[Research Paper]

Methanol, Ethanol, 2-Propanol 그리고 1-Butanol 이성분 혼합계에 대한 101.3 kPa에서의 인화점 측정 및 예측

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The Measurement and Prediction of Flash Point for Binary Mixtures of Methanol, Ethanol, 2-Propanol and 1-Butanol at 101.3 kPa

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요   약

인화점은 화재 및 액체의 폭발 위험의 가능성을 결정하는 데 사용되는 가장 중요한 물리적 특성이고, 산업공정에서 안정성 평가시 중요한 연소특성 가운데 하나이다. 따라서 본 연구는 4류 위험물 중 알코올계 혼합물인 {methanol + 1-butanol}, {ethanol + 1-butanol} 그리고 {2-propanol + 1-butanol} 이성분계 101.3 kPa에서 최소인화점을 SETA closed cup flash point tester를 이용하여 측정하였다. 각 이성분계에 대하여 Wilson, NRTL 및 UNIQUAC 파라미터를 이용하여 혼합물에 대한 인화점 예측하고 실험 결과와 비교하였다. 비교결과 모든 예측값과 실험값은 유사한 값을 보였고 편차가 1.14 K 이내의 결과를 보였다.

ABSTRACT

Flash point is one of the most important variables used to characterize fire and explosion hazard of liquids. The lower flash point data were measured for the binary systems {methanol + 1-butanol}, {ethanol + 1-butanol} and {2-propanol + 1-butanol} at 101.3 kPa. Experiments were performed according to the standard test method (ASTM D 3278) using a SETA closed cup flash point tester. The measured flash points were compared with the predicted values calculated using the following activity coefficient models: Wilson, Non-Random Two Liquid (NRTL), and UNIversal QUAsiChemical (UNIQUAC). The measured FP data agreed well with the predicted values of Raoult's law, Wilson, NRTL and UNIQUAC models. The average absolute deviation between the predicted and measured lower FP was less than 1.14 K.

Keywords : Flash point, Seta closed cup tester, Alcohols, Activity coefficient models

1. Introduction

The flash point (FP) is one of the most important variables used to characterize fire and explosion hazard of those liquids[1]. The lower flammable limit (LFL) provides the knowledge necessary for understanding the fundamental physical and chemical processes of combustion. As temperature increases, the vapor pressure increases and the amount of evaporated flammable liquid in equilibrium with the air also increases. When the FP is reached, a simple ignition source is able to combust the mixture[2]. Experi-

mental FP data have clearly become important in ensuring safe storage of flammable materials, and for this reason a series of studies for predicting the FP of pure substances and their mixtures can be encountered.

Recently, several method have been developed for the prediction or estimation of low flash points of pure compound and mixtures[3-5]. The methanol, ethanol, 2-propanol and 1-butanol are very useful solvents for petrochemical materials and industrially significant plastics. The purpose of this study was to predict the FPs for the flammable binary mixtures by using representative industrial solvents

with alkyl alcohols.

In the present work, the lower FPs at 101.3 kPa were analytically determined for the following binary systems using SETA closed cup flash point tester: {methanol (1) + 1-butanol (2)}, {ethanol (1) + 1-butanol (2)} and {2-propanol (1) + 1-butanol (2)}. The experimental FP data for these binary systems were compared with predicted values from a variety of activity coefficient models, including the Wilson[6], Non-Random Two-Liquid (NRTL)[7] and UNIversal QUASiChemical (UNIQUAC)[8] models.

2. Material and Methods

2.1 Materials

Commercial, analytical-grade chemicals were used in this investigation. Methanol (CH_4O, $M = 32.04$ g · mol^{-1}, CAS-RN 67-56-1, 99.9%), Ethanol (C_2H_6O, $M = 46.07$ g · mol^{-1}, CAS-RN 64-17-5, 99.9%) and 2-propanol (C_3H_8O, $M = 60.10$ g · mol^{-1}, CAS-RN 67-63-0, 99.9%) were supplied by J. T Baker Chemical Co. 1-Butanol ($C_4H_{10}O$, $M = 74.12$ g · mol^{-1}, CAS-RN 71-36-3, 99.9%) was obtained from Aldrich Co. All of the chemicals were dried using molecular sieves with a pore diameter of 0.3 nm. The water content of the chemicals, determined using a Karl-Fischer titrator (Metrohm 684 KF-Coulometer), was less than 7×10^{-5} g/g. The purity of the chemicals was assessed by gas chromatography and by a comparison of the densities with values reported in the literature[9]. The densities, purities, FPs and UNIQUAC parameters of the chemicals are listed in Table 1 along with the reported values.

2.2 Procedure

A SETA closed cup flash point tester (Series 8 SETA FLASH, model 82000-0, Surrey, UK) was used to measure the FPs for the three miscible mixtures. The SETA closed cup flash point tester was operated according to the standard test method, ASTM D 3278[11]. It consists of four

parts: a sample cup, a test flame device with flame controller, a temperature-measuring system with a temperature controller, and a time controller. The injection volume was 2 ml, and the measured temperature range was set from 253.15 K to 573.15 K. The temperature of the liquid sample in the sample cup was regulated by the temperature controller, which has an accuracy of 0.1 K. Calibration of the SETA closed cup flash point tester was carried out periodically using standard tester solvent. Approximately 2 ml of the sample mixtures were weighed using a microbalance (Ohaus DV215CD) with a precision of 1×10^{-5} g. The heavier component of the binary mixtures was weighed first to minimize vaporization. The systematic error associated with the experiments was estimated to be less than 1×10^{-4} mole fraction. A time interval of 15 min between measurements was chosen to attain a constant temperature and stability in oscillation.

3. Results and Discussion

Le Chatelier's rule[12] for a flammable mixture of vapor and air may be expressed as follows:

$$1 = \sum_i \frac{y_i}{LFL_i} \tag{1}$$

where y_i is the vapor phase composition of a flammable substance i and LFL_i is the lower flammable limit of the pure component i. The LFL_i is expressed in relation to the pure component i vapor pressure at its FP, $P_{i, FP}^{sat}$, as

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

where P in the equation above represents the ambient pressure. The FP of a pure substance is measured at atmospheric pressure. Under this condition the vapor phase usually exhibits an ideal behavior. In the case of a liquid mixture containing flammable substances in the presence

Table 1. The Densities, Purities, FPs and UNIQUAC Parameters of Chemicals used in this Work

Chemicals	ρ/g · cm^3 at 298.15 K		G.C. analysis (wt%)	Flash point (K) at 101.3 kPa		UNIQUAC	
	This work	Reference^a		This work	Reference^b	r-Value^a	q-Value^a
Methanol	0.78657	0.78660	> 99.9	283.45	284.15	1.4311	1.4320
Ethanol	0.78511	0.78500	> 99.9	284.75	286.15	2.1055	1.9720
2-Propanol	0.79979	0.79970	> 99.9	287.95	287.15	2.7799	2.5120
1-Butanol	0.80598	0.80600	> 99.9	308.65	310.15	3.4543	3.0520

^{a}Ref. [9].
^{b}Ref. [10].

of the non-condensable components of air, the vapor-liquid equilibrium of component i is given by

$$y_i P = x_i \gamma_i P_i^{sat} \tag{3}$$

where γ_i is the liquid phase activity coefficient.

As proposed by Liaw et al.[3], the substitution Eq. (2) and Eq. (3) into Eq. (1) results in Eq. (4), which allows evaluation of FPs for a flammable liquid mixture:

$$\sum_i \frac{x_i \gamma_i P_i^{sat}}{P_{i,FP}^{sat}} = 1 \tag{4}$$

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

$$\log P^{sat}(\text{mmHg}) = A - \frac{B}{C + T/^o C} \tag{5}$$

Antoine coefficients A, B and C were adapted from the literature[9] and are given in Table 2.

For an ideal solution assumption, the activity coefficients of the liquid phase are equal to unity. Therefore Eq. (4) was reduced to Raoult's law, this being expressed as[13]:

$$\sum_i \frac{x_i P_i^{sat}}{P_{i,FP}^{sat}} = \frac{x_1 P_1^{sat}}{P_{1,FP}^{sat}} + \frac{x_2 P_2^{sat}}{P_{2,FP}^{sat}} = 1 \tag{6}$$

The temperature, which satisfies Eq. (6), is determined to be the flash point of the binary mixtures.

Table 2. The Antoine Coefficients of the Components

Components	Antoine coefficients[a]		
	A	B	C
Methanol	8.08097	1582.27	239.726
Ethanol	8.11220	1592.86	226.184
2-Propanol	8.00308	1505.52	211.600
1-Butanol	7.92484	1617.52	203.296

[a]Ref. [6].

For non-ideal liquid mixtures, activity coefficients (γ_i) were estimated with the optimum binary interaction parameters of the Wilson[6], NRTL[7] and UNIQUAC[8] equations.

Wilson equation:

$$\ln\gamma_i = -\ln\left(\sum_{j=1}^n x_j \Lambda_{ij}\right) + 1 - \sum_{k=1}^n \frac{x_j \Lambda_{ji}}{\sum_{j=1}^n x_j \Lambda_{kj}} \tag{7}$$

with

$$\Lambda_{ij} = \frac{V_j^2}{V_i^2} \exp\left(-\frac{\lambda_{ij} - \lambda_{ii}}{RT}\right)$$

NRTL equation:

$$\ln\gamma_i = \frac{\sum_j \tau_{ji} G_{ji} x_j}{\sum_k G_{ki} x_k} + \sum_j \frac{x_j G_{ij}}{\sum_k G_{kj} x_k}\left(\tau_{ij} - \frac{\sum_k x_k \tau_{kj} G_{kj}}{\sum_k G_{kj} x_k}\right) \tag{8}$$

with

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

UNIQUAC equation:

$$\ln\gamma_i = \ln\gamma_i^C + \ln\gamma_i^R \tag{9}$$

$$\ln\gamma_i^C = 1 - J_i + \ln J_i - 5q_i\left(1 - \frac{J_i}{L_i} + \ln\frac{J_i}{L_i}\right)$$

$$\ln\gamma_i^R = q_i\left(1 - \ln S_i - \sum_j \theta_j \frac{\tau_{ij}}{S_j}\right)$$

with

$$J_i = \frac{r_i}{\sum_j r_j x_j} \qquad L_i = \frac{q_i}{\sum_j q_j x_j} \qquad S_i = \sum_l \theta_l \tau_{li}$$

$$\theta_i = \frac{x_i q_i}{\sum_j x_j q_j} \qquad \tau_{ij} = \exp\frac{-(u_{ij} - u_{ii})}{RT}$$

The optimized binary parameters for the equations to estimate the activity coefficients were taken from litera-

Table 3. The Optimized Binary Parameters of the Wilson, NRTL and UNIQUAC Equations for Each Binary System

Systems	Wilson		NRTL			UNIQUAC	
	A_{12} /J·mol^{-1}	A_{21} /J·mol^{-1}	A_{12} /J·mol^{-1}	A_{21} /J·mol^{-1}	α	A_{12} /J·mol^{-1}	A_{21} /J·mol^{-1}
{Methanol (1) + 1-butanol (2)}[a]	253.80	707.80	−988.94	857.02	0.3038	513.74	−132.25
{Ethanol (1) + 1-butanol (2)}[b]	−341.32	1159.44	24357.06	−17972.67	0.0433	3602.95	−2060.51
{2-Propanol (1) + 1-butanol (2)}[c]	1868.53	−2006.83	−315.90	92.20	13.5436	−725.39	673.89

[a]Ref. [14].
[b]Ref. [15].
[c]Ref. [16].

Table 4. The Experimental and Predicted FPs for Each Binary System at 101.3 kPa

Mole factions	Flash points (K)				
x₁	Exp.	Raoult's law	Wilson	NRTL	UNIQUAC
{Methanol (1) + 1-butanol (2)}					
0.0000	308.65	-	-	-	-
0.0505	306.45	306.55	306.67	306.79	306.68
0.0986	304.35	304.66	304.85	305.06	304.88
0.2007	300.25	301.02	301.23	301.58	301.30
0.2990	297.25	297.92	298.08	298.49	298.17
0.3999	294.75	295.10	295.17	295.61	295.27
0.5001	292.45	292.62	292.59	293.02	292.69
0.5972	290.05	290.46	290.36	290.75	290.46
0.7017	287.95	288.38	288.24	288.56	288.32
0.8001	286.15	286.60	286.48	286.70	286.54
0.9000	284.45	284.96	284.90	284.99	284.92
0.9504	283.85	284.18	284.16	284.20	284.17
1.0000	283.45	-	-	-	-
A.A.D	-	0.41	0.43	0.71	0.50
{Ethanol (1) + 1-butanol (2)}					
0.0000	308.65	-	-	-	-
0.0508	306.95	306.36	306.32	307.77	306.81
0.0995	305.15	304.37	304.29	306.74	305.11
0.2024	301.65	300.70	300.54	304.06	301.71
0.3045	298.65	297.64	297.40	300.91	298.59
0.4005	296.45	295.15	294.88	297.79	295.89
0.5001	294.25	292.90	292.61	294.65	293.32
0.5996	292.35	290.92	290.64	291.82	291.00
0.7001	290.25	289.13	288.90	289.43	288.92
0.8026	288.35	287.49	287.34	287.50	287.14
0.8997	286.65	286.08	286.01	286.06	285.82
0.9495	285.55	285.40	285.38	285.41	285.28
1.0000	284.75	-	-	-	-
A.A.D	-	0.92	1.09	1.07	0.61
{2-Propanol (1) + 1-butanol (2)}					
0.0000	308.65	-	-	-	-
0.0507	307.15	306.73	307.29	307.60	307.11
0.1008	305.25	304.99	305.91	306.17	305.64
0.1977	301.95	302.05	303.26	303.15	302.95
0.2971	298.87	299.46	300.66	300.29	300.40
0.4003	296.55	297.15	298.16	297.71	297.99
0.4965	294.45	295.25	296.05	295.64	295.94
0.6003	292.45	293.43	293.99	293.68	293.94
0.6996	290.85	291.86	292.23	292.02	292.21
0.8023	289.45	290.41	290.61	290.49	290.60
0.8999	288.35	289.14	289.22	289.18	289.22
0.9495	288.15	288.54	288.58	288.56	288.57
1.0000	287.95	-	-	-	-
A.A.D	-	0.63	1.14	1.00	1.02

ture, and are given in Table 3[(14-16)].

The experimental binary FP data for the systems {methanol + 1-butanol}, {ethanol + 1-butanol} and {2-propanol + 1-butanol} are given in Table 4. These binary data were compared with predicted values using the Raoult's law, Wilson, NRTL and UNIQUAC models. The binary param-

eters of each model equation were used to calculate activity coefficient for the same composition with experimental condition, and the initial temperature was given numerical average temperature of each mixture sample. Then the FP was obtained from adjustment of initial temperature by satisfying the Le Chatelier's rule (eq. 4). The objective function (OF) used was

$$OF = \min\left[\left(\sum_i \frac{x_i \gamma_i P_i^{sat}}{P_{i,FP}^{sat}}\right) - 1\right] \qquad (10)$$

For the Raoult's law, the activity coefficient is equal to unity with the assumption of ideal liquid phase.

The average absolute deviation (A.A.D) between the experimental and calculated values is included in Table 4.

The A.A.D was defined as:

$$A.A.D = \sum_{i=1}^{N} \frac{\left|T_i^{exp} - T_i^{cal}\right|}{N} \qquad (11)$$

where the T_i^{exp} is the experimental lower FP of component i, and T_i^{cal} is the estimated lower flash point of component i.

The each binary system at 101.3 kPa was plotted in Figures 1 to 3. The parameters for the Wilson, NRTL and UNIQUAC models are given in Table 3, along with the A.A.D between the experimental and predicted values. The

estimation results of FP are not dependant to the measurement of this work, because the activity coefficient model parameters just have been chosen from the literatures (ref.
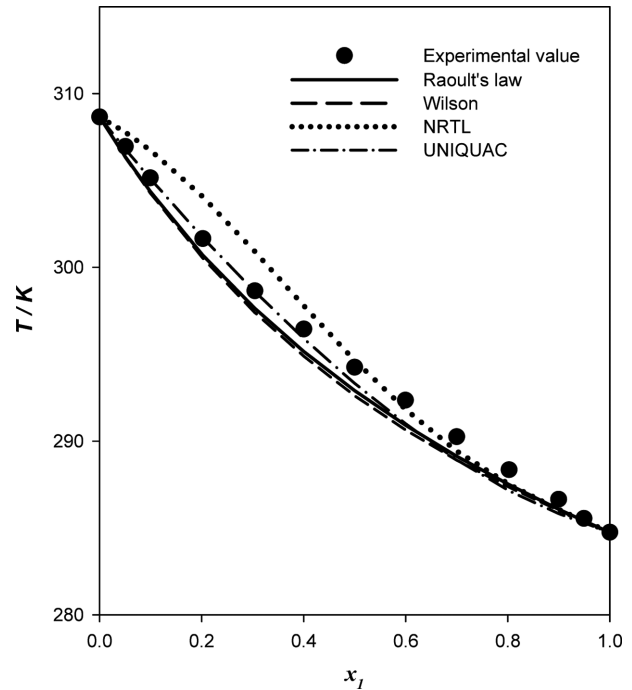

Figure 2. The comparison of the flash point prediction curves with the experimental data for the binary system {ethanol (1) + 1-butanol (2)} at 101.3 kPa.
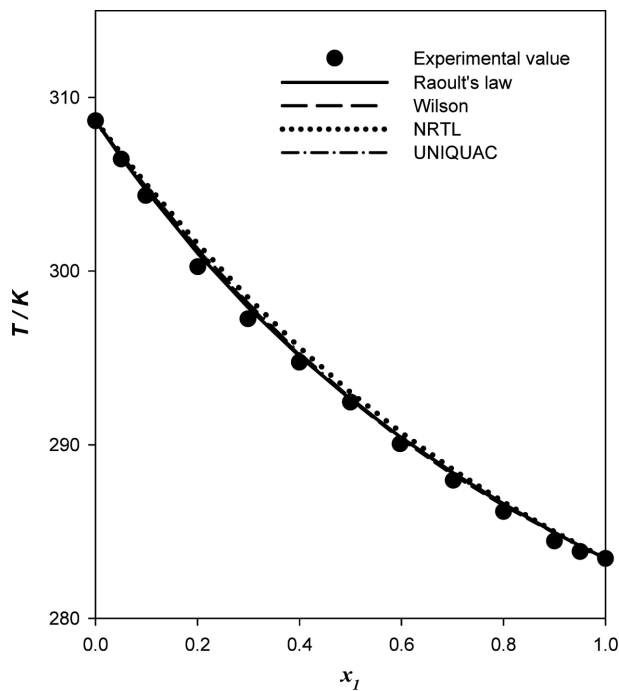

Figure 1. The comparison of the flash point prediction curves with the experimental data for the binary system {methanol (1) + 1-butanol (2)} at 101.3 kPa.
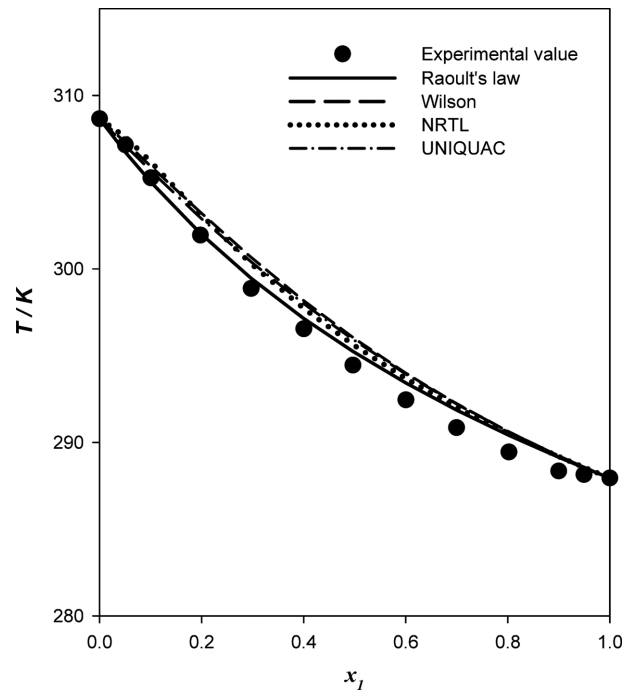

Figure 3. The comparison of the flash point prediction curves with the experimental data for the binary system {2-propanol (1) + 1-butanol (2)} at 101.3 kPa.

11~13). All of set for FP data agreed very well, as illustrated in the figures. However, the calculation result of NRTL model has higher deviation from the measured FP point at lower ethanol composition range for {ethanol (1) + 1-butanol (2)} system. A minimum flash points behavior was not observed in all binary systems. For the investigated systems, the A.A.D between the predicted and measured lower FP was less than 1.14 K.

4. Conclusions

Lower FP data for the {methanol + 1-butanol}, {ethanol + 1-butanol} and {2-propanol + 1-butanol} binary systems were analytically determined at 101.3 kPa. A minimum flash points behaviour (MFPB) was not observed in all binary systems. The measured FP data agreed well with the predicted values of Raoult's law, Wilson, NRTL and UNIQUAC models. The average absolute deviation between the predicted and measured lower FP was less than 1.14 K. The lower FP values from ideal solution (Raoult's law) were also represented for the two binary system {methanol + 1-butanol} and {2-propanol + 1-butanol}.

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