

The Flash Points of the Butylacetate+2-Propanol System Measured By Air Blowing Tester

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Abstract : The lower and upper flash points of the flammable binary system, butylacetate+2-propanol were measured by air blowing tester. The shape of the concentration-temperature region of flash depended on the components of the mixture in solution. The experimental data were compared with the values calculated by the reduced model under an ideal solution assumption and the flash point-prediction models based on Van Laar equation. Good qualitative agreement was obtained with these models. The prediction results of these models can thus be applied to incorporate inherently safer design for chemical process, such as the determination of the safe storage conditions for flammable solutions.

Key words : lower and upper flash points, flammable, butylacetate+2-Propanol, air-blowing tester, the reduced model, van laar equation

Nomenclatures

A, B, C	: Antoine coefficients
f	: fugacity [kPa]
ΔH_c	: heat of combustion in kJ/mol
LFL	: lower flammable limit
UFL	: upper flammable limit
N	: number of data
P	: ambient pressure [kPa]
P^{sat}	: saturated vapor pressure [kPa]
T	: temperature [K]
T^{cal}	: calculated flash point temperature [K]
T^{exp}	: experimentally derived flash point temperature [K]
t	: temperature [°C]
x	: liquid phase composition
y	: vapor phase composition

Greek Letters

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

Subscripts

i : species i

1. Introduction

The flash points is one of the most important physical properties used to determine the potential for fire and explosion hazards of industrial materials. The flash points are used by virtually all the environmental, health, and safety organizations in both government and industry to classify flammable liquids for safety and transportation regulations.

An accurate knowledge of the flash point is important in developing appropriate preventive and control measures in industrial fire protection [1]. The stringent regulations related to material safety have also made accurate measurements of flash points essential.

The experimental flash point data are readily available in the several literatures. The most published flash point data were for pure components. However, the flash points of the binary solution that have flammable components, have seen a little study and the data that did exist were inconsistent. Therefore, the purpose of this

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study was to measure and predict the lower and upper flash points for the system to aid in evaluating the safety of flammable liquid mixtures.

Ha et al. [2] performed that experimental flash points for binary system were compared with the calculated values by using Raoult's law and Van Laar equation.

The lower and upper flash points for the system, butylacetate+2-propanol, were measured by air-blowing tester, and compared with the values calculated by using the reduced model under an ideal solution assumption and the flash point prediction model based on the Van Laar equation [3].

2. Flash Point

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

Many flammable and combustible liquids are volatile in nature; that is, they evaporate quickly and are continually giving 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 temperature 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 [4] 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 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.

3. Experimental Section

3-1. Chemicals

Butylacetate and 2-propanol were purchased from Sunjong Chemical Co., Korea with a minimum purity of 99%. All these chemicals were used directly without any purification.

3.2. Experimental Apparatus and Procedure

The basic system configuration of air blowing tester is given in Fig. 1. The apparatus consist of the constant temperature bath, combustion chamber and refrigerator etc..

The procedure for measuring the flash point is as follows.

After maintaining 50% ethylene glycol aqueous solution bath at the prescribed temperature, the combustion chamber containing a sample liquid is sunk with a weight. The chamber is left for 1 hour to reach the saturated vapor concentration due to the natural evaporation of the liquid sample and than an electric discharge is induced between two platinum electrodes by means

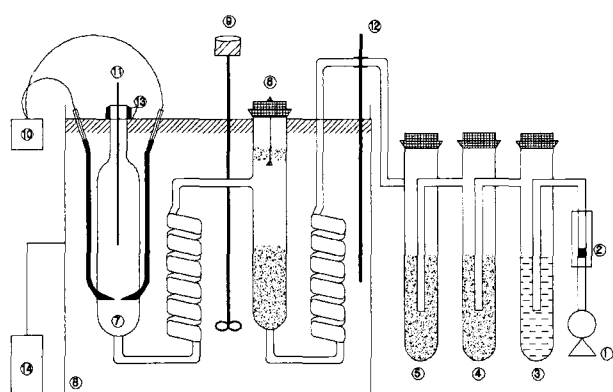


Fig. 1. Schematic diagram of experimental apparatus.

- ① Blower
- ② Air flow meter
- ③ E.G. column
- ④ CaCl₂ column
- ⑤ Evaporator
- ⑥ Saturator
- ⑦ Combustion chamber
- ⑧ Constant temperature bath
- ⑨ Agitator
- ⑩ Neon transformer
- ⑪ Thermocouple
- ⑫ Bath
- ⑬ Heater
- ⑭ Refrigerator

Table 2. Comparison of experimental and calculated lower flash points by the reduced model and Van Laar equation for butylacetate(x₁)+2-propanol(x₂) system

Mole fraction		The Lower Flash Point (°C)		
x ₁	x ₂	Exp.	Reduced	Van Laar
0.0	0.1	0.2	0.3	0.4
0.5	0.6	0.7	0.8	0.9
1.0	1.0	0.9	0.8	0.7
0.6	0.5	0.4	0.3	0.2
0.1	0.0	14.0	15.0	14.0
16.0	19.0	19.0	20.0	20.0
20.0	22.0	26.0	11.91	12.74
13.63	14.57	15.57	16.66	17.83
19.11	20.51	22.06	23.80	11.91
12.21	12.46	12.91	13.47	14.17
15.07	16.25	17.87	20.20	23.80
A.A.D		-	1.61	3.16

Table 3. Comparison of experimental and calculated upper flash points by the reduced model and Van Laar equation for butylacetate(x_1)+2-propanol(x_2) system

Mole fraction		The Upper Flash Point (°C)		
x_1	x_2	Exp.	Reduced	Van Laar
0.0	0.1	0.2	0.3	0.4
0.5	0.6	0.7	0.8	0.9
1.0	1.0	0.9	0.8	0.7
0.6	0.5	0.4	0.3	0.2
0.1	0.0	36.0	38.0	38.0
39.0	38.0	40.0	42.0	46.0
47.0	52.0	57.0	37.96	39.08
40.28	41.59	43.00	44.56	46.27
48.20	50.37	52.89	55.86	37.96
38.40	38.97	39.65	40.47	41.48
42.75	44.43	46.77	50.21	55.86
A.A.D			2.67	1.22

of a neon transformer of 15000 V.

A flash is judged by the eye or an output of thermocouples depending on whether flame propagation can reach the end point of the thermocouples. The flash point is determined from the bath temperature at which the flash occurred.

4. Results And Discussion

4.1. Experimental Results

The results obtained in this study for the system, butylacetate(1)+2-propanol(2), are presented in Table 2 and Table 3 and Fig. 2. Concentrations of component i are given in mole fraction, x_i .

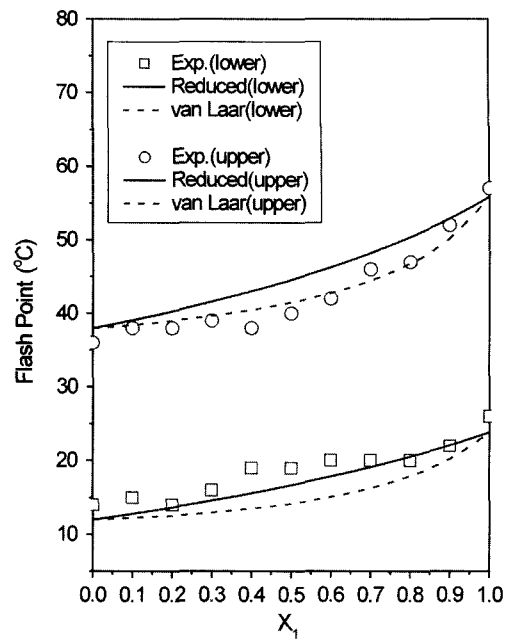
As shown in Fig. 2, the lower and upper flash points of the systems plotted as a function of butylacetate concentration. The shape of the concentration-temperature region of flash depended on the components of the mixture in solution. As the concentration of butylacetate increased, the lower and upper flash points also increased.

4.2. Calculation of the Lower and Upper Flash Points

4.2.1. Mathematical formulation for the flash point prediction model

The flash point for a pure flammable liquid i can be written as the flash temperature T_F for which

$$\frac{P_i^{sat}}{LFL_i} = 1, \quad \frac{P_i^{sat}}{UFL_i} = 1 \quad (1)$$

**Fig. 2.** Comparison of the experimental data and the calculated values for butylacetate(x_1)+2-propanol(x_2) system.**Table 1.** Antoine constants, flammability limits and heats of combustion for butylacetate+2-propanol System

Propertiese Components	A	B	C	LFL	UFL	ΔH_{ci}
Butylacetate	7.02845	1368.50	204.00	1.38	7.6	3590.4
2-Propanol	8.87829	2010.33	252.636	2.5	12	2051.1

Le Chatelier [5] has presented an analogous equation for binary and multicomponent mixtures containing N flammable compounds.

$$\sum \frac{P_i}{LFL_i} = \frac{P_1}{LFL_1} + \frac{P_2}{LFL_2} = 1 \quad (2)$$

$$\sum \frac{P_i}{UFL_i} = \frac{P_1}{UFL_1} + \frac{P_2}{UFL_2} = 1 \quad (3)$$

In this equation P_i is the actual partial pressure of component i in a vapour-air mixture which is in equilibrium with the liquid mixture. LFL_i and UFL_i are the partial pressure in a gas-air mixture with a composition corresponding to the lower flammability limit and the upper flammability of pure component i .

The lower flammability limit, LFL_i and the upper flammability limit, UFL_i are the function of the temperature and of the heat of combustion. The heat of combustion is the net the heat of combustion since the reactants and the combustion products all are in the gaseous state.

Over moderate ranges of temperature there are only small changes in LFL_i and UFL_i . Zabetakis [6] accounted for the temperature effect for various types of substances by means of the expression which may be written as :

$$LFL_i(t) = LFL_i(25) - 0.182(t-25)/\Delta H_{ci} \quad (4)$$

$$UFL_i(t) = UFL_i(25) + 0.182(t-25)/\Delta H_{ci} \quad (5)$$

where ΔH_{ci} is the heat of combustion in kJ/mol and listed in Table 1. $LFL_i(t)$ and $LFL_i(25)$ are the lower flammability limits at $t^\circ\text{C}$ and 25°C respectively. $UFL_i(t)$ and $UFL_i(25)$ are the upper flammability limits at $t^\circ\text{C}$ and 25°C respectively.

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 :

$$y_i \Phi_i P = x_i \gamma_i f_i \quad (i = 1, 2, \dots, N) \quad (6)$$

At low pressure, the vapor phase can be approximated as an ideal gas, then the vapor phase solutions fugacity coefficient for component i is reduced to :

$$\Phi_i = 1 \quad (7)$$

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

$$f_i \cong P_i^{sat} \quad (8)$$

where P_i^{sat} is the vapor pressure of pure i at the system temperature.

Therefore, the vapor-liquid equilibrium relation is reduced as :

$$f_i = x_i \gamma_i P_i^{sat} \quad (i = 1, 2, \dots, N) \quad (9)$$

where x_i is the mole of component i , γ_i is the activity coefficient of component i , and P_i^{sat} is the vapour pressure of component i at temperature T .

Substitution Eq. (9) into Eq. (2) and Eq. (3) :

$$1 = \sum \frac{x_i \gamma_i P_i^{sat}}{LFL_i} = \frac{x_1 \gamma_1 P_1^{sat}}{LFL_1} + \frac{x_2 \gamma_2 P_2^{sat}}{LFL_2} \quad (10)$$

$$1 = \sum \frac{x_i \gamma_i P_i^{sat}}{UFL_i} = \frac{x_1 \gamma_1 P_1^{sat}}{UFL_1} + \frac{x_2 \gamma_2 P_2^{sat}}{UFL_2} \quad (11)$$

The saturated vapor pressure variation with temperature for a pure substance i can be estimated by the Antonine equation :

$$\log P_i^{sat} = A_i - \frac{B_i}{T + C_i} \quad (12)$$

where A_i , B_i and C_i are the Antonine coefficients and were

adapted from the literature [3] and are listed in Table 1.

The activity coefficient (γ_i) which were presented in Eq. (10) and (11), can be estimated by the use of the following Van Laar equation.

$$\ln \gamma_1 = A_{12} \left(\frac{A_{12} x_2}{A_{12} x_1 + A_{12} x_2} \right)^2 \quad (13)$$

$$\ln \gamma_2 = A_{21} \left(\frac{A_{12} x_1}{A_{12} x_1 + A_{12} x_2} \right)^2 \quad (14)$$

The binary parameters of the Van Laar equation were abstracted from the literature [7].

The flash point-prediction model developed for the flammable binary solution included the modified equation of Le Chatelier, the Antonine equation and the Van Laar equation.

The solution of Eq. (2) provides iteratively the desired lower flash point temperature. The values of LFL_i are calculated from Eq. (4) while P_i values are obtained from Eq. (9) and (12) with the activity coefficients predicted by means of Van Laar equation.

While the solution of Eq. (3) provides iteratively the desired upper flash point temperature. The values of UFL_i are calculated from Eq. (5) while P_i values are obtained from Eq. (9) and (12) with the activity coefficients predicted by means of Van Laar equation.

4.2.2. Reduced model under 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 equation, Eq. (9), was able to be reduced to Raoult's law for this study, this being described as :

$$P_i = x_i P_i^{sat} \quad (i = 1, 2, \dots, N) \quad (15)$$

Therefore, the modified equation of Le Chatelier, Eq. (2) and (3), was reduced to Eq. (16) and (17), respectively :

$$1 = \sum \frac{x_i P_i^{sat}}{LFL_i} = \frac{x_1 P_1^{sat}}{LFL_1} + \frac{x_2 P_2^{sat}}{LFL_2} \quad (16)$$

$$1 = \sum \frac{x_i P_i^{sat}}{UFL_i} = \frac{x_1 P_1^{sat}}{UFL_1} + \frac{x_2 P_2^{sat}}{UFL_2} \quad (17)$$

this being the equation used by White et al. [8] to estimate the flash point of the systems, JP-4/JP-8 and JP-5/JP-8. The Antonine equation, Eq. (12), was still deemed by us to be useful to estimate P_i^{sat} .

The reduced model developed for the flammable binary solution included the modified equation of Le Chatelier, the Antonine equation and the Raoult's law.

The solution of Eq. (16) provides iteratively the desired lower flash point temperature. The values of LFL_i are calculated from Eq. (4) while P_i values are obtained from Eq. (15) and (12) with the activity coefficients predicted by means of Raoult's law.

While the solution of Eq. (17) provides iteratively the desired upper flash point temperature. The values of UFL_i are calculated from Eq. (5) while P_i values are obtained from Eq. (15) and (12) with the activity coefficients predicted by means of Raoult's law.

4.2.3. Comparison of the calculated values with the experimental data

In this study, the flash point prediction models proposed in section 4.2.1 and 4.2.2 was used to predict the lower and upper flash points of the binary system, butylacetate+2-propanol. The prediction results obtained were presented in Table 2 and Table 3.

And included in Table 2 and Table 3 is the average absolute deviation (A.A.D.) defined as [9]

$$A.A.D. = \sum_{i=1}^N \left[\frac{|T_i^{\text{exp}} - T_i^{\text{cal}}|}{N} \right] \quad (18)$$

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

Fig. 2 compares the lower and upper flash point variation between the model predictive curves and the experimentally-derived data for the binary solution, butylacetate+2-propanol.

As seen from Fig. 2, the curve predicted by the flash point prediction models proposed in section 4.2.1 and 4.2.2 appears to be consistent with the experimentally-derived data. And as can be seen from A.A.D. in Table 2 and Table 3, good qualitative agreement was obtained with the reduced model and the flash point prediction model based on the Van Laar Equation.

The calculated lower flash points based on the reduced model were found to be better than those based on Van Laar equation, while the calculated upper flash points based on Van Laar equation were found to be better than those based on the reduced model.

5. Conclusions

The lower and upper flash points of the flammable

binary system, butylacetate+2-propanol were measured by air-blowing tester.

The experimental data were compared with the values calculated by the reduced model and the flash point prediction models based on the Van Laar equation. The agreement between experimental data and calculated values is generally very good as can be seen from Fig. 2 and from A.A.D. in Table 2-3.

The prediction results of these models can thus be applied to incorporate inherently safer design for chemical process, such as the determination of the safe storage conditions for flammable (or combustible) solutions.

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