

## Measurement and estimation of the lower flash points for the flammable binary systems using a Tag open cup tester

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**Abstract**—Lower flash points for flammable binary systems, ethylbenzene+n-propanol, n-propionic acid+ethylbenzene and n-propionic acid+o-xylene, were measured by Tag open cup tester. These binary solutions exhibited the minimum flash point behavior, which leads to a minimum on the flash point vs composition curve. The experimental data were compared with the values calculated by the flash point prediction models based on the van Laar and Wilson equations. As can be seen from the A.A.D., 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, Tag Open Cup Tester, van Laar Equation, Wilson Equation, Minimum Flash Point Behavior

### INTRODUCTION

The lower flash point is the lowest temperature at which application of a test flame causes the vapor of a specimen to ignite under specified test conditions. To form a flammable vapor-air mixture above the surface of a flammable liquid solution, the temperature of the solution must be sufficiently high to produce vapor concentration above the solution surface at or above the lower flammability limit (LFL) of the vapor. In other words, the lower flash point is the temperature at which the vapor pressure divided by the pressure of the atmosphere is equal to the LFL expressed in mole fraction [1].

The flash point is the best known and most widely used flammability property for the evaluation of the flammability hazard of combustible liquids. It is an important criterion for the fire-hazard rating of these liquids [2,3]. A liquid that exhibits a flash point value below ambient temperature, and can thus give rise to flammable mixtures under ambient conditions, is generally considered to be more hazardous than one reflecting a higher flash point [4].

Affens and McLaren [5] have developed a model based upon Raoult's law, in order to predict the flash point for hydrocarbon solutions. White et al. [6] reduced Affens and McLaren's model to a simpler equation by ignoring the temperature effect upon the LFL. However, neither the Affens and McLaren's model nor the equation of White et al. is able to effectively predict the measured the flash point for a non-ideal solution [7]. Ha et al. [8,9] predicted the lower and upper flash point for a non-ideal solution. Ha et al. [10,11] developed a model based on Raoult's law and van Laar equation, in order to estimate the lower flash point for the binary mixtures containing non-flammable component.

The experimental flash point data are readily available in several literatures. However, the most published flash point data was for pure components and the flash points of the binary solution that

have flammable components, have seen a little study and the data that did exist was inconsistent. Therefore, the purpose of this study was to measure and predict the lower flash points for the system to aid in evaluating the safety of flammable liquid mixtures.

The lower flash points for the three binary solutions, ethylbenzene+n-propanol, n-propionic acid+ethylbenzene and n-propionic acid+o-xylene, were measured by Tag open cup tester, and compared with the values calculated by using the flash point prediction models based on the van Laar [12] and Wilson equations [13].

### FLASH POINT AND FLAMMABLE LIMIT

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 continually give 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 [14] 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.

Flammable limits refer to the range of flammable gas or vapor concentrations between which ignition will occur if an ignition source is present. The LFL is the lower flammable limit; the UFL is the upper flammable limit. All concentrations between LFL and UFL are in the flammable range, and special precautions are needed to prevent ignition or explosion.

### EXPERIMENTAL SECTION

#### 1. Chemicals

Ethylbenzene was purchased from Samchun Chem. Co., Korea

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with a minimum purity of 99.8% and o-xylene from Lancaster, with a minimum purity of 99.0%. n-Propionic acid was supplied from Acros Organics, USA with a minimum purity of 99.0%. The minimum purity of n-propanol from Carlo Erba Co. was 99.5%. All these chemicals were used directly without any purification.

Three mixtures were selected for the samples: ethylbenzene(1)+n-propanol(2), n-propionic acid(1)+ethylbenzene(2) and n-propionic acid(1)+o-xylene(2).

## 2. Experimental Apparatus and Procedure

The basic system configuration of the Tag open cup tester manufactured by Koehler Instrument Co. is given in Fig. 1. The apparatus consists of a sample cup, water bath, test flame device, level gauge, electrical heater, overflow path, thermometer and temperature controller [15].

The Tag open cup tester is operated according to the standard test method, ASTM D 1310-86 [16]. The pure component is added by mass and the sample cup (70 ml) is filled with the mixture. The water bath is heated with electrical heater, adjusting the heat so that the solution temperature increases at a rate of  $1 \pm 0.25$  °C/min. A test flame is passed at a uniform rate across the sample cup at a specific interval, 0.5 K until a flash occurs. The lower flash point is recorded as the lowest temperature of the bulk at which this results in a flash.

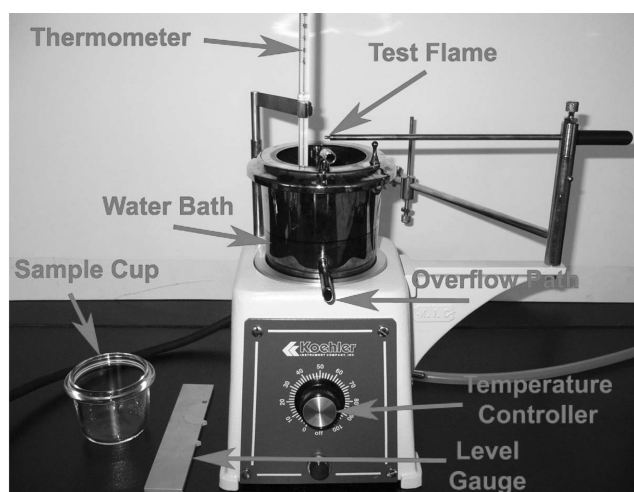


Fig. 1. The basic system configuration of the Tag open cup tester.

Table 1. The experimental and the calculated flash points for the ethylbenzene(1)+n-propanol(2) system

Mole fractions		Flash points (°C)		
$x_1$	$x_2$	Exp.	van Laar	Wilson
0.000	1.000	28.5	-	-
0.099	0.901	25.5	25.96	25.31
0.205	0.795	23.0	24.77	23.96
0.304	0.696	23.0	24.29	23.42
0.508	0.492	21.5	24.10	23.16
0.705	0.295	22.0	24.63	23.53
0.908	0.092	27.0	27.18	25.87
1.000	0.000	30.5	-	-
A.A.D.	-	-	1.49	0.98

Table 2. The experimental and the calculated flash points for the n-propionic acid(1)+ethylbenzene(2) system

Mole fractions		Flash points (°C)		
$x_1$	$x_2$	Exp.	van Laar	Wilson
0.000	1.000	30.5	-	-
0.098	0.902	28.5	31.01	30.63
0.296	0.704	32.0	32.34	31.76
0.501	0.499	34.0	34.54	34.14
0.701	0.299	40.0	38.85	38.75
0.903	0.097	47.0	48.73	48.78
1.000	0.000	59.0	-	-
A.A.D.	-	-	1.25	1.11

Table 3. The experimental and the calculated flash points for the n-propionic acid(1)+o-xylene(2) system

Mole fractions		Flash points (°C)		
$x_1$	$x_2$	Exp.	van Laar	Wilson
0.000	1.000	37.0	-	-
0.092	0.908	36.5	37.16	36.74
0.298	0.702	39.0	38.22	37.54
0.501	0.499	39.5	40.00	39.34
0.703	0.297	41.0	43.50	43.02
0.900	0.100	54.5	51.10	50.85
1.000	0.000	59.0	-	-
A.A.D.	-	-	1.57	1.51

## RESULTS AND DISCUSSION

### 1. Experimental Results

The results obtained in this work for the systems, ethylbenzene+n-propanol, n-propionic acid+ethylbenzene and n-propionic acid+o-xylene, are presented in Tables 1-3 and Figs. 2-4.

The concentrations of component  $i$  are given in mole fraction,  $x_i$ . As shown in Figs. 2-4, the lower flash points of the flammable binary systems are plotted as a function of mole fraction.

### 2. Mathematical Formulation for the Lower Flash Point Prediction of the Flammable Binary Mixture

Le Chatelier's rule [17] for a flammable vapor-air mixture of multicomponents is as follows:

$$\sum_{i=1}^N \frac{y_i}{\text{LFL}_i} = 1 \quad (1)$$

where  $y_i$  is the composition of a flammable substance  $i$  in the vapor phase, and  $\text{LFL}_i$  is the lower flammable limit (LFL) of the pure component  $i$ . From the definition of the flash point, the  $\text{LFL}_i$  is expressed relative to its saturated vapor pressure at flash point,  $P_{i,fp}^{sat}$ , as:

$$\text{LFL}_i = \frac{P_{i,fp}^{sat}}{P} \quad (2)$$

where  $P$  is the ambient pressure. The composition of flammable substance  $i$  in the vapor phase,  $y_i$ , can be derived from the vapor-liquid equilibrium (VLE).

For every component  $i$  in the mixture, the condition for equilib-

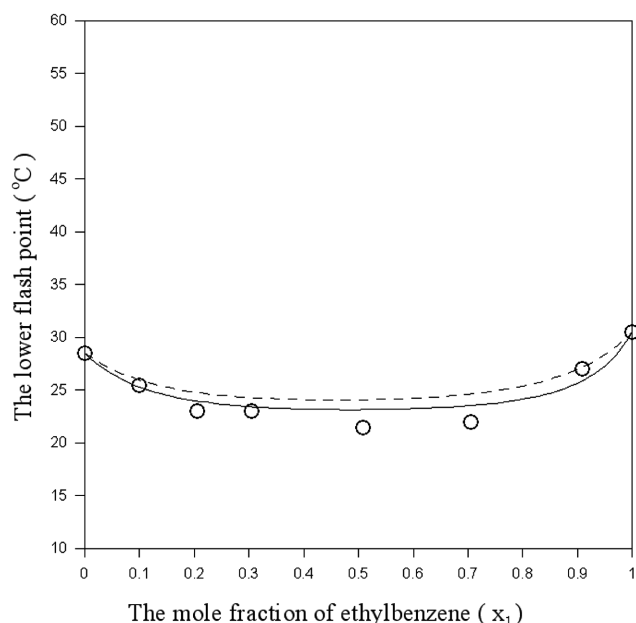


Fig. 2. A comparison of the lower flash point prediction curves with the experimental data for the ethylbenzene(1)+n-propanol(2) system: experimental data by this work (○), calculated values based on the Wilson equation (—), calculated values based on the van Laar equation (---).

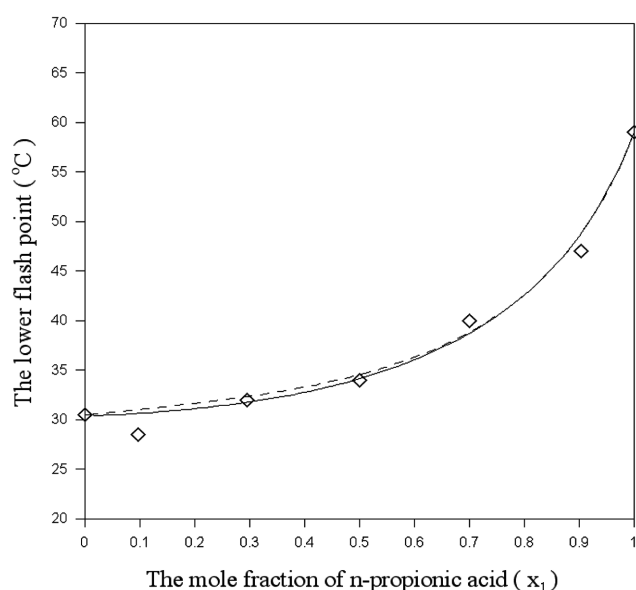


Fig. 3. A comparison of the lower flash point prediction curves with the experimental data for the n-propionic acid(1)+ethylbenzene(2) system: experimental data by this work (◇), calculated values based on the Wilson equation (—), calculated values based on the van Laar equation (---).

rium between a liquid phase and a vapor phase at the same  $T$  and  $P$  is given by:

$$y_i \Phi_i P = x_i \gamma_i f_i \quad (i=1, 2, \dots, N) \quad (3)$$

At low pressure, the vapor phase can be approximated as an ideal gas, then the vapor phase solution's fugacity coefficient for compo-

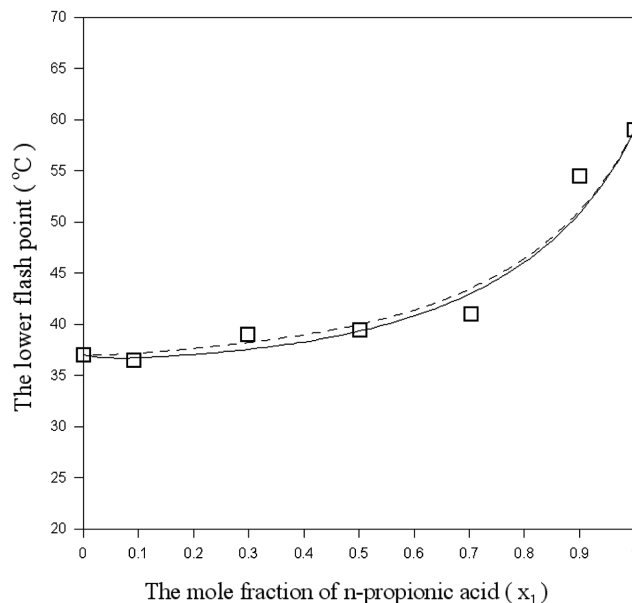


Fig. 4. A comparison of the lower flash point prediction curves with the experimental data for the n-propionic acid(1)+o-xylene(2) system: experimental data by this work (□), calculated values based on the Wilson equation (—), calculated values based on the van Laar equation (---).

nent is reduced to:

$$\Phi_i = 1 \quad (4)$$

and the fugacity of pure liquid  $i$ , at the temperature and pressure of the system can be simplified as:

$$f_i \cong P_i^{sat} \quad (5)$$

where  $P_i^{sat}$  is the vapor pressure of pure  $i$  at the system temperature. Therefore, the vapor-liquid equilibrium relation is reduced as:

$$y_i P = x_i \gamma_i P_i^{sat} \quad (6)$$

or

$$y_i = \frac{x_i \gamma_i P_i^{sat}}{P} \quad (7)$$

Substitution Eq. (2) and Eq. (7) into Eq. (1) results in:

$$\sum_{i=1}^N \frac{x_i \gamma_i P_i^{sat}}{P_{i,fp}^{sat}} = \frac{x_1 \gamma_1 P_1^{sat}}{P_{1,fp}^{sat}} + \frac{x_2 \gamma_2 P_2^{sat}}{P_{2,fp}^{sat}} = 1 \quad (8)$$

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

$$\log P_i^{sat} = A_i - \frac{B_i}{T + C_i} \quad (9)$$

where  $A_i$ ,  $B_i$  and  $C_i$  are the Antoine coefficients and  $T$  is the temperature in degree Celsius (°C). The Antoine coefficients,  $A_i$ ,  $B_i$  and  $C_i$ , were adapted from the literature [12] and are listed in Table 4.

The vapor pressure of pure substance  $i$  at its flash point  $P_{i,fp}^{sat}$ , as presented in Eq. (8), can be estimated by substituting  $T_{i,fp}$ , the flash point of component  $i$ , into the Antoine equation.

The activity coefficients ( $\gamma_i$ ), which were presented in Eq. (8),

**Table 4. The Antoine coefficients of the components**

Components	Coefficients		
	A	B	C
n-Propanol	8.3789	1788.02	227.438
n-Propionic Acid	7.9906	1929.30	236.430
Ethylbenzene	6.9658	1429.55	213.767
o-Xylene	7.0015	1476.393	213.872

can be estimated by the use of two different equations, such as the van Laar equation and the Wilson equation. The binary parameters of those equations were abstracted from the literature [18] and are listed in Table 5.

The flash point-prediction model developed for the flammable binary mixture included the modified equation of Le Chatelier, the Antoine equation, and the models for estimating activity coefficients. These are described using Eq. (8) and Eq. (9) and the models for estimating activity coefficients (the van Laar equation and Wilson equation). The temperature, which satisfies these equations, is deemed by us to be the lower flash points of the flammable binary mixture [7].

### 3. The Comparison of the Predicted and Measured Lower Flash Points

In this study, the flash point prediction models proposed in section 2 were used to predict the flash points of the binary systems, ethylbenzene+n-propanol, n-propionic acid+ethylbenzene and n-propionic acid+o-xylene. The prediction results obtained were presented in Table 1-3 and Fig. 2-4.

And included in Table 1-3 is the A.A.D. (average absolute deviation) defined [19] as follows:

$$\text{A.A.D.} = \frac{\sum_{i=1}^N |T_i^{\text{exp}} - T_i^{\text{cal}}|}{N} \quad (12)$$

where the A.A.D. is a measure of agreement between the experimental data and the calculated values, the  $T_i^{\text{exp}}$  is the experimental lower flash point of component  $i$ , and  $T_i^{\text{cal}}$  is the estimated lower flash point of component  $i$ .

As can be seen from Fig. 2-4, the experimental results are in good agreement with the predictive curves, which use the van Laar and Wilson equations to estimate the activity coefficients.

Tables 1-3 also depict the results of comparing the predictive curves of the flash point prediction model using different equations for estimating the corresponding activity coefficients. The Wilson equation is more accurate than the van Laar equation, as can be seen from the A.A.D. in Tables 1-3. This is the reason that the Wilson equation was more effective than the van Laar equation at describing the activity coefficients for non-ideal solution systems, ethyl-

benzene+n-propanol, n-propionic acid+ethylbenzene and n-propionic acid+o-xylene [12].

### 4. Minimum Flash Point Behavior

The surprising finding for the binary solutions of ethylbenzene+n-propanol, n-propionic acid+ethylbenzene and n-propionic acid+o-xylene, was that the flash points of the solutions over a wide or narrow composition range were lower than those recorded for the individual solution components, i.e., these solutions exhibit the minimum flash point behavior.

The minimum value of the flash point for a binary solution is not necessarily equivalent to that of individual component displaying the lower value. It may be equivalent to a value for a specific composition located somewhere between the composition values for the individual components. This phenomenon is attributable to the observation that this particular non-ideal solutions reflects a highly-positive deviation from the behavior of an ideal solution, for which the activity coefficients are observed to be much larger than unity, that such behavior results in a substantial reduction of the solutions' flash point [7]. By contrast, another highly non-ideal solution, methyl acetate+methanol, does not exhibit minimum flash point behavior, although it does reveal a minimum boiling azeotrope at 101.3 kPa [20].

Clearly, not all liquid solutions, which reveal a minimum boiling azeotrope, are able to exhibit minimum flash-point behavior. Therefore, it must be emphasized that chemical process safety design based upon the lower flash point value of individual solution components cannot necessarily be guaranteed safe for a binary solution because the resultant solution may reveal minimum flash point behavior [7].

## CONCLUSION

The flash points for the binary systems, ethylbenzene+n-propanol, n-propionic acid+ethylbenzene and n-propionic acid+o-xylene, were measured by Tag open cup tester.

The experimental data were compared with the values calculated by the flash point models based on the van Laar and Wilson equations. The experimental results are in good agreement with the predictive curves, which use the van Laar and Wilson equation to estimate activity coefficients. However, the predictive curve of the flash point prediction model based on the Willson equation described the experimentally-derived data more effectively than was the case when the prediction model was based upon the van Laar equation.

The prediction results of this model can thus be applied to incorporate inherently safer design for chemical processes, such as the determination of the safe storage conditions for highly non-ideal solutions containing flammable components.

It is important to emphasize here that some highly non-ideal so-

**Table 5. The binary parameters of the van Laar and Wilson equations for each binary system**

Systems	Parameters		Wilson*			
	van Laar					
	A <sub>12</sub>	A <sub>21</sub>	A <sub>12</sub>	A <sub>21</sub>	V <sub>1</sub> <sup>L</sup>	V <sub>2</sub> <sup>L</sup>
Ethylbenzene(1)+n-Propanol(2)	1.3297	12417	234.0213	950.7209	123.07	75.14
n-Propionic acid(1)+Ethylbenzene(2)	1.3743	0.7223	1565.483	-410.1934	74.98	123.07
n-Propionic acid(1)+o-Xylene(2)	1.252	0.7636	1375.7728	-319.1018	74.98	121.2

\* Wilson: A<sub>12</sub>=λ<sub>12</sub>-λ<sub>11</sub>, A<sub>21</sub>=λ<sub>21</sub>-λ<sub>22</sub> (cal/mol).

lutions, such as ethylbenzene+n-propanol, n-propionic acid+ethylbenzene and n-propionic acid+o-xylene, may exhibit the minimum in the flash point vs. composition curve.

## NOMENCLATURE

A, B, C : Antoine coefficients  
 $f$  : fugacity [mmHg]  
 LFL : lower flammable limit  
 N : number of data  
 $P$  : ambient pressure [mmHg]  
 $P^{sat}$  : saturated vapor pressure [mmHg]  
 $P_i^{sat}$  : saturated vapor pressure of component  $i$  at flash point [mmHg]  
 $T$  : temperature [ $^{\circ}\text{C}$ ]  
 $T^{cal}$  : calculated flash point temperature [ $^{\circ}\text{C}$ ]  
 $T^{exp}$  : experimentally derived flash point temperature [ $^{\circ}\text{C}$ ]  
 $T_{i,fp}$  : flash point temperature of pure component  $i$  [ $^{\circ}\text{C}$ ]  
 $x$  : liquid phase composition  
 $y$  : vapor phase composition

## Greek Letters

$\Phi$  : fugacity coefficient  
 $\gamma$  : activity coefficient

## Superscripts

sat : saturated  
 exp : experimental value  
 cal : calculated value

## Subscripts

fp : flash point  
 $i$  : species  $i$

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