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Water와 Acetic Acid 혼합용액의 인화점

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The Lower Flash Points of the Water+Acetic Acid Liquid Mixture

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1. INTRODUCTION

The flash point are used to classify combustible liquids according to their relative flammability. 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 important in the chemical industry.[1]

Experimental flash point data for most single component flammable liquids are readily available in the literature. Most published flash point data was for pure components. However, the flash points of mixtures that have a non-flammable component, such as 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. Therefore, 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 flash points for the system, water+acetic acid, were measured by Pensky-Martens closed cup tester, and compared with the values based on Van Laar equation[2] and Wilson equation[3].

2. EXPERIMENTAL SECTION

2-1. Chemicals

Acetic acid was purchased from Junsei, Japan with a minimum purity of 99.7%,

and water was supplied by J.T. Baker, USA. All these chemicals were used directly without any purification.

2-2. Experimental Apparatus and Procedure

Pensky-Martens closed cup tester[4] is used. The apparatus consist of a test cup, cover and stove.

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.

3. RESULTS AND DISCUSSION

3-1. Experimental Results

The results obtained in this work for the system, water(1)+acetic acid(2), are presented in Table 1. The concentrations of component i are given in mole fraction, x_i .

Table 1. The experimental data and the calculated values for the system, water(1)+acetic acid(2)

Mole fraction		Flash point ((C)		
x_1	x_2	Exp.	Van Laar	Wilson
0.707	0.293	70	73.27	70.95
0.605	0.395	59	66.08	64.07
0.506	0.494	57	60.57	59.02
0.394	0.606	51	55.27	54.27
0.312	0.688	50	51.82	51.17
0.211	0.789	43	47.95	47.65
0.111	0.889	43	44.45	44.37
0.000	1.000	41	41	41
A.A.D.	–	–	3.23	2.31

3-2. Calculation of the Lower Flash Points
The Le Chatelier has presented the following equation for multicomponent

mixtures containing flammable compounds.

The following equation applies to vapor-liquid equilibrium.

$$P_i = P_i^0 \alpha_i = P_i^0 \gamma_i x_i \qquad (1)$$

where P_i is the partial vapor pressure of component i(mmHg), P_i^0 is the vapor pressure of component i(mmHg), α_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 equation can be applied to binary systems.[5]

$$\frac{dlnP_i}{dT} = \frac{\Delta H_i}{RT^2} \qquad (2)$$

where T is the flash point in absolute temperature(K), ΔH_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. For the estimation of the enthalpy of vaporization, Wastson equation were used.[2]

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

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

where $P_{i,0}^0$ 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.

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

$$P_1 = P_{1,0}^0 = Constant \qquad (5)$$

where the subscript 1 indicates the flammable component.

Substituting Equation (5) into Equation (3),

$$\frac{1}{T^L} = \frac{1}{T_0^L} + \left(\frac{R}{\Delta H_1} \right) \cdot \ln(\gamma_1 \cdot x_1) \qquad (6)$$

where the superscript L indicates the lower flash point, T_0^L is the lower flash point temperature of the flammable component, and ΔH_1 is the average of the enthalpy of vaporization near T_0^L.

The activity coefficients(γ_i) were estimated by the Van Laar equation and the Wilson equation and the binary parameters of those equations were abstracted from the literature.[6]

The flash points prediction models developed for flammable and non-flammable binary systems included the modified equation of the enthalpy of vaporization, the Antoine equation, the pure flash point value, and a model for estimating activity coefficients.

And included in the tables is the average absolute deviation(A.A.D.) defined as[7]

$$A.A.D. = \sum_{i=1}^{N} \left(\frac{\mid T_i^{\exp} - T_i^{cal} \mid}{N} \right) \tag{7}$$

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

The calculated values based on both the Van Laar equation and the Wilson equation gave good representation of the experimental data for the system, water+acetic acid acid. However, the Wilson equation is more accutate than the Van Laar equation, as can be seen from the A.A.D..

4. CONCLUSION

The flash points for the binary system containing non-flammable component, water, were measured by Pensky-Martens closed cup tester. The experimental data were compared with the values calculated by the Van Laar equation and the Wilson equation. Good qualitative agreement was obtained with these equations. However, the calculated values based on Wilson equation were found to be better than those based on Van Larr equation.

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