

The Prediction of Lower Flash Points by Optimization Method

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Abstract : The flash point is the most widely used flammability property for the evaluation of the flammability hazard of combustible liquid mixtures. In this paper, the reported flash points for the binary systems, ethylbenzene+n-butanol and ethylbenzene+n-hexanol were correlated by the optimization method. The optimization method based on the van Laar and Wilson equations were compared with the Raoult's law. The calculated values based on the optimization method were found to be better than those based on the Raoult's law.

Key Words: flash point, raoult's law, van laar, wilson, optimization method

1. Introduction

The flash point is defined as the lowest temperature at which application of an ignition source causes the sample vapour to ignite under specified test conditions [1]. 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 [2,3].

A liquid that exhibits a flash point value below ambient temperature, and can thus give rise to flammable mixtures under ambient conditions, is generally considered to be more hazardous than one reflecting a higher flash point [4].

Affens and McLaren [5] developed a predictive model for the flash points of binary hydrocarbon mixtures using Raoult's law. White et al. [6] reduced Affens and McLaren's model to a simpler equation by ignoring any dependence of the LFL on temperature. However, neither the Affens and McLaren's model nor the equation of White et al. is able to effectively predict the measured flash point for a non-ideal solution [7].

Liaw et al. [8] developed a mathematical model for the flash points of highly non-ideal solutions using activity coefficient models, such as Wilson, NRTL and UNIQUAC models. Surely, the Liaw's model needs the

binary interaction parameters of activity coefficient model to calculate the flash points. Without the binary interaction parameters, the Liaw's model cannot be able to predict the flash points for the binary solutions.

Lately, Ha et al. [9] measured the lower flash points of the binary solutions exhibited the minimum flash point behavior and calculated the flash points by using the prediction models based on the van Laar and Wilson equations.

The experimental flash point data are readily available in the several literatures. However, 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.

The purpose of this study was to predict the lower flash points for the binary mixtures to aid in evaluating the safety of flammable liquid mixtures. The reported flash points [10] for the two binary solutions, ethylbenzene+n-butanol and ethylbenzene+n-hexanol, were correlated with the optimization method using the van Laar and Wilson equations [11]. The calculated values based on the optimization method were compared with the reported calculation values [10] based on Raoult's law.

2. Mathematical formulation for the lower flash point prediction

The Le Chatelier's rule [12] for the flammable vapor-air mixture of multicomponents is as follows :

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

where y_i is the composition of a flammable substance i in the vapor phase, and LFL_i is the lower flammable limit(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, $P_{i,fp}^{sat}$, 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 :

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

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

$$y_i P = x_i \gamma_i P_i^{sat} \quad (6)$$

or

$$y_i = \frac{x_i \gamma_i P_i^{sat}}{P} \quad (7)$$

Substitution Eq. (2) and Eq. (7) into Eq. (1) results in :

$$\sum_{i=1}^N \frac{\chi_i \gamma_i P_i^{sat}}{P_{i,fp}^{sat}} = \frac{\chi_1 \gamma_1 P_1^{sat}}{P_{1,fp}^{sat}} + \frac{\chi_2 \gamma_2 P_2^{sat}}{P_{2,fp}^{sat}} = 1 \quad (8)$$

The saturated vapor pressure variation with tempera-

Table 1. The Antoine coefficients of the components

Components	Coefficients		
	A	B	C
Ethylbenzene	6.9658	1429.55	213.767
n-Butanol	7.838	1558.19	196.881
n-Hexanol	7.9059	1819.57	205.086

ture for a pure substance i can be estimated by the Antoine equation [11] :

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

where A_i , B_i and C_i are the Antoine coefficients and T is the temperature in degree Celsius($^{\circ}\text{C}$). The Antoine coefficients, A_i , B_i and C_i , were adapted from the literature[13] 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. (8), 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. (8) was reduced to Raoult's law, this being described as :

$$\sum_{i=1}^N \frac{x_i P_i^{sat}}{P_{i,fp}^{sat}} = \frac{x_1 P_1^{sat}}{P_{1,fp}^{sat}} + \frac{x_2 P_2^{sat}}{P_{2,fp}^{sat}} = 1 \quad (10)$$

The temperature, which satisfies Eq. (10), is determined to be the lower flash point of the binary mixtures.

3. The Optimization of the Binary Interaction Parameters

The van Laar and Wilson equations are used to correlate the reported experimental data[10] for two binary solutions, these equations being described as :

van Laar equation :

$$\ln \gamma_1 = A_{12} \left(\frac{A_{21} x_2}{A_{12} x_1 + A_{21} x_2} \right)^2 \quad (11)$$

Wilson equation :

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

where Λ is as following

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

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

$$F = \sum_{j=1}^N ABS(T_j^{\text{exp}} - T_j^{\text{cal}}) \quad (13)$$

where, N is the number of experimental data, ABS is absolute value, T_j^{exp} is the experimental lower flash point of component j, T_j^{cal} and is the calculated lower flash point of component j which satisfies Eq. (8), is determined to be the lower flash point of the binary mixtures.

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

Using the SIMPLEX [14] method, the binary interaction parameters of the van Laar and Wilson equations,

van Laar : A_{12}, A_{21}

Wilson : $A_{12} (= \lambda_{12} - \lambda_{11}), A_{21} (= \lambda_{21} - \lambda_{22})$ were calculated.

The binary interaction parameters calculated in this way are shown in Table 2 and the calculated flash points are presented in Table 3~4.

4. Result

In this study, the prediction results obtained were presented in Table 3~4 and Fig. 1~2. And included in Table 3~4 is the A.A.D.(average absolute deviation)

Table 2. The optimized binary parameters of the van Laar and Wilson equations for each binary system

Parameters	van Laar		*Wilson	
	A_{12}	A_{21}	A_{12}	A_{12}
Ethylbenzene(1) +n-Butanol(2)	1.5996	2.1679	52.0100	3577.9693
Ethylbenzene(1) +n-Hexanol	0.9808	2.9180	23.9953	3472.5059

*Wilson : $A_{12} (= \lambda_{12} - \lambda_{11}), A_{21} (= \lambda_{21} - \lambda_{22})$ (cal/mol)

defined [15] as follows :

$$A.A.D. = \sum_{i=1}^N \frac{|T_i^{\text{exp}} - T_i^{\text{cal}}|}{N} \quad (14)$$

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

The calculated values using the optimization method and the Raoult's law for the systems are presented in table 3~4. The calculated values based on the optimization method were found to be better than those based on the Raoult's law for the systems, ethylbenzene+n-butanol and ethylbenzene+n-hexanol.

Table 3. The experimental and the calculated flash points for ethylbenzene(x_1)+n-butanol(x_2) system

Mole fractions			Flash points (°C)		
x_1	x_2	Exp.[10]	Raoult's law[10]	van Laar	Wilson
1.000	0.000	30.5	-	-	-
0.901	0.099	26.5	31.50	28.00	26.92
0.713	0.287	27.5	33.51	27.55	26.93
0.506	0.494	28.0	35.90	27.67	27.54
0.305	0.695	29.5	38.39	28.64	29.49
0.100	0.900	34.0	41.11	34.01	35.36
0.000	1.000	42.5	-	-	-
A.A.D.		-	6.98	0.55	0.56

Table 4. The experimental and the calculated flash points for ethylbenzene(x^1)+n-hexanol(x^2) system

Mole fractions			Flash points (°C)		
x_1	x_2	Exp.[10]	Raoult's law[10]	van Laar	Wilson
1.000	0.000	30.5	-	-	-
0.913	0.087	29.9	31.98	30.32	29.90
0.704	0.296	30.5	36.16	30.36	30.58
0.502	0.498	31.0	41.36	31.80	32.60
0.299	0.701	40.5	48.46	36.69	37.36
0.100	0.900	49.5	58.57	49.51	49.50
0.000	1.000	65.5	-	-	-
A.A.D.		-	7.11	1.12	1.04

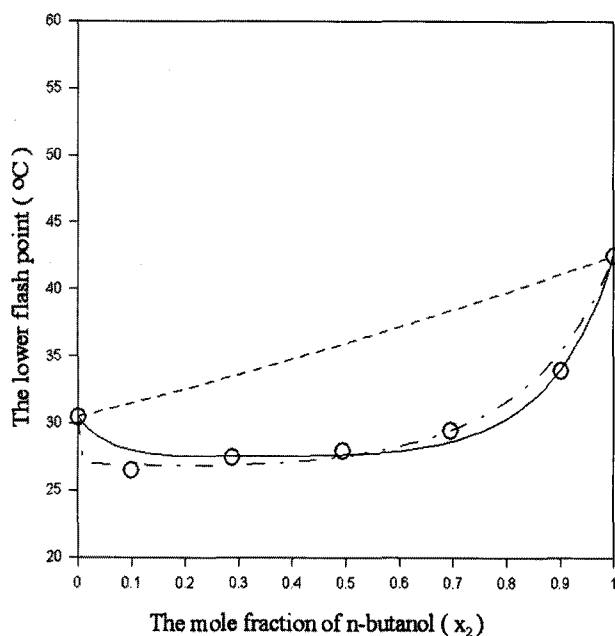


Fig. 1. The comparison of the lower flash point prediction curves with the reported experimental data for the ethylbenzene(x_1)+n-butanol(x_2) system : calculated values based on the Raoult's law (---) : calculated values based on van Laar equation (—) : calculated values based on Wilson (- · - · -) : experimental lower flash points (○)

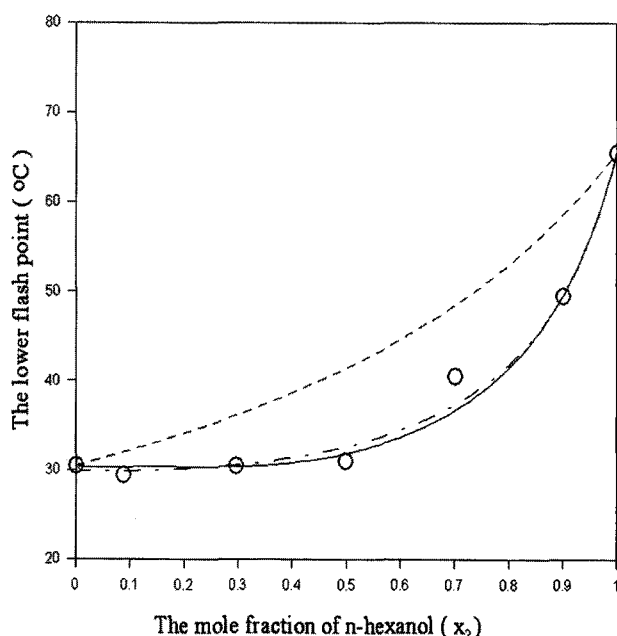


Fig. 2. The comparison of the lower flash point prediction curves with the reported experimental data for the ethylbenzene(x_1)+n-hexanol(x_2) system : calculated values based on the Raoult's law (---) : calculated values based on van Laar equation (—) : calculated values based on Wilson (- · - · -) : experimental lower flash points (○).

5. Conclusion

The reported flash points for the the binary systems, ethylbenzene+n-butanol and ethylbenzene+n-hexanol were correlated by the optimization method. The optimization method using the van Laar and Wilson equations were compared with the Raoult's law. The calculated values based on the optimization method were found to be better than those based on the Raoult's law.

The prediction method in this study 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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