice.

2. EXPERIMENTAL SECTION

2-1. Chemicals

Propionic acid was purchased from Acros, USA with a minimum purity of 99.0%, and water was supplied by J.T. Baker, USA. All these chemicals were used directly without any purification.

2-2. Experimental Apparatus and Procedure

Pensky-Martens closed cup tester is used. The apparatus consist of a test cup, cover and stove.

The volume of the test cup is 100 ml and was made of brass. The flange is equipped with devices for locating the position of the test cup in the stove. The cover consists of cover proper, shutter, flame-explosure device, pilot flame and stirring device. Heat is supplied to the cup by means of the stove. The stove consists of an air bath and a top plate.

The pure components are added by mass and the test cup is filled with the mixture (65ml). The mixture is heated at a rate of 5 to 6 K/min with continual stirring (90 to 120 rpm). A small flame is directed into the test cup at regular intervals with simultaneous interruption of stirring. The flash point is the lowest temperature at which application of the test flame causes the vapor above the mixture to ignite.

3. RESULTS AND DISCUSSION

3-1. Experimental Results

The results obtained in this work for the system, water(1)+propionic acid(2), are presented in Table 1. The concentrations of component i are given in mole fraction, x_i .

3-2. Calculation of the Lower Flash Points

The Le Chatelier has presented the following equation for multicomponent mixtures containing flammable compounds.

The following equation applies to vapor-liquid equilibrium.

$$P_i = P_i^0 \alpha_i = P_i^0 \gamma_i x_i \tag{1}$$

where P_i is the partial vapor pressure of component i(mmHg), P_i^0 is the vapor pressure of component i(mmHg), α_i is the activity of component i, γ_i is the activity coefficient of component i and x_i is the mole fraction of component i in the liquid phase.

Assuming vapor-liquid equilibrium in the Pensky-Martens closed cup tester, the Clausius-Clapeyron equation can be applied to binary systems[5].

$$\frac{d\ln P_i}{dT} = \frac{\Delta H_i}{RT^2} \tag{2}$$

where T is the flash point in absolute temperature(K), ΔH_i is the enthalpy of vaporization of component i(kJ/mol), and R is the gas constant, 8.314 (J/mol/K).

The enthalpy of vaporization is a function of temperature and was estimated by use of Watson equation[3] in this study.

Integrating Equation (2), and substituting Equation (1) results in the following:

$$\ln P_i = \ln \left(P_{i,0}^0 \gamma_i x_i \right) + \frac{\Delta H_i}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right) \tag{3}$$

where $P_{i,0}^0$ is the saturated vapor pressure of component i, while T and T_0 are the flash points of the liquid mixture and pure flammable component, respectively.

The saturated vapor pressure variation with temperature for a pure substance can be estimated by the Antoine equation :

$$\ln P_{i,0}^0 = A_i - \frac{B_i}{t + C_i} \tag{4}$$

Below we assume that a flash occurs at the lower limit of flammability in the fuel-air system without the additive,

$$P_1 = P_{1,0}^0 = Constant \tag{5}$$

where the subscript 1 indicates the flammable component.

Substituting Equation (5) into Equation (3),

$$\frac{1}{T^L} = \frac{1}{T_0^L} + \left(\frac{R}{\Delta H_1}\right) \cdot \ln(\gamma_1 \cdot x_1) \tag{6}$$

where the superscript L indicates the lower flash point, T_0^L is the lower flash point temperature of the flammable component, and ΔH_1 is the average of the enthalpy of vaporization near T_0^L.

The activity coefficients(γ_i) were estimated by the Van Laar equation and the Wilson equation and the binary parameters of those equations were abstracted from the literature[6].

The flash points prediction models developed for flammable and non-flammable binary systems included the modified equation of the enthalpy of vaporization, the Antoine equation, the pure flash point value, and a model for estimating activity coefficients.

And included in the tables is the average absolute deviation(A.A.D.) defined as[7]

$$A.A.D. = \sum_{i=1}^{N} \left(\frac{|T_i^{\exp} - T_i^{cal}|}{N}\right) \tag{7}$$

The A.A.D. is a measure of agreement between the experimental data and the calculated values.

The calculated values based on both the Van Laar equation and the Wilson equation gave good representation of the experimental data for the system, water+acetic acid acid. However, the Wilson equation is more accutate than the Van Laar equation, as can be seen from the A.A.D..

Table 1. The experimental data and the calculated values
for water(X_1)+propionic acid(X_2) system

Mole fraction		Flash point (C)		
X_1	X_2	Exp.	Van Laar	Wilson
0.690	0.310	62	66.24	63.27
0.596	0.404	59	64.30	61.45
0.513	0.487	58	62.44	59.95
0.306	0.694	55	57.38	56.22
0.220	0.780	54	55.23	54.58
0.136	0.864	53	53.15	52.58
0.000	1.000	50	50	50
A.A.D.	-	-	2.54	1.13

4. CONCLUSION

The flash points for the binary system containing non-flammable component, water, were measured by Pensky-Martens closed cup tester. The experimental data were compared with the values calculated by the Van Laar equation and the Wilson equation. Good qualitative agreement was obtained with these equations. However, the calculated values based on Wilson equation were found to be better than those based on Van Laar equation.

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