Tag 개방식 장치를 이용한 n-Propanol+n-Decane 계의 하부인화점 측정 및 예측

하 동 명

세명대학교 안전공학과
(2005. 1. 10. 접수 / 2005. 4. 10. 채택)

Measurement and Prediction of the Lower Flash Point for n-Propanol+n-Decane System Using the Tag Open-Cup Apparatus

Dong-Myeong Ha

Department of Safety Engineering, Semyung University, Jecheon, Korea
(Received January 10, 2005 / Accepted April 10, 2005)

Abstract : The lower flash points for the n-propanol+n-decane flammable mixture were measured by the Tag open-cup apparatus(ASTM D 1310). The experimental results of mixture exhibited the lower flash point than those of pure component in the flash point versus composition curve. The experimental value of the minimum flash point is 27℃ at a mole fraction of n-propanol of 0.71, and the flash point of n-propanol was 28℃. The experimentally obtained data were compared with the values that had been calculated by use of the prediction model, which assumes an ideal solution, and the flash point prediction models based on the van Laar equation were used to estimate the activity coefficients. The predictive curve based on an ideal solution deviated from the experimental data for this system. The experimental results demonstrate a close agreement with the predicted curves, which used the van Laar equation. The average absolute deviation(A.A.D.) from using the van Laar equation is 0.83℃.The methodology proposed here in this paper can thus be applied to incorporate an inherently safer design for chemical processes, such as determining safe storage and handling conditions for flammable solutions.

초록 : 노말프로판올과 노말데칸의 가연성혼합물의 하부인화점을 Tag 개방식 장치를 이용하여 측정하였다. 실험 결과 인화점과 조성의 관계에서 혼합물 보다 낮은 인화점을 보여주었다. 노말 프로판올의 몰분율 0.71에서 27℃였으며, 노말프로판올의 인화점은 28℃였다. 실험 결과는 이상용액을 근거로 한 예측값과 활동도계수 예측식인 van Laar식을 사용하여 계산된 값을 각각 비교하였다. 이상용액 개념을 이용한 예측값은 실험값과 차이를 보였으나, van Laar 식에 의한 예측값은 실험값과 일치하였으며, van Laar식에 의한 예측값과 실험값은 평균 0.83℃차이를 보였다. 본 연구에서 제시된 방법론은 가연성물질에 대해 안전한 저장 및 취급하는 조건의 결정과 같은 화학공정 설계의 본질적 안전 설계에 적용할 수 있다.

Key Words : flash points, flammable mixture, Tag open-cup apparatus, ideal solution model, van Laar equation

Nomenclature

A, B, C : Antoine coefficients
f : fugacity [kPa]
LFL : lower flammable limit
n : number of data
P : ambient pressure [kPa]

P^{sat} : saturated vapor pressure [kPa]
P_i^{sat} : saturated vapor pressure of component i at flash point [kPa]
r : coefficient of correlation
T : temperature [K]
T^{cal} : calculated flash point temperature [K]
T^{exp} : experimentally derived flash point temperature [K]

hadm@semyung.ac.kr

x   : liquid phase composition
Y   : predicted value by the fitted model
y   : vapor phase composition

Greek Letters

Φ : fugacity coefficient of species i in solution
γ : activity coefficient

Superscripts

F   : flash point
exp.   : experimental value
cal.   : calculated value

Subscripts

i   : species I

1. Introduction

The flash point is the best known and most widely used flammability property for the evaluation of the hazard of flammability liquids. Also, the flash point is one of the major safety properties specified in a typical material safety data sheet(MSDS)[1].

The experimental flash point data are readily available in the various literatures. However, most of the data published on the flash points were for pure components, while the flash points of binary solutions that have flammable components determined by the closed cup apparatus have seen in a little study and the data that does exist was inconsistent. Therefore, the purpose of this study was to measure and predict the lower flash points for the binary system to aid in evaluating the safety of flammable liquid mixtures by using an open cup flash point tester.

Affens and McLaren[2] have developed the model based on Raoult's law, which was used to predict the flash point for hydrocarbon solutions. White et al.[3] reduced Affens and Mclaren's model to a simpler equation by ignoring the temperature effect upon LFL(Lower Flammability Limit). Ha et al.[4,5] determined experimentally the lower and upper flash points for a binary system. Then these results were compared with the calculated values by using Raoult's law and the van Laar equation. Ha et al.[6,7] developed that

experimental lower flash points for binary system containing non-flammable component were compared with the calculated values by using Raoult's law and van Laar equation.

The flash points are generally measured by using the flash point testers. There are two methods for measuring the flash point of combustible liquids, the closed cup and open-cup apparatus. The open-cup flash point temperature is a few degrees higher than the closed cup flash point temperature, because the open cup tester can not be readily be made for multi-component due to the distillation of the mixture during heating.

In this study, n-propanol+n-decane system was selected to aim at prediction of the flash points of non-ideal flammable solutions. The flash points for the n-propanol+n-decane system were measured by the Tag open cup apparatus(TOC, ASTM D1310)[8], and compared with the values calculated by using the flash point prediction models based on Raoult's law and van Laar equation.

2. Relationship Between Flash Points and Flammability Limits for Flash Point Calculation

Flammable substances are gases, liquids and solids that ignite and continue to burn in air if exposed to a source of ignition.

Most flammable and combustible liquids are volatile by nature; that is, they evaporate quickly and are continue to give off vapors. The rate of evaporation varies greatly from one liquid to another and increases with temperature. It is their vapors combined with air, not the liquid or solids themselves, that ignite and burn. In many instances, an increase in just temperature all one creates a more hazardous condition because of the increase in the rate at which vapors are evolved.

The flash point is defined by the National Fire Protection Association[9] as the lowest temperature at which a flammable liquid gives off sufficient vapor to form an ignitable mixture with air near its surface or within a vessel. The open cup(O.C.) flash points are generally somewhat higher than the closed cup

(C.C.) flash points for the same materials. Special precautions should be taken when the product has a low flash point. Materials having a low flash point are a greater fire hazard than materials having a high flash point.

The flammable limits refer to the range of flammable gas or vapor concentrations which ignition will occur if an ignition source is present. LFL means the lower flammable limit. UFL means the upper flammable limit. All concentrations between LFL and UFL are in the flammable range, and special precautions are needed to prevent ignition or explosion.

From the definition of flash point, the flash point of a combustible liquid is defined as that temperature at which the vapor pressure of the specified liquid produces such as to produce a concentration of vapor in the air that corresponds to the lower flammable limit.

3. Experiment

3.1. Chemicals

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

3.2. Experimental Apparatus and Procedure

The Tag open-cup apparatus(TOC) consists of a sample cup, water bath, test flame, level gauge and electric heater[9].

The pure components are added by mass and the test cup is filled with the mixture solution, and a glass cup is filled with solution to a level 1/8" from the edge of the cup.

The thermometer are placed so that it is half-way between the center and edge of cup, with the bottom of the bulb 1/4" from the inside bottom of the cup.

The flame taper is lighted and adjust the flame to 5/32" diameter, using the bead as a guide. The flame taper is passed over the top of the cup so that the flame is in a plane 1/8" over the top rim of the cup, and across the center of the cup, using the swivel device provided.

Table 1. The experimental and calculated flash points for n-propanol(x_1)+n-decane(x_2) system by using TOC

Mole fractions		Flash points (℃)		
x_1	x_2	Exp.	Ideal solution	van Laar
1.000	0.000	28	28.01	28.01
0.887	0.113	27	29.48	27.40
0.710	0.290	27	32.12	27.57
0.504	0.496	28	35.96	27.75
0.309	0.691	29.5	40.80	28.79
0.108	0.892	31.5	48.12	35.35
0.000	1.000	54	54.02	54.02
A.A.P.E	-	-	21.10	2.74
A.A.D.	-	-	6.21	0.83

The bath is heated with electrical heater, adjusting the heat so that the solution temperature increases at a rate of 2±0.5°F(1±0.25℃)/min, until flash occurs. The pass should be in one direction only, and should take about one second to pass over sample. The flash point the lowest temperature at which application of the test flame causes the vapor above the mixture to ignite.

4. Results and Discussion

4.1. Flash Points for n-Propanol+n-Decane System Measured by the Tag Open-cup Apparatus

The results obtained in this work for the n-propanol (1)+n-decane(2) system are presented in Table 1 and Fig. 1.

The concentrations of component i are given in the mole fraction, xi . As shown in Fig. 1, the lower flash points of the system are plotted as a function of n-decane concentration.

4.2. Calculation of Lower Flash Points for the Tag Open-cup Apparatus

4.2.1. Flash point prediction model by using the activity coefficient

It is necessary to calculate the component activity coefficients of the mixtures of flammable solvents in the determination of the vapor-liquid equilibrium, as they often exhibit strongly non-ideal solution behavior. Many expressions have been proposed to calculate
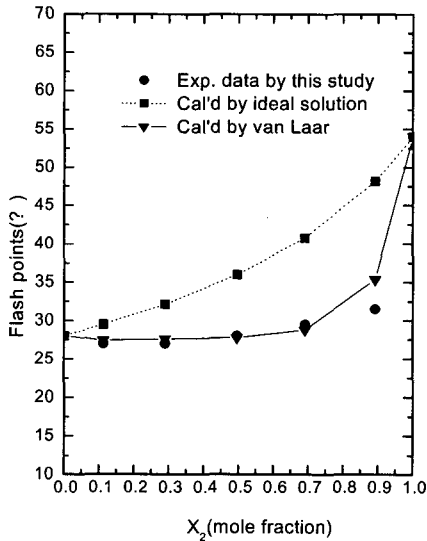
Fig. 1. Comparison of the flash point prediction curves with experimental data for n-propanol(x_1)+n-decane(x_2) system.

the activity coefficients of such mixtures. Some examples, which are discussed in reference[10], are the equations of Margules, van Laar, and Wilson, the Non-Random Two Liquid (NRTL) method, and group contribution methods like the Analytical Solution of Groups (ASOG), the Universal Quasi-Chemical (UNIQUAC) method, and its modification UNIFAC.

According to the authors of the reference[10], the methods of Margules and van Laar are mathematically simpler than the others, and give good results for many moderately non-ideal binary mixtures.

Walsham's method[11] of calculating the flash points of mixture of oxygenated and hydrocarbon solvents was also used here. This method is the modification of the Le Chatelier equation[12],

$$\sum_{i=1} p_i \gamma_i x_i / p_i^F = 1 \tag{1}$$

where p_i is vapor pressure of pure i at test T(K) in mmHg, γ_i is activity coefficient of component i at test T(K), x_i is mole fraction i, and p_i^F is vapor pressure of i at its TOC flash point. Walsham found that this equation was not significantly more accurate than simply using the flash point of the lowest

flashing component as the mixture flash point.

In this study, the Le Chatelier[12] has presented the following equation for multicomponent mixtures containing flammable compounds.

$$\sum_{i=1}^{N} \frac{y_i}{LFL_i} = 1 \tag{2}$$

where y_i is the composition of a flammable substance i in the vapor phase, and LFL_i the lower flammable limit(LFL) of the pure component i. From the definition of flash point, LFL_i is expressed relative to its saturated vapor pressure at flash point, P_i^F, as :

$$LFL_i = \frac{P_i^F}{P} \tag{3}$$

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 :

$$y_i \Phi_i P = x_i \gamma_i f_i (\text{ i} = 1, 2, \cdots, \text{N}) \tag{4}$$

At the 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 :

$$\Phi_i = 1 \tag{5}$$

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

$$f_i \cong P_i^{sat} \tag{6}$$

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

$$y_i = \frac{x_i \gamma_i P_i^{sat}}{P} \quad (\text{ i} = 1, 2, \cdots, \text{N}) \tag{7}$$

Table 2. Antoine constants of n-propanol and n-decane

Constants Components	A	B	C
n-Propanol	8.37895	1788.02	227.438
n-Decane	7.44000	1843.12	230.220

Substitution Eq. (2) and Eq. (7) into Eq. (1), the flammable vapor-air mixture of two components is as follows :

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

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

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

where A_i, B_i and C_i are the Antoine coefficients, and T is temperature(℃). These coefficients were adapted form the literature[13] and listed in Table 2.

The vapor pressure of pure substance i at its flash point P_i^F, as presented in Eq. (9), can be estimated by substituting $T_{i,fp}$, the flash point of component i, into the Antoine equation.

The activity coefficients(γ_i) which were presented in Eq. (8), can be estimated by the use of two different equations including : the van Laar equation. The binary parameters of those equations were abstracted from the literature[13].

The flash point-prediction model developed for the flammable binary solution included by using the Le Chatelier, the Antoine equation, and the models for estimating activity coefficients. These are described using Eq. (8), Eq. (9) and the models for estimating activity coefficients(van Laar equation). The temperature, which satisfies these equations, is deemed by us to the flash point of the solution.

4.2.2. Prediction model development by an ideal solution assumption

For the ideal solution, the activity coefficients of the liquid phase are equal to unity, and the flash point prediction model may be reduced to a simpler form. Under this condition, the vapor-liquid equilibrium(VLE) equation, Eq. (7), could be reduced to Raoult's law for this study, this being described as :

$$y_i = \frac{x_i P_i^{sat}}{P} \qquad (i = 1, 2, \cdot \cdot \cdot, N) \qquad (10)$$

Therefore, the modified equation of the Le Chatelier, Eq. (8), was reduced to :

$$\sum_{i=1}^{N} \frac{x_i P_i^{sat}}{P_i^F} = \frac{x_1 P_1^{sat}}{P_1^F} + \frac{x_2 P_2^{sat}}{P_{2,}^F} = 1 \qquad (11)$$

The Antoine equation, Eq. (9), was still deemed by us to useful to estimate P_i^{sat} and P_i^F for this prediction model. Therefore, the prediction model for the flash point under an ideal solution assumption can be described using Eq. (7) and (11).

4.3. Evaluation Criteria Used[14]

4.3.1. Average absolute percent errors(A.A.P.E.) and average absolute deviations(A.A.D.)

The A.A.P.E. is a non-dimensional quantity that permits an accurate quantitative comparison between the reported value and predicted value. The average absolute percent errors(A.A.P.E.) is :

$$A.A.P.E. = \frac{\sum \left| \frac{T_i^{cal} - T_i^{exp}}{T_i^{exp}} \right|}{n} \times 100 \qquad (12)$$

where the T_i^{exp} is the experimental flash point, and T_i^{cal} is the estimated flash point and n is the number of data.

The A.A.D. is another index, replacing A.A.P.E. in situation when an accurate quantitative comparison between the reported value and estimated value are attempted. The average absolute deviations(A.A.D.) is:

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

where the A.A.D. is a degree of agreement between the experimental data and the calculated values.

4.3.2. The coefficient of determination(r^2), coefficient of correlation(r) and standard deviation

The determination of determination(r^2) and the coefficient of correlation(r) measure the proportion of the variation in the response around the mean that can be attributed to terms in the model rather than to random error and it is determined by

$$r^2 = \frac{SS_r}{SS_{yy}} = 1 - \frac{SS_E}{SS_{yy}} \tag{14}$$

$$r = \pm \sqrt{r^2} \tag{15}$$

where SS_E is the sum of squares of the residual errors $(= \sum_{i=1}^{n}(y_i - Y_i)^2)$ where Y_i is the predicted value by the fitted model. SS_R is the sum of squares due to regression $(= \sum_{i=1}^{n}(Y_i - y)^2)$ where y is the overall average of y_i, SS_{yy} is the total sum of squares about the mean given by

$$SS_{yy} = SS_E + SS_R = \sum_{i=1}^{n}(y_i - y)^2 \tag{16}$$

The standard deviation(S) is :

$$S = \sqrt{\frac{\sum(y_i - Y_i)^2}{n-1}} \tag{17}$$

where n is the number of data.

4.4. Comparison of the calculated values with the experimental values

In this study, the flash point prediction models proposed in section 4.2.1 and 4.2.2 was used to predict the flash point of the n-propanol+n-decane system. The prediction results obtained were presented in Table 1 and Fig. 1.

As shown in Fig. 1, the experimental results agreed well with the predicted curves, which use the

van Laar equation to estimate activity coefficients. The predictive curves simulated from the prediction model proposed in section 4.2.2, are also displayed in Fig. 1. From this figure, it is apparent that the predictive curves based on the reduced model deviate from the experimental results for this highly non-ideal solution, n-propanol+n-decane system.

Fig. 1 also depicts the results of comparing the predictive curves of the flash point prediction model using different equations for estimating the corresponding activity coefficients. It is apparent that the flash point prediction model based on the van Laar equation which described by the experimentally-derived data is more effective than that of the flash point prediction model based on the Raoult's law. The average absolute deviations(A.A.D.) by using van Laar equation is 0.83℃. The average absolute percent errors(A.A.P.E.) is 2.74% and the coefficient of correlation(r) is 0.986. The values estimated by the van Laar equation agreed well with the experimental values.

The surprising finding for the solution of n-propanol+n-decane system, was that a flash point of the solution over a wide composition was lower than that recorded for the individual components of solution : i.e., this solution exhibits minimum flash point behavior. The minimum value of the flash point for a binary solution is not necessarily equivalent to that of an individual component displaying the lower value. It may be equivalent to a value between a specific composition located somewhere and a composition value for the individual components. This phenomenon is attributable to the observation that this particular non-ideal solution reflects a highly-positive deviation from the behavior of an ideal solution, for which the activity coefficients are observed to be much larger than unity, that such behavior results in a substantial reduction of the solution's flash point.

Therefore, it must be emphasized that chemical process safety design based upon the lower flash point value of individual solution components cannot necessarily be guaranteed safe for a binary solution because the resultant solution may reveal minimum flash point behavior.

5. Conclusions

The flash points for the n-propanol+n-decane flammable mixture were measured by Tag open-cup apparatus(TOC, ASTM D1310).

The experimental results exhibited the flash point, i. e., less than those of pure component in the flash point versus composition curve. The experimental value of the minimum flash point is 27℃ at a mole fraction of n-propanol of 0.71, and the flash point of n-propanol was 28℃.

The experimental data were compared with the values calculated by the prediction model based on an ideal solution and the flash point models based on the van Laar. The predictive curve based upon an ideal solution deviated form the experimental data. The experimental results are in good agreement with the predictive curves, which use the van Laar to estimate activity coefficients.

The average absolute deviations(A.A.D.) by using van Laar equation is 0.83℃. The average absolute percent errors(A.A.P.E.) is 2.74% and the coefficient of correlation(r) is 0.986. The values estimated from the van Laar equation agreed well with the experimental values.

The predictive results of this model can thus be applied to incorporate inherently safer design for chemical processes, such as the determination of the safe storage and handling conditions for the non-ideal solutions containing flammable components.

References

1) E. Meyer, "Chemistry of Hazardous Materials", 2nd ed., Prentice- Hall, 1990.

2) W. A. Affens and G. W. McLaren, "Flammability Properties of Hydrocarbon Solutions in Air", J. Chem. Eng. Data, Vol. 17, pp. 482~488, 1972.

3) D. White, C. L. Beyler, C. Fulper and J. Leonard, "Flame Spread on Aviation Fuels", Fire Safety Journal, Vol. 38, pp. 1~31, 1997.

4) D. M. Ha, Y. S. Mok and J. W. Choi, "Flash Points of a Flammable Liquid Mixture of Binary System", HWAHAK KONGHAK, Vol. 37, No. 2, pp. 146~150, 1997.

5) D. M. Ha and S. K. Lee, "A Study on Flash Points of a Flammable Substances - Focused on Prediction of Flash Points in Ternary System by Solution Theory-", T. of Korea Institute of Fire Sci. & Eng., Vol. 15, No. 3, pp. 14~20, 2001.

6) D. M. Ha, Y. C. Choi and S. J. Lee, "The Flash Points of Water+n-propanol System Using Closed Cup Measurement Apparatus", J. of Korean Institute for Industrial Safety, Vol. 17, No. 4, pp. 140~145, 2002.

7) S. J. Lee and D. M. Ha, "The Lower Flash Points for Binary Systems Containing Non-flammable Component", Korea J. Chem. Eng., Vol. 20, No. 5, pp. 799~802, 2003.

8) ASTM, "Standard Test Method for Flash-Point and Fire point of Liquids Tag Open-cup Apparatus (ASTM D 1310-86)", American Society for Testing Materials, Philadelpia, PA, 1990.

9) D. M. Ha, S. J. Lee and Y. H. Song, "Measurement of Fire Point and Flash Point for Alcohols using Tag Open-Cup Apparatus", J. of the Korean Society of Safety, Vol. 19, No. 4, pp. 69~73, 2004.

10) C. R. Reid, J. M. Prausnitz and B. E. Poling, "The Properties of Gases and Liquids", 4nd ed., McGraw-Hill, New York, 1998.

11) J. G. Walsham, "Prediction of flash points for solvent mixture", Advan. Chem. Ser. Publ. 73, Ser. 124, American Chemical Society, Washington, DC, pp. 56~69, 1973.

12) H. Le Chatelier, "Estimation of Fire Damp by Flammability limits", Ann. Mines, Vol. 19, No. 8, pp. 388~392, 1891.

13) J. Gmehing, U. Onken and W. Arlt, "Vapor-Liquid Equilibrium Data Collection", Vol. 1, Part 1-Part 7, DECHEMA, 1980.

14) D. M. Ha and S. J. Lee, "Prediction of the Net Heats of Combustion of Organic Halogenated Compounds based on the Atomic Contribution Method", T. of Korea Institute of Fire Sci. & Eng., Vol. 17, No. 4, pp.7~13, 2003.