

The Lower Flash Points of the n-Butanol+n-Decane System

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ABSTRACT

The lower flash points for the binary system, n-butanol+n-decane, were measured by Pensky-Martens closed cup tester. The experimental results showed the minimum in the flash point versus composition curve. 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 the Van Laar and Wilson equations. The predictive curve based upon the reduced model deviated from the experimental data for this system. The experimental results were in good agreement with the predictive curves, which use the Van Laar and Wilson equations to estimate activity coefficients. However, the predictive curve of the flash point prediction model based on the Willson equation described the experimentally-derived data more effectively than that of the flash point prediction model based on the Van Laar equation.

Keywords : Lower Flash Points, Flammable, Pensky-Martens Closed Cup Tester, Reduced Model, Van Laar Equation, Wilson Equation

1. Introduction

The flash point is the best known and most widely used flammability property for the evaluation of the flammability hazard of combustible liquids. It is an important criterion for the fire-hazard rating of these liquids.¹⁾

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

Affens and McLaren²⁾ have developed a model based upon 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)} performed

that experimental lower and upper flash points for binary system were compared with the calculated values by using Raoult's law and Van Laar equation.

The flash points of the closed cup tester were measured rather than the flash points of the open cup tester, because the open cup tester of multicomponent systems cannot be readily made, due to distillation of the mixture during heating. Further, the flash points of the closed cup tester are most widely used to characterize flammable substance hazards in practice.

In this study, n-butanol+n-decane system was selected to aim for prediction of the flash point of non-ideal flammable solutions. The flash points for the system, n-butanol+n-decane, were measured by Pensky-Martens closed cup tester, and compared with the values calculated by using the flash point prediction models based on Raoult's law, Van Laar equation⁶⁾ and Wilson equation.⁷⁾

2. Experimental

2.1 Chemicals

n-Decane was purchased from Lancaster, England with a minimum purity of 99%, and n-butanol from

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Junsei, Japan with a minimum purity 99%. All these chemicals were used directly without any purification.

2.2 Experimental apparatus and procedure

The basic system configuration of Pensky-Martens closed cup tester⁸⁾ is given in Fig. 1. The apparatus consist of a test cup, cover and stove.

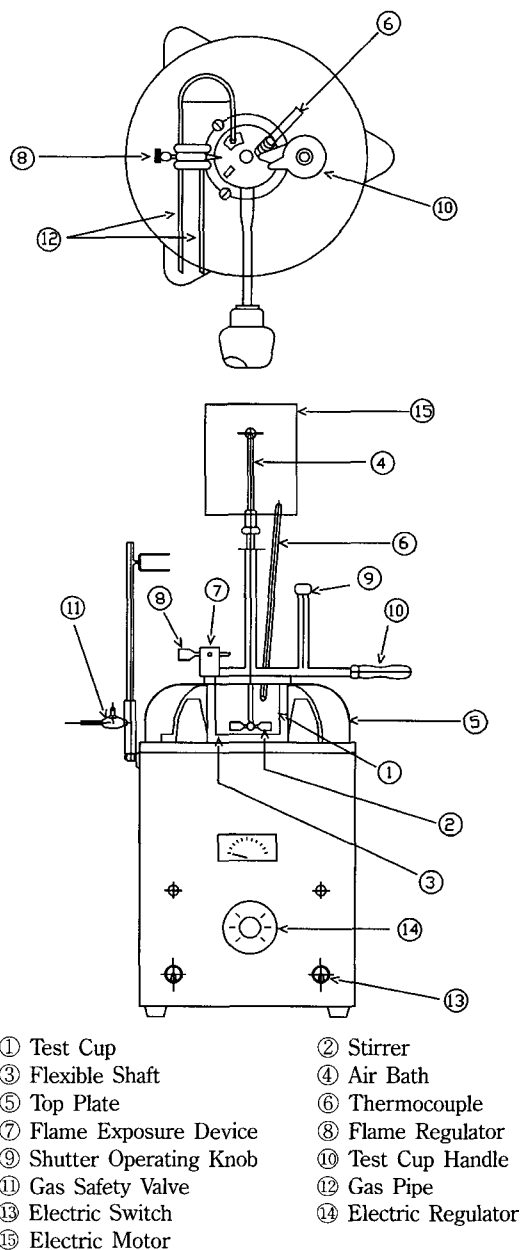


Fig. 1. Schematic diagram of experimental apparatus.

The volume of the test cup is 100 ml and was made of brass. The flange is equipped with devices for locating the position of the test cup in the stove. The cover consists of cover proper, shutter, flame-exposure device, pilot flame and stirring device. Heat is supplied to the cup by means of the stove. The stove consists of an air bath and a top plate.

The pure components is added by mass and the test cup is filled with the mixture (65 ml). The mixture is heated at a rate of 5 to 6 K/min with continual stirring (90 to 120 rpm). A small flame is directed into the test cup at regular intervals with simultaneous interruption of stirring. The flash point(± 0.1 K) is the lowest temperature at which application of the test flame causes the vapor above the mixture to ignite.

3. Results and Discussion

3.1 Flash points for n-butanol+n-decane system measured by Pensky-Martens closed cup tester

The results obtained in this work for the system, n-butanol(1)+n-decane(2), are presented in Table 1 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 system plotted as a function of n-decane concentration.

Table 1. The experimental data and the calculated values for the system, n-butanol(1)+n-decane(2)

Mole fraction		Flash point(C)			
x_1	x_2	Exp.	Reduced	Van Laar	Wilson
1.000	0.000	31	31.84	31.84	31.84
0.904	0.096	29	32.73	31.17	30.65
0.796	0.204	30	33.88	31.14	30.53
0.505	0.495	30	37.59	31.86	31.08
0.390	0.610	30	39.42	32.56	31.62
0.304	0.696	32	40.96	33.48	32.32
0.209	0.791	33	42.91	35.25	33.74
0.095	0.905	34	45.68	39.56	37.73
0.000	1.000	44	48.51	48.51	48.51
A.A.D.	-	-	6.72	2.49	1.67

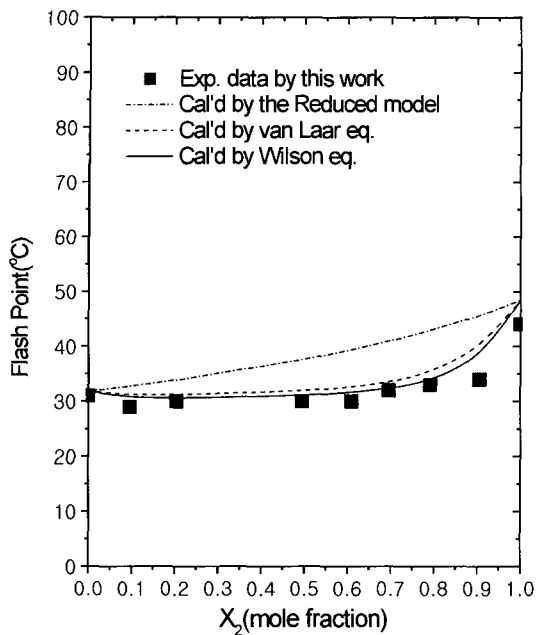


Fig. 2. Comparison of the flash point prediction curves with experimentally-derived data for n-butanol(1)+n-decane(2).

3.2 Calculation of the lower flash points

3.2.1 Flash points and flammability limits

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

Most 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 liquids 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

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

Constants	A	B	C
n-butanol	7.838	1558.19	196.881
n-decane	6.95707	1503.568	194.738

Protection Association⁹) 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.

Flammability limits refer to the range of flammable gas or vapor concentrations between which ignition will occur if an ignition source is present. LFL means the lower flammable limit. UFL means to 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.

3.2.2 Mathematical formulation for the flash point prediction model

The Le Chatelier¹⁰) has presented the following equation for multicomponent mixtures containing flammable compounds.

$$\sum_{i=1}^N \frac{y_i}{LFL_i} = 1 \quad (1)$$

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, $P_{i,fp}^{sat}$, as:

$$LFL_i = \frac{P_{i,fp}^{sat}}{P} \quad (2)$$

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 :

$$y_i \Phi_i P = x_i \gamma_i f_i \quad (i = 1, 2, \dots, N) \quad (3)$$

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 :

$$\Phi_i = 1 \quad (4)$$

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

$$f_i \cong P_i^{\text{sat}} \quad (5)$$

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

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

or

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

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

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

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

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

where A_i , B_i and C_i are the Antonine coefficients and were adapted from the literature⁶⁾ and listed in Table 2.

The vapor pressure of pure substance i at its flash point $P_{i,fp}^{\text{sat}}$, as presented in Eq. (8), can be estimated by substituting $T_{i,fp}$, the flash point of component i , into the Antonine 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 and Wilson equations. The binary parameters of those equations were abstracted from the literature.¹¹⁾

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

flash point of the solution.

3.2.3 Reduced model development 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. (7), was able to be reduced to Raoult's law for this study, this being described as :

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

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

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

this being the equation used by White *et al.*³⁾ to estimate the flash point of the systems, JP-4/JP-8 and JP-5/JP-8. The Antonine equation, Eq. (9), was still deemed by us to be useful to estimate P_i^{sat} and $P_{i,fp}^{\text{sat}}$ for this reduced model. Therefore, the reduced model for the flash point-prediction under an ideal solution assumption can be described using Eq. (7) and (11).

3.2.4 Comparison of the calculated values with the experimental data

In this study, the flash point prediction models proposed in section 3.2.2 and 3.2.3 were used to predict the flash point of the binary system, n-butanol+n-decane. The prediction results obtained were presented in Table 1 and Fig. 2.

And included in table 1 is the average absolute deviation (A.A.D.)¹²⁾ defined as

$$\text{A.A.D.} = \sum_{i=1}^N \frac{|T_i^{\text{exp}} - T_i^{\text{cal}}|}{N} \quad (12)$$

where the A.A.D. is a measure of agreement between the experimental data and the calculated values, the T_i^{exp} is the experimental flash point, and T_i^{cal} is the estimated flash point.

As shown in Fig. 2, the experimental results are in good agreement with the predictive curves, which use the Van Laar, Wilson equations to estimate activity coefficients. The predictive curves simulated by the reduced model proposed in section 3.2.3, are

also displayed in Fig. 2. 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-butanol+n-decane.

Fig. 2 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 predictive curve of the flash point prediction model based on the Willson equation described the experimentally-derived data more effectively than that of the flash point prediction model based on the Van Laar equation, because the Wilson equation was more effective than the Van Laar equation at describing the activity coefficients for strongly non-ideal solutions.⁶⁾

The surprising finding for the solution of n-butanol+n-decane, was that the flash point of the solution over a wide composition range was lower than that recorded for the individual solution components, 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 individual component displaying the lower value. It may be equivalent to a value for a specific composition located somewhere between the composition values 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 solutions 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.

4. Conclusions

The flash points for the binary system, n-butanol +n-decane, were measured by Pensky-Martens closed cup tester.

The experimental data were compared with the values calculated by the reduced model and the flash point models based on the Van Laar and Wilson equation. The predictive curve based upon the reduced model deviated from the experimental data for this system. The experimental results are in good agreement with the predictive curves, which use the Van Laar and Wilson equation to estimate activity coefficients. However, the predictive curve of the flash point prediction model based on the Willson equation described the experimentally-derived data more effectively than that of the prediction model based upon the Van Laar equation. The prediction results of this model can thus be 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.

It is important to emphasize here that some highly non-ideal solutions, such as n-butanol+n-decane, may show the minimum in the flash point versus composition curve.

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]
T	: temperature [K]
T^{cal}	: calculated flash point temperature [K]
T^{exp}	: experimentally derived flash point temperature [K]
$T_{i, \text{fp}}$: flash point temperature of pure component i [K]
x	: liquid phase composition
y	: vapor phase composition

Greek Letters

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

Subscripts

fp : flash point
i : species i

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