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Flash Point for Ternary Flammable Solutions of Liquid Using Modified UNIFAC Methods

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Abstract:- Ternary liquid mixtures are important in many engineering applications. The study of flash point for ternary flammable solutions of liquid is of great significance in fire prevention to ensure the safety of dangerous flammable liquids and when conducting fire fighting. Experimental data were obtained using a Pensky - Marten closed-cup tester and calculated using an approximate model using equation Wilson, Uniquac, NRTL or Modified UNIFAC methods.

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

I. INTRODUCTION

Flash point is a key characteristic used to determine the fire hazard of liquids in safe practice when handling and storing liquid mixtures and to assess the exact level of risk. It is defined as the minimum temperature at which a vapor appears above a liquid at equilibrium to form a flammable mixture when mixed with air.

The flash point for a mixture of two water can be determined experimentally or estimated by calculation with available information. The information required for the prediction of the mixed flash point is the flash point of each component, the vapor pressure and the activity coefficient as a function of the temperature for each component of the mixture. Full test data are not available and other ways of determining background information are required. The process of evaluating the flash point of a ternary mixture using the modified Unifac method is quick and efficient.

The basic assumption in Liaw et al [1-3] is that the liquid phase is in equilibrium with the vapor, and the vapor phase is behaving as an ideal gas:

$$\sum_{i=1}^{2} \frac{x_i \gamma_i P_i^{sat}}{P_{i,fp}^{sat}} = 1 \quad (1)$$

Where xi, γi, 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.

For a mixture of water (component 1) and liquid (component 2) (aqueous mixtures) [4], water is a non-flammable substance and has no flash point temperature Tf. So the first quantity can be ignored:

$$P_2^{sat} = \frac{P_{2,fp}^{sat}}{x_2 \gamma_2} \quad (2)$$

For the ideal tenary liquid solution becomes :

$$1 = \sum \frac{x_i P_i^{sat}}{P_{i,fp}^{sat}} = \frac{x_1 P_1^{sat}}{P_{1,fp}^{sat}} + \frac{x_2 P_2^{sat}}{P_{2,fp}^{sat}} + \frac{x_3 P_3^{sat}}{P_{3,fp}^{sat}} \quad (3)$$

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

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

Table 1. Antoine coefficients for the involved components

Formula	*Component*	A_i	B_i	C_i
$CHCl_3$	Chloroform	9.39360	2696.249	–46.918
CH_2Cl_2	Dichloromethane	10.44014	3053.085	–20.53
CH_2O	Formaldehyde	9.94883	2234.878	–29.026
CH_2O_2	Formic acid	9.37044	2982.446	–55.150
CH_3NO_2	Nitromethane	10.14657	3331.696	–45.550
CH_4O	Methanol	11.98705	3643.314	–33.424
C_2H_6O	Ethanol	12.05896	3667.705	–46.966
C_3H_6O	Acetone	9.76775	2787.498	–43.486
C_3H_8	Propane	9.10434	1872.824	–25.101
C_3H_8O	1–propanol	11.21152	3310.394	–74.687
C_3H_8O	2–propanol	13.82295	4628.956	–20.514
$C_3H_8O_2$	2–methoxy–ethanol	11.45476	4130.796	–36.273

The activity coefficient γ2 in Eq. (2) can be estimated using the Wilson equation [6].

$$\ln \gamma_2 = -\ln(x_1\Lambda_{21} + x_2) - x_1\left(\frac{\Lambda_{12}}{x_1 + x_2\Lambda_{12}} - \frac{\Lambda_{21}}{x_1\Lambda_{21} + x_2}\right) \quad (5)$$

$$\Lambda_{12} = \frac{v_2}{v_1}\exp\left(\frac{-A_{12}}{RT}\right)$$

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By Uniquac equation:

$$\ln \gamma_i = \ln\frac{\Phi_i}{x_i} + \frac{z}{2}q_i \ln\frac{\theta_i}{\Phi_i} + l_i - \frac{\Phi_i}{x_i}\sum_j^N x_j l_j$$

$$-q_i \ln\left(\sum_j^N \tau_{ji}\theta_j\right) + q_i - q_i \sum_j^N \frac{\theta_j \tau_{ji}}{\sum_j^N \tau_{jk}\theta_k} \quad (6)$$

Where:

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

$$\theta_i = \frac{x_i q_i}{\sum_k^N x_k q_k} \qquad l_i = \frac{z}{2}(r_i - q_i) - (r_i - 1)$$

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

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.

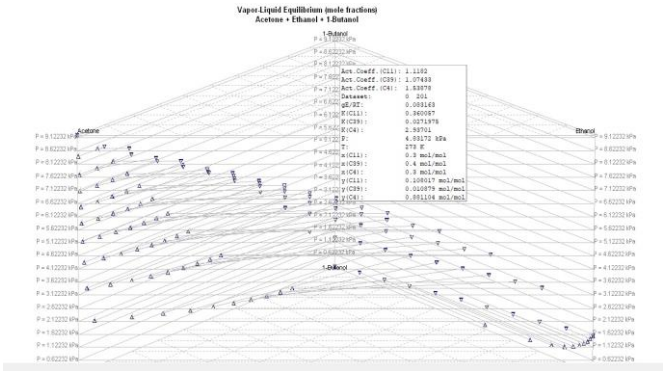

Figure 1. *Vapor liquid equilibrium Acetone , Ethanol and 1-Butanol by Unifac*

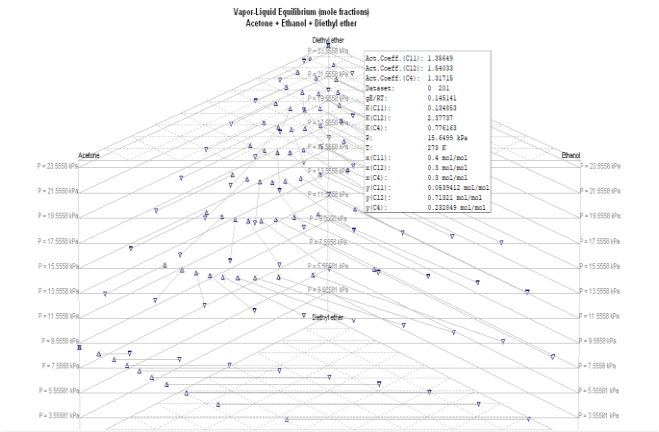

Figure 2. *Vapor liquid equilibrium Acetone , Ethanol and Dietylether by Unifac*

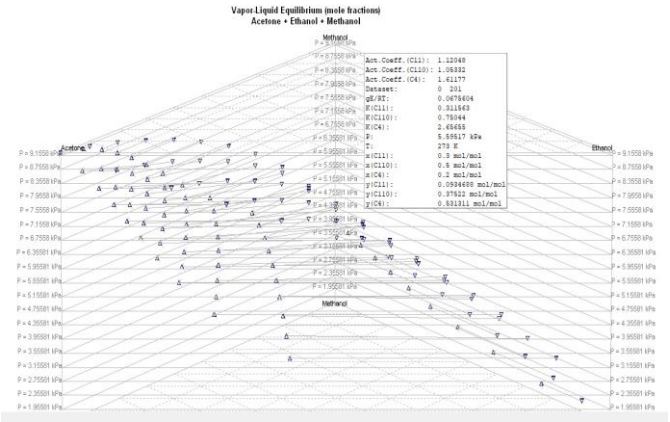

Figure 3. *Vapor liquid equilibrium Acetone , Ethanol and Methanol by Unifac*

IV. CONCLUSIONS

The calculted flash point of ternary liquid mixtures using modified Unifac method 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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