

Prediction and measurement of the lower flash points for flammable binary solutions by using a setaflash closed cup tester

Dong-Myeong Ha^{*,†} and Sungjin Lee^{**}

^{*}Department of Occupational Health and Safety Engineering, Semyung University, Jecheon 390-711, Korea

^{**}Department of Clinical Laboratory Science, Semyung University, Jecheon 390-711, Korea

(Received 14 March 2010 • accepted 10 November 2010)

Abstract—The flash point is one of the most important physical properties used to determine the potential for fire and explosion hazards of industrial materials. The purpose of this study was to measure and predict the lower flash points for the binary mixtures to aid in evaluating the safety of flammable liquid mixtures. The lower flash points for the flammable binary systems, n-hexanol+propionic acid, n-butyric acid+m-xylene and n-pentanol+n-butanol, were measured by Setaflash closed cup tester. The experimentally derived data were correlated with the Wilson and UNIQUAC (UNiversal QUasi Chemical) equations using the binary interaction parameters. Both equations correlated with a good accuracy.

Key words: Lower Flash Points, Setaflash Closed Cup Tester, Wilson Equation, UNIQUAC Equation, Binary Interaction Parameter

INTRODUCTION

The flash point is the lowest temperature at which a liquid produces flammable vapor near its surface that ignites spontaneously when brought in contact with air and a spark or a flame [1].

The flash point is one of the most important physical properties used to determine the potential for fire and explosion hazards of industrial materials [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] developed a predictive model for the flash points of binary hydrocarbon mixtures using Raoult's law. White et al. [6] reduced Affens and McLaren's model to a simpler equation by ignoring any dependence of the lower flammable limit (LFL) on temperature. 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.

Liaw et al. [7] developed a mathematical model for the flash points of highly non-ideal solutions using activity coefficient models, such as Wilson, NRTL and UNIQUAC models. Surely, the Liaw's model needs the binary interaction parameters of activity coefficient model to calculate the flash points. Without the binary interaction parameters, Liaw's model cannot predict the flash points for the binary solutions.

Lately, Ha et al. [8] measured the lower flash points of the binary solutions that exhibited the minimum flash point behavior and calculated the flash points by using the prediction models based on the van Laar and Wilson equations.

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 solutions that have flammable components appear to be scarce in the literature.

The purpose of this study was to measure and predict the lower flash points for the binary mixtures to aid in evaluating the safety of flammable liquid mixtures.

The lower flash points for the three binary solutions, n-hexanol+propionic acid, n-butyric acid+m-xylene and n-pentanol+n-butanol, were measured by Setaflash closed tester and correlated with the Wilson and UNIQUAC equations using binary interaction parameters [9].

EXPERIMENTAL DETAILS

n-Hexanol, propionic acid, n-butyric acid, m-xylene, and n-pentanol were purchased from Acros Organic Co. with a minimum purity

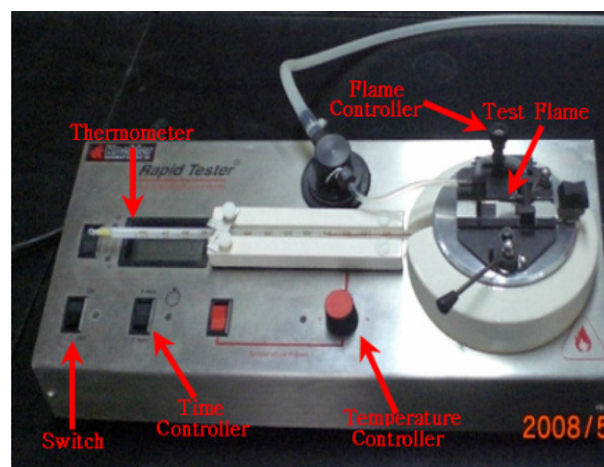


Fig. 1. The basic system configuration of the Setaflash closed cup tester.

[†]To whom correspondence should be addressed.
E-mail: hadm@semyung.ac.kr

of 99.0%. n-Butanol was purchased from Acros Organic Co. with a minimum purity of 99.5%. All these chemicals were used directly without any purification.

Three mixtures were selected for the samples: n-hexanol(1)+propionic acid(2), n-butyric acid(1)+m-xylene(2) and n-pentanol(1)+n-butanol(2).

The Setaflash closed cup tester manufactured by Koehler Instrument Co. was used to measure the lower flash points of three binary solutions. The basic system configuration is given in Fig. 1. The apparatus consisted of a sample cup, time controller, test flame device, thermometer and temperature controller. The Setaflash closed cup tester is operated according to the standard test method, ASTM D 3278 [10].

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

Mole fractions		Flash points (°C)			
x_1	x_2	Exp.	Raoult's law	Wilson	UNIQUAC
0.000	1.000	49.0	-	-	-
0.095	0.905	51.5	49.96	51.02	50.74
0.300	0.700	55.5	52.17	55.95	55.43
0.500	0.500	59.5	54.53	59.34	59.52
0.700	0.300	61.0	57.13	61.00	61.64
0.900	0.100	61.0	59.97	61.50	61.83
1.000	0.000	61.5	-	-	-
A.A.D.		-	2.95	0.32	0.46

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

Mole fractions		Flash points (°C)			
x_1	x_2	Exp.	Raoult's law	Wilson	UNIQUAC
0.000	1.000	26.0	-	-	-
0.101	0.899	26.5	27.72	26.74	26.87
0.300	0.700	28.5	31.77	28.50	28.52
0.497	0.503	32.5	37.05	31.84	31.85
0.702	0.298	37.0	44.90	38.33	38.47
0.902	0.098	52.0	57.38	52.00	51.99
1.000	0.000	67.0	-	-	-
A.A.D.		-	4.46	0.45	0.50

Table 3. The experimental and the calculated flash points for the n-pentanol(1)+n-butanol(2) system

Mole fractions		Flash points (°C)			
x_1	x_2	Exp.	Raoult's law	Wilson	UNIQUAC
0.000	1.000	36.0	-	-	-
0.101	0.899	38.0	36.96	36.92	36.90
0.298	0.702	39.0	39.02	38.89	38.84
0.483	0.517	41.0	41.26	41.00	41.00
0.701	0.299	44.0	44.39	43.96	44.13
0.899	0.101	47.0	47.89	47.50	47.75
1.000	0.000	50.0	-	-	-
A.A.D.		-	0.52	0.36	0.43

RESULTS AND DISCUSSION

1. Experimental Results

The experimental results obtained in this work for the systems, n-hexanol(1)+propionic acid(2), n-butyric acid(1)+m-xylene(2) and n-pentanol(1)+n-butanol(2), 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 plotted as a function of mole fraction.

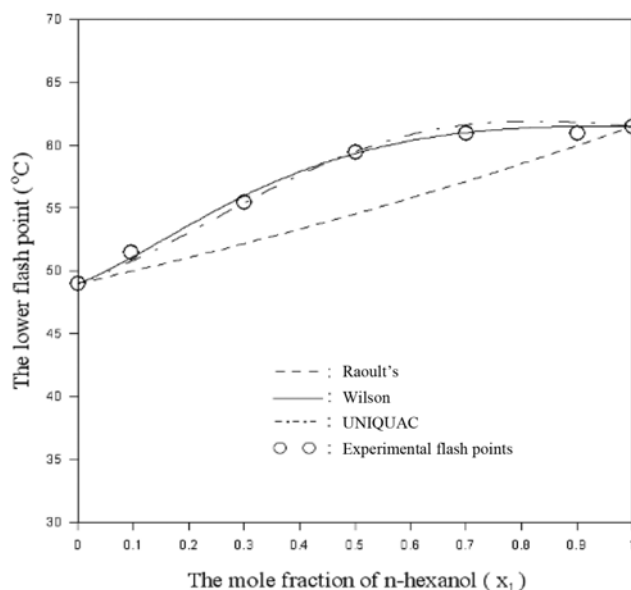


Fig. 2. The comparison of the lower flash point prediction curves with the experimental data for the n-hexanol(1)+propionic acid(2) system.

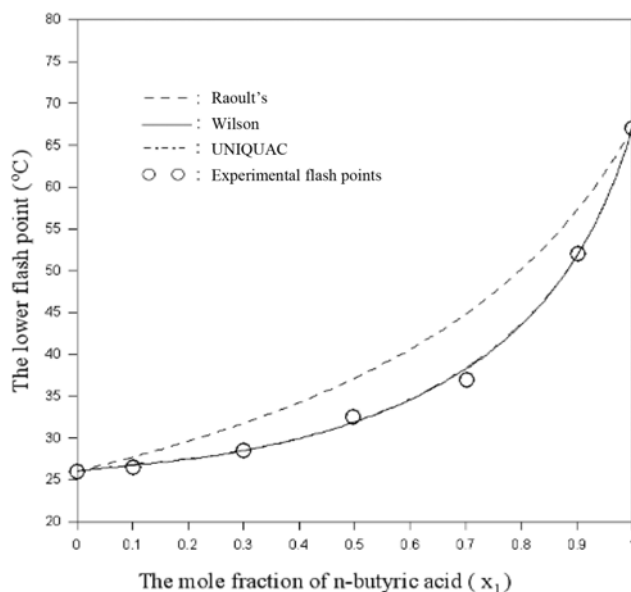


Fig. 3. The comparison of the lower flash point prediction curves with the experimental data for the n-butyric acid(1)+m-xylene(2) system.

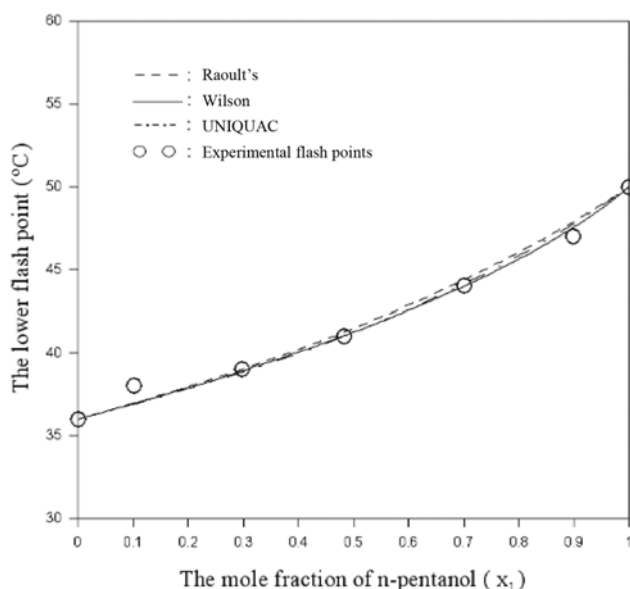


Fig. 4. The comparison of the lower flash point prediction curves with the experimental data for the n-pentanol(1)+n-butanol (2) system.

2. The Prediction of the Lower Flash Points Based on the Raoult's Law

Le Chatelier's rule [11] 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 LFL_i is the LFL of the pure component i . From the definition of the flash point, the LFL_i is expressed relative to its saturated vapor pressure at flash point, $P_{i,fp}^{\text{sat}}$, as :

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

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

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

At low pressure, the vapor phase can be approximated as an ideal gas; then the vapor phase solution's fugacity coefficient for component i 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 :

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

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

Table 4. The Antoine coefficients of the components

Components	Coefficients		
	A	B	C
n-Hexanol	7.90584	1819.57	205.00
Propionic acid	7.99064	1929.3	236.43
n-Butyric acid	7.7399	1764.68	199.892
m-Xylene	7.00909	1462.266	215.11
n-Pentanol	7.39824	1435.57	179.798
n-Butanol	7.838	1558.19	196.881

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

or

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

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

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

The saturated vapor pressure variation with temperature for a pure substance i can be estimated by the Antoine equation [9] :

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

where A_i , B_i and C_i are the Antoine coefficients and T is the temperature in degrees 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 $P_{i,fp}^{\text{sat}}$, as presented in Eq. (8), can be estimated by substituting $T_{i,fp}$, the flash point of component i , into the Antoine equation.

Under an ideal solution assumption, the activity coefficients of the liquid phase are equal to unity. Therefore Eq. (8) was reduced to Raoult's law [13], this being described as :

$$\sum_{i=1}^N \frac{x_i P_i^{\text{sat}}}{P_{i,fp}^{\text{sat}}} = \frac{x_1 P_1^{\text{sat}}}{P_{1,fp}^{\text{sat}}} + \frac{x_2 P_2^{\text{sat}}}{P_{2,fp}^{\text{sat}}} = 1 \quad (10)$$

The temperature which satisfies Eq. (10) is determined to be the lower flash point of the binary mixtures [13]. The calculated results are presented in Tables 1-3.

3. The Optimization of the Binary Interaction Parameters

The above-mentioned method based on Raoult's law is only adequate for an almost ideal solution. In this study, the Wilson and UNIQUAC equations are used to estimate the activity coefficients of nonideal binary solutions, because the equations are useful methods for evaluating the activity coefficients.

The Wilson and UNIQUAC equations are used to correlate the experimentally derived data for three binary solutions, these equations being described as :

Wilson equation :

$$\begin{aligned} \ln \gamma_1 &= -\ln(x_1 + A_{12}x_2) + x_2 \left(\frac{A_{12}}{x_1 + A_{12}x_2} - \frac{A_{21}}{A_{21}x_1 + x_2} \right) \\ \ln \gamma_2 &= -\ln(x_2 + A_{21}x_1) + x_1 \left(\frac{A_{12}}{x_1 + A_{12}x_2} - \frac{A_{21}}{A_{21}x_1 + x_2} \right) \end{aligned} \quad (11)$$

Table 5. The optimized binary parameters of the Wilson and UNIQUAC equations for each binary system

Systems	Parameters	Wilson*				UNIQUAC**	
		A_{12}	A_{21}	v_1^L	v_2^L	U_{12}	U_{21}
n-Hexanol(1)+propionic acid(2)		90.7771	-435.2170	125.23	74.98	48.8111	-219.2924
n-Butyric acid(1)+m-xylene(2)		1657.8277	-411.2998	92.43	123.47	-424.9692	920.6098
n-Pentanol(1)+n-butanol(2)		-407.9056	583.8628	108.63	91.97	-163.5492	204.8874

*Wilson: $A_{12}=\lambda_{12}-\lambda_{11}$, $A_{21}=\lambda_{21}-\lambda_{22}$ (cal/mol)

**UNIQUAC: $U_{12}=g_{12}-g_{11}$, $U_{21}=g_{21}-g_{22}$ (cal/mol)

where A is as the following:

$$A_{12} = \frac{v_2}{v_1} e^{-\frac{\lambda_{12}-\lambda_{11}}{RT}}, \quad A_{21} = \frac{v_1}{v_2} e^{-\frac{\lambda_{21}-\lambda_{22}}{RT}}$$

where the partial molar volumes, v_1 and v_2 , were adapted from the literature [9] and are listed in Table 5.

UNIQUAC equation :

$$\ln \gamma_i = \ln \frac{\phi_i^*}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\phi_i^*} + l_i - \frac{\phi_i^*}{x_i} \sum_{j=1}^m x_j l_j - q_i' \ln \left(\sum_{j=1}^m \theta_j' \tau_{ji} \right) + q_i' - q_i \sum_{j=1}^m \frac{\theta_j' \tau_{ij}}{\sum_{k=1}^m \theta_k' \tau_{kj}} \quad (12)$$

where,

$$\tau_{ji} = \frac{g_{ji} - g_{ij}}{RT}$$

$$l_j = \frac{z}{2} (r_j - q_j) - (r_j - 1), \quad z = 10$$

The objective function was used to minimize the difference between the experimental and calculated flash points, this being described as :

$$F = \sum_{j=1}^N \text{ABS}(T_j^{\text{exp}} - T_j^{\text{cal}}) \quad (13)$$

where, N is the number of experimental data, ABS is absolute value, T_j^{exp} is the experimental lower flash point of component j , and T_j^{cal} is the calculated lower flash point of component j . T_j^{cal} , which satisfies Eq. (8), is determined to be the lower flash point of the binary mixtures.

The values of the binary interaction parameters that minimized this objective function (F) were sought, using both the Wilson and the UNIQUAC equations.

Using the SIMPLEX [14] method, the binary interaction parameters of the Wilson and UNIQUAC equations,

$$\text{Wilson: } A_{12} (= \lambda_{12} - \lambda_{11}), A_{21} (= \lambda_{21} - \lambda_{22})$$

$$\text{UNIQUAC: } U_{12} (= g_{12} - g_{11}), U_{21} (= g_{21} - g_{22})$$

were calculated.

The binary interaction parameters calculated in this way are shown in Table 5. And the calculated flash points are presented in Tables 1-3.

4. The Comparison of the Predicted and Measured Lower Flash Points

In this study, the prediction results obtained were presented in

Tables 1-3 and Figs. 2-4.

And included in Tables 1-3 is the A.A.D. (average absolute deviation) defined [15] as follows :

$$\text{A.A.D.} = \frac{\sum_{i=1}^N \frac{|T_i^{\text{exp}} - T_i^{\text{cal}}|}{N}}{N} \quad (14)$$

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

As can be seen from Figs. 2-4, the experimental results are generally in bad agreement with the predictive curves based on Raoult's law and in good agreement with the predictive curves based on the optimization method using the Wilson and UNIQUAC equations.

Tables 1-3 also depict the results of comparing the predictive curves provided by the optimized binary interaction parameters in the Wilson equation and UNIQUAC equation for estimating the corresponding activity coefficients. The Wilson equation is a little more accurate than the UNIQUAC equation, as can be seen from the A.A.D. in Tables 1-3.

CONCLUSIONS

The lower flash points for three binary systems, n-hexanol+propionic acid, n-butyric acid+m-xylene, and n-pentanol+n-butanol, were measured by Setaflash closed cup tester.

The experimental data were compared with the calculated values based on Raoult's law and are generally in bad agreement with those.

The calculated flash points based on the optimization method using the Wilson and UNIQUAC equations are very similar to the experimental data. However, the predictive curves based on the Wilson equation described the experimentally-derived data more effectively than those based on the UNIQUAC.

The prediction method in this study 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.

ACKNOWLEDGEMENT

This study was supported by a Semyung University Research Grant of 2009.

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 [$^{\circ}\text{C}$]
 v_i^L : partial molar volume of pure component i for liquid phase
 x : liquid phase composition
 y : vapor phase composition

Greek Letters

Φ : fugacity coefficient of species i in solution
 γ : activity coefficient

Superscripts

sat : saturated
 exp : experimental value
 cal : calculated value

Subscripts

fp : flash point
 i : species i

REFERENCES

1. A. R. Katritzky, D. A. Stoyanova-SlavovovKong, D. A. Dobchev and M. Karelson, *J. Molecular Graphics and Modelling*, **26**, 529 (2007).
2. F. Gharagheizi and R. F. Alamdari, *QSAR Comb. Sci.*, **27**, 679 (2008).
3. D. A. Crowl and J. F. Louvar, Chemical Process Safety Fundamentals with Applications, Prentice Hall, *Englewood Cliffs*, New Jersey (1990).
4. F. P. Lees, Loss Prevention in the Process Industries, 2nd Ed., Butterworth-Heinemann Vol. 1, Oxford (1996).
5. W. A. Affens and G. W. McLaren, *J. Chem. Eng. Data*, **17**, 482 (1972).
6. D. White, C. L. Beyler, C. Fulper and J. Leonard, *Fire Safety Journal*, **38**, 1 (1997).
7. H. J. Liaw, C. T. Chen, C. C. Cheng and Y. T. Yang, *J. Loss Prevention in the Process Industries*, **15**, 429 (2002).
8. D. M. Ha, S. J. Lee and M. H. Back, *Korean J. Chem. Eng.*, **24**, 551 (2007).
9. B. E. Poling, J. M. Prausnitz and J. P. O'Connell, The Properties of Gases and Liquids, 5th Ed., McGraw-Hill, New York (2001).
10. American Society for Testing Materials, Annual Book of ASTM Standards, Vol. 06.01 (1999).
11. H. Le Chatelier, *Ann. Minnes*, **19**, 388 (1891).
12. J. Gmehling, U. Onken and W. Arlt, Vapor-Liquid Equilibrium Data Collection, 1, Part1-Part7, DECHEMA (1980).
13. D. M. Ha and S. J. Lee, *J. Korea Ins. Fire Sci. & Eng.*, **22**, 65 (2008).
14. J. L. Kuester and J. H. Mize, Optimization Techniques with Fortran, McGraw-Hill, New York (1973).
15. S. J. Lee and D. M. Ha, *Korean J. Chem. Eng.*, **20**, 799 (2003).

1. A. R. Katritzky, D. A. Stoyanova-SlavovovKong, D. A. Dobchev