Mathematical Prediction of Binary Mixtures Flash-Points

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Abstract**—**The flash points of three organic binary mixtures containing alcohols were measured in the present work. The experimental data was obtained using the Pensky-Martens closed cup tester. The experimental data were compared with the values calculated by the approximation model. Activity coefficients were calculated by the Wilson equation. The accuracy of predicted flash point values is dependent on the thermodynamic model used for activity coefficient.

Keywords**—**approximation function, binary mixture, flash point, prediction.

I. INTRODUCTION

THE flash point of a mixture will vary depending on the composition. The total characterization of a mixture requires significant experimental work and time. Probably, that is why the available experimental flash point data of mixtures are scarce. In a given liquid, the flash point is defined as the lowest temperature at which a liquid generates flammable vapours which can be ignited in air by a flame above its surface [1]. The lower flash-point value indicates relatively greater fire and explosion hazard. The value of the flash point is a key parameter for the flammable liquids classification, as defined in European CLP Regulation. In addition to the usage and accumulation of flammable liquids, such as is outlined above, the transportation requirements for these mixtures are primarily related to their flash-point values. This parameter plays special role in closed containers, when liquid-vapor equilibrium can be established. In this case, the atmosphere in the container consists of a homogeneous mixture of vapor and air and, if the vapor concentration is included in the flammability range, comprised between the lower flammability limit (LFL) and the upper flammability limit (UFL), an explosive atmosphere is present in the closed container. The lower point of explosion (LPE) of a liquid is defined as the temperature at which the concentration of vapors emitted by this liquid, in thermodynamic liquid-vapor equilibrium conditions and when mixing with air at atmospheric pressure, is equal to the lower flammability limit (LFL) [1]. The first purpose of the contribution is to show the erroneous prediction that could be made if an ideal solution is assumed when the solution is non-ideal. The second purpose of this contribution is to developed FP approximation of binary aqueous mixtures by a reasonable relationship allowing predicting easily FP when only the concentration of the flammable component is known.

II. THERMODYNAMIC MODEL

Phase equilibria (VLE, LLE, SLE) data are described by activity coefficient models selected by the user from the set of supported models: Wilson, NRTL, UNIQUAC, Margules, Redlich-Kister, and van Laar. Predictions of the activity coefficients generated for mixtures are covered by the various versions of the models, including [1].

The flash point for a solution can be estimated by Liaw´s model by equation of Le Chatelier [2-4] and an extended Antoine equation for estimating the saturated vapor pressure [5] and a model for estimating activity coefficients for given temperature and pressure conditions [6]. The model for predicting the flash point of mixtures take into account the non-ideality of the solution through liquid phase activity coefficients and have been used to predict efficiently the flash point of several mixtures [2, 7-11].

The flash point of a binary mixture can be estimated by model developed by Liaw et al., 2002 [2]

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

where P_i^{sat} = vapor pressure at temperature T, (Pa); $P_{i,fp}^{sat}$ = vapor pressure at the flash point temperature (Pa), x_i = liquid

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mole fraction of component I (-), γ_i = activity coefficients for Wilson equation (-).

If the mixture is an ideal, $\gamma_i = 1$ and (1) become

$$\frac{x_1 P_1^{sat}}{P_{1,fp}^{sat}} + \frac{x_2 P_2^{sat}}{P_{2,fp}^{sat}} = 1 \tag{2}$$

where P_i^{sat} = vapor pressure at temperature T (Pa), $P_{i,fp}^{sat}$ = vapor pressure at the flash point temperature (Pa), x_i = liquid mole fraction of component I (-).

The temperature that satisfies (1) or (2) is the flash point temperature of the mixture. The vapour pressure can be estimated from an equation, such as Antoine´s equation, if the required constants are known

$$\log P_i^{sat} = A_i + \frac{B_i}{T} + C_i T + D_i T^{E_i} \tag{3}$$

where P_i^{sat} = vapor pressure at temperature T (Pa), A_i, B_i, C_i, D_i and E_i are the regression coefficients for compound I, T = thermodynamic temperature (K).

This correlation should not be used outside the temperature range (T_{min}= 183 K, T_{max}= 512 K) at which the parameters were obtained. In Table 1 are the Antoine equation parameters used for the calculation [12].

$$ln\gamma_i = -\ln\left(x_i + \Lambda_{ij}\, x_j\right) + x_j \left(\frac{\Lambda_{ij}}{x_i + \Lambda_{ij} x_j} - \frac{\Lambda_{ji}}{\Lambda_{ji} x_i + x_j}\right) \tag{4}$$

where γ_i = activity coefficients for Wilson equation (-), x_i, x_j= liquid mole fraction of component (-), Λ = Wilson model parameter, i, j = indexes of chemicals.

$$\Lambda_{ij} = \frac{v_j^l}{v_i^l}\exp\left(-\frac{\lambda_{ij} - \lambda_{ii}}{RT}\right) \tag{5}$$

where Λ_{ji}, Λ_{ij} = Wilson model parameter (-), v^l = Molar volume of liquid (m³/mol), λ_{ji}, λ_{ij} = binary parameters of the Wilson equation (J/mol), i, j = indexes of chemicals.

The activity coefficients were calculated by using Wilson model.

Table 1. Binary interaction parameters of the Wilson equation for the binary systems of methanol (A), ethanol (B), 1-propanol (C), 1-butanol (D) and 1-pentanol (E).

Mixtures	Wilson activity coefficients		Reference
	λ_{12}	λ_{21}	
A + B	-68.35	66.46	[7]
A + C	66.79	-70.54	[7]
D + E	-133.80	648.30	[3]

Wilson equation: $A_{12}=(\lambda_{12}-\lambda_{11})/R.A_{21}=(\lambda_{21}-\lambda_{22})/R$

III. EXPERIMENTS

Two flash point analyzers have been used in the present study. One employed the Pensky-Martens (SN: 0746 11 4101, Petrotest GmbH, Germany) semi-automatic closed cup tester. Measurements of the flash points in the 20-50 °C region were obtained using the Abel (SN: 0723 12 1001, Petrotest GmbH, Germany) semi-automatic closed cup tester. Both set up consists of an external cooling system, test cup, heating block, electric igniter, and sample thermometer. The apparatus incorporates control devices that program the instrument to heat the sample at a specified heating rate within a temperature range close to the expected flash point. The flash point has been tested using an electric igniter at specified temperature test intervals. A magnetic stirrer provides sufficient agitation for the test samples (120/min.). The prepared mixtures were stirred for 10 min. before the flash-point test. Flash points values of the pure liquid flammable substances were determined experimentally according to EN ISO 2719: 2002 and EN ISO 13736:2013 European standards with the accuracy of 0.5 °C. The mole fraction of each component was determined by measuring the mass using a Sartorius digital balance (sensitivity 0.0001 g, maximum load 100 g). The sample was prepared and transferred to the cup of the apparatus at least 10ºC below the expected flash point. The sample was not stirred while the flame was lowered into the cup. The flash point was the temperature at which the test flame application caused a distinct flash in the interior of the cup. The measured value was the mean of two measurements which do not differ by more than 2ºC. All materials used in this study were purchased from Merck. Purities were at least 99.8% (analytical grade) for all compounds used for these experimental flash point determinations.

IV. RESULTS AND DISCUSSION

To confirm the predictive efficiency of the derived flash-points, the model was verified by comparing the predicted values with the experimental data for the studied mixtures: methanol + ethanol; methanol + 1-propanol; 1-butanol + 1-pentanol.

Table 2. Comparison of FP values adopted from the literature with experimentally-derived data for some alcohols.

	Predicted	Experiment	SFPE	Merck	DIPPR
A	10.0	10.0 ±0.4[a]	12	10	11
B	13.0	13.0±0.3[a]	13	13	13
C	22.9	23.0±0.9[b]	15	22	18
D	36.9	37.0±0.5[b]	29	34	33
E	49.9	49.0±0.6[b]	33	49	47

[a][7], [b][2]

The value of the flash point for 1-propanol adopted from Society of Fire Protection Engineers (SFPE) Handbook [13], Design Institute for Physical Property Research (DIPPR) [12], and the Merck Index (Merck) [14] (15, 22 and 18°C, respectively) clearly appear to be quite different. The corresponding value provided by the chemical supplier of the 1-propanol used herein Merck is 22°C, which appears to be quite similar to that value predicted.

Table 3. Flash-point approximations developed.

Mixtures	Approximations developed	
	Polynomial [a]	Reciprocal [b]
A + B	a = 9.90100 b = 6.99224 c = -5.55918 d = 2.77797 e = -1.86772 f = 0.76923 R^2 = 0.99999	a = 0.12787 b = -0.0519 c = 0.18734 R^2 = 0.98783
A + C	a = 9.98287 b = 11.10672 c = 1.33584 d = 4.49248 e = -6.52331 f = 2.60256 R^2 = 1	a = 0.11083 b = -0.06793 c = 0.49151 R^2 = 0.99772
D + D	a = 36.63493 b = -0.48609 c = 12.69344 d = 0.91801 e = -4.60781 f = 4.34615 R^2 = 1	a = 0.0274 b = -0.00721 c = 1.77037 R^2 = 0.99995

[a] $y = b_0 + b_1x + b_2x^2 + b_3x^3 + b_4x^4 + b_5x^5$

[b] $y = \frac{1}{a+bx^c}$

Table 4. Mixture FP methanol (1) + ethanol (2).

Ethanol fraction	Model predictions (present work)			Approximations [a] (present work)			
	T_{FPI}	T_{FPW}	Δ_{WI}	T_{FPP}	Δ_{PI}	T_{FPR}	Δ_{RI}
1.0	12.9	13.0	0.1	13.0	0.1	13.1	0.2
0.9	12.6	12.9	0.3	12.9	0.3	13.0	0.4
0.8	12.3	12.8	0.5	12.8	0.5	12.8	0.5
0.7	12.0	12.7	0.7	12.7	0.7	12.6	0.6
0.6	11.7	12.5	1.2	12.5	0.8	12.4	0.7
0.5	11.4	12.2	0.8	12.2	0.8	12.1	0.7
0.4	11.1	11.9	0.8	11.9	0.8	11.9	0.8
0.3	10.8	11.5	0.7	11.5	0.7	11.5	0.7
0.2	10.5	11.0	0.5	11.0	0.5	11.2	0.7
0.1	10.2	10.5	0.3	10.5	0.3	10.6	0.4

[a] $\Delta = (T_{predicted} - T_{approximation})$

In the prediction model, it was assumed that the vapour phase and the liquid phase of a solution were in equilibrium. The predicted data was only adequate for the data determined by the closed cup test method, and may not be appropriate to apply to the data obtained from the open cup test method because of its condition having deviated from the vapour-liquid equilibrium. The experimentally-derived value of the flash point for ethanol is the same as that adopted from various literature sources [13,14], although there did appear to exist some slight deviation between our predicted and experimentally-derived data and the analogous value reported for methanol and propanol in the literature. As a result of data presented in Table 3 the prediction well satisfied the experimental and published values. Data correlations by equations developed in Table 3 for methanol (1) + ethanol (2), methanol (1) + 1-propanol (2) and butanol (1) + 1-pentanol (2) based on the basis of Harris reciprocal and 5th order polynomial functions were performed together with iterative Levenberg-Marquardt calculations [15,16]. In Figs. 1-3, the flash point variation between the model predictive curves and the experimentally derived data for the binary solutions are compared. Most liquid mixtures made of members of homologous series are practically ideal. The propanol-pentanol mixture exhibits no deviation from ideal behaviour and no azeotropes are present. These mixtures have properties that can be predicted with a simple mixing rule that ignores interactions among the individual components because these chemicals are very similar. In the presented mixtures, a minimum flash point value is observed.

The effect of assuming an ideal solution for the mixture flash point prediction is presented in Figures 1-3. In general, the mixture flash point of an ideal mixture will have a linear trend, whereas the mixture flash point of a non-ideal mixture will be curved. The shape of this curve will depend on the components of the mixture. Non-idealities have a strong effect on mixture flash point, and the assumption of ideal solution can lead to erroneous estimates that conceal the risk associated with a specific mixture. The conceived reciprocal function fits the experimental data better than the 5rd polynomial expressions. Errors comparable to those provided by the polynomial relationships were observed with methanol-propanol mixtures (Table 4) only.

Data correlations by equations developed in Table 4 for methanol (1) + ethanol (2), methanol (1) + 1-propanol (2) and butanol (1) + 1-pentanol (2) based on the basis of Harris reciprocal and 5th order polynomial functions were performed together with iterative Levenberg-Marquardt calculations. Similar trend could be recognized from Figures 2-3.

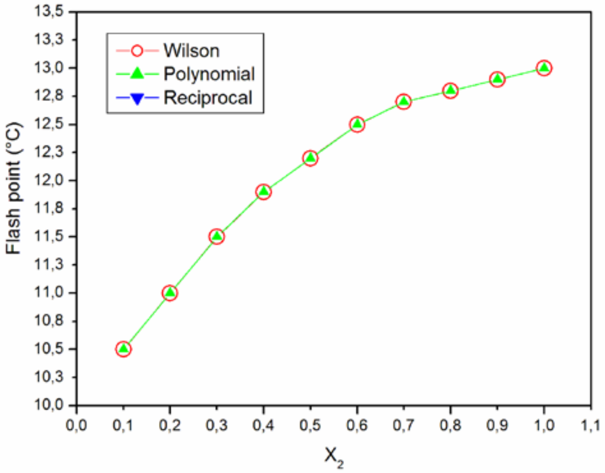

Figure 1. Comparison of polynomial approximation and reciprocal approximation with the standard Wilson model for methanol (1) + ethanol (2) mixture.

Table 5. Mixture FP methanol (1) + 1-propanol (2).

1-propanol fraction	Model predictions (present work)			Approximations (present work)			
	T_{FPI}	T_{FPW}	Δ_{WI}	T_{FPP}	Δ_{PI}	T_{FPR}	Δ_{RI}
1.0	23.0	22.9	0.1	23.0	0.0	23.3	0.3
0.9	21.4	21.5	0.1	21.5	0.1	21.7	0.3
0.8	19.8	20.2	0.4	20.2	0.4	20.0	0.2
0.7	18.4	18.8	0.4	18.8	0.4	18.5	0.1
0.6	17.0	17.4	0.4	17.4	0.4	17.2	0.2
0.5	15.7	16.1	0.4	16.1	0.4	15.9	0.2
0.4	15.4	14.7	0.7	14.7	0.7	14.8	0.6
0.3	13.2	13.5	0.3	13.4	0.2	13.6	0.4
0.2	12.1	12.2	0.1	12.2	0.1	12.5	0.4
0.1	11.0	11.1	0.1	11.1	0.1	11.2	0.2

[a] $\Delta = (T_{predicted}-T_{approximation})$

Fig. 1 and Table 5 show that predicted results by the Wilson equation and as ideal solution are in excellent agreement with the experimental data. The flash point of differing concentration methanol+1-propanol solution covering the entire composition range of methanol in propanol was tested herein. The results were plotted against the predictive curves from the flash point prediction model for a binary organic compound.

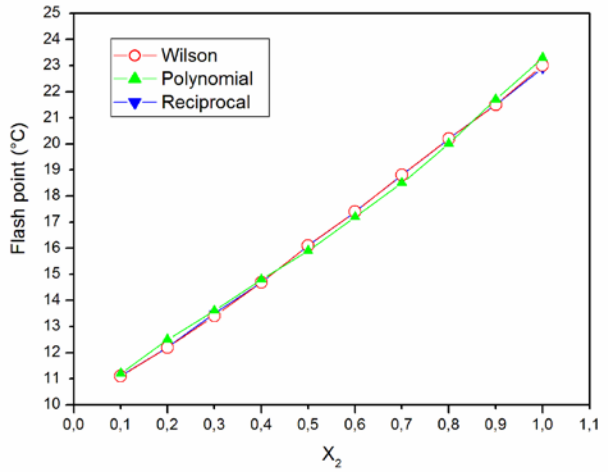

Figure 2. Comparison of polynomial approximation and reciprocal approximation with the standard Wilson model for methanol (1) + 1-propanol (2).

Table 6. Mixture FP butanol (1) + 1-pentanol (2).

1-pentanol fraction	Model predictions (present work)			Approximations (present work)			
	T_{FPI}	T_{FPW}	Δ_{WI}	T_{FPP}	Δ_{PI}	T_{FPR}	Δ_{RI}
1.0	49.5	49.4	0.1	49.6	0.1	49.5	0.0
0.9	47.7	46.6	1.1	46.7	1.0	46.9	0.8
0.8	46.0	44.3	1.7	44.4	1.6	44.3	1.7
0.7	44.5	42.4	2.1	42.5	2.0	42.3	2.2
0.6	43.2	40.8	2.4	40.8	2.4	40.8	2.4
0.5	41.9	39.5	2.4	39.5	2.4	39.5	2.4
0.4	40.8	38.4	2.4	38.5	2.3	38.5	2.3
0.3	39.7	37.6	2.1	37.6	2.1	37.6	2.1
0.2	38.7	37.0	1.7	37.0	1.7	37.0	1.7
0.1	37.7	36.7	1.0	36.7	1.0	36.6	1.1

[a] $\Delta = (T_{predicted}-T_{approximation})$

In Table 6 the flash point butanol (1) + 1-pentanol (2) variation between the model predictive curves and the experimentally-derived data for the binary solutions are compared. For all mixtures, the predicted values based upon an ideal solution assumption and Wilson equation (non-ideal behaviour) are accurate with experimental measurements.

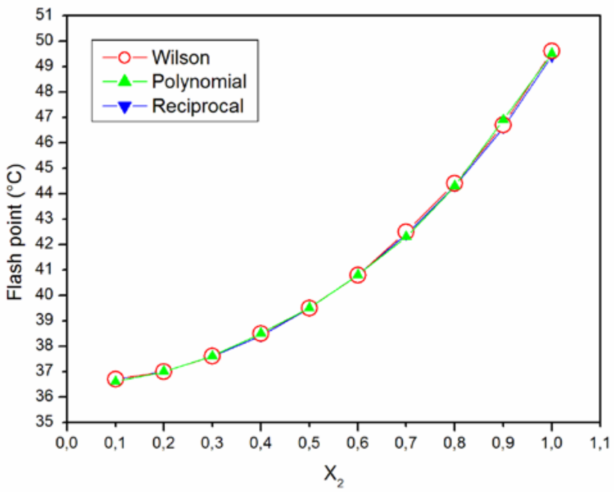

Figure 3. Comparison of polynomial approximation and reciprocal approximation with the standard Wilson model for butanol (1) + 1-pentanol (2).

All the results concerning sample mixtures are summarized in Tables 5-7. The data summarized indicate almost equal level of approximation (based on the absolute point-wise errors) of both the empirical approximations and the prediction of the thermodynamic models. The predicted flash point value for the flammable mixtures of alcohols was obtained for methanol + ethanol; methanol + 1-propanol and butanol + 1-pentanol mixtures. The formulae are based on data obtained from flash-point predictions. The proposed approach requires only one coefficient, molar fraction of components, to be known in advance. Our results reveal that immiscibility in the two liquid phases should not be ignored in the prediction of flash point. Based on this evidence, therefore, it appears reasonable to suggest further experimental investigation of this phenomenon as our future studies. The conceived reciprocal function fits the experimental data better than the 5rd polynomial expressions. Errors comparable to those provided by the polynomial relationships were observed with methanol-propanol mixtures (Table 5) only.

V. CONCLUSION

The predicted flash point value for the flammable mixtures of alcohols was obtained for methanol + ethanol; methanol + 1-propanol and butanol + 1-pentanol mixtures. The predictive results of applied model describe the experimental data from [2] and [3] well within the error two times lower than experimental one. Based on this evidence, therefore, it appears reasonable to suggest potential application for our model in assessment of fire and explosion hazards, and development of inherently safer designs for chemical processes containing binary mixtures of flammable solvents. Dimensionless mathematical formulae based on rational reciprocal and polynomial functions for correlation of flashpoint data of binary mixtures of two flammable components have been applied. The formulae are based on data obtained from flash-point predictions. The proposed approach requires only one coefficient, molar fraction of components, to be known in advance [17-18]. Our results reveal that immiscibility in the two liquid phases should not be ignored in the prediction of flash point. Based on this evidence, therefore, it appears reasonable to suggest further experimental investigation of this phenomenon as our future studies.

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