Vol. 9, No. 2, pp. 6-10, December 2010

INTERNATIONAL JOURNAL OF SAFETY

www.kosos.or.kr

The Measurement and Prediction of Minimum Flash Point Behaviour for Flammable Binarry Solution Using Pensky-Martens Closed Cup Tester

Dong-Myeong Ha, Yong-Chan Choi[1] and Sung-Jin Lee[2]*

Department of Occupational Health and Safety Engineering, Semyung University, Jecheon, 390-711, korea
[1]POSCO Engineering & construction Co. Ltd. Seoul, 135-769, Korea
[2]Department of Clinical Laboratory Science, Semyung University, Jecheon, 390-711, Korea

(Received July 5, 2010; Accepted December 2, 2010)

Abstract: The flash point of liquid solution is one of the most important flammability properties that used in hazard and risk assessments. Minimum flash point behaviour (MFPB) is showed when the flash point of a liquid mixture is below the flash points of the individual components. In this paper, the lower flash points for the flammable binary system, n-decane+n-octanol, were measured by Pensky-Martens closed cup tester. This binary mixture exhibited MFPB. The measured flash points were compared with the values calculated by the Raoult's law and the optimization method using van Laar and UNIQUAC equations. The optimization method were found to be better than those based on the Raoult's law, and successfully estimated MFPB. The opimization method based on the van Laar equation described the experimentally-derived data more effectively than was the case when the prediction model was based upon the UNIQUAC.

Key words: Flash point, Minimum flash point behaviour, van Laar, UNIQUAC, Optimization method

1. Introduction

The flash point is a primary property used to determine the fire and explosion hazards of a liquid solution [1]. The flash point is the lowest temperature at which there is sufficient vapour to form an ignitable mixture with air [2].

The flash point of most mixtures vary depending on the composition. Some of mixtures exhibit minimum flash point behaviour, which leads to the minimum on the flash point vs composition curve. This behaviour can lead to a very hazardous situation [3].

The flash points are measured by heating the liquid in a container and then introducing a small flame just above the liquid surface. Two general experimental apparatus are the closed cup tester and open cup tester. In the closed cup tester the liquid is enclosed, while in the open cup tester the liquid is exposed to open air. The flash points measured with the closed cup tester are usually lower than the open cup tester because the vapour are prevented form escaping [1].

There are different methods for calculation the flash points of binary mixture. Affens and McLaren [4] developed a predictive model for the flash points of binary hydrocarbon mixtures using Raoult's law. However, the Affens and McLaren's model is not able to effectively predict the measured the flash point for a non-ideal solution.

Liaw et al. [5] developed a mathmatical 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, the Liaw's model cannot be able to predict the flash points for the binary solutions.

Kim and Lee [6] established a general empirical model to estimate the flash point of binary liquid mixtures using the partial least squares (PLS) method, which is one of the multivariate statistical analysis methods.

Ha et al. [7,8] predicted the lower flash points of the flammable binary solutions by using the prediction models based on activity coefficient model.

The purpose of this study was to measure and predict the flash points for the binary mixture exhibiting MFPB to aid in evaluating the safety of flammable liquid mix-

---

*Corresponding author: pappi68@hanmail.net tures. The flash points for the binary solution, n-decane+n-octanol were measured by Pensky-Martens closed cup tester and compared with the Raoult's law and optimization method based on van Laar and UNIQUAC equations [9].

2. Experimental Details

n-Decane and n-octanol were purchased from Lancaster, England with a minimum purity of 99%. All these chemicals were used directly without any purification.

The basic system configuration of Pensky-Martens closed cup tester [10] consists 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-exposure 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 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. Mathematical formulation for the lower flash point prediction

3.1 The Prediction of the lower flash points based on the Raoult's law

The Le Chatelier's rule [11] for the flammable vapor-air mixture of multicomponent is as follows :

$$\sum_{i=1}^{N} \frac{y_i}{LFL_i} = 1 \tag{1}$$

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, $P_{i,fp'}^{sat}$, as :

$$LFL_i = \frac{P_{i,fp}^{sat}}{P} \tag{2}$$

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 :

$$y_i \Phi_i P = x_i \gamma_i f_i \qquad (i = 1,\ 2,\ \cdots,\ N) \tag{3}$$

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 :

$$\Phi_i = 1 \tag{4}$$

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

$$f_i \cong P_i^{sat} \tag{5}$$

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

$$y_i P = x_i \gamma_i P_i^{sat} \tag{6}$$

or

$$y_i = \frac{x_i \gamma_i P_i^{sat}}{P} \tag{7}$$

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

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

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

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

where A_i, B_i and C_i are the Antoine coefficients and T is the temperature in degree Celsius (°C). The Antoine coefficients for n-decane and n-octanol, were adapted from the literature [12] and are listed in Table 1.

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.

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 :

Table 1. The Antoine coefficients of the components

Coefficients Components	A	B	C
n-Decane	7.44	1843.12	230.22
n-Octanol	7.0845	1457.76	151.58

Table 2. The optimized binary parameters of the van Laar and UNIQUAC equations for each binary system

Parameters	van Laar		UNIQUAC	
Systems	A_{12}	A_{21}	A_{12}	A_{12}
n-Decane(1)+n-Octanol(2)	0.6304	26.6568	1995.7221	-592.5629

Table 3. The experimental and the calculated flash points for n-decane(x_1)+n-octanol(x_2) system

Mole fractions		Flash points (°C)			
x_1	x_2	Exp.	Raoult's law	van Laar	UNIQUAC
1.000	0.000	44.0	-	-	-
0.764	0.236	39.0	48.38	39.00	39.61
0.696	0.304	40.0	49.88	40.12	40.01
0.597	0.403	42.0	52.29	42.25	41.75
0.503	0.497	46.0	54.90	44.80	44.45
0.395	0.605	49.0	58.40	48.49	48.68
0.307	0.693	53.0	61.75	52.30	53.01
0.196	0.804	58.0	66.81	58.69	59.84
0.103	0.897	64.0	71.99	66.27	67.28
0.000	1.000	79.0	-	-	-
A.A.D.		-	9.18	0.72	0.98

$$\sum_{i=1}^{2}\frac{x_i P_i^{sat}}{P_{i,fp}^{sat}} = \frac{x_1 P_1^{sat}}{P_{1,fp}^{sat}} + \frac{x_2 P_2^{sat}}{P_{2,fp}^{sat}} = 1 \tag{10}$$

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 Table 3.

3.2 The optimization of the binary interaction parameters

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

The van Laar and UNIQUAC equations are used to correlate the experimentally derived data for flammable binary system, n-decane+n-octanol, these equations being described as :

van Laar equation :

$$\ln\gamma_1 = A_{12}\left(\frac{A_{21}x_2}{A_{12}x_1 + A_{21}x_2}\right)^2$$

$$\ln\gamma_2 = A_{21}\left(\frac{A_{12}x_1}{A_{12}x_1 + A_{21}x_2}\right)^2 \tag{11}$$

UNIQUAC equation :

$$\ln\gamma_i = \ln\frac{\Phi_i^*}{x_i} + \frac{z}{2}q_i\ln\frac{\theta_i}{\Phi_i^*} + l_i - \frac{\Phi_i^*}{x_i}\sum_{j=1}^{m}x_j l_j \tag{12}$$

$$-q'_i\ln\left(\sum_{j=1}^{m}\theta'_j\tau_{ji}\right) + q'_i - q'_i\sum_{j=1}^{m}\frac{\theta'_j\tau_{ij}}{\sum_{k=1}^{m}\theta'_k\tau_{kj}}$$

where,

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

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

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

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

where, N is the number of experimental data, ABS is absolute value, $T_j^{\exp}$ is the experimental lowver 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 van Laar and the UNIQUAC equations.

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

van Laar : A_{12}, A_{21}

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

were calculated.

4. Results

4.1 Experimental Results

The results obtained in this work for the system, n-decane(1)+n-octanol(2) [15], are presented in Table 3. Concentrations of component i are given in mole fraction, x_i. As shown in Figure 2, the lower flash points of the systems plotted as a function of mole fraction. This binary mixture exhibited MFPB (minimum flash point behavior), which leads to the minimum on the flash point vs composition curve.

4.2 The comparison of the experimental and calculated lower flash points

The binary interaction parameters calculated in this study

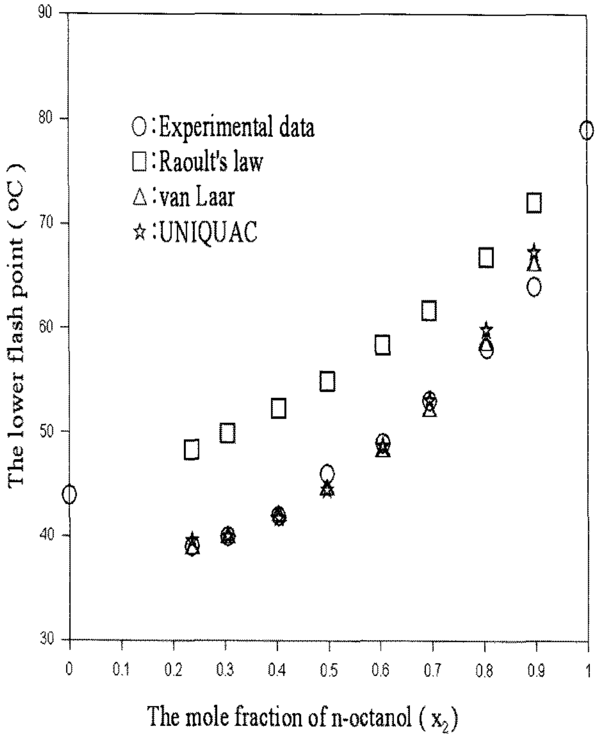

Fig. 1. The comparison of the lower flash point prediction curves with the experimental data for n-decane(x_1)+n-octanol(x_2) system.

are shown in Table 2, and the predicted flash pointss were presented in Table 3 and Figure 2. Included in Table 3 is the A.A.D. (average absolute deviation) defined [16] as follows :

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

where the 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 Figure 1, the experimental results are generally in bad agreement with the predicted values based on the Raoul's law and in good agreement with the predicted values based on the optimization method using the van Laar and UNIQUAC equations. And the optimization method successfully estimated MFPB.

Table 3 also depict the results of comparing the predicted values provided by the optimized binary interaction parameters in the van Laar equation and UNIQUAC equation for estimating the corresponding activity coefficients. The van Laar equation is a little more accurate than the UNIQUAC equation, as can be seen from the A.A.D. in Table 3.

5. Conclusion

The flash points for flammable binary system, n-decane +n-octanol, were measured by Pensky-Martens closed cup tester. This binary mixture exhibited MFPB (minimum flash point behavior), which leads to the minimum on the flash point vs composition curve. The experimental data were compared with the values calculated by the Raoult's law and optimization methods. The calculated values based on the optimization methods were found to be better than those based on the Raoult's law. The van Laar equation is a little more accurate than the UNIQUAC equation, as can be seen from the A.A.D.

The prediction method in this study can thus be applied to incorporate inherently safer design for chemical process, such as the determination of the safe storage conditions for flammable (or combustible) solutions.

References

[1] M. Vidal, W. J. Rogers and M. S. Mannan, "Prediction of Minimum Flash Point Behavious for Binary Mixtures", *Process Safety and Environment Protection*, Vol. 84(B1), pp. 1-9, 2006.

[2] D. A. Crowl and J. F. Louvar, "Chemical Process Safety : Fundamentals with Applications", *Englewood Cliffs*, New Work, 1990.

[3] H. H. Liaw, T. P. Lee, J. S. Tai, W. H. Hsiao, M. H. Chen and T. T. Hsu, "Binary Liquid Solutions Exhibiting Minimum Flash-Point Behavior", *J. of Loss Prevention in the Process Industries*, Vol. 15, pp. 173-186, 2003.

[4] W. A. Affens and G. W. McLaren, "Flammability Properties of Hydrocarbon Solutions in Air", *J. Chem. Eng. Data*, Vol. 17, No. 4, pp. 482-488, 1972.

[5] H. J. Liaw, Y. H. Lee, C. L. Tang, H. H. Hsu. and J. H. Liu, "A Mathematical Model for Predicting the Flash Point of Binary Solutions", *J. of Loss Prevention in the Process Industries*, Vol. 15, pp. 429-438, 2002.

[6] S. Y. Kim and B. S. Lee, "A Prediction Model for the Flash Point of Binary Liquid Mixtures", *J. of Loss Prevention in the Process Industries*, Vol. 23, pp. 166-169, 2010.

[7] D. M. Ha, S. J. Lee. and M. H. Back., "Measurement and Estimation of the Lower Flash Points for the Flammable Binary System Using a Tag Open Cup Tester", *Korea J. Chem. Eng.*, Vol. 24, pp. 551-555, 2007.

[8] D. M. Ha and S. J. Lee, "The Measurement and Estimation of Minimum Flash Point Behavior for Binary Mixtures Using Tag Open-Cup Tester", *Journal of the Korean Institute of Gas*, Vol. 12, pp. 50-55, 2009.

[9] B. E. Poling, J. M. Prausnitz and J. P. O'connell, "The Properties of Gases and Liquids", *5th Edition., McGraw-Hill*, New York, 2001.

[10] D. M. Ha, S. J. Lee and Y. C. Choi, "Flash Points of Water+n-Propanol System Using Closed-Cup Measurement Apparatus", *Journal of the KOSOS*, Vol. 17, No. 4, pp. 140-145, 2003.

[11] H. Le Chatelier, "Estimation of Firedamp by Flammability Limits", *Ann. Minmes*, Vol. 19, pp. 388, 1891.

[12] J. Gmehing, U. Onken and W. Arlt, "Vapor-Liquid Equilibrium Data Collection", 1, Part1-Part7, DECHEMA, 1980.

[13] D. M. Ha and S. J. Lee, "Estimation of the Flash Points for n-Propanol+Formic acid System Using the Binary Parameters Optimization Method", *J. of Korea Institute of Fire Sci. & Eng.*, Vol. 22, pp. 65-69, 2008.

[14] J. L. .Kuester and J. H. Mize, "Optimization Techniques with Fortran", *McGraw-Hill*, New York, 1973.

[15] Y. C. Choi, "Prediction and Measurement of Flash Points of Mixtures Using Closed Tester", M.S. Dissertation, Semyung University, Jecheon, Korea, 2003.

[16] D. M. Ha and S. J. Lee, "The Measurement and Estimation of the Lower Flash Points for tert-Pentanol+Propionic Acid and p-Xylene+Propionic Acid Systems Using Open-Cup Apparatus", *J. of Korea Institute of Fire Sci. & Eng.*, Vol. 23, pp. 161-166, 2009.