Tag 개방식 장치를 이용한 tert-Pentanol+n-Decane 계의 하부인화점 측정

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The Measurement of Lower Flash Point for tert-Pentanol+n-Decane System Using Tag Open-Cup Tester

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요 약

인화점은 공기 속 가연성 증기의 농도가 연소하한계(lower flammability limit)에 도달할 때의 최저 온도이며, 산업현장에서 사용하는 물질들의 화재와 폭발의 위험성을 결정하는 중요한 물성치이다. 단일 성분의 인화점 정보는 여러 문헌에서 얻을 수 있으나, 이성분계 혼합물의 인화점은 충분히 제공되어 있지 않다. 본 연구에서는 tert-pentanol+n-decanel 계의 인화점을 Tag 개방식 장치를 이용하여 측정하였다. 실험값은 Raoult의 법칙과, Wilson 식과 NRTL 식을 활용한 최적화 기법에 의해 계산된 값들과 비교되었다. 최적화 기법에 의한 계산값이 Rauolt의 법칙에 의한 계산값 보다 실험값에 더욱 근접하였다.

Abstract - The flash point the lowest temperature at which the concentration of vapor of the substance in the air reaches the lower flammability limit(LFL), and is one of the most important physical properties used to determine the potential for fire and explosion hazards of industrial materials. 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. In the present study, the flash points of tert-pentanol+n-decane system were measured by Tag open-cup tester. The measured data were compared with the values calculated by the Raoult's law and the optimization methods based on the Wilson and NRTL equations. The calculated values by optimization methods were found to be better than those based on the Raoult's law.

Key words : flash point, tag open-cup tester, tert-pentanol+n-decane system, wilson equation, NRTL equation

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I. INTRODUCTION

The Flammability is an important factor of safe practices for handling and storage of liquid mixtures[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].

The flash point is the lowest temperature at which a liquid gives off enough vapor to form a flammable air-vapour mixture. Generally the lower the flash point temperature, the greater the fire hazard[4].

The flash point is measured by different type of test methods. Two types which are commonly used are open cup and closed cup testers. The flash points measured by closed cup tester are lower than those measured by open cup tester. As it is apparent, in open cup tester, some of the vapours produced by hitting up the spaceman escapes to the atmosphere nearby, in closed cup tester it is prevented to let the vapours escape by using a liquid[1].

Several researchers attempted to develop the predictive model. Catoire and Paulmier[5] developed the model for combustible mixtures. Affens and McLaren[6] developed a predictive model based on the Le Chatelire rule[7]. 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. Liaw et al.[8] developed a mathematical model for highly non-ideal solutions using activity coefficient equations, such as Wilson, NRTL and UNIQUAC models. Ha et al.[9-12] calculated the lower flash points by using the prediction models based on the activity coefficient equation for the binary solutions exhibited the minimum flash point behavior based on the activity coefficient models.

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

In this study, the flash points of tert-pentanol+ n-decane system were measured by Tag open-cup tester. The measured data were compared with the values calculated by the Raoult's law and the optimization methods based on the Wilson and NRTL equations.

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

According to the Le Chatelier's rule, the flash point of flammable vapor-air mixture of multi-component is the temperature which satisfies Eq. (1) :

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

where y_i is the vapour mole fraction of flammable component i, in equilibrium with liquid 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, $P^{sat}_{i,fp}$, as :

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

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 :

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

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 :

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

Substitution Eq. (2) and Eq. (6) into Eq. (1) results in :

$$\sum_{i=1}^{N} \frac{x_i \gamma_i P_i^{sat}}{P_{i,fp}^{sat}} = \frac{x_1 \gamma_1 P_1^{sat}}{P_{1,fp}^{sat}} + \frac{x_2 \gamma_2 P_2^{sat}}{P_{2,fp}^{sat}} = 1 \tag{7}$$

The saturated vapor pressure variation with temperature for a pure substance i can be estimated by the Antoine equation[13] :

$$\log P_i^{sat} = A_i - \frac{B_i}{T + C_i} \tag{8}$$

where A_i, B_i and C_i are the Antoine coefficients and T is the temperature in degree Celsius (℃). The Antoine coefficients, A_i, B_i and C_i, were adapted from the literature[14] 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. (7), 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. (7) was reduced to Raoult's law[15], this being described as :

$$\sum_{i=1}^{N} \frac{x_i P_i^{sat}}{P_{i,fp}^{sat}} = \frac{x_1 P_1^{sat}}{P_{1,fp}^{sat}} + \frac{x_2 P_2^{sat}}{P_{2,fp}^{sat}} = 1 \tag{9}$$

Table 1. The Antoine coefficients of the components

Coefficients Components	A	B	C
tert-Pentanol	8.3767	1821.9	230.0
n-Decane	7.44	1843.12	230.22

The temperature, which satisfies Eq. (9), is determined to be the lower flash point of the binary mixtures[8].

III. 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 Wilson and NRTL 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 NRTL equations are used to correlate the experimentally derived data for tert-pentanol+n-decane system, these equations being described as :

Wilson equation :

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12} x_2) + x_2 \left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} - \frac{\Lambda_{21}}{\Lambda_{21} x_1 + x_1} \right)$$
$$\ln \gamma_2 = -\ln(x_2 + \Lambda_{21} x_1) + x_1 \left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} - \frac{\Lambda_{21}}{\Lambda_{21} x_1 + x_2} \right) \tag{10}$$

where Λ is as following.

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

where the partial molar volumes, v_1 and v_2, were adapted from the literature[14].

NRTL equation :

$$\ln \gamma_i = \frac{\sum_{j=1}^{m} \tau_{ji} G_{ji} x_j}{\sum_{l=1}^{m} G_{li} x_l} + \sum_{j=1}^{m} \frac{x_j G_{ij}}{\sum_{l=1}^{m} G_{lj} x_l} \left(\tau_{ij} - \frac{\sum_{r=1}^{m} x_r \tau_{rj} G_{rj}}{\sum_{l=1}^{m} G_{lj} x_l} \right) \tag{11}$$

where,

$$\tau_{ji} = \frac{g_{ji} - g_{ii}}{RT}$$
$$G_{ji} = \exp(-\alpha_{ji} \tau_{ji}) \quad (\alpha_{ji} = \alpha_{ij})$$

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

Table 2. The optimized binary parameters of Wilson and NRTL equations for tert-pentanol (1)+n-decane(2) system.

Parameters / Systems	Wilson		NRTL		
	A_{12}	A_{21}	A_{12}	A_{21}	α_{12}
tert-Pentanol(1) +n-Decane(2)	1483.58	-234.99	-110.96	1245.51	0.3

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

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. (7), is determined to be the lower flash point of the binary mixture.

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

Using the SIMPLEX[16] method, the binary interaction parameters of the Wilson and NRTL equations,

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

were calculated.

The binary interaction parameters calculated in this way are shown in Table 2. and the calculated flash points are presented in Table 3.

IV. EXPERIMENTAL SECTION

4.1. Chemicals

Tert-pentanol(99.0%) and n-decane(99.0%) was purchased from Acros Company. All these chemicals were used directly without any purification.

4.2. Experimental Apparatus and Procedure

Tag open-cup tester manufactured by Koehler Instrument Co.(USA) was used to measure the flash points. The basic system configuration of the tester is given in Fig.1. The tester consist of a sample cup, water bath, test flame device, level gauge,
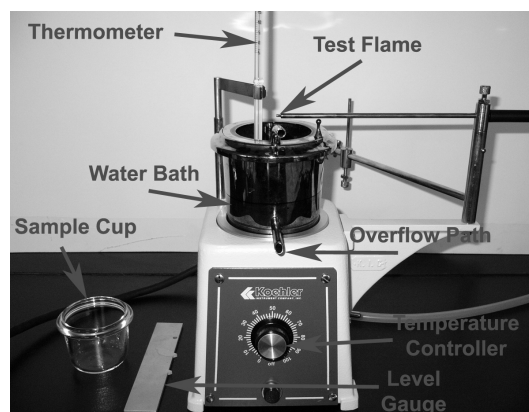
Fig. 1. Experimental apparatus.

electrical heater, overflow path, thermometer and temperature controller.

The Tag open cup tester is operated according to the standard test method, ASTM D 1310-86[17]. The pure components is added by mass and the sample cup(70ml) was filled with the mixture. The water bath is heated with electrical heater, adjusting the heat so that the solution temperature increases at a rate of 1±0.25 ℃/min. A test flame is passed at a uniform rate across the sample cup at specific interval, 0.5 K until a flash occurs. The lower flash point is recorded as the lowest temperature of the bulk at which this results in a flash.

V. RESULTS AND DISCUSSION

In the present study, the flash points for the tert-pentanol+n-decane mixture were measured by Tag open-cup tester. The experimental values are presented in Table 3 and Fig. 2.

The concentrations of component i are given in mole fraction, x_i. As shown in Fig. 2, the lower flash points of the flammable binary mixture plotted as a function of mole fraction. The prediction results obtained were presented in Table 3 and Fig. 2.

Included in Table 3 is the A.A.D.(average absolute deviation) defined[15] as follows :

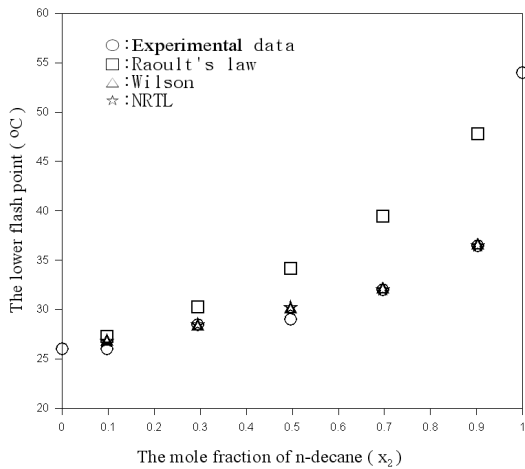$$A.A.D. = \sum_{i=1}^{N} \frac{|T_i^{\exp} - T_i^{cat}|}{N} \qquad (13)$$

Fig. 2. The comparison of the presented flash points with the measured flash points tert-pentanol(x_1)+n-decane(x_2) system

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

Mole Fraction (x_1 : x_2)	Exp. (℃)	Raoult's law	Wilson	NRTL
1.000 : 0.000	26.0	-	-	-
0.902 : 0.098	26.0	27.29	26.72	26.79
0.705 : 0.295	28.5	30.30	28.28	28.48
0.504 : 0.496	29.0	34.20	30.00	30.23
0.303 : 0.697	32.0	39.48	32.00	32.00
0.097 : 0.903	36.5	36.50	36.50	36.50
0.000 : 1.000	54.0	-	-	-
A.A.D.	-	5.42	0.39	0.41

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

As can be seen from Fig. 2, the experimental results are generally in bad agreement with the predictive results based on the Raoul's law and in good agreement with the predictive results based

on the optimization method using the Wilson and NRTL equations.

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

VI. CONCLUSIONS

The lower flash points for tert-pentanol+n-decane were measured by Tag open-cup tester. The measured data were compared with the calculated values based on the Raoult's law and are generally in bad agreement with those. The calculated flash points based on the optimization method using the Wilson and NRTL equations are very similar to the experimental data.

The optimized method in this study can be thus 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.

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