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이성분계 가연성 혼합물의 인화점 측정

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The Flash Point Measurement for Binary Flammable Mixture

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요 약

가연성 액체 혼합물의 화재 위험성을 특징짓는 주된 물리적 성질은 인화점이다. 본 연구는 이성분계 가연성 혼합물의 인화점을 측정하고 예측하고자 한다. Seta flash 밀폐식 장치를 이용하여 n-propanol+propionic acid 계의 인화점을 측정하였다. van Laar 식과 NRTL 식을 이용한 최적화 기법을 통해 인화점을 예측하였다. 이 계산치와 라울의 법칙에 의한 계산치를 비교하였다. 그 결과, 최적화 기법에 의한 계산치가 라울의 법칙에 의한 계산치 보다 측정값에 보다 근사하였다.

Abstract - The flash point is the major physical property used to characterize the fire hazard of flammable liquid solutions. In the present study, the main focus is on measuring and estimating the flash points for binary flammable mixture. The flash points for n-propanol+propionic acid were measured by Seta flash closed cup apparatus. The experimental data were correlated with the van Laar and NRTL equations through the optimization method. The results estimated by these correlations were compared with the values calculated by the method based on Raoult's law. The optimization method were found to be better than the method based on the Raoult's law.

Key words : flash point, seta flash closed cup, n-propanol+propionic acid, van Laar and NRTL equations

I. INTRODUCTION

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, the greater the fire hazard[1]. The flash point is the major physical property used to characterize the fire and explosion hazard of flammable liquid solutions[2].

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The flash point can be generally measured by the testers of two types. The open and closed cup testers are two major flash point analyzers for the determination of the experimental flash point[3]. In this study, Seta flash closed cup tester is selected.

Because the flash points of all the liquid solutions are not available, the development of its estimation method is desirable for the analysis of the fire and explosion hazard. Several researchers have tried to develop the reliable predictive method.

Affens and McLaren[4] proposed the predictive model for the flash point of binary solutions ac-

cording to ideal solution assumption. White et al[5]. reduced Affens model to a simpler equation by ignoring any dependence of the lower flammable limit(LFL) on temperature. However, these models are unable to accurately predict the flash point for non-ideal solution.

Gmehling and Rasmussen[6] proposed the model to calculate the flash point of binary mixtures using UNIFAC equation to the activity coefficients.

Liaw et al.[7] proposed the predictive model for the flash point of binary non-ideal solutions using the activity coefficient models(Wilson, NRTL and UNIQUAC equation). This model needs the binary interaction parameters of activity coefficient model to calculate the flash point. Without the information regarding the binary interaction parameters, this model is unable to calculate the flash point of the binary mixtures.

The flash point data of pure components are readily available in the several literatures. However, the flash points of liquid mixtures containing the flammable components, appear to be scarce in the literature.

Therefore, the main focus of this work was to measure and calculate the flash points for binary flammable mixture to aid in the safety analysis of flammable mixtures.

The flash points for n-propanol+propionic acid, were measured by Seta flash closed cup apparatus. The flash points were calculated by the method based on the Raoult's law. The measured experimental data were correlated with the van Laar and NRTL equations[8] through the optimization method. The results estimated by these correlations were compared with the values calculated by the method based on Raoult's law.

II. FLASH POINT MEASUREMENT

Propionic acid was supplied by Acros Organic Company with a minimum purity of 99.0 %. n-Propanol(99.0%) was obtained from Samchun Company. Two these chemicals were used directly without further purification.

The Seta flash closed cup apparatus manufactured by Koehler Instrument Company was used to measure the flash points of binary liquid solution at different compositions. The basic system configuration was presented in our previous paper[9]. The apparatus consist of a sample cup, time controller, test flame device, flame controller, thermometer, temperature controller, etc. The Seta flash closed cup apparatus was operated according to the standard test method, ASTM D 3278[10].

III. CALCULATION OF THE FLASH POINT

3.1. The Calculation of the flash point based on the Raoult's law

Le Chatelier's rule[11] for the flammable mixture of vapor-air can be expressed as :

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

where y_i is the vapor phase composition of the flammable component i in equilibrium with the liquid phase and LFL_i is the lower flammable limit(LFL) of the pure component i.

LFL_i of each component can be expressed in relation to the saturated vapor pressure of the component i at its flash point, $P_{i,fp}^{sat}$, as :

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

where P in the equation above is the ambient pressure.

The saturated vapor pressure of the studied pure components is a function of temperature and can be calculated by the Antoine equation[8] :

$$\log P_i^{sat} = A_i - \frac{B_i}{T + C_i} \tag{3}$$

where A_i, B_i and C_i are the Antoine coefficients and T is the temperature in degree Celsius(℃). The Antoine coefficients of the studied pure components were adopted from the literature[12] and are listed in Table 1.

The flash point of liquid mixture is measured at the atmospheric pressure. Under this condition the

Table 1. The Antoine coefficients of the studied pure components

	A	B	C
n-Propanol	7.9058	1819.57	205.00
Propionic Acid	7.9906	1929.30	236.43

vapor phase can be approximated as ideal gas, then the vapor phase fugacity coefficient of each component is equal to unity. In case of the non-condensable liquid mixture, the vapor-liquid equilibrium relation of component i can be expressed as :

$$y_i P = x_i \gamma_i P_i^{sat} \tag{4}$$

or

$$y_i = \frac{x_i \gamma_i P_i^{sat}}{P} \tag{5}$$

where x_i is the liquid phase composition of the component i in equilibrium with the vapor phase and r_i is the liquid phase activity coefficient of the component i.

According to being proposed by Liaw et al.[13], the substitution Eq. (2) and Eq. (5) into Eq. (1) results in :

$$\sum_{i=1}^{N} \frac{x_i \gamma_i P_i^{sat}}{P_{i,fp}^{sat}} = \frac{x_1 \gamma_1 P_1^{sat}}{P_{1,fp}^{sat}} + \frac{x_2 \gamma_2 P_2^{sat}}{P_{2,fp}^{sat}} = 1 \tag{6}$$

$P_{i,fp}^{sat}$, presented in Eq. (6), can be calculated by substituting $T_{i,fp}$, (the flash point of the pure component i) into Eq. (3).

Under an ideal solution assumption, the liquid phase activity coefficients of all components are equal to unity. Therefore Eq. (5) was able to be reduced to Raoult's law, then Eq. (6) was reduced as[5] :

$$\sum_{i=1}^{N} \frac{x_i P_i^{sat}}{P_{i,fp}^{sat}} = \frac{x_1 P_1^{sat}}{P_{1,fp}^{sat}} + \frac{x_2 P_2^{sat}}{P_{2,fp}^{sat}} = 1 \tag{7}$$

The temperature which satisfies Eq. (7), was determined to be the flash point of the binary flammable mixture[7].

3.2. The optimization of the binary interaction parameters

The above explained method based on Raoult's law is adequate only for almost ideal solution. In this paper, the wilson and NRTL equations is used to calculate the liquid phase activity coefficient of the binary flammable mixture. Because these equations are effective methods for evaluating the liquid phase activity coefficients.

The van Laar and NRTL equations was used to correlate the experimentally derived data for three binary solutions, these equations being described as :

van Laar :

$$\ln\gamma_1 = A_{12}\left(\frac{A_{21}x_2}{A_{12}x_1 + A_{21}x_2}\right)^2$$
$$\ln\gamma_2 = A_{21}\left(\frac{A_{12}x_1}{A_{12}x_1 + A_{21}x_2}\right)^2 \tag{8}$$

where A_{12} and A_{21} are the binary parameters.

NRTL equation :

$$\ln\gamma_i = \frac{\sum_{j=1}^{m}\tau_{ji}G_{ji}x_j}{\sum_{l=1}^{m}G_{li}x_l} + \sum_{j=1}^{m}\frac{x_j G_{ij}}{\sum_{l=1}^{m}G_{lj}x_l}\left(\tau_{ij} - \frac{\sum_{r=1}^{m}x_r\tau_{rj}G_{rj}}{\sum_{l=1}^{m}G_{lj}x_l}\right) \tag{9}$$

where

$$\tau_{ji} = \frac{g_{ji} - g_{ii}}{Rt} \tag{10}$$

$$G_{ji} = \exp(-\alpha_{ji}\tau_{ji}) \qquad (\alpha_{ji} = \alpha_{ij}) \tag{11}$$

where R is ideal gas constant and t is absolute temperature(K).

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

$$F = \sum_{j=1}^{N} ABS(T_j^{\exp} - T_j^{cal}) \quad (12)$$

where N is the number of the experimental data, ABS is absolute value, $T_j^{\exp}$ is the experimental flash point of component j, and T_j^{cal} is the calculated flash point of component j. T_j^{cal}, which satisfies Eq. (6), was determined to be the flash point of the binary flammable mixtures.

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

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

van Laar : A_{12}, A_{21}
NRTL : A_{12} $(=g_{12}-g_{11})$, A_{21} $(=g_{21}-g_{22})$

were calculated and the flash points were determined.

IV. RESULTS AND DISCUSSION

4.1. Experimental Results

The experimental flash points obtained in this work for n-propanol(1)+propionic acid(2), are presented in Table 2 and Fig. 1.

The concentrations of component i are given in mole fraction, x_i. As shown in Fig. 1, the flash points of the binary flammable system plotted as a function of mole fraction.

4.2. The comparison of the calculated and measured flash points

The experimental flash pointsIn this study, the prediction results obtained were presented in Table 2 and Fig. 1. The calculated binary interaction parameters using the optimization method are shown in Table 3.

The A.A.E.(average absolute error) included in Table 2 is defined as follows[15,16] :

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

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

From Table 2, for n-propanol+propionic acid system, the A.A.E.s of the optimization methods

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

Mole Fractions		Flash points (℃)			
x_1	x_2	Exp.	Raoult's law	van Laar	NRTL
1.000	0.000	21.0	-	-	-
0.899	0.101	25.0	22.28	25.00	22.53
0.700	0.300	27.0	25.22	27.50	26.61
0.501	0.499	32.0	28.99	31.07	31.96
0.300	0.700	37.0	34.24	35.99	37.54
0.102	0.898	42.0	42.31	43.29	42.01
0.000	1.000	49.0	-	-	-
A.A.E.		-	2.12	0.75	0.69

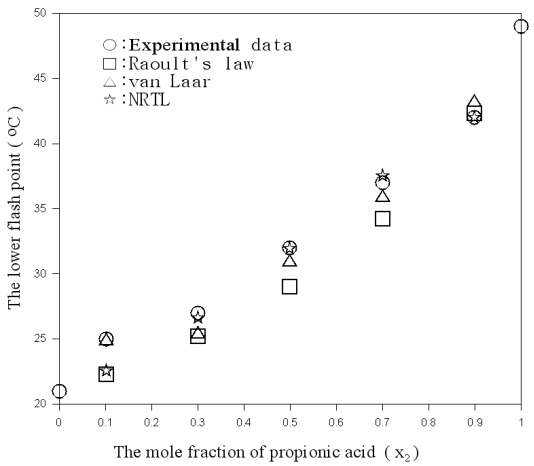

Fig. 1. The comparison of calculated flash points with experimental flash points for the n-propanol(1)+propionic acid(2) system.

Table 3. The optimized binary parameters of the van Laar and NRTL equations for n-propanol(1)+propionic acid(2) system

Parameter / System	van Laar		NRTL*	
	A_{12}	A_{21}	A_{12}	A_{21}
n-Propanol(1) + propionic acid(2)	-0.1526	13.2371	-1116.572	2507.004
*NRTL : $A_{12}=g_{12}-g_{11}$, $A21=g_{21}-g_{22}$ (cal/mol)				

using the van Laar and NRTL equations are 0.75 ℃ and 0.69 ℃ respectively. The A.A.E. of the method based on Raoult's law is 2.12 ℃.

As can be seen from the A.A.E., it is clear that there is a good agreement between the measured flash points and those calculated by the optimization method proposed in this study.

Table 2 also depict the results of comparing the values calculated by the method based on the Raoult's law, and the optimization method based on the van Laar and NRTL equations. The optimization method is more accurate than the method based on the Raoult's law, as can be seen from the A.A.E.

In case of being unable to adopt the binary parameter from the literature, the optimization method proposed in this paper has the advantage of being able to predict effectively the flash point for the binary flammable mixture.

V. CONCLUSIONS

The flash points for n-propanol+propionic acid, were measured using Seta flash closed cup apparatus.

The experimental flash points were compared with the calculated flash points based on the Raoult's law, and the optimization method using the van Laar and NRTL equations.

The predictive values by the optimization method described the experimentally-derived data more effectively than those by the method based on the Raoult's law.

The optimization method proposed in this study can thus be useful to predict the flash point for the binary flammable mixture and to help analyse the fire and explosion hazard.

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NOMENCLATURE

A, B, C : Antoine coefficients
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 [℃]
T^{cal} : calculated flash point temperature [℃]
$T^{\exp}$: experimentally derived flash point temperature [℃]
$T_{i,fp}$: flash point temperature of pure component i [℃]
x : liquid phase composition
y : vapor phase composition

GREEK LETTERS

γ : activity coefficient

REFERENCES

[1] Catoire, L., Paulmier, S., and Naudet, V., "Experimental determination and estimation of closed cup flash points of mixtures of flammable solvents", *Process Safety Progress*, **25**, 1, 33-39, (2006)

[2] H.J. Liaw, W.H. Lu, V. Gerbaud and C.C. Cheng, "Flash-point prediction for binary partially miscible mixtures of flammable solvents", *J. of Hazardous Materials*, **153**, 1165-1175, (2008)

[3] Khalili, T. and Moghadam, A.Z., "Measurement and calculation of flash point of binary aqueous-organic and organic-organic solutions", *Fluid Phase Equilibria,* **312**, 101-105, (2011)

[4] Affens, W.A. and Mclaren, G.W., "Flammabili-

ty Properties of Hydrocarbon Solutions in Air", *J. of Chem. & Eng. Data*, **17**(4), 482-488, (1972)
[5] White, D., Beyler, C.L., Fulper, C., and Leonard, J., "Flame spread on aviation fuels", *Fire Safety Journal*, **28**, 1-31, (1997)
[6] Gmehling, J. and Rasmussen, P., "Flash points of flammable liquid mixtures using UNIFAC", *Ind. Eng. Chem. Fundam.*, **2**, 186.-188, (1982)
[7] Liaw, H.J., Chen, C.T., Cheng, C.C., and Yang, Y.T., "A mathematical model for predicting the flash point of binary solution", *J. of Loss Prevention in the Process Industries*, **15**, 429-438, (2002)
[8] Poling, B.E., Prausnitz, J.M., and O'connell, J.P., *The Properties of Gases and Liquids*, 5th Edition., McGraw-Hill, New York, (2001)
[9] D.M. Ha and S.J. Lee, "Prediction and measurement of the lower flash points for flammable binary solutions by using a setaflash closed cup tester", *Korean J. Chem. Eng.*, **28**, 5, 1161-1165, (2011)
[10] American Society for Testing Materials, Annual Book of ASTM Standards, Vol. **06.01,** (1999)
[11] Le Chatelier, "Esimation of Firedamp by Flammability limits", *Ann. Minmes*, **19**, 388-392, (1891)
[12] Gmehing, J., Onken, U., and Arlt, W., *Vapor-Liquid Equilibrium Data Collection*, **1**, Part1-Part7, DECHEMA, (1980)
[13] Liaw, H.J., Tang, C.L., and Lai, J.S., "A Model for Predicting the Flash Point of Ternary Flammable Solutions of Liquid", *Combust Flame*, **138**, 308-319, (2004)
[14] Kuester J.L. and J.H. Mize, *Optimization Techniques with Fortran*, McGraw-Hill, New York, (1973)
[15] S.J. Lee and D.M. Ha, "The Lower Flash Points of Binary Systems Containing Non-Flammable Component", *Korean J. Chem. Eng.*, **20**(5), 799-802, (2003)
[16] J. Lim, S. Jang, H. Kim, H.K. Cho and M.S. Shin, "Solubility of triclocarban in pure alkanols at different temperatures", *Korean J. Chem. Eng.*, **30**, 1, 181-186, (2013)