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Measurement and prediction of binary mixture flash point

Research Article

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Abstract: The flash points of three binary mixtures, containing n-heptane, o-xylene, m-xylene and ethylbenzene, were measured by Pensky-Martens closed cup tester. The experimental data were compared with the calculated values using Liaw`s Model with the application of Raoult`s Law and Wilson equation. These equations were in good qualitative agreement.

Keywords: *Flash point • Binary mixture • Pensky-Martens Closed Cup Tester*

1. Introduction

Flammability is an important factor to consider in developing safe methods for storing and handling solids and liquids [1]. Laboratories and industries commonly use flammable substances. Corresponding mixtures are used to carry out certain experiments and processes. It is important to take note of the physical properties of the substances to avoid any of the hazards associated with them. Liquids that have a flashpoint of 93°C or less are subject to the hazard class flammable liquids of the GHS (Globally Harmonized System of Classification and Labelling of Chemicals). The flashpoint is the lowest temperature of the liquid, corrected to a barometric pressure of 101.3 kPa, at which the application of a test flame causes the vapour of the liquid to ignite momentarily and a flame to propagate across the surface of the liquid under the specified conditions of test [2]. This means, the lower flammability limit (LFL) is exceeded at the flashpoint.

The flashpoint is determined by standardized equilibrium or non-equilibrium methods. Normally a closed-cup method is used because its results tend to be more reliable. Test results from open-cup measurements are not always reliable since volatile compounds may escape from the measuring equipment. Therefore, they are acceptable only in special cases with an explicit justification.

The measurement of a flash point is defined in test methods that are maintained by standardization bodies such as the Energy Institute in the UK, ASTM in the USA, CEN in Europe and ISO internationally. In the last decade, new standards and completely automated methods for measuring flash point were introduced, but older methods are still accepted and are widely used throughout the world.

Experimental flash point data for pure substances are readily available in the literature. As one of the major safety data items, the flash point is specified in a standard material safety data sheet (MSDS). The flash points for pure substances can also be found in many engineering handbooks and databases. The flash point data corresponding to various mixtures appear to be scarce in the literature and are valid for a specific mixture composition.

The experimental measurement of the flash point is expensive and time consuming and therefore, several authors attempted to develop predictive models. By using these models, the flash points of various liquid solutions would be predicted relatively easily from a limited number of initial data.

Affens and McLaren [3] have developed a model based on Raoult's Law to predict the flash point for hydrocarbon solutions. White *et al*. [4] reduced Affens and McLaren's model to a simpler equation by ignoring the temperature effect upon the LFL for prediction of the

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flash points of two aviation-fuel mixtures. Gmehling and Rasmussen [5] proposed the model according to the non-ideal liquid phase solution and LFL dependence on temperature. Crowl and Louvar [6] suggested that the flash point of a liquid solution with only one flammabale component could be estimated using Raoult's Law. This model is only adequate for a composition's range in which the flammable substance composition lies close to unity. Catoire *et al*. developed a simple formulation for the estimation of flash points of miscible combustible solvents mixtures [7]. It consists of an equation which was previously validated for pure compounds [8].

A new trend to estimate the flash temperature is based on the quantitative structure property relationship (QSPR), which incorporates in its procedure theoretical molecular calculations for geometrical, topological, quantum mechanical and electronic properties [9-12]. In general, the QSPR method requires special computer programs. Moreover, the training set of the QSPR procedure should contain large number of compounds with different molecular structures to obtain suitable results.

Since 2002, Liaw *et al*. have developed many models for total miscible flammable mixtures, partially miscible and aqueous-organic mixtures [13-20].

This study measured and predicted the flash point of three binary mixtures, n-heptane+o-xylene, n-heptane+m-xylene, n-heptane+ethylbenzene. The flash points were measured by Pensky-Martens closed cup tester, and compared with the values calculated by using the Liaw Model, Raoult's Law and Wilson equation.

2. Experimental procedure

2.1. Materials

All components were purchased from the Merck Company (Germany) with a minimum purity of 99.5%. Three mixtures were selected for the samples: n-heptane (1)+o-xylene (2), n-heptane (1)+m-xylene (2) and n-heptane (1)+ethylbenzene (2).

2.2. Experimental Apparatus and Procedure

The experimental data were obtained using the Pensky-Martens Closed Cup tester (Fig. 1) model PM 1, SUB (Berlin, Germany).The closed cup tester was operated according to the standard test method, BDS EN ISO 2719 [21]. A modification of this standard test method was implemented because most of the investigated flash points were below room temperature. The modification consisted of cooling the testing cup with a sample in a refrigerated chamber, and then allowing the temperature of the test sample to rise slowly as the experiments began. The ramping rate was reduced to about 1ºC min^{-1} to test the assumption of thermal equilibrium in the tester cup. The ISO 2719 gradient was 1.5ºC min^{-1}. The temperature control was sustained by electrical heating.

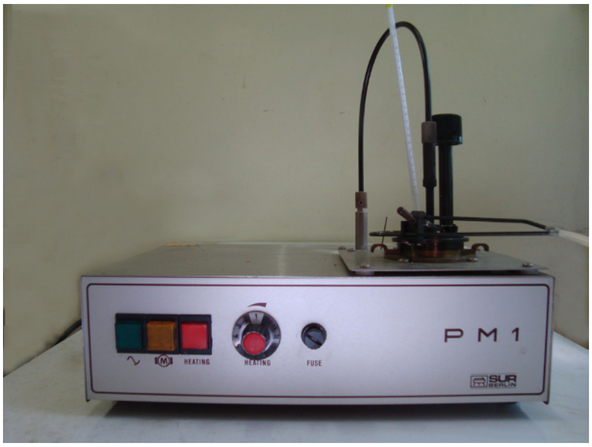

Figure 1. Photograph of the experimental apparatus.

A tester thermometer with a range from -7 to +110ºC was used. The ambient barometric pressure was observed and recorded at the time of the test. When the pressure differed from 760 mm Hg (101.3 kPa), the flash point was corrected as follows:

$$\text{Corrected flash point} = T_0 + 0.25(101.3 - P)$$

where T_0 is observed flash point (ºC); P is barometric pressure (kPa).

The mole fraction of each component was determined by measuring the mass using the 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 the two measurements which did not differ more than 2ºC.

3. Theory

3.1. Calculation model

The properties of mixtures are difficult to predict because a simple mixing rule will not work when interactions among the mixture components are strong. The flash point of a liquid mixture depends on the composition of the mixture and on the types of chemicals involved [16].

The flash point of a flammable liquid is the temperature at which the vapor pressure of the liquid is such that it produces a concentration of vapor in the air that corresponds to its lower flammable limit (LFL) [1]. Thus, at the flash point of a liquid solution, Le Chatelier's rule, that describes the lower flammable limit of a gas mixture, is followed:

$$1=\sum_i \frac{y_i}{LFL_i} \tag{1}$$

where y_i is the mole fraction of the flammable substance *I* in the vapor phase, LFL_i is its lower flammable limit.

From the definition of flash point [1], it is the temperature at which the vapour pressure is equivalent to the lower flammable limit composition in air:

$$LFL_i=\frac{P_{i,fp}^{sat}(T_f)}{P} \tag{2}$$

where $P_{i,fp}^{sat}(T)$ is the vapour pressure at the flash point temperature and P is the ambient pressure.

Another assumption of the model is that the liquid and vapour phases of the mixture are in equilibrium [13]. Thus, the vapor-phase composition, y_i, can be derived from the vapor–liquid equilibrium (VLE) between a non-ideal liquid and a perfect gas as

$$y_i=\frac{x_i\gamma_i P_i^{sat}}{P} \tag{3}$$

Substituting Eqs. 2 and 3 into Eq. 1 the flash point of binary mixture can be calculated:

$$\sum_{i=1}^{2}\frac{x_i\gamma_i P_i^{sat}}{P_{i,fp}^{sat}}=1 \tag{4}$$

where x_i, γ_i, and P_i^{sat} are the mole fraction in liquid phase, activity coefficient and vapour pressure at temperature *T*, of the mixture components, respectively.

The vapour pressure P_i^{sat} can be estimated from an equation such as Antoine's equation, if the required constants are known:

$$\log P_i^{sat}=A_i-\frac{B_i}{T+C_i} \tag{5}$$

where A_i, B_i and C_i are the parameters of compound *i*. The parameters for the Antoine equation can be obtained from different collections [23,24].

From the classic thermodynamics, we know that the activity coefficient is introduced as the revision and judgment for the non-ideality of the mixture [25-27]. If the activity coefficient is equal to unity, the interactions between dissimilar or same molecules are always identical, and the mixture is in the ideal state; if the activity coefficient is away from unity, the mixture is in the non-ideal state. The concept of activity coefficient is used for the liquid phase. The liquid-phase activity coefficient models include the Margules equation [24], van Laar equation [24], Wilson equation [28], NRTL equation [29], UNIFAC equation [30], and so on. In this work, the Wilson equation was used to calculate activity coefficient:

$$\ln\gamma_1=-\ln(x_1+x_2\Lambda_{12})+x_2\left(\frac{\Lambda_{12}}{x_1+x_2\Lambda_{12}}-\frac{\Lambda_{21}}{x_1\Lambda_{21}+x_2}\right) \tag{6}$$

$$\ln\gamma_2=-\ln(x_1\Lambda_{21}+x_2)-x_1\left(\frac{\Lambda_{12}}{x_1+x_2\Lambda_{12}}-\frac{\Lambda_{21}}{x_1\Lambda_{21}+x_2}\right) \tag{7}$$

$$\Lambda_{ij}=\frac{V_j^L}{V_i^L}\exp\left(-\frac{\lambda_{ij}-\lambda_{ii}}{RT}\right) \tag{8}$$

where V_i^L is the molar volume of pure liquid i, λ_{ij} is an energy parameter characterizing the interaction of molecule i with molecule j, *R* is the universal gas constant, *T* is the temperature (K).

If the mixture is an ideal, Eq. 4 becomes:

$$\frac{x_1P_1^{sat}}{P_{1,fp}^{sat}}+\frac{x_2P_2^{sat}}{P_{2,fp}^{sat}}=1 \tag{9}$$

The temperature that satisfies Eqs. 4 or 9 is the flash point temperature of the mixture.

3.2. Data input

The parameters required for the calculation include the pure components flash points and the Antoine coefficients.

The measured flash points of the pure components are compared with values provided by the supplier and are listed in Table 1.

The experimental flash points for n-heptane and ethylbenzene are identical to values reported by the supplier. The values for o-xylene and m-xylene are almost identical to those provided by the supplier. Experimental flash points of pure components were used (Table 1) for the calculations in this study.

The Antoine coefficients and binary interaction parameters of the Wilson equation were taken from the literature and are listed in Tables 2 and 3.

4. Results and discussion

The flash points of of n-heptane(1)+o-xylene(2), n-heptane(1)+m-xylene(2) and n-heptane(1)+ethylbenzene(2) mixtures were tested over the entire composition range. The results

Table 1. Molar volume, experimental flash points and flash points from supplier for pure components.

Substance	CAS №	V^L (cm^3 mol^{-1})	Flash point Exp. (°C)	Flash point from suppl. (°C)
n-heptane	142-82-5	147.6	-4	-4
o-xylene	95-47-6	120.8	32	30
m-xylene	108-38-3	122.3	26	25
Ethyl benzene	100-41-4	123.07	15	15

Table 2. Antoine coefficients of the components* [24].

Substance	A	B	C
n-heptane	6.89385	1264.37	216.635
o-xylene	6.99891	1474.679	213.686
m-xylene	7.00908	1462.266	215.105
Ethyl benzene	6.95719	1424.255	213.206

$\log P(mmHg) = A - \dfrac{B}{T(^0C) + C}$

Table 3. Binary parameters of the Wilson equation* [31].

System	A_{12}	A_{21}
n-heptane (1)+o-xylene (2)	-84.2388	235.4754
n-heptane (1)+m-xylene (2)	-139.8292	250.8485
n-heptane (1)+ethylbenzene (2)	-266.22	454.42

$A_{ij} = (\lambda_{ij} - \lambda_{ii})/R$

Table 4. Experimental flash points and predictions for n-heptane (1) + o-xylene mixture.

X_1	Exp. (°C)	Ideal	ΔT_{fp} /°C	Wilson	ΔT_{fp} /°C
0	32.0	32.00	0.00	32.00	0.00
0.1	20.5	23.53	3.03	21.73	1.23
0.2	15.0	17.13	2.13	15.09	0.09
0.3	11.0	12.41	1.41	10.58	0.42
0.4	6.9	8.72	1.82	7.23	0.33
0.5	4.5	5.72	1.22	4.60	0.10
0.6	2.5	3.20	0.70	2.42	0.08
0.7	1.0	1.04	0.04	0.56	0.44
0.8	-0.9	-0.84	0.06	-1.09	0.19
0.9	-1.9	-2.51	0.61	-2.59	0.69
1.0	-4.0	-4.00	0.00	-4.00	0.00

Table 5. Experimental flash points and predictions for n-heptane (1) + m-xylene mixture.

X_1	Exp. (°C)	Ideal	ΔT_{fp} /°C	Wilson	ΔT_{fp} /°C
0	26.0	26.00	0.00	26.00	0.00
0.1	17.0	19.47	2.47	18.5	1.50
0.2	14.0	14.57	0.57	13.36	0.64
0.3	9.0	10.72	1.72	9.55	0.55
0.4	6.5	7.57	1.07	6.57	0.07
0.5	3.9	4.94	1.04	4.14	0.24
0.6	2.5	2.68	0.18	2.10	0.40
0.7	0.2	0.71	0.51	0.33	0.13
0.8	-0.9	-1.04	0.14	-1.24	0.34
0.9	-2.0	-2.59	0.59	-2.67	0.67
1.0	-4.0	-4.00	0.00	-4.00	0.00

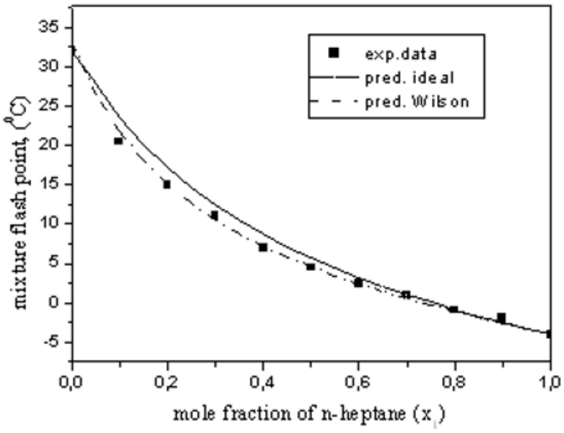

Figure 2. Comparison of the flash point prediction curves with the experimental data for n-heptane (1) + o-xylene (2) system.

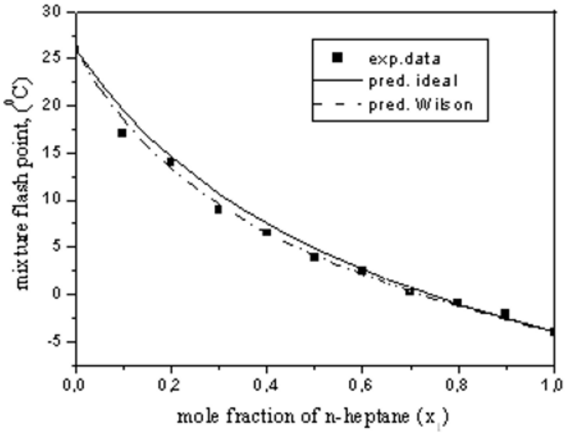

Figure 3. Comparison of the flash point prediction curves with the experimental data for n-heptane (1) + m-xylene (2) system.

from experiments and predicted by Liaw's model are presented in Tables 4-6 respectively, where $\Delta T_{fp} = \left|T_{experimental} - T_{predicted}\right|$.

In Figs. 2-4 the flash point 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. As confirmed by the activity coefficient *vs*. composition (Table 7), all mixtures reveal a positive deviation from that of an ideal solution. The activity coefficients are very

Table 6. Experimental flash points and predictions for n-heptane (1) + ethyl benzene mixture.

X_1	Exp. (°C)	Ideal	DT_{fp} /°C	Wilson	DT_{fp} /°C
0	15.0	15.00	0.00	15.00	0.00
0.1	11.0	11.94	0.94	11.25	0.25
0.2	8.5	9.28	0.78	8.26	0.24
0.3	5.5	6.94	1.44	5.81	0.31
0.4	3.2	4.87	1.67	3.77	0.57
0.5	2.5	3.02	0.52	2.03	0.47
0.6	0.8	1.35	0.55	0.54	0.26
0.7	-0.3	-0.17	0.13	-0.77	0.47
0.8	-1.7	-1.55	0.15	-1.93	0.23
0.9	-2.9	-2.82	0.08	-3.00	0.10
1.0	-4.0	-4.00	0.00	-4.00	0.00

Table 7. Calculated activity coefficients of binary mixtures.

X_1	n-hepnane(1) + o-xylene(2)		n-hepnane(1) + m-xylene(2)		n-hepnane(1)+ ethylbenzene(2)	
	γ_1	γ_2	γ_1	γ_2	γ_1	γ_2
0.0	1.26	1.00	1.17	1.00	1.19	1.00
0.1	1.21	1.00	1.14	1.00	1.16	1.00
0.2	1.17	1.01	1.12	1.01	1.14	1.00
0.3	1.13	1.02	1.09	1.01	1.12	1.01
0.4	1.10	1.04	1.07	1.02	1.09	1.02
0.5	1.07	1.06	1.05	1.04	1.07	1.04
0.6	1.05	1.09	1.03	1.06	1.05	1.07
0.7	1.03	1.14	1.02	1.09	1.03	1.10
0.8	1.01	1.19	1.01	1.13	1.02	1.15
0.9	1.00	1.25	1.00	1.17	1.00	1.23
1.0	1.00	1.33	1.00	1.23	1.00	1.34

Table 8. Average absolute deviation (A.A.D.) between calculated and experimental flash point for binary mixtures of n-heptane, o-xylene, m-xylene and ethylbenzene.

Solution	Ideal	Wilson
n-heptane + o-xylene	1.02	0.37
n-heptane + m-xylene	0.78	0.44
n-heptane + ethylbenzene	0.58	0.19

close to unity; therefore it can be concluded that these mixtures are almost-ideal solutions. This is the reason for the small differences between the flash points that were predicted as an ideal solution and by using the Wilson equation.

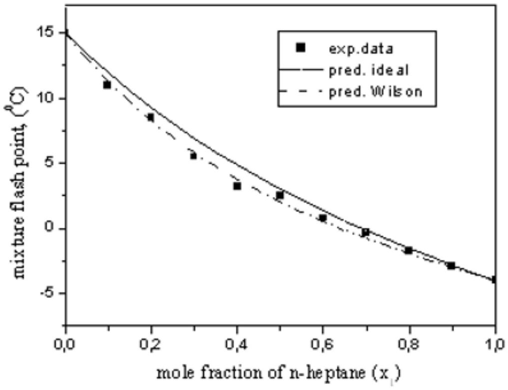

Figure 4. Comparison of the flash point prediction curves with the experimental data for n-heptane (1) + ethylbenzene (2) system.

Table 8 includes average absolute deviation (A.A.D.) for three binary solutions:

$$A.A.D. = \frac{\sum_{i=1}^{n} \left| T_i^{\exp} - T_i^{cal} \right|}{n} \tag{10}$$

A.A.D. is a measure of agreement between the experimental data and the calculated values.

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.

5. Conclusions

The flash points of three binary mixtures containing n-heptane, o-xylene, m-xylene and ethylbenzene, were measured by the Pensky-Martens closed cup tester. The experimental data were compared with the values calculated by using Raoult`s Law and the Wilson equation. Good qualitative agreement was obtained with these equations. However, the calculated values based on the Wilson equation were found to be better than those based on Raoult`s Law.

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