

Seta Flash 밀폐식 장치를 이용한 Water-Methanol과 Water-Ethanol계의 인화점 측정

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The Measurement of Flash Point of Water-Methanol and Water-Ethanol Systems Using Seta Flash Closed Cup Tester

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요 약

인화점은 액체 혼합물의 화재와 폭발의 위험성을 특징짓는 주된 성질이다. 인화점은 가연성 액체에 불꽃이 가해졌을 때 점화가 발생하는 가장 낮은 온도로 정의된다. Seta flash 밀폐식 장치를 이용하여 이성분계 수용성 혼합물인 water-methanol계와 water-ethanol계의 인화점을 측정하였다. Wilson 식과 UNIQUAC 식과 같은 활동도 모델식을 활용한 방법을 이용하여 인화점을 계산하였다. 이 계산치와 라울의 법칙에 의한 계산치를 비교하였다. 그 결과, 활동도 계수 모델식에 의한 계산치가 라울의 법칙에 의한 계산치 보다 측정값에 보다 근접하였다.

ABSTRACT

The flash point is the major property to characterize fire and explosion hazard of liquid mixtures. The flash point is the lowest temperature at which a liquid gives off enough vapor to form a flammable air-vapor mixture. The flash points of two aqueous mixtures, water-methanol and water-ethanol, were measured using Seta flash closed cup tester. A prediction method based on activity coefficient models, Wilson and UNIQUAC equations, was used to calculate the flash point. The calculated flash points were compared to the results by the calculating method using Raoult's law. The calculated values based on activity coefficients models were found to be better than those based on the Raoult's law.

Keywords : Flash point, Seta flash closed cup, Water+methanol, Water+ethanol, Wilson, UNIQUAC

1. Introduction

The flash point is the important property of the flammable liquid mixtures to analyze the safety in chemical processes⁽¹⁾. The flash point is the lowest temperature at which a liquid gives off enough vapor to form a flammable air-vapor mixture. Generally the lower the flash point temperature has the greater the fire hazard⁽²⁾.

The flash point can be measured using either open cup tester or closed cup tester. Generally the flash point measured by open cup tester results in a higher value than that

measured by closed cup tester, because open cup tester permits the emission of the low-boiling-point component in the mixture into the surrounding atmosphere prior to the application of the flame^(2,3). On the contrary, the mixture in closed cup tester is separated from the surrounding atmosphere, thereby inhibiting mass transfer between the mixture and the surrounding atmosphere. Reliable and consistent flash point can be obtained using closed cup tester, particularly for multicomponent mixtures^(3,4). Therefore the flash point by closed cup tester are most widely used to characterize flammable substance hazards in practice.

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United Nations (UN) recommended the worldwide implementation of Globally Harmonized System of Classification and Labeling of Chemicals (GHS) in 2008 and the flash point of liquid mixtures is the crucial reference property in the classification of flammable liquids within it⁽⁵⁾. Unfortunately experimental flash point data of liquid mixtures are scarce. Particularly the flash points of the mixtures that have non-flammable component, such as water, have seen little study and the data that did exist was inconsistent.

Deriving the flash point data using closed cup tester is a time-consuming work and the cost of obtaining the flash point data is vary high⁽⁵⁾. Therefore various alternative methods to predict the flash point of liquid mixture have been proposed.

Affens and McLaren⁽⁶⁾ developed a predictive model for the flash points of alkane mixtures by combined Raoult's law, Dalton's law, and Le Chatelier's rule. The model better predict the flash point of the hydrocarbon mixture. However, its application is limited to ideal solutions.

White et al.⁽⁷⁾ reduced Affens and McLaren's model to a simpler equation by ignoring any dependence of the lower flammable limit (LFL) on temperature. However, the equation of White et al. is only valid for ideal solutions.

Liaw et al.⁽⁸⁾ developed a mathematical model for the flash point of highly non-ideal solutions using activity coefficient 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 is not able to predict the flash points for the binary solutions.

Ha et al.⁽⁹⁾ predicted the flash point of the binary flammable mixtures using the optimizing methods based on the van Laar and NRTL equations.

Methanol is mixed with water and injected into high performance diesel and gasoline engines for an increase of power and a decrease in intake air temperature in a process known as water-methanol injection. Ethanol is miscible with water and is a good general purpose solvent. It is found in paints, tinctures, markers, and personal care products such as perfumes and deodorants.

The purpose of this study was to measure and predict the flash point to aid in evaluating the safety of such binary liquid mixtures (water-methanol and water-ethanol). The flash points for two systems, water-methanol and water-ethanol, were measured using Seta flash closed cup tester. The prediction methods based on activity coefficient models, Wilson and UNIQUAC equations⁽¹⁰⁾, were used to esti-

mate the flash points. The calculated results were compared with the experimental flash points. Also the results were compared to the results by the calculating method using Raoult's law.

2. Experimental Section

Two binary aqueous solutions (water-methanol and water-ethanol) were selected for the experimental samples. Methanol and Ethanol were purchased from CARLO Erba Reagents (Italy) with a minimum purity of 99.9%. Water (HPLC grade) was supplied by J.T. Baker, USA. All these chemicals were used without any purification.

The Seta flash closed cup tester manufactured by Koehler Instrument Company (USA) was used to determine the flash point of binary liquid solutions at different compositions.

The basic system configuration of the Seta flash closed cup tester was presented in our previous paper⁽¹¹⁾. The tester consists of a sample cup, time controller, test flame device, flame controller, thermometer, temperature controller, etc. The Seta flash closed cup tester was operated according to the standard test method, ASTM D 3278⁽¹²⁾.

3. Flash Point Calculation of Binary Aqueous Mixture

3.1 Flash point prediction using activity coefficient model

The vapor-liquid equilibrium relation of the component *i* can be expressed as the following equation⁽¹⁰⁾.

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

where P_i is the partial vapor pressure of component *i*, P_i^0 is the vapor pressure of component *i*, 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 Seta flash closed cup tester, the Clausius-Clapeyron equation can be applied to binary systems⁽¹⁰⁾.

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

where T is the flash point in absolute temperature, ΔH_i is the enthalpy of vaporization of component *i*, and R is the gas constant.

The enthalpy of vaporization is a function of temperature and is calculated using Watson equation⁽¹⁰⁾ in this study.

Table 1. The Binary Parameters of Wilson and UNIQUAC Equations for Each Binary System

Systems	Parameters	Wilson*		UNIQUAC**	
		A ₁₂	A ₂₁	A ₁₂	A ₂₁
Water (HPLC grade)-methanol (99.9%)		433.0681	271.1382	697.5569	-404.8062
Water (HPLC grade)-ethanol (99.9%)		960.9534	307.4162	188.6515	86.5941

*Wilson : A₁₂ = λ₁₂ - λ₁₁, A₂₁ = λ₂₁ - λ₂₂.

**UNIQUAC : A₁₂ = g₁₂ - g₁₁, g₂₁ = g₂₁ - λ₂₂.

Integrating Equation (2), and Substituting Equation (1) results in :

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

where P_{i,0}⁰ is the saturated vapor pressure of component i, T is the flash point of binary aqueous mixture, and T₀ are the flash point of pure flammable component.

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

$$P_2 = P_{2,0}^0 = \text{constant} \quad (5)$$

where the subscript 2 indicates the flammable component.

Substituting Equation (5) into Equation (3) results in :

$$\frac{1}{T} = \frac{1}{T_0} + (R/\Delta H_2) \cdot \ln(\gamma_2 \cdot x_2) \quad (6)$$

The activity coefficient (γ₂) of component 2, which were presented in Equation (6), can be calculated using two activity coefficient models, Wilson and UNIQUAC equations. These equations being described as :

Wilson equation :

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12} x_2) + x_2 \left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} - \frac{\Lambda_{21}}{\Lambda_{21} x_1 + x_2} \right)$$

$$\ln \gamma_2 = -\ln(x_2 + \Lambda_{21} x_1) + x_1 \left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} - \frac{\Lambda_{21}}{\Lambda_{21} x_1 + x_2} \right) \quad (7)$$

where Λ is as following

$$\Lambda_{12} = \frac{v_2}{v_1} e^{-\frac{\lambda_{12}-\lambda_{11}}{RT}}, \quad \Lambda_{21} = \frac{v_1}{v_2} e^{-\frac{\lambda_{21}-\lambda_{22}}{RT}} \quad (8)$$

UNIQUAC equation :

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

$$- q'_i \ln \left(\sum_{j=1}^m \theta'_j \tau_{ji} \right) + q'_i - q'_i \sum_{j=1}^m \frac{\theta'_j \tau_{ij}}{\sum_{k=1}^m \theta'_k \tau_{kj}} \quad (9)$$

where,

$$\tau_{ji} = \frac{q_{ji} - q_{ij}}{RT} \quad (10)$$

$$l_j = \frac{z}{2} (r_j - q_j) - (r_j - 1), \quad z = 10 \quad (11)$$

The binary parameters of Wilson and UNIQUAC equations were abstracted from the literature⁽¹³⁾ and are listed in Table 1.

The temperature (T) which satisfies Equation (6), was determined to be the flash point of binary aqueous mixture. The results are presented in Table 2~3.

3.2 Flash points prediction using Raoult's law

Under an ideal solution assumption, the liquid phase activity coefficient of component 2 is equal to unity. Therefore Equation (6) was reduced to Raoult's law, this being described as :

$$\frac{1}{T} = \frac{1}{T_0} + (R/\Delta H_2) \cdot \ln(x_2) \quad (12)$$

The temperature (T) which satisfies Equation (12), was determined to be the flash point of binary aqueous mixture. The results are presented in Table 2~3.

4. Results

4.1 Experimental results

The flash points of binary aqueous mixtures, water (1)-methanol (2) and water (1)-ethanol (2), are listed in Table 2~3 and Figure 1~2.

The concentrations of component i are given in mole fraction, x_i. As shown in Figure 1 and Figure 2, the flash points of the systems plotted as a function of mole fraction.

As can be seen from the figures, the non-flammable component (water) inhibits the flash. The flash point of aqueous mixtures will be vary depending on the composition of the non-flammable component. The more non-flammable component was obtained as having a the higher the flash point temperature.

Table 2. The Experimental and The Calculated Flash Points for Water (x_1)-Methanol (x_2) System

Mole fractions		Flash points (°C)			
x_1	x_2	Exp.	Raoult's law	Wilson	UNIQUAC
0.000	1.000	10.0	-	-	-
0.102	0.898	11.5	11.85	11.77	11.80
0.315	0.685	16.0	16.69	15.76	16.07
0.500	0.500	21.0	22.63	19.79	20.66
0.700	0.300	26.0	33.15	25.73	27.66
0.900	0.100	46.0	60.99	41.19	44.56
0.950	0.050	58.0	85.12	55.99	59.28
A.A.E.		-	8.66	1.47	0.85

Table 3. The Experimental and The Calculated Flash Points for Water (x_1)-Ethanol (x_2) System

Mole fractions		Flash points (°C)			
x_1	x_2	Exp.	Raoult's law	Wilson	UNIQUAC
0.000	1.000	12.0	-	-	-
0.103	0.897	14.0	13.68	13.49	13.57
0.305	0.695	16.0	17.75	16.04	16.56
0.508	0.492	20.0	23.55	18.35	19.33
0.700	0.300	24.0	32.52	20.83	21.99
0.900	0.100	31.0	56.25	28.02	29.72
0.950	0.050	43.0	75.51	36.15	38.70
A.A.E.		-	11.98	2.53	1.54

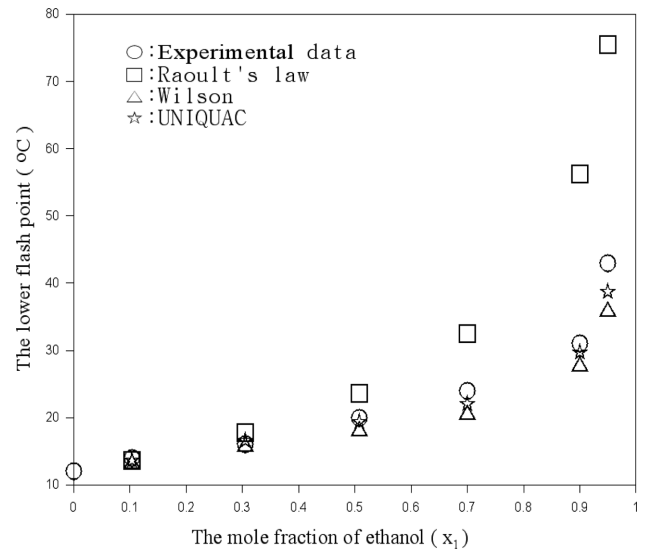
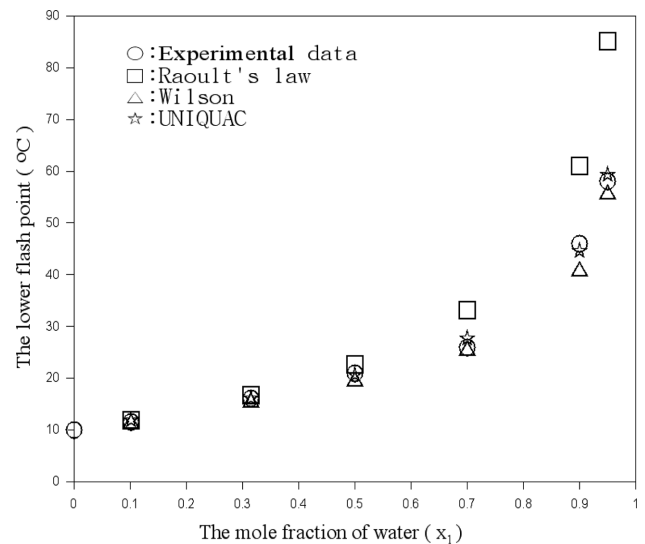
4.2 The comparison of the experimental and calculated flash point

The calculated flash points were presented in Table 2~3. The average absolute error (AAE) included in the tables is defined⁽¹⁴⁾ as :

$$AAE = \sum_{i=1}^N \frac{|T_i^{\text{exp}} - T_i^{\text{cal}}|}{N} \quad (13)$$

where N is the number of experimental data, the T_i^{exp} is the experimental flash point of component i , and T_i^{cal} is the calculated flash point of component i . The AAE is a measure of agreement between the experimental flash points and the calculated flash points.

A comparison between the experimental data and the calculated results of water-methanol system is presented in Table 2. The AAEs of the results calculated by the methods using the Wilson and UNIQUAC equations are 1.47°C and 0.85°C, respectively. The AAE of the results calculated by the method based on Raoult's law is also

**Figure 1.** The comparison of flash points of experimental and calculated for water (x_1)-methanol (x_2) system.**Figure 2.** The comparison of flash points of experimental and calculated for water (x_1)-ethanol (x_2) system.

8.66°C.

As shown in Table 3, for water-ethanol system, the AAEs between the experimental data and the results calculated by the methods using the Wilson and UNIQUAC equations are 2.53°C and 1.54°C, respectively. The AAE of the results calculated by the method based on Raoult's law is also 11.98°C.

It is clear that there is a good agreement between the measured flash points and those calculated by the activity coefficient method performed in this study, as can be seen from the AAEs. The activity coefficient method is also more accurate than the method based on the Raoult's law.

5. Conclusion

The flash points for two aqueous mixtures, water-methanol and water-ethanol, were determined using Seta flash closed cup tester.

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

On the other hand, the flash points calculated by the method using the Wilson and UNIQUAC equations are very similar to the experimental data. The activity coefficient method can thus be useful to calculate the flash point of binary aqueous mixture and to help analyse the fire and explosion hazard.

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