

The Lower Flash Points of Binary Systems Containing Non-flammable Component

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

Key words: Lower Flash Points, Non-flammable, Water, Pensky-Martens Closed Cup Tester, Van Laar Equation, Wilson Equation

INTRODUCTION

Flash points are used to classify combustible liquids according to their relative flammability [Crowl and Louvar, 1990]. 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 importance in the chemical industry.

Experimental flash point data for most single component flammable liquids are readily available in the literature. Most published flash point data are 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 do exist are 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. [1999] performed that the experimental lower and upper flash points for flammable liquid mixtures were compared with the calculated values by Raoult's law and the Van Laar equation.

The flash points for the systems, water+acetic acid and water+propionic acid, were measured by Pensky-Martens closed cup tester, and compared with the values based on the Van Laar equation [Reid et al., 1998] and Wilson equation [Wilson, 1964].

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.

FLASH POINT

Flammable substances are those gases, liquids and solids that will ignite and continue to burn in air if exposed to a source of ignition.

Many flammable and combustible liquids are volatile in nature;

that is, they evaporate quickly and are continually giving off vapors. The rate of evaporation varies greatly from one liquid to another and increases with temperature. It is their vapors combined with air, not the liquid or solids themselves, that ignite and burn. In many instances, an increase in temperature creates a more hazardous condition because of the increase in the rate at which vapors are evolved.

The flash point is defined by the National Fire Protection Association [NFPA, 1991] as the lowest temperature at which a flammable liquid gives off sufficient vapor to form an ignitable mixture with air near its surface or within a vessel. The open cup (O.C.) flash points are generally somewhat higher than the closed cup (C.C.) flash points for same materials. Special precautions should be taken when the product has a low flash point. Materials having a low flash point are a greater fire hazard than materials having a high flash point.

EXPERIMENTAL SECTION

1. Chemicals

Acetic acid was purchased from Junsei, Japan with a minimum purity of 99.7%, and propionic acid from Acros, USA with a minimum purity 99%. Water was supplied by J. T. Baker, USA. All these chemicals were used directly without any purification.

Two mixtures were selected for the samples: water+acetic acid and water+propionic acid systems.

2. Experimental Apparatus and Procedure

The basic system configuration of Pensky-Martens closed cup tester [ASTM, 1994] is given in Fig. 1. 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 (65 ml). 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 interrup-

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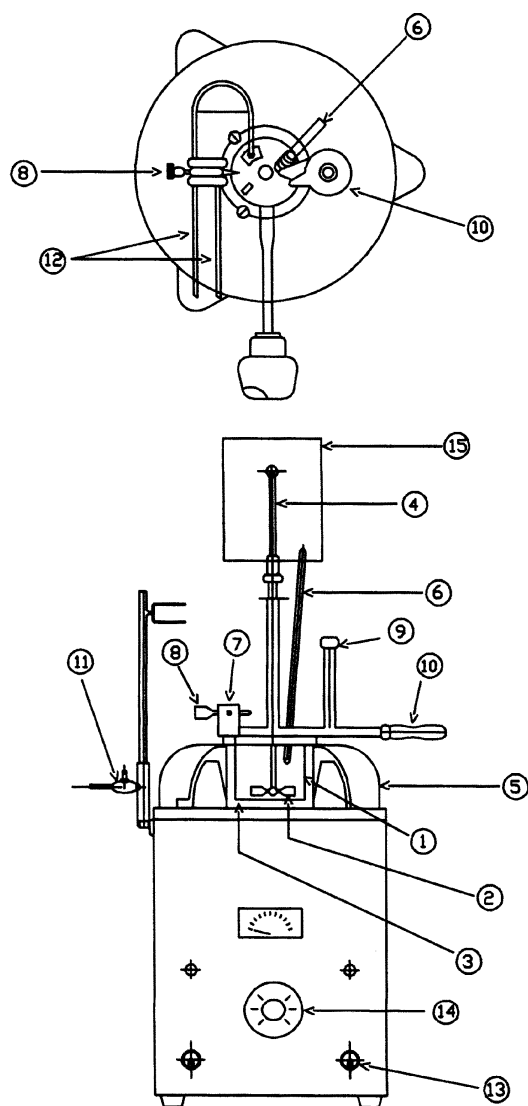


Fig. 1. Schematic diagram of experimental apparatus.

- | | |
|--------------------------|---------------------------|
| 1. Test cup | 9. Shutter operating knob |
| 2. Stirrer | 10. Test cup handle |
| 3. Flexible shaft | 11. Gas safety valve |
| 4. Air bath | 12. Gas pipe |
| 5. Top plate | 13. Electric switch |
| 6. Thermocouple | 14. Electric regulator |
| 7. Flame exposure device | 15. Electric motor |
| 8. Flame regulator | |

tion of stirring. The flash point is the lowest temperature at which application of the test flame causes the vapor above the mixture to ignite.

RESULTS AND DISCUSSION

1. Experimental Results

The results obtained in this work for the systems, water(1)+acetic acid(2) and water(1)+propionic acid(2), are presented in Table 1 and Table 2, respectively. Concentrations of component *i* are given in mole fraction, x_i .

As shown in Fig. 2 and Fig. 3, the lower flash points of the sys-

Table 1. The experimental data and the calculated values for the system, water (x_1)+acetic acid (x_2)

Mole fraction		Flash point (°C)		
x_1	x_2	Exp.	Van Laar	Wilson
0.707	0.293	70	73.27	70.95
0.605	0.395	59	66.08	64.07
0.506	0.494	57	60.57	59.02
0.394	0.606	51	55.27	54.27
0.312	0.688	50	51.82	51.17
0.211	0.789	43	47.95	47.65
0.111	0.889	43	44.45	44.37
0.000	1.000	41	41	41
A.A.D.	-	-	3.23	2.31

Table 2. The experimental data and the calculated values for the system, water (x_1)+propionic acid (x_2)

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

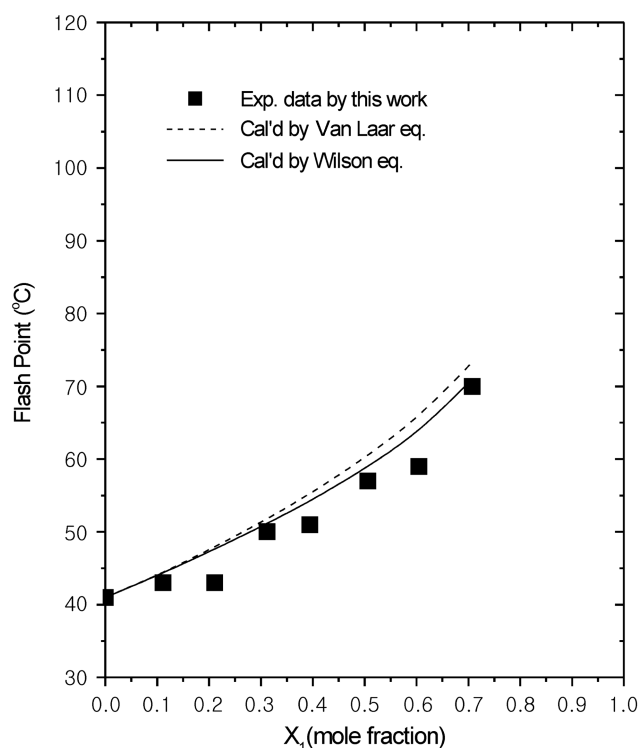


Fig. 2. Comparison the experimental data with the calculated values for the system, water (x_1)+acetic acid (x_2).

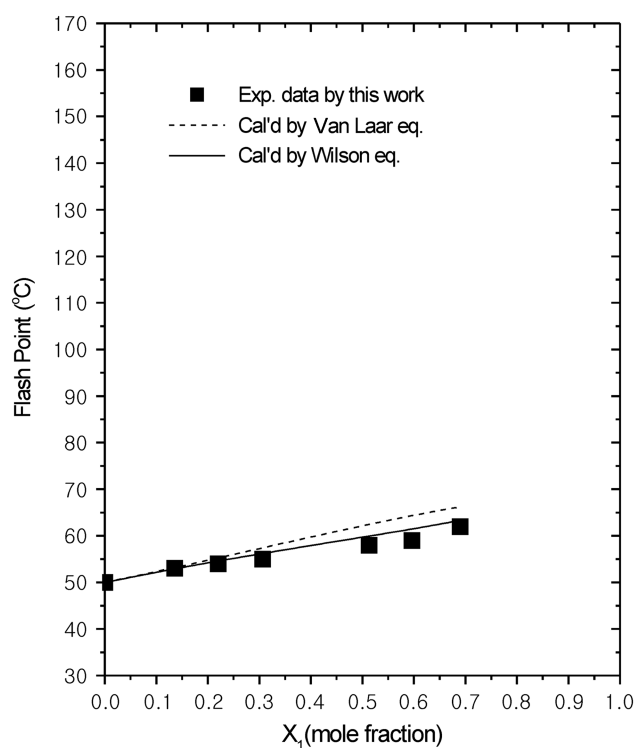


Fig. 3. Comparison the experimental data with the calculated values for the system, water (x_1) + propionic acid (x_2).

tems plotted as a function of water concentration. As water concentration increased, the lower flash points also increased.

2. Calculation of the Lower Flash Points

The following equation applies to vapor-liquid equilibrium:

$$P_i = P_i^0 \alpha_i = P_i^0 \gamma_i x_i \quad (1)$$

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 [Godefroy and Jones, 2002].

$$\frac{d \ln P_i}{dT} = \frac{\Delta H_i}{RT^2} \quad (2)$$

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 the use of the Watson equation [Reid et al., 1998] in this study.

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

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

where P_i^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.

Table 3. The Antoine coefficients of the components

Components	A	B	C
Water	8.07131	1730.63	233.426
Acetic acid	8.021	1936.01	258.451
Propionic acid	7.99064	1929.3	236.43

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

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

The Antoine coefficients, A_i , B_i and C_i , for these species were adapted from the literature [Reid et al., 1998] and are listed in Table 3.

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

$$P_1 = P_{1,0}^0 = \text{Constant} \quad (5)$$

where the subscript 1 indicates the flammable component.

Substituting Eq. (5) into Eq. (3),

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

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 [Gmehling et al., 1980] and are listed in Table 4.

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 [Park et al., 1996]

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

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

The calculated values using both the Van Laar equation and the Wilson equation for the systems are presented in Fig. 2 and Fig. 3.

Fig. 2 graphically shows the relationship between experimental and predicted flash point for water+acetic acid system, and Fig. 3 shows water+propionic acid system.

The calculated values based on both the Van Laar equation and the Wilson equation gave good representation of the experimental

Table 4. The parameters of the Van Laar and Wilson equations

Systems	Van Laar equation		Wilson equation ^a	
	A_{12}	A_{21}	A_{12}	A_{21}
Water+acetic acid	0.5203	1.1066	731.7231	107.2566
Water+propionic acid	0.9330	2.1748	1215.6694	500.9146

^aWilson: $A_{12} = (\lambda_{12} - \lambda_{11})/R$, $A_{21} = (\lambda_{21} - \lambda_{22})/R$.

data for the systems, water+acetic acid and water+propionic acid. However, the Wilson equation is more accurate than the Van Laar equation, as can be seen from the A.A.D. in Table 1 and Table 2. This is the reason that the Wilson equation was more effective than the Van Laar equation at describing the activity coefficients for strongly non-ideal solution systems, water+acetic acid and water+propionic acid [Reid et al., 1998].

CONCLUSION

The flash points for two binary systems 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.

NOMENCLATURE

A_i, B_i, C_i : Antoine coefficients of component i
 ΔH_i : enthalpy of vaporization of component i [kJ/mol]
 N : number of data
 P_i : partial vapor pressure of component i [mmHg]
 P_i^0 : vapor pressure of component i [mmHg]
 $P_{i,0}^0$: saturated vapor pressure of component i [mmHg]
 R : universal gas constant [J/mol-K]
 T : flash point of liquid mixture [K]
 T_0 : flash point of pure flammable component [K]
 T^L : lower flash point of liquid mixture [K]
 T_0^L : lower flash point of the flammable component [K]
 T_i^{exp} : experimental flash point of component i [K]
 T_i^{cal} : calculated flash point of component i [K]

x_i : mole fraction of component i

Greek Letters

α_i : activity of component i

γ_i : activity coefficient of component i

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