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Flash Point for Binary Mixtures Liquids using UNIQUAC Equation

Le Viet Vu
The University of fire prevention and fighting
243 Khuat duy tien – Hanoi – VietNam

Abstract:- Flash point is a very important parameter in fire protection. It is used to assess the fire and explosion hazards of liquid fuels. The determination of the flash point has practical implications for the storage, transportation and use of today's flammable liquids. For binary liquid solution, determining the flash point through the Uniquac equation is extremely difficult by calculating the parameters. In this article, the author studies the relationship between calculation by Unifac, Uniquac equation and experimentally.

Keywords:- *Unifac, Liquid, Binary Mixture, Flash Point, Uniquac Equation.*

I. INTRODUCTION

We used flash point as a major property to determine the fire and explosion risks of a liquid. Flash point is the lowest temperature, at which a flammable mixture created by mixing the vapor above the liquid at the balance state with air. Flash point for binary mixtures can be determined by experimental or estimated method by calculation method with available information. The information needed for the composite flash point prediction is the flash point of each component, the vapor pressure and activity coefficient as functions of temperature for each mixed component. The full test data is not available and other ways to identify basic information are needed. A flash point assessment procedure of a binary mixture using the Uniquac equation, Uniquac equaton.. is proposed especially using calculationby Unifac, providing techniques that can be used to estimate a parameter necessary determination for binarry mixtures [1-4].

$$1=\sum_{i=1} \frac{x_i \gamma_i P_i^{sat}}{P_{i,fp}^{sat}} \quad (1)$$

where x_i, γ_i, Pisat and Pi,fp sat are the mole fraction, activity coefficient, vapour pressure at temperature T and vapour pressure at the flash point temperature of the mixture.

The activity coefficient γ_2 in Eq. (1) can be estimated using the Uniquac equation.

$$\ln\gamma_i = \ln\frac{\Phi_i}{x_i} + \frac{z}{2} q_i \ln\frac{\theta_i}{\Phi_i} + l_i - \frac{\Phi_i}{x_i}\sum_j^N x_j l_j - q_i \ln\left(\sum_j^N \tau_{ji}\theta_j\right) + q_i - q_i \sum_j^N \frac{\theta_j \tau_{ji}}{\sum_j^N \tau_{jk}\theta_k} \quad (2)$$

Where:

$$\ln\tau_{ij} = -\frac{u_{ij}-u_{jj}}{RT} \qquad \Phi_i = \frac{x_i r_i}{\sum_k^N x_k r_k}$$

$$\theta_i = \frac{x_i q_i}{\sum_k^N x_k q_k}$$

$$l_i = \frac{z}{2}(r_i - q_i) - (r_i - 1)$$

For the ideal binary liquid solution becomes :

$$1=\sum \frac{x_i P_i^{sat}}{P_{i,fp}^{sat}} = \frac{x_1 P_1^{sat}}{P_{1,fp}^{sat}} + \frac{x_2 P_2^{sat}}{P_{2,fp}^{sat}} \quad (3)$$

where x_1, x_2, P_1sat, P_2sat and P_1,fp sat, P_2,fp are the mole fraction, activity coefficient and vapour pressure at the flash point temperature of the mixture.

The saturated vapor pressure of each pure component i varies with temperature according to the Antoine equation [5].

$$P_i^{sat} = \exp\left(A_i - \frac{B_i}{T+C_i}\right) \quad (4)$$

II. MATERIALS AND METHODS

All chemicals were purchased as reagent grade and used without further purification. Solvents were distilled and/or dried according to standard methods . PM-93 Pensky-Martens Flash Point Tester (Stanhope-Seta, London Street, Chertsey, Surrey, KT16 8AP, UK). Measure of flash point in +5 °C to 400 °C, fast heating rate (>10 °C/min) and standard; 5.5 °C/min; 3 °C/min; 1.3 °C/min; 1 °C/min. Results are recorded in accordance with ASTM D6299 (Standard Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance).

III. RESULTS AND DISCUSSION

Because the activity coefficient of Uniquac equation more effective for other [6-8], the author chose to use the Uniquac equation as the main factor. To calculate the activity coefficients of Uniquac equations using some parameters are presented in Table 1.

System	***A12***	***A21***
Methanol - Ethanol	-162.67	240.45
Ethanol - Acetone	73.0960	22.5570
Methanol - Acetone	-37.323	197.251

Table 1:- Parameters for Uniquac equations

Basing on the methods “original UNIFAC” and “modified UNIFAC (Dortmund)”, using the algorithm the UNIFAC software could be calculates flash points of flammable liquid mixtures to determine the paramaters. For calculation by Unifac we can calculate the saturated vapor pressure of binary liquid or tenary liquid then easily calculate the flammability limits of the mixture at different rates. Functional groups on the molecules make up the binary liquid to calculate activity coefficients by UNIFAC. For pure components we can use the Antone equation to compute the saturated vapor pressures.

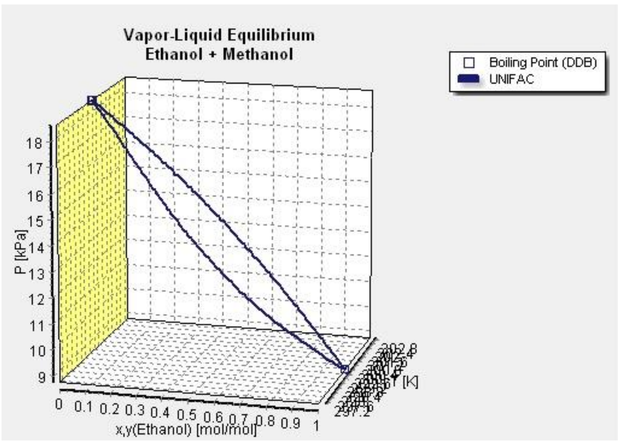

Fig 1:- Vapor liquid equilibrium Methanol and Ethanol

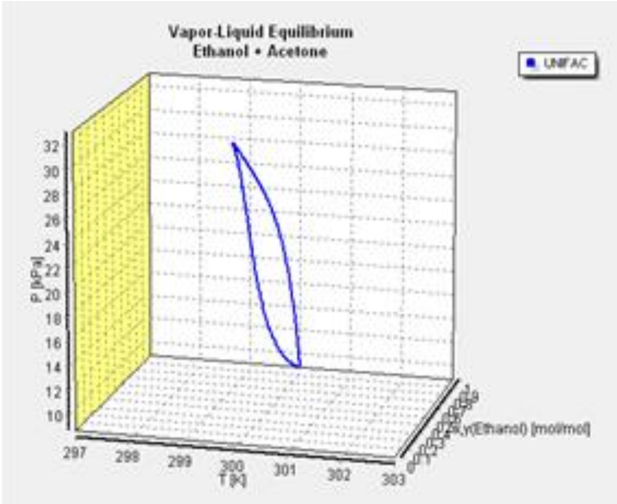

Fig 2:- Vapor liquid equilibrium Acetone and Ethanol

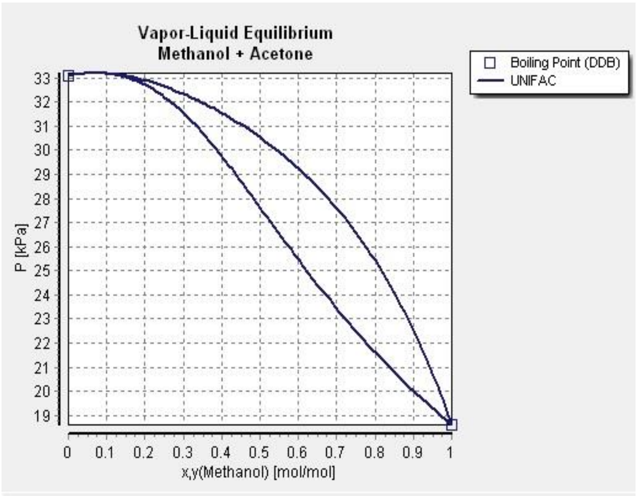

Fig 3:- Vapor liquid equilibrium Methanol and Acetone

The flash point result for the binary liquid mixture is shown in Figure 4.

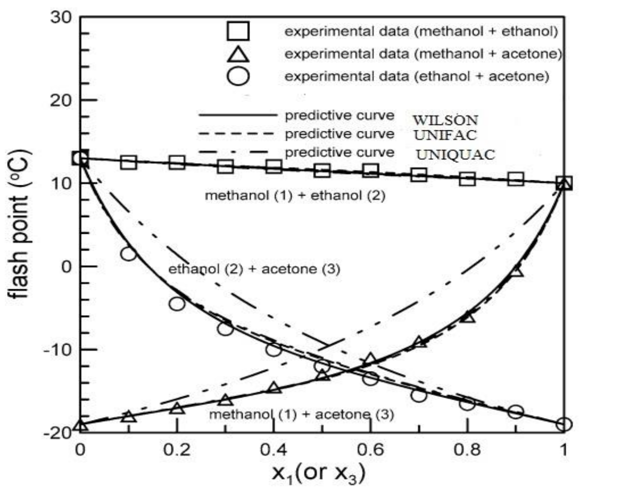

Fig 4:- Comparison of the flash point prediction curves based upon binary parameters

IV. CONCLUSIONS

The calculted flash point of mixtures by Unifac are in good agreement with experimental data. It opens a new direction in solving the problem of applying experimental replacement calculations.

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