

## **n-Propanol+Acetic Acid, n-Propanol+Propionic Acid, 2-Propanol+Acetic Acid 계의 클리브랜드 개방식 장치를 이용한 하부인화점 측정 및 예측**

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### **The Lower Flash Point Measurement and Prediction of n-Propanol+Acetic Acid, n-Propanol+Propionic Acid and 2-Propanol+Acetic Acid Systems Using Cleveland Open Cup Apparatus**

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## **1. Introduction**

Flash point is defined as the minimum temperature at which the vapor present over a liquid forms a flammable mixture when mixed with air[1]. The flash point of a flammable liquid therefore acts as an important criterion for regulatory authorities to classify flammable and combustible liquids [2], so that they are able to set apropos and reasonable regulations on the treatment of the liquids.

In the study, n-propanol+acetic acid, n-propanol+propionic acid and 2-propanol+acetic acid systems are selected. The study mainly focuses on the comparison of actual flash points and predicted flash points by several prediction methods. Flash points of the selected systems are measured by Cleveland Open Cup Tester and are compared to the predicted values by prediction models based on Raoult's Law, Van Laar equation, and Wilson Equation. The author hopes that the information in this paper would be useful for flash point prediction study and industrial safety.

## **2. Experiment**

### **2.1 Chemicals and Experimental Apparatus**

N-propanol from Samchun Chemical, Korea and 2-propanol from Acros, USA are used throughout the experiment. Acetic acid and propionic acid are all from Junsei, Japan. Every chemical used in the experiment has a minimum purity of 99.0 percents.

Cleveland Open Cup Tester is used for the measuring of actual flash points of materials in the experiment. This apparatus consists of a test cup, a heating plate, a test flame applicator, a heater, supports, and a thermometer [3].

### **2.3 Experiment Procedure**

The test cup is filled to a specified level with the sample. The temperature of the sample is increased rapidly at first and then at a slow constant rate, approximately 6 degrees Celsius per 60 seconds, as the flash point is approached. At specified intervals, at every 0.5 degrees Celsius, a small test flame is passed across the cup. The lowest temperature at which application of the test flame causes the vapors above the surface of the liquid to ignite is taken as the flash point [3].

### **3. Flash Point Prediction**

The fundamental idea in the prediction is that vapor-liquid equilibrium of the whole components must be assumed. Then the basis for the prediction is Le Chatelier's Law, which says:

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

where  $i$  refers to a component of a mixture,  $y$  refers to the mole fraction of a vapor component, and LFL refers to lower flammability limit.

The letter  $y$  can be substituted for a function of component pressure in a saturated solution using Modified Raoult's Law, which is:

$$y_i P = x_i P_i^s \gamma_i \quad (2)$$

where  $P$  indicates the pressure of the whole vapor components,  $x$  refers to the mole fraction of a saturated component, and  $\gamma$  indicates the activity constant of a component.

Also, LFL can be substituted for a function of component pressure in a saturated solution at flash point of the pure component, using:

$$LFL_i = \frac{P_{i,T_f}^s}{P} \quad (3)$$

The fundamental Le Chatelier's Law then becomes:

$$\sum_{i=A}^B \frac{x_i P_i^s \gamma_i}{P_{i,T_f}^s} = 1 \quad (4)$$

Here,  $x$  can be obtained from the experiment, since the experiment sets mole fractions of the components and the pressures can be gotten from Antoine equation [4], which states:

$$\log P_i^s = A + \frac{B}{C + t} \quad (5)$$

where A, B, and C are Antonine constants which are already available in data sources [5] and t indicates a Celsius temperature.

Also,  $\gamma$  can be substituted for a function of t and  $x$ ; in the study three methods are employed for the calculation of  $\gamma$ : Raoult's Law, Van Laar Equation[6], and Wilson Equation[5].

Raoult's Law basically assumes that every phase is ideal; therefore, the law which is used to substitute  $\gamma$ , Modified Raoult's Law, becomes:

$$y_i P = x_i P_i^s \quad (6)$$

and there is no need to get the value of  $\gamma$ .

When all substitutions are done, basic Le Chatelier's Law becomes an equation of the flash point t, and the prediction can be conducted with the equation.

#### 4. Experiment Results and Comparison

##### 4.1 Tables of Experiment Results and Predictions

Table 1. Actual flash points and flash point predictions of n-propanol+acetic acid systems.

mole fraction (n-propanol:acetic acid)	observed	Raoult's Law	Van Laar Equation	Wilson Equation
1.000 : 0.000	32.3	32.30	32.30	32.30
0.922 : 0.078	32.5	33.25	33.28	33.28
0.709 : 0.291	35.0	36.26	36.40	36.41
0.501 : 0.499	43.8	40.01	40.32	40.35
0.299 : 0.701	47.8	44.98	45.46	45.51
0.097 : 0.903	49.8	52.65	53.09	53.11
0.000 : 1.000	58.5	58.50	58.50	58.50
A.A.D.	-	2.294	2.258	2.248

Table 2. Actual flash points and flash point predictions of n-propanol+propionic acid systems.

mole fraction (n-propanol:propionic acid)	observed	Raoult's Law	Van Laar Equation	Wilson Equation
1.000 : 0.000	32.3	32.30	32.30	32.30
0.904 : 0.096	33.3	33.58	33.70	33.73
0.703 : 0.297	36.3	36.70	37.28	37.41
0.499 : 0.501	42.3	40.69	41.96	42.24
0.298 : 0.702	49.3	45.97	47.84	48.25
0.089 : 0.911	54.5	54.24	55.61	55.88
0.000 : 1.000	59.5	59.50	59.50	59.50
A.A.D.	-	1.176	0.858	0.806

## 4.2 Explanation

As shown above, the overall pattern of the experimental data is similar to that of the Table 3. Actual flash points and flash point predictions of 2-propanol+acetic acid systems.

mole fraction (2-propanol:acetic acid)	observed	Raoult's Law	Van Laar Equation	Wilson Equation
1.000 : 0.000	22.0	22.00	22.00	22.00
0.904 : 0.096	23.5	23.38	23.54	23.53
0.697 : 0.303	25.5	26.91	27.72	27.71
0.500 : 0.500	33.0	31.29	32.86	32.98
0.298 : 0.702	41.0	37.68	39.87	40.21
0.094 : 0.906	47.7	48.78	50.57	50.97
0.000 : 1.000	58.5	58.50	58.50	58.50
A.A.D.	-	1.528	1.280	1.264

prediction data. Prediction models using Van Laar Equation and Wilson Equation show relative precision in prediction than the model using Raoult's Law does. This is because the two includes an activity constant, which is a modification of aberrations in unideal solutions.

## 5. Conclusion

Flash points of three binary systems, n-propanol+acetic acid, n-propanol+propionic acid and 2-propanol+acetic acid, were measured with Cleveland Open Cup Tester. Actual flash points of the systems from the experiment are compared to the predicted values from several prediction models, which are the models using Raoult's Law, Van Laar Equation, and Wilson Equation.

All the prediction models employed in the study slightly deviate from the observed data. However, among the three the prediction model using Wilson Equation relatively corresponds well with the observed data.

## Reference

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