Calculation of Flash Point for Aqueous Binary Mixtures Using Closed Cup Tester

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Abstract: ***Mixtures of water with alcohols are important in numerous engineering applications. A queous solution of various alcohols was selected for investigation in this study. The experimental data was obtained using the Pensky - Marten closed cup tester and calculated by approximation model. Activity coefficients were calculated by the Wilson equation.***

Keywords: Aqueous solutions, Pensky – Marten, binary mixture, flash point, wilson equation

1. Introduction

Flash point is a major property used to identify the fire hazard of liquids in the safe practice of handling and storing liquid mixtures and to assess the exact level of risk. It is defined as the minimum temperature that vapor appears on the liquid in equilibrium to form a flammable mixture when mixed with air.

Flash point for aqueous binarry 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 Wilson equation is proposed, providing techniques that can be used to estimate a parameter necessary determination for aqueous binarry mixtures.

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:

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

where x_i, γ_i, P_i^{sat} and $P_{i,fp}^{sat}$ 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 T_f. So the first quantity can be ignored:

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

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

$$P_i^{sat} = \exp\left(A_i - \frac{B_i}{T + C_i} \right) \qquad (3)$$

Table 1: Antoine coefficients for the involved components

Formula	Component	T_b	A_i	B_i	C_i	T_{min}- T_{max}
Ar	Argon	87.3	9.31039	832.778	2.361	73–133
CCl_4	Tetrachloromethane	349.70	9.22001	2790.781	–46.741	287–350
$CHCl_3$	Chloroform	334.40	9.39360	2696.249	–46.918	263–333
CH_2Cl_2	Dichloromethane	313.20	10.44014	3053.085	–20.53	233–313
CH_2O	Formaldehyde	254.00	9.94883	2234.878	–29.026	164–373
CH_2O_2	Formic acid	373.70	9.37044	2982.446	–55.150	299–381
CH_3NO_2	Nitromethane	374.30	10.14657	3331.696	–45.550	329–409
CH_4O	Methanol	337.80	11.98705	3643.314	–33.424	288–357
CO	Carbon monoxide	81.60	9.26679	769.935	1.637	52–121
CO_2	Carbon dioxide	185.50	10.77151	1956.255	–2.112	146–285
C_2H_3N	Acetonitrile	354.80	10.28058	3413.099	–22.627	246–355
C_2H_4O	Acetaldehyde	293.70	9.97724	2532.406	–39.205	191–293
$C_2H_4O_2$	Acetic acid	391.10	11.84896	4457.828	–14.699	291–391

C_2H_6	Ethane	184.50	9.27428	1582.178	–13.762	145–284
C_2H_6O	Ethanol	351.50	12.05896	3667.705	–46.966	293–366
C_3H_6O	Acetone	329.40	9.76775	2787.498	–43.486	260–328
C_3H_8	Propane	231.10	9.10434	1872.824	–25.101	192–331
C_3H_8O	1–propanol	370.40	11.21152	3310.394	–74.687	333–378
C_3H_8O	2–propanol	355.40	13.82295	4628.956	–20.514	247–356
$C_3H_8O_2$	2–methoxy–ethanol	397.60	11.45476	4130.796	–36.273	290–447
C_4H_8O	2–butanone	352.80	9.64438	2904.340	–51.181	316–361
C_4H_8O	Tetrahydrofuran	339.10	9.48686	2768.375	–46.896	296–373
C_6H_6O	Phenol	455.00	9.33802	3183.669	–113.657	336–455
$C_4H_{10}O$	Diethylether	307.70	9.91763	2847.722	–20.110	308–432

The activity coefficient γ_2 in Eq. (2) can be estimated using the Wilson equation [6].

$$\ln \gamma_2 = -\ln(x_1\Lambda_{21} + x_2) - x_1\left(\frac{\Lambda_{12}}{x_1 + x_2\Lambda_{12}} - \frac{\Lambda_{21}}{x_1\Lambda_{21} + x_2}\right) \quad (4)$$

$$\Lambda_{12} = \frac{v_2}{v_1}\exp\left(\frac{-A_{12}}{RT}\right) \quad \Lambda_{12} = \frac{v_1}{v_2}\exp\left(\frac{-A_{21}}{RT}\right)$$

2. 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).

3. Results and Discussion

Following the activity coefficients of wilson equation more effective for other [7-8], the author chose to use the Wilson equation as the main factor. The parameters were used in the Wilson equations for the calculation of activity coefficients needed for the flash point predictions are presented in Table 2.

Table 2: Parameters for Wilson equations

System	A_{12}	A_{21}
Water - Methanol	908.46	-359.74
Water - Ethanol	481.44	179.66
Water - 1-propanol	597.52	527.50
Water - 2-propanol	650.35	380.59

The predictions for water-alcohol mixtures are presented in **Fig. 1-4**.

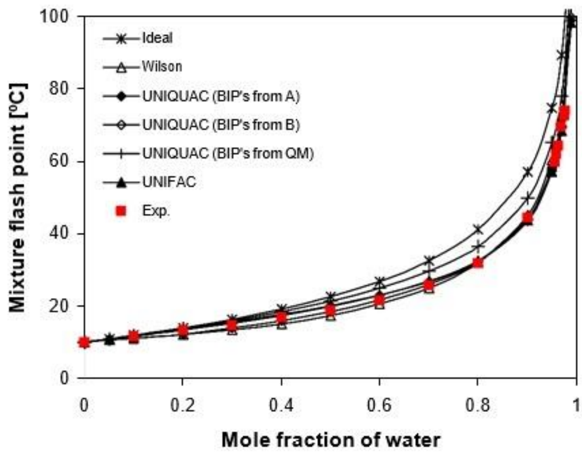

Figure 1: Prediction of the water - methanol mixture flash point

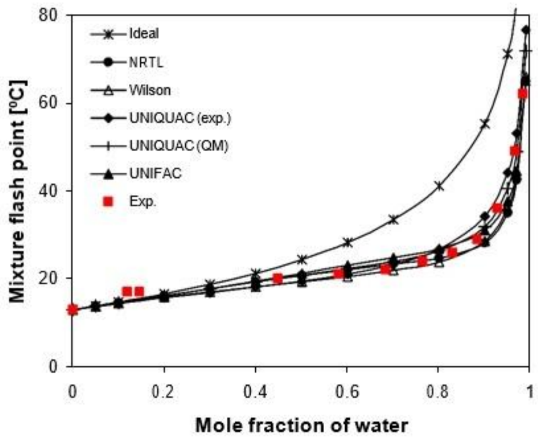

Figure 2: Prediction of the water - ethanol mixture flash point

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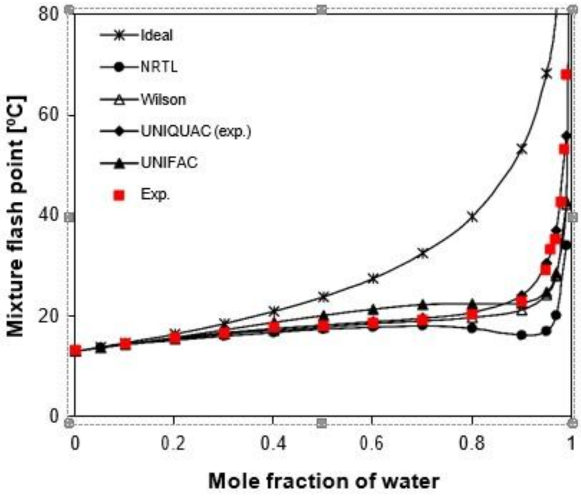

Figure 3: Prediction of the water - 1- propanol mixture flash point

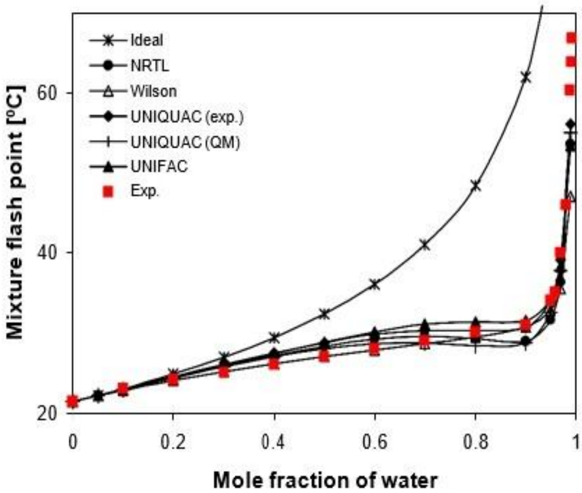

Figure 4: Prediction of the water - 2 - propanol mixture flash point

4. Conclusions

The calculated flash points of aqueous mixtures 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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