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Measurement and Prediction of the Flash Points for Flammable Liquid Mixtures with Non-flammable Component

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Abstract : Lower flash points for the binary systems, carbon tetrachloride+o-xylene and water+n-butanol were measured by Pensky-Martens closed cup tester. The Raoult's law and optimization method using van Laar equation were used to predict the lower flash points and were compared with experimental data. 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, pensky-martens closed cup apparatus, raoult's law, van laar equation, optimization method

1. Introduction

The flash points are used to classify combustible liquids according to their relative flammability[1]. The regulations for the safe handling, transportation, and storage of such substances are dependent on this classification, and the flash points are therefore of great importance in the chemical industry.

The flash points of the closed cup tester were measured rather than the flash points of the open cup tester. Owing to distillation of the mixture during heating, the open cup tester of multicomponent systems cannot be readily made. Further, the flash points of the closed cup tester are most widely used to characterize flammable substance hazards in practice[2].

Experimental flash point data for most single component flammable liquids are readily available in the literature. However, the flash points of mixtures that have non-flammable components, such as carbon tetrachloride and water, have seen little study and the data that did exist was inconsistent. The non-flammable components add to flammable liquids to inhibit the flash. The flash points of the mixtures will be vary depending on the composition.

Ha *et al.*[3,4] performed that experimental flash points for flammable liquid mixtures were compared with the calculated values by using Raoult's law and van Laar equation.

The purpose of this study was to measure and predict the lower flash points for these systems to aid in evaluating the safety of flammable and non-flammable liquid mixtures. The lower flash points for the systems, carbon tetrachloride+o-xylene and water+n-butanol, were measured by Pensky-Martens closed cup tester, and compared with the Raoult's law and optimization method using van Laar equation[5].

2. Mathematical Formulation for the Lower Flash Point Prediction

2.1 The Prediction of the lower flash points based on the Raoult's law

The following equation applies to vapor-liquid equilibrium[6].

$$P_i = P_i^0 \alpha_i = P_i^0 \gamma_i x_i \tag{1}$$

where P_i is the partial vapor pressure of component i(mmHg), P^0_i is the vapor pressure of component i(mmHg), a_i is the activity of component i, γ_i is the activity coefficient of component i and x_i is the mole fraction of component i in the liquid phase.

Assuming vapor-liquid equilibrium in the Pensky-Martens closed cup tester, the Clausius-Clapeyron equa-

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tion can be applied to binary systems[7].

$$\frac{d\ln P_i}{dT} = \frac{\Delta H_i}{RT^2} \tag{2}$$

where T is the flash point in absolute temperature(K), H_i is the enthalpy of vaporization of component i(kJ/mol), and R is the gas constant, 8.314(J/mol/K).

The enthalpy of vaporization is a function of temperature and was estimated by use of the Watson equation[5] in this study.

Integrating Equation (2), and substituting Equation (1) results in the following :

$$\ln P_i = \ln(P^0_{i,0}\gamma_i x_i) + \frac{\Delta H_i}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right) \tag{3}$$

where $P^0_{i,0}$ is the saturated vapor pressure of component i, while T and T_0 are the flash points of the liquid mixture and pure flammable component, respectively.

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

$$\ln P^0_{i,0} = A_i - \frac{B_i}{t + C_i} \tag{4}$$

The Antonine coefficients, A_i, B_i and C_i, for these species were adapted from the literature[5] and are listed in Table 1.

Below we assume that a flash occurs at the lower limit of flammability in the fuel-air system without the additive,

$$P_2 = P^0_{2,0} = constant \tag{5}$$

where the subscript 2 indicates the flammable component.

Substituting Equation (5) into Equation (3),

$$\frac{1}{T^L} = \frac{1}{T^L_0} + (R/\Delta H_2)\cdot \ln(\gamma_2 \cdot x_2) \tag{6}$$

where the superscript L indicates the lower flash point, T^L_0 is the lower flash point temperature of the flammable component, and H_2 is the average of the enthalpy of vaporization near T^L_0.

Under an ideal solution assumption, the activity coefficients of the liquid phase are equal to unity. Therefore Equation. (6) was reduced to Raoult's law[8], this being decribed as :

$$\frac{1}{T^L} = \frac{1}{T^L_0} + (R/\Delta H_2)\cdot \ln(x_2) \tag{7}$$

The temperature, which satisfies Equation. (7), is determined to be the lower flash point of the binary mixtures[8]. The calculated results are presented in Table 3 and Table 4.

2.2 The optimization of the binary interaction parameters

The van Laar equation is used to correlate the experimentally derived data for three binary solutions, these equations being described as :

van Laar equation :

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

$$\ln\gamma_2 = A_{21}\left(\frac{A_{12}x_1}{A_{12}x_1 + A_{21}x_2}\right)^2 \tag{8}$$

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

$$F = \sum_{j=1}^{N} ABS(T_j^{exp} - T_j^{cal}) \tag{9}$$

where, N is the number of experimental data, ABS is absolute value, T_j^{exp} is the experimental lower flash point of component j, and T_j^{cal} is the calculated lower flash point of component j. T_j^{cal}, which satisfies Equation. (6), 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 the van Laar equation. Using the SIMPLEX[9] method, the binary interaction parameters(A_{12}, A_{21}) of the van Laar equation were calculated. The binary interaction parameters calculated in this way are shown in Table 2.

Table 1. The Antoine coefficients of the components

Components \ Coefficients	A	B	C
Carbon tetrachloride	6.84083	1177.910	220.576
o-Xylene	7.00154	1476.393	213.872
Water	8.07131	1730.630	233.426
n-Butanol	7.838	1558.19	227.438

Table 2. The optimized binary parameters of the van Laar equation for each binary system

Systems \ Parameters	van Laar	
	A_{12}	A_{21}
Carbon tetrachloride(1)+o-Xylene(2)	14.3123	0.4246
Water(1)+n-Butanol(2)	0.0327	1.8312

3. Experimental

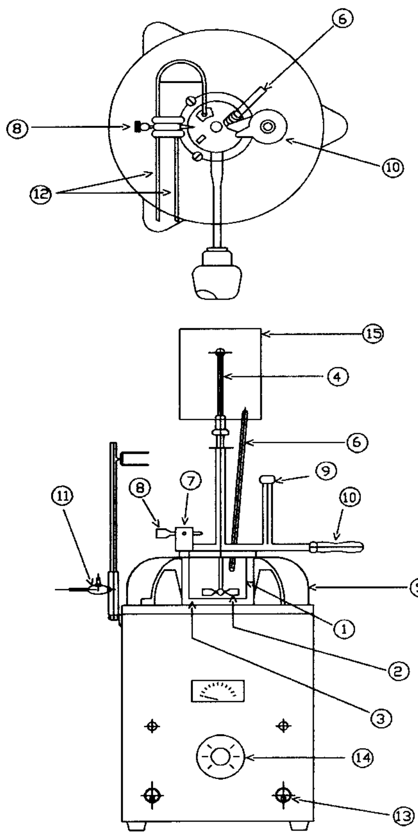
3.1 Chemicals

n-Butanol was purchased from Junsei, Japan with a minimum purity of 99%. Carbon tetrachloride was purchased from Kanto, Japan with a minimum purity of 99.5% and o-xylene from Lancaster, USA with a minimum purity 99%. Water was supplied by J.T. Baker, USA. All these chemicals were used directly without any purification.

Two mixtures were selected for the samples : carbon tetrachloride+o-xylene and water+n-butanol systems.

3.2 Apparatus and Procedure

The basic system configuration of Pensky-Martens closed cup tester[10] is given in Fig. 1. This apparatus consists of a test cup, cover and stove.



① Test Cup ② Stirrer
③ Flexible Shaft ④ Air Bath
⑤ Top Plate ⑥ Thermocouple
⑦ Flame Exposure Device ⑧ Flame Regulator
⑨ Shutter Operating Knob ⑩ Test Cup Handle
⑪ Gas Safety Valve ⑫ Gas Pipe
⑬ Electric Switch ⑭ Electric Regulato
⑮ Electric Motor

Fig. 1. Schematic diagram of experimental apparatus.

The volume of the test cup is 100ml 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 are added by mass and the test cup is filled with the mixture (65ml). 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 is the lowest temperature at which application of the test flame causes the vapor above the mixture to ignite.

4. Results

4.1 Experimental Results

The results obtained in this work for the systems, carbon tetrachloride(1)+o-xylene(2) and water(1)+n-butanol(2), are presented in Table 3 and Table 4, respectively. Concentrations of component i are given in mole fraction, x_i. As shown in Fig. 2 and Fig. 3, the lower flash points of the systems plotted as a function of mole fraction.

Table 3. The experimental and the calculated flash points for carbon tetrachloride(x_1)+o-xylene(x_2) system

Mole fractions		Flash points (°C)		
x_1	x_2	Exp.	Raoult's law	Optimization method
0.261	0.739	29.0	28.30	28.31
0.204	0.796	27.0	26.98	26.98
0.094	0.906	25.0	24.70	24.71
0.000	1.000	23.0	-	-
A.A.D.			0.34	0.33

Table 4. The experimental and the calculated flash points for water(x1)+n-butanol(x2) system

Mole fractions		Flash points (°C)		
x_1	x_2	Exp.	Raoult's law	Optimization method
0.515	0.485	36.0	44.42	35.99
0.312	0.688	31.0	37.79	31.00
0.000	1.000	31.0	-	-
A.A.D.			7.61	0.05

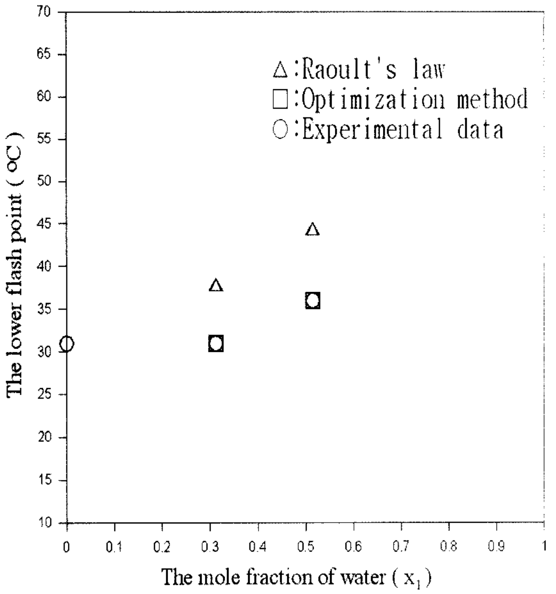


Fig. 3. Comparison of lower flash points of experimental and predicted for water(x_1)+n-butanol(x_2) system.

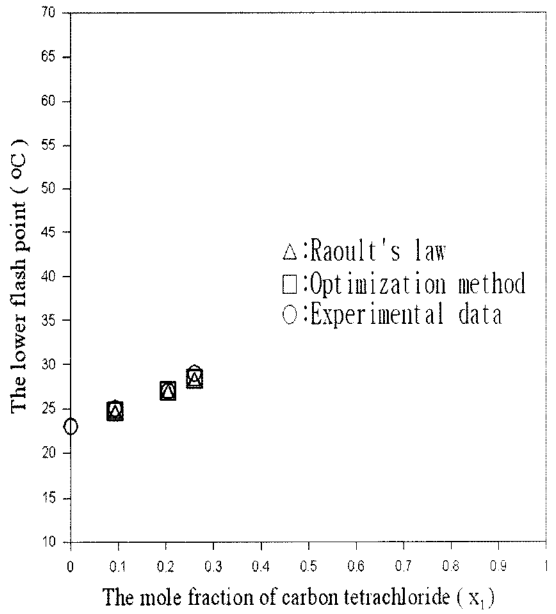


Fig. 2. Comparison of lower flash points of experimental and predicted for carbon tetrachloride(x_1)+o-xylene(x_2) system.

4.2 The comparison of the experimental and calculated lower flash points

Included in the tables is the average absolute deviation(A.A.D.) defined as [11,12] :

$$A.A.D. = \sum_{i=1}^{N}\left(\frac{\left|T_i^{\exp} - T_i^{cal}\right|}{N}\right) \quad (10)$$

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

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, carbon tetrachloride+o-xylene and water+n-butanol.

5. Conclusion

The flash points for two binary systems containing non-flammable component, were measured by Pensky-Martens closed cup tester. The experimental data were compared with the values calculated by the Raoult's law and optimization method. 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 containing non-flammable component.

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