

클리브랜드 개방식 장치를 이용한 2성분계의 인화점 Flash Points of the Binary Solutions Using Cleveland Open Cup Tester

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(2010. 12. 9 접수/2011. 2. 11. 채택)

요 약

인화점은 공정안전을 평가할 때 산업공정에서 가연성 액체의 중요한 연소 특성 가운데 하나이다. 본 연구에서는 클리브랜드 개방식 장치를 사용하여 n-propanol + formic acid계와 acetic acid + propionic acid계의 인화점을 측정하였다. 실험값은 Raoult의 법칙과 최적화 기법에 의해 추산된 값과 비교하였다. 그 결과, 최적화 기법에 의한 추산값이 Raoult의 법칙에 의한 추산값 보다 실험값에 더욱 근접하였다.

ABSTRACT

The flash point is one of the most significant combustion properties of flammable liquids in industrial processes when evaluation process safety. In this paper, Cleveland open cup tester is used to measure the flash points for the two binary systems (n-propanol + formic acid and acetic acid + propionic acid). The measured flash points were compared with the values calculated by the Raoult's law and the optimization method using van Laar and Wilson equations. The calculated values based on the optimization method were found to be better than those based on the Raoult's law.

Key words : Flash point, Raoult's law, van Laar, Wilson, Optimization method

1. Introduction

The flash point is one of the most significant physical properties of flammable liquid mixtures in industrial processes when evaluation process safety.¹⁾ The flash point is defined as the lowest temperature at which a liquid produces enough vapour to ignite in the presence of a source of ignition.²⁾

The knowledge of the flash point of materials is essential in many pharmaceutical and chemical unit operations. For example, in some processes powdered materials are handled at low relative humidity (weighing, mixing, fluidization, drying, storage, transportation), in which frictional electricity may be generated.³⁾

There are many methods for prediction of the flash point in the literature. Walsham⁴⁾ proposed the calculation method of the Tag open cup flash points for

various solvent mixtures using the sum of flashing indexes method. Affens and McLaren⁵⁾ developed a predictive model for the flash points of binary hydrocarbon mixtures using Raoult's law, and White et al.⁶⁾ reduced Affens and McLaren's model to a simpler equation by ignoring any dependence of the LFL on temperature. Lee and Ha⁷⁾ calculated the flash point of binary liquid mixtures based on van Laar and Wilson equations, and compared the results with experimental data. Liaw et al.⁸⁾ developed a mathematical model for the flash points of highly non-ideal solutions using activity coefficient models, such as Wilson, NRTL and UNIQUAC models. Vidal et al.⁹⁾ evaluated prediction methods of the flash point behavior of binary mixtures using quantum chemical calculation methods such as COSMO-RS and theoretical methods such as UNIFAC. Kim and Lee¹⁰⁾ established a general empirical model to estimate the flash point of binary liquid mixtures using the partial least squares (PLS) method, which is

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one of the multivariate statistical analysis methods.

The experimental flash point data are readily available in the several literatures. However, the most published flash point data was for pure components and the flash points of the binary solutions that have the flammable components, appear to be scarce in the literature.

The objective 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 flash points for the two binary solutions, n-propanol + formic acid and acetic acid + propionic acid, were measured by Cleveland open cup tester and compared with the Raoult's law and optimization method using van Laar and Wilson equations.¹¹⁾

2. Experimental Details

2.1 Chemicals

n-Propanol (99.0%) and acetic acid (99.5%) were purchased from Samchun, Korea. Formic acid and propionic acid were purchased from Acros, Belgium with a minimum purity of 99.0%. All these chemicals were used directly without any purification.

2.2 Apparatus and Procedure

The basic system configuration of Cleveland open cup tester is given in Figure 1. This apparatus consists of test cup (80 mL), thermometer, test flame applicator, heating plate, hose to a gas source, heater inside, and current Regulator.

The pure components are added by mass and the test cup is filled with the mixture. The mixture is heated at a rate of 5 to 6 K/min. 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 rule¹²⁾ for the flammable vapor-air mixture of binary component is as follows:

$$\sum_{i=1}^2 \frac{y_i}{LFL_i} = 1 \quad (1)$$

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

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

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 equilibrium between liquid phase and 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 component i is reduced to:

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

and the fugacity of pure liquid i , at the temperature and



Figure 1. Photograph of cleveland open cup apparatus. ① A thermometer A test flame applicator, ② A test cup A heating plate, ③ A hose to a gas source A heater inside, ④ A current Regulator.

pressure of the system can be simplified as:

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

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

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

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:

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

The saturated vapor pressure variation with temperature for a pure substance i can be estimated by the Antoine equation(11):

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

where A_i , B_i and C_i are the Antoine coefficients of i component and T is the temperature in degree Celsius ($^{\circ}\text{C}$). The Antoine coefficients for n-propanol, formic acid, acetic acid and propionic acid, were adapted from the literature¹³⁾ and are listed in Table 1.

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, activity coefficients of the liquid phase are equal to unity. Therefore Eq. (8) was reduced to Raoult's law,¹⁴⁾ this being described as:

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

Table 1. The Antoine Coefficients of the Components

Components	Coefficients		
	A	B	C
n-Propanol	8.3789	1788.020	227.438
Formic acid	6.9446	1295.250	218.000
Acetic acid	7.5596	1644.048	233.524
Propionic acid	7.9906	1929.300	236.430

The temperature, which satisfies Eq. (10), is determined to be the lower flash point of the binary mixtures. The calculated results are presented in Table 3~4.

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, van Laar and Wilson equations is used to estimate the activity coefficients of the nonideal binary solutions. Because the equations are useful methods for evaluating the activity coefficients.

The van Laar and Wilson equations are used to correlate the experimentally derived data for flammable binary systems, these equations being described as:

van Laar equation:

$$\begin{aligned} \ln \gamma_1 &= A_{12} \left(\frac{A_{21} x_2}{A_{12} x_1 + A_{21} x_1} \right)^2 \\ \ln \gamma_2 &= A_{21} \left(\frac{A_{12} x_1}{A_{12} x_1 + A_{21} x_2} \right)^2 \end{aligned} \quad (11)$$

Wilson equation:

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

where Λ is as following

$$\Lambda_{ij} = \frac{v_j}{v_i} e^{-\frac{\lambda_{ij} - \lambda_{ii}}{RT}}$$

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

Table 2. The Optimized Binary Parameters of the van Laar and Wilson Equations for Each Binary System

Systems	Parameters	van Laar		Wilson	
		A ₁₂	A ₂₁	A ₁₂	A ₁₂
n-Propanol(1) + Formic acid(2)		0.2425	0.2613	-154.2185	546.6781
Acetic acid(1) + Propionic acid(2)		2.1029	1.6274	998.6914	773.1992

both the van Laar and the Wilson equations.

Using the SIMPLEX¹⁵⁾ method, the binary interaction parameters of the van Laar and Wilson equations,

van Laar: A₁₂, A₂₁

Wilson: A₁₂ (= λ₁₂ - λ₁₁), A₂₁ (= λ₂₁ - λ₂₂)

were calculated.

4. Results and Discussion

4.1 Experimental Results

The flash points measured in this work for two binary systems, n-propanol (1) + formic acid (2) and acetic acid (1) + propionic acid (2), are presented in Table 3~4 and Figure 2~3. Concentrations of component

Table 3. The Experimental and the Calculated Flash Points for n-Propanol(x₁) + Formic Acid(x₂) System

Mole Fractions		Flash Points (°C)			
x ₁	x ₂	Exp.	Raoult's Law	van Laar	Wilson
1.000	0.000	32.0	-	-	-
0.700	0.300	33.0	36.69	33.01	33.44
0.495	0.505	33.0	41.18	33.67	34.67
0.299	0.701	36.0	47.44	34.15	35.95
0.099	0.901	39.0	59.05	39.00	39.01
0.000	1.000	72.0	-	-	-
A.A.D.		-	10.34	0.63	0.54

Table 4. The Experimental and the Calculated Flash Points for Acetic Acid(x₁) + Propionic Acid(x₂) System

Mole Fractions		Flash Points (°C)			
x ₁	x ₂	Exp.	Raoult's Law	van Laar	Wilson
1.000	0.000	58.5	-	-	-
0.904	0.096	60.0	59.56	59.24	59.03
0.702	0.298	61.0	61.95	61.00	60.66
0.502	0.498	62.0	64.51	63.11	62.94
0.298	0.702	66.0	67.36	65.88	66.01
0.000	1.000	72.0	-	-	-
A.A.D.		-	1.32	0.50	0.56

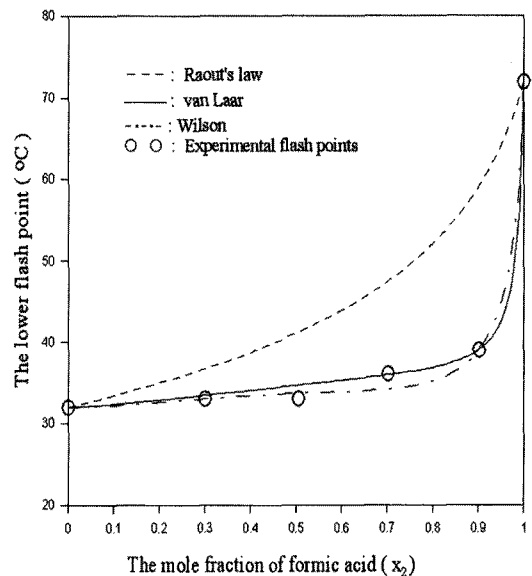
i are given in mole fraction, xi. As shown in Figure 2~3, the lower flash points of the systems plotted as a function of mole fraction.

4.2 The Comparison of the Experimental and Calculated Lower Flash Points

In this study, the binary interaction parameters calculated are shown in Table 2. The calculated flash points are presented in Table 3~4 and Figure 2~3. Included in Table 3~4 is the A.A.D. (average absolute deviation) defined¹⁶⁾ as follows:

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

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.

**Figure 2.** The comparison of the lower flash point prediction curves with the experimental data for n-propanol(x₁) + formic acid(x₂) system.

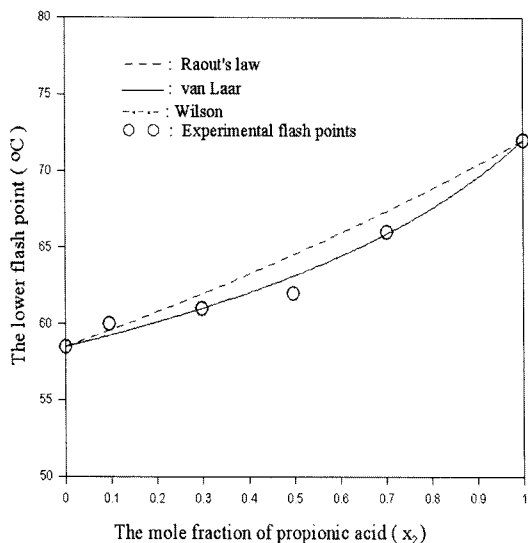


Figure 3. The comparison of the lower flash point prediction curves with the experimental data for acetic acid(x_1) + propionic acid(x_2) system.

As can be seen from Figure 2~3, the experimental results are generally in bad agreement with the predictive curves based on the Raoult's law and in good agreement with the predictive curves based on the optimization method using the van Laar and Wilson equations.

Table 3~4 also depict the results of comparing the predictive curves provided by the optimized binary interaction parameters in the van Laar equation and Wilson equation for estimating the corresponding activity coefficients. In n-propanol + formic acid system, Wilson equation is a little more accurate than van Laar equation, as can be seen from the A.A.D. in Table 3. In acetic acid + propionic acid system, van Laar equation is a little more accurate than Wilson equation, as can be seen from the A.A.D. in Table 4.

5. Conclusion

The flash points for two binary mixtures, n-propanol + formic acid and acetic acid + propionic acid, were measured by Cleveland open cup tester. 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. In n-propanol + formic acid system, Wilson equation is a little more accurate than van Laar equation, as can be seen from the A.A.D. In acetic acid + propionic acid

system, van Laar equation is a little more accurate than Wilson equation.

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.

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