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Flash-point prediction for binary partially miscible mixtures of flammable solvents

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Abstract

Flash point is the most important variable used to characterize fire and explosion hazard of liquids. Herein, partially miscible mixtures are presented within the context of liquid-liquid extraction processes. This paper describes development of a model for predicting the flash point of binary partially miscible mixtures of flammable solvents. To confirm the predictive efficacy of the derived flash points, the model was verified by comparing the predicted values with the experimental data for the studied mixtures: methanol + octane; methanol + decane; acetone + decane; methanol + 2,2,4-trimethylpentane; and, ethanol + tetradecane. Our results reveal that immiscibility in the two liquid phases should not be ignored in the prediction of flash point. Overall, the predictive results of this proposed model describe the experimental data well. 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 partially miscible mixtures of flammable solvents.

Keywords: Flash point; Prediction; Partially miscible mixtures; Vapor–liquid equilibrium; Liquid–liquid equilibrium

1. Introduction

In a given liquid, the flash point is the temperature determined experimentally at which the substance emits sufficient vapor to form a combustible mixture with air [1], with a lower flash-point value indicating relatively greater fire and explosion hazard [2]. Recently, the importance of flash point was dramatically highlighted in Taiwan after a series of explosions of essential oils and the Shengli event. In the former series of accidents, six blasts occurring from January through August of 2003, left eight people badly burnt. The fire and explosion hazard of liquids, such as essential oils, is primarily characterized by their flash point [3]. The Shengli event subsequently resulted in the temporary storage of large quantities of waste organic solutions at various factory sites and industrial park precincts [4,5]. Thus, flash-point data knowledge for these mixtures has become increasingly important to ensure the safety of this voluminous storage. 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 [6].

Flash-point data of mixtures are scarce in the literature, although composition ranges for specific mixtures used or produced in an industrial process can vary quite substantially. Since the cost of flash-point data derived from test instruments is very expensive in Taiwan (NT$20,000/US$600 per sample), a model for predicting the flash point of a given mixture is useful. Partially miscible mixtures are used in liquid–liquid extraction processes [7,8]. The flash-point value for a given substance is relative to its vapor pressure [2]. As the estimation of vapor pressure for partially miscible mixtures is quite different from that for miscible analogues, we infer that flash point behavior for the two mixture types will be quite different. Thus, a model that allows prediction of the flash point of partially miscible mixtures is urgently required to facilitate evaluation of fire and explosion hazard.

Crowl and Louvar [3] have suggested a method for the estimation of the flash point of a liquid solution with a single flammable

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Nomenclature

A, B, C	Antoine coefficients
A_{ij}	coefficient in Table 1 (J/mol)
a_{ij}	parameter in Table 1 (J/mol)
B_{ij}	coefficient in Table 1 (J/mol K)
b_{ij}	parameter in Table 1 (J/mol K)
C_{ij}	coefficient in Table 1 (J/mol K^2)
D_{ij}	coefficient in Table 1 (J/mol K^3)
G	defined in Table 1
g	binary parameters of the NRTL equation (J/mol)
L	coefficient used for calculating liquid molar volumes (m^3 mol^{-1})
LFL	lower flammable limit
M	coefficient for calculating liquid molar volumes (m^3 mol^{-1} K^{-1})
N	coefficient for calculating liquid molar volumes (m^3 mol^{-1} K^{-2})
P	ambient pressure (kPa)
P^{sat}	saturated vapor pressure (kPa)
P_{c}	critical pressure (kPa)
$P_{i,\mathrm{fp}}^{\mathrm{sat}}$	saturated vapor pressure of component, i, at flash point (kPa)
R	gas constant (8.314 J/mol K)
T	temperature (K)
T_{C}	upper critical solution temperature (UCST) (K)
T_{c}	critical temperature (K)
$T_{i,\mathrm{fp}}$	flash point temperature of pure component, i (K)
T_{r}	reduced temperature (K)
$\underline{v}^{\mathrm{l}}$	molar volume of liquid (m^3/mol)
x	liquid-phase composition
y	vapor-phase composition
Z_{RA}	modified Rackett equation parameter

Greek letters

α_{ij}	NRTL parameter
β	defined in Table 1
β_{v}	defined in Table 1
γ	activity coefficient
Λ	defined in Table 1
λ	binary parameters of the T–K–Wilson equation (J/mol)
τ	defined in Table 1

Subscripts

2LP	two liquid phases
exp.	experimental data
fp	flash point
i	species i
pred.	predictive value

Superscripts

α	α-phase
β	β-phase

component. However, it was shown to be adequate only when the flammable component composition approaches unity for binary aqueous–organic solutions [5], and it is not applicable to solvent/salt systems, even in a similar composition range [9]. Introducing activity coefficient models to model the non-ideal behavior of liquids, various models have been proposed recently for predicting the flash point of binary aqueous–organic and solvent/salt systems [5,9], with successful verification based on comparison with the experimental data. Previously, Affens and McLaren [10] have developed a predictive model to determine the flash points of binary hydrocarbon mixtures based on Raoult's law. White et al. [11] have reduced this model to a simpler equation by ignoring any dependence of the lower flammable limit on temperature. A model for predicting the flash point of multi-component mixtures of only flammable compounds was also proposed [12] and verified using experimental data for ternary solutions. This model can be simplified for binary solutions, as proposed previously [4], with prediction of flash points verified for both ideal and non-ideal mixtures [4,13,14]. The model for binary solutions has been applied in deriving the criteria for determining whether a binary mixture may form a minimum/maximum flash point solution (below/above the pure-substance flash points) or not [13,14]. Garland and Malcolm [15] developed a statistical model to predict the flash point of a single organic acid–water solutions: acetic acid + propionic acid + butyric acid + water. However, it deviated significantly from the experimental measurements for multiple organic–water solutions [16].

Overall, application of the former models [3,10,11,15] is limited to solutions that can be assumed as ideal within the composition range considered. The new models taking into account non-ideality of the solution through liquid phase activity coefficients have to be used to predict efficiently the flash point of these miscible mixtures [4,5,9,12,16]. Non-ideality of the liquid phase is in particular responsible to the occurrence of extreme flash-point behavior such as minimum and maximum flash-point behavior [13,14]. This is similar to minimum boiling and maximum-boiling azeotropic behavior in vapor–liquid equilibrium. In the vapor–liquid equilibrium area, stronger non-ideality may often result to the partial miscibility of the liquid phase, eventually coupled with the occurrence of a so-called heteroazeotrope. We suspect that similar behaviors happen for flash point. However, to our knowledge no applicable model has been available for partially miscible mixtures. In this manuscript, a model for such mixtures was developed and investigated using the partially miscible mixtures: methanol + octane; methanol + decane; acetone + decane; methanol + 2,2,4-trimethylpentane; and, ethanol + tetradecane [7,8].

Based upon the definition of flash point [2], it is necessary to estimate the vapor-phase composition of flammable substances from a vapor–liquid equilibrium equation in order to predict their flash point. Furthermore, it is acknowledged that partial miscibility occurs because of significant interaction within non-ideal liquid solution. For such solutions, liquid-phase activity coefficients must be taken into account in the vapor–liquid equilibrium equation by means of thermodynamic models. The original Wilson thermodynamic model [17] is not applicable for evaluating the liquid-phase activity coefficients for mixtures that exhibit a miscibility gap [18]. Unlike Wilson's equation, the NRTL [19] and UNIQUAC thermodynamic models [20] are applicable to both vapor–liquid and liquid–liquid equilibria [18]. The Wilson thermodynamic model was modified as T–K–Wilson thermodynamic model by Tsuboka and Katayama to be applicable to liquid–liquid equilibria [21].

2. Experimental protocol

Two flash point analyzers, the HFP 360-Pensky Martens and the HFP 362-Tag (Walter Herzog GmbH, Germany), were used to measure the flash points for a variety of mixtures (methanol + octane, methanol + decane, acetone + decane, methanol + 2,2,4-trimethylpentane and ethanol + tetradecane) at different compositions. The former apparatus was operated according to the standard ASTM D93B test protocol [22], and the latter according to ASTM D56 [23]. The standard method, ASTM D93B, is applicable for determination of flash points in the range 40–360 °C, while ASTM D56 covers −25 to 99 °C. 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 is automatically tested using an igniter at specified temperature test intervals. If the expected flash point is lower than or equal to the change temperature, heating rate-1 is used and the igniter is fired at test interval-1. If the expected flash point is higher, heating rate-2 is adopted and the igniter is fired at test interval-2. The first flash-point test series is initiated at a temperature equivalent to the expected flash point minus the start-test value. If the flash point is not determined when the test temperature exceeds the sum of the expected flash point plus the end-of-test value, the experimental iteration is terminated. The following set of selected parameters is used in ASTM D93B [22]: start test 23 °C; end of test 20 °C; heat rate-1 1.3 °C/min; heat rate-2 1.3 °C/min; change temperature 110 °C; test interval-1 1.0 °C; and, test interval-2 2.0 °C. The following set of selected parameters was adopted for the other standard ASTM D56 test protocol [23]: start test 5 °C; end of test 20 °C; heat rate-1 1 °C/min; heat rate-2 3 °C/min; change temperature 60 °C; test interval-1 0.5 °C; and, test interval-2 1.0 °C. The liquid mole fraction is determined from mass measured using a Setra digital balance (EL-410D: sensitivity 0.001 g, maximum load 100 g). Both methanol and acetone were HPLC/Spectro-grade reagents (Tedia Co. Inc.; USA); octane and 2,2,4-trimethylpentane were also sourced from Tedia. Ethanol (99.5 vol%) was purchased from NASA enterprises (USA). Decane was obtained from Alfa Aesar (Lancaster, England), and tetradecane from Tokyo Kasei Kogyo Co., Ltd. (Japan).

3. Mathematical formulation

Within the mutual-solubility region of a binary partially miscible mixture, only one liquid phase is present and the variation of the vapor pressure with liquid-phase composition identical to that for a miscible mixture. Thus, the flash point in such a region can be evaluated by the method for a binary miscible mixture of flammable solvents [4]:

$$1=\frac{x_1\gamma_1P_1^{\mathrm{sat}}}{P_{1,\mathrm{fp}}^{\mathrm{sat}}}+\frac{x_2\gamma_2P_2^{\mathrm{sat}}}{P_{2,\mathrm{fp}}^{\mathrm{sat}}} \quad (1)$$

Table 1
Some models for activity coefficients of partially miscible mixtures using only pure-component and binary parameters

Name	Activity coefficient for component *i*
NRTL	$\ln\ \gamma_i=\frac{\sum_j^N\tau_{ji}G_{ji}x_j}{\sum_k^N G_{ki}x_k}+\sum_j^N\frac{x_jG_{ij}}{\sum_k^N G_{kj}x_k}\left(\tau_{ij}-\frac{\sum_k^N x_k\tau_{kj}G_{kj}}{\sum_k^N G_{kj}x_k}\right)$ where $\ln G_{ij}=-\alpha_{ij}\tau_{ij}$ $\tau_{ij}=\frac{g_{ij}-g_{jj}}{RT}$ $g_{12}-g_{22}=A_{12}+B_{12}(T_\mathrm{C}-T)+C_{12}(T_\mathrm{C}-T)^2+D_{12}(T_\mathrm{C}-T)^3$ $g_{21}-g_{11}=A_{21}+B_{21}(T_\mathrm{C}-T)+C_{21}(T_\mathrm{C}-T)^2+D_{21}(T_\mathrm{C}-T)^3$ or $\tau_{ij}=\frac{a_{ij}+b_{ij}T}{RT}$
T–K–Wilson	$\ln\ \gamma_i=\ln\frac{x_i+\underline{v}_j^lx_j/\underline{v}_i^l}{x_i+\Lambda_{ij}x_j}+(\beta-\beta_v)x_j$ where $\beta=\frac{\Lambda_{ij}}{x_i+\Lambda_{ij}x_j}-\frac{\Lambda_{ji}}{x_j+\Lambda_{ji}x_i}$ $\beta_v=\frac{\underline{v}_j^l/\underline{v}_i^l}{x_i+\underline{v}_j^lx_j/\underline{v}_i^l}-\frac{\underline{v}_i^l/\underline{v}_j^l}{x_j+\underline{v}_i^lx_i/\underline{v}_j^l}$ $\Lambda_{ij}=\frac{\underline{v}_j^l}{\underline{v}_i^l}\exp\left(-\frac{\lambda_{ij}-\lambda_{ii}}{RT}\right)$ $\lambda_{12}-\lambda_{11}=A_{12}+B_{12}(T_\mathrm{C}-T)+C_{12}(T_\mathrm{C}-T)^2+D_{12}(T_\mathrm{C}-T)^3$ $\lambda_{21}-\lambda_{22}=A_{21}+B_{21}(T_\mathrm{C}-T)+C_{21}(T_\mathrm{C}-T)^2+D_{21}(T_\mathrm{C}-T)^3$ $\underline{v}_i^l=L_i+M_iT+N_iT^2$ or $\underline{v}_i^l=\frac{RT_{\mathrm{c},i}}{P_{\mathrm{c},i}}Z_{\mathrm{RA},i}^{1+(1-T_{\mathrm{r},i})^{2/7}}$

$$\log\ P_i^{\text{sat}} = A_i - \frac{B_i}{T + C_i} \quad i = 1, 2 \tag{2}$$

The vapor pressure of the pure substance, i, at its flash point, $P_{i,\text{fp}}^{\text{sat}}$, can be estimated by substituting $T_{i,\text{fp}}$, the flash point of component i, into the Antoine equation (Eq. (2)). Liquid-phase activity coefficients γ_i enable to tackle the non-ideal behavior of the liquid phase that results in the partial-miscibility. Vapor phase is assumed to behave as a perfect gas as is usual under low to moderate pressure condition [24].

Within the partially miscible region of a binary partially miscible mixture, two liquid phases are in equilibrium with compositions defining a so-called tie line. Since any liquid composition located on this tie-line, in particular the composition of both liquid phases in equilibrium, is in equilibrium with a single vapor composition located on the so-called vapor line [24,25], the flash point in this region should keep constant whatever the liquid composition on the liquid–liquid equilibrium tie line.

The compositions between liquid phases in equilibrium can be estimated by the equilibrium equality of the compound activities in each phase:

$$(x_i\gamma_i)^{\alpha} = (x_i\gamma_i)^{\beta} \quad i = 1, 2 \tag{3}$$

where α and β designate the two coexisting liquid phases. The activity coefficients γ_i in Eqs. (1) and (3), should be estimated using thermodynamic activity coefficient models adequate for partially miscible mixtures, such as the NRTL [19] or T–K–Wilson equations [21]; both were employed in this study (Table 1). The temperature derived from the problem solution of Eqs. (1)–(3) is deemed to be the flash point in the two liquid phases.

The flash point prediction model developed for a binary partially miscible mixture of flammable solvents is described using Eqs. (1)–(3), and any suitable thermodynamic model for estimating liquid-phase activity coefficient. The procedure for evaluating the flash point for binary partially miscible mixtures is depicted in Fig. 1. The two liquid phase region and the flash point in this region were first estimated by Eqs. (1)–(3). Then, the flash point in the mutual-solubility region is calculated using Eqs. (1)–(2). The iterative procedure is analogous to

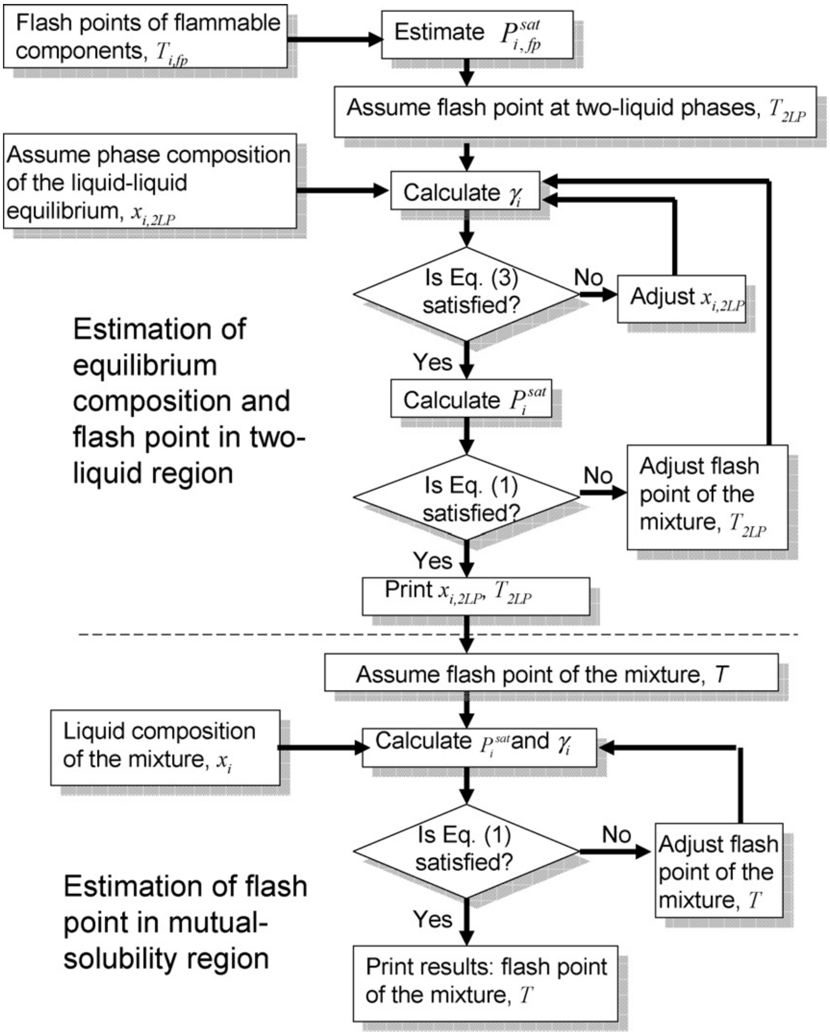

Fig. 1. Procedure for evaluation of flash point for partially miscible mixtures of flammable solvents.

Table 2
Parameters of the NRTL and T-K-Wilson equations for the binary systems, methanol + octane, ethanol + tetradecane, methanol + 2,2,4-trimethylpentane, methanol + decane and acetone + decane

System	T_C (K)	α_{12}	Parameters	ij		Reference
				12	12	
NRTL equation						
Methanol (1) + octane (2)	339.69	0.2	A_{ij}	6.24395×10^{3}	5.25942×10^{2}	[7]
			B_{ij}	1.52260×10	6.96300×10	
			C_{ij}	-1.7556	7.89985×10^{-2}	
			D_{ij}	2.11364×10^{-2}	-5.53227×10^{-3}	
Ethanol (1) + tetradecane (2)	307.81	0.4	A_{ij}	5.789005×10^{3}	1.769883×10^{3}	[8]
			B_{ij}	1.711979×10	1.707391×10^{2}	
			C_{ij}	-3.233318×10^{-1}	-6.227185	
			D_{ij}	8.925731×10^{-3}	1.003282×10^{-1}	
Methanol (1) + 2,2,4-trimethyl pentane (2)	316.84	0.2	A_{ij}	4.93912×10^{3}	1.22776×10^{3}	[7]
			B_{ij}	5.20020×10	5.22268×10	
			C_{ij}	-4.88841	1.47937	
			D_{ij}	8.89400×10^{-2}	-4.74041×10^{-2}	
Methanol (1) + decane (2)	363.92	0.4	A_{ij}	7.055479×10^{3}	1.815871×10^{3}	[8]
			B_{ij}	2.640328×10	1.452246×10^{2}	
			C_{ij}	-2.781241×10^{-1}	-1.878796	
			D_{ij}	1.957136×10^{-3}	1.122525×10^{-2}	
Acetone (1) + decane (2)	–	0.3	a_{ij}	7914.504	2941.470	[27]
			b_{ij}	−25.143	7.858	
T–K–Wilson equation						
Methanol (1) + octane (2)	339.69	–	A_{ij}	6.98028×10^{3}	-2.41862×10^{3}	[7]
			B_{ij}	-6.58055	6.00017×10	
			C_{ij}	1.77902	-1.28347	
			D_{ij}	-2.16660×10^{-2}	1.34946×10^{-2}	
Ethanol (1) + tetradecane (2)	307.81	–	A_{ij}	5.759423×10^{3}	-2.758062×10^{3}	[8]
			B_{ij}	-9.587510×10	1.080870×10^{2}	
			C_{ij}	9.962493	-6.356456	
			D_{ij}	-2.302148×10^{-1}	1.370958×10^{-1}	
Methanol (1) + 2,2,4-trimethyl pentane (2)	316.84	–	A_{ij}	7.89465×10^{3}	-2.66211×10^{3}	[7]
			B_{ij}	-7.65730×10	6.26064×10	
			C_{ij}	6.2988	-2.08306	
			D_{ij}	-1.17529×10^{-1}	3.21490×10^{-2}	
Methanol (1) + decane (2)	363.92	–	A_{ij}	6.724470×10^{3}	-3.685977×10^{3}	[8]
			B_{ij}	1.815153×10	5.283316×10	
			C_{ij}	3.564183×10^{-1}	-7.313433×10^{-1}	
			D_{ij}	-2.017083×10^{-3}	5.335632×10^{-3}	

that used for calculating the boiling and dew points of mixtures [26].

4. Results and discussion

4.1. Parameters used in this manuscript

The flash-point model for partially miscible mixtures of two flammable solvents was used for methanol + octane, methanol + decane, acetone + decane, methanol + 2,2,4-trimethylpentane, and ethanol + tetradecane mixtures. The prediction results were compared with experimental data. The liquid-phase activity coefficients for these five mixtures were estimated using the NRTL [19] and T–K–Wilson equations [21], with parameters adopted from the literature [7,8,27] (Table 2). The parameters used for calculating the liquid molar volumes required for the T–K–Wilson equation (also obtained from the literature [7,8]) are listed in Table 3. The

Table 3
Pure component parameters used for calculating liquid molar volumes

Component	$L \times 10^{5}$ m^{3} mol^{-1}	$M \times 10^{8}$ m^{3} mol^{-1} K^{-1}	$N \times 10^{10}$ m^{3} mol^{-1} K^{-2}	T_c K	P_c MPa	Z_{RA}	Reference
Methanol	3.68717	−2.19582	1.17085	512.64	8.097	0.23230	[7,8]
Ethanol	–	–	–	513.92	6.148	0.25041	[8]
Octane	12.7105	5.64444	2.20316	–	–	–	[7]
2,2,4-Trimethyl pentane	13.7850	−1.02976	3.52000	–	–	–	[7]
Decane	–	–	–	617.70	2.110	0.25074	[8]
Tetradecane	–	–	–	693.00	1.570	0.24322	[8]

Table 4
Antoine coefficients for solution components[a]

Material	A	B	C	Reference
Methanol	5.20277	1580.080	−33.650	[18]
Ethanol	5.33675	1648.220	−42.232	[18]
Acetone	4.21840	1197.010	−45.090	[18]
Octane	4.05075	1356.360	−63.515	[18]
2,2,4-Trimethyl pentane	3.93646	1257.850	−52.383	[18]
Decane	4.06853	1495.170	−79.292	[18]
Tetradecane	4.13790	1740.880	−105.430	[18]

[a] $\text{Log}(P/\text{bar}) = A - B/[(T/\text{K}) + C]$.

Antoine coefficients were also sourced from the literature [18] (Table 4).

The flash points for the pure substances used in this study were measured using the Flash Point Analyzer, with these values compared with their literature-derived analogues (Table 5). The ASTM D56 test protocol was used for all mixtures [23] except for tetradecane, where ASTM D93B [22] was used because its flash point is outside of the test range of the former. Flash-point literature reported data for methanol, octane, decane, tetradecane and 2,2,4-trimethylpentane differ from one source to the other, however. Our experimental flash point for ethanol is identical to the literature-derived values [28,29]. Our measurements for methanol and octane are identical to the values reported by Oxford University [30]. The value for 2,2,4-trimethylpentane is almost identical to that reported by Chevron Phillips [31], and close to that provided by the supplier, Tedia (USA), and values reported by some sources [30,32], although it is different from those adopted from Merck [28] and SFPE [29]. The experimental data for acetone is close to the Merck [28] and SFPE values [29]. The deviations between our measurements and the published flash points of ASTM [22,23] for decane and tetradecane are slight and acceptable.

The standard methods ASTM D56 [23] and ASTM D93B [22] were used to measure the flash points of ethanol (1) + tetradecane (2) in the composition $x_1 = 0.01$ as the flash point values are within the effective test ranges for both standards. The flash points of the other mixtures were determined using ASTM D56 [23].

Table 5
Comparison of flash-point values adopted from the literature with experimentally derived data for some alcohols

Component	Experimental data (°C)	Literature (°C)
Methanol	10.0 ± 0.4	12 [28,29] 10 [30]
Ethanol	13.0 ± 0.3	13 [28,29]
Acetone	−18.6 ± 0.4	−18 [28,29]
Octane	15.0 ± 0.4	13 [29] 15 [30]
Decane	51.8 ± 0.5	44 [29] 52.8 ± 2.3 [22] 50.9 ± 2.3 [23]
Tetradecane	110.4 ± 1.0	99 [30] 107 [31] 121 [33] 109.3 ± 4.8 [22]
2,2,4-Trimethylpentane	−8.1 ± 0.7	−7[a] [30,32] −12 [28,29] −8 [31]

[a] Provided by Tedia.

4.2. Comparison of predicted and measured flash points

The flash points of methanol + octane were tested over the entire composition range (Table 6). The measured values were almost constant in the region of two liquid phases, where the methanol composition ranged between 0.06 and 0.97 (Table 6, Fig. 2). The flash points predicted by the proposed model and the corresponding measured values are compared in Fig. 2. Predictions are all in excellent agreement with the experimental data over the entire composition range (Table 7, Fig. 2), when the NRTL or T–K–Wilson is used in conjunction with the equation describing the partial miscibility (Eq. (3)). When Eq. (3) is discarded (see Fig. 2) a pseudo-homogeneous liquid flash point curve is predicted and is substantially less than the experimental data. Besides, its smooth concave then convex shape is similar to the shape of pseudo-homogeneous boiling temperature–composition curve predicted in vapor–liquid equilibrium calculations when neglecting partial miscibility of partially miscible mixtures [25]. Table 7 also demonstrates that the model that considers partial-miscibility behavior is superior to the model that does not. Thus, it can be concluded that the property of immiscibility should not be ignored in the two liquid phases.

The constant flash point behavior within the two liquid phases coexisting region is also observed in other mixtures of this study, methanol + decane, acetone + decane, methanol + 2,2,4-trimethylpentane and ethanol + tetradecane, which are displayed

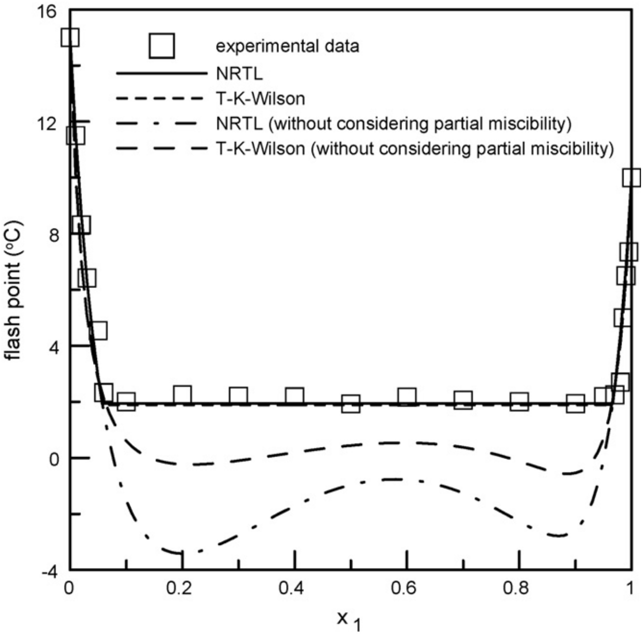

Fig. 2. Comparison of predicted flash point and experimental data for methanol (1) + octane (2).

Table 6
Measured flash point for partially miscible mixtures

x_1	Methanol (1) + octane (2) (°C)	Methanol (1) + decane (2) (°C)	Acetone (1) + decane (2) (°C)	Methanol (1) + 2,2,4-trimethyl pentane (2) (°C)	Ethanol (1) + tetradecane (2) (°C)
0	15.0	51.8	51.8	−8.1	110.4[a]
0.01	11.5	32.3	30.0	–	41.3[a] 39.5
0.02	8.3	18.5	16.0	–	29.4
0.03	6.4	15.0	4.0	–	–
0.04	–	12.5	–	–	–
0.05	4.5	11.0	−2.0	−9.0	24.3
0.06	2.3	–	–	–	–
0.1	2.0	11.5	−12.4	−10.1	20.0
0.12	–	–	−15.5	–	–
0.13	–	–	−16.5	–	–
0.15	–	–	–	–	17.6
0.2	2.3	10.9	−17.5	−10.4	14.2
0.22	–	–	−17.5	–	–
0.25	–	–	−17.5	–	–
0.27	–	–	−17.6	–	–
0.3	2.2	10.2	−18.0	−10.4	14.5
0.4	2.2	10.4	−17.8	−10.5	14.5
0.5	1.9	10.4	−18.4	−11.0	13.5
0.6	2.2	10.1	−17.9	−10.5	13.7
0.7	2.1	10.1	−18.2	−10.3	14.2
0.8	2.0	10.3	−18.5	−10.3	13.9
0.9	1.9	9.6	−18.3	−10.5	13.0
0.92	–	–	−18.6	–	–
0.93	–	–	−18.4	–	–
0.95	2.2	9.3	−18.6	−10.4	13.0
0.97	2.3	–	−18.6	−9.9	13.4
0.98	2.7	8.9	−19.9	−6.6	–
0.985	5.0	–	–	–	–
0.99	6.5	9.0	−19.2	−1.2	–
0.995	7.4	–	−18.5	5.7	–
1.0	10.0	10.0	−18.6	10.0	13.0

[a] ASTM D93B.

in Figs. 3–6. It arises because of the particular behavior enounced above that any composition on a liquid–liquid–vapor equilibrium tie line is in equilibrium with a single vapor composition [24,25]. The flash point being a feature of the vapor, it is constant when the composition and temperature of the vapor is also constant.

The predictive curves for methanol + decane and acetone + decane are presented in Figs. 3 and 4. Table 7

Table 7
Deviation between calculated and experimental flash points, ΔT_{fp} [a], for the studied ternary solutions comparing models

Mixture	Model for partially miscible mixtures		Model ignoring partial miscibility	
	NRTL	T–K–Wilson	NRTL [b]	T–K–Wilson [b]
Methanol (1) + octane (2)	0.37 [b] 0.18 [c]	0.50 [b] 0.21 [c]	2.05	1.27
Methanol (1) + decane (2)	1.08 [b] 0.97 [c]	1.03 [b] 1.05 [c]	1.43	3.02
Acetone (1) + decane (2)	1.65 [b] 0.73 [c]	–	2.78	–
Methanol (1) + 2,2,4-trimethylpentane (2)	0.42 [b] 0.17 [c]	1.34 [b] 1.62 [c]	1.39	1.29
Ethanol (1) + tetradecane (2)	6.21 [b] 0.56 [c]	5.36 [b] 0.55 [c]	6.29	5.69

[a] Deviation of flash point: $\Delta T_{\mathrm{fp}} = \sum_{N} |T_{\mathrm{fp,exp.}} - T_{\mathrm{fp,pred.}}|/N$.

[b] ΔT_{fp} over the entire composition range.

[c] ΔT_{fp} for two liquid phases.

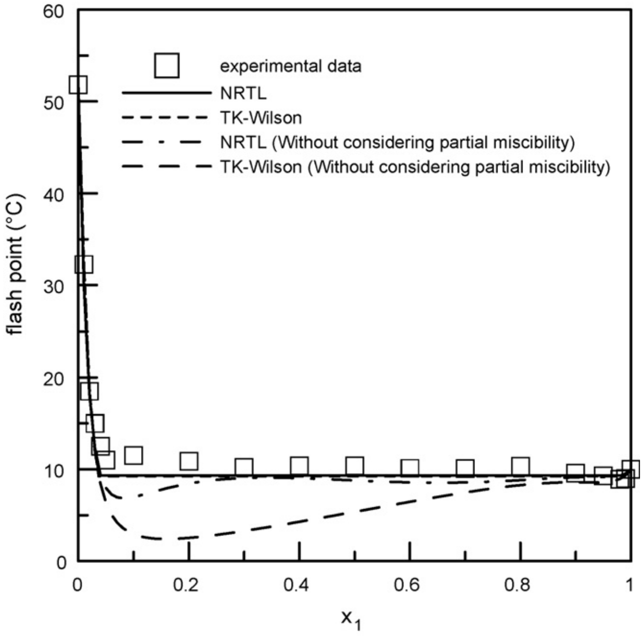

Fig. 3. Comparison of predicted flash point and experimental data for methanol (1) + decane (2).

demonstrates that the predictions are acceptable for the two mixtures, although some differences arise in the decane-rich phase. The reason of this deviation is attributed to the inability of the liquid-phase activity coefficient models to represent accurately the whole composition range and in particular the span of the two liquid phase region. It likely comes because the set of LLE data that was used to regress the activity coefficient model binary parameters lacks data in the decane-rich side [8,27].

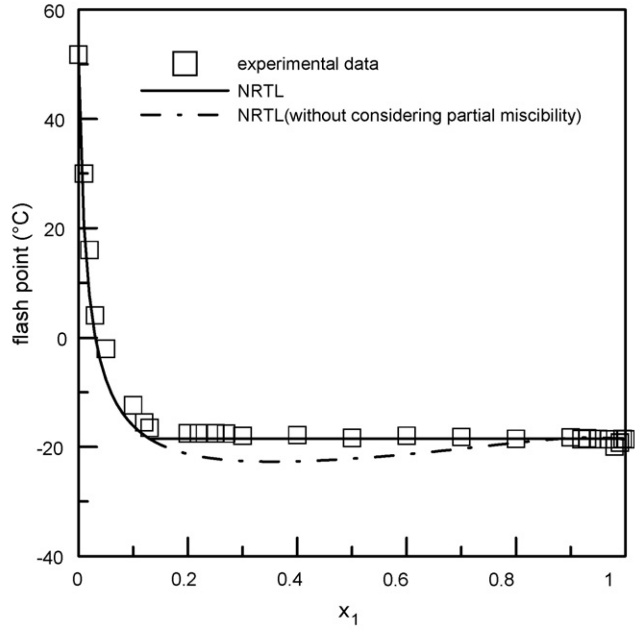

Fig. 4. Comparison of predicted flash point and experimental data for acetone (1) + decane (2).

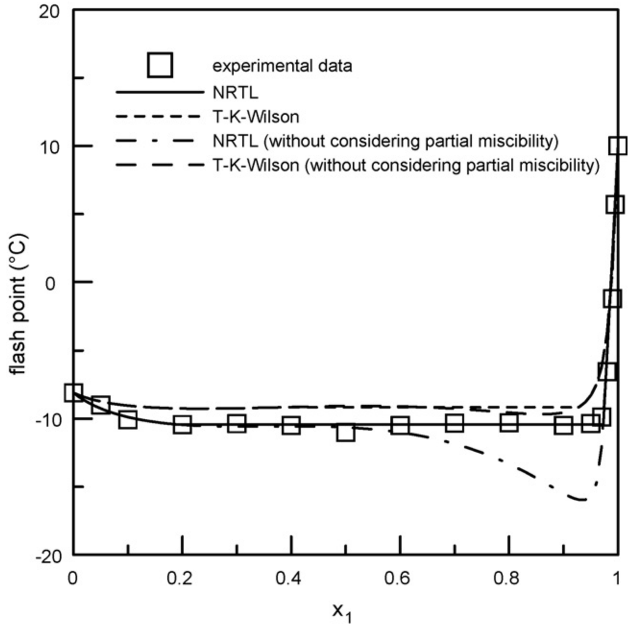

Fig. 5. Comparison of predicted flash point and experimental data for methanol (1) + 2,2,4-trimethylpentane (2).

The flash points for the mixture, methanol + 2,2,4-trimethylpentane, were computed and compared with the corresponding experimental data (Fig. 5; Table 6). There are some differences between the predicted flash points when the NRTL or T–K–Wilson equation is used to estimate the relevant activity coefficients. NRTL provides good agreement with the experimental data over the entire composition range. T–K–Wilson shows some deviations from the measurements for the two liquid phases (Fig. 5, Table 7).

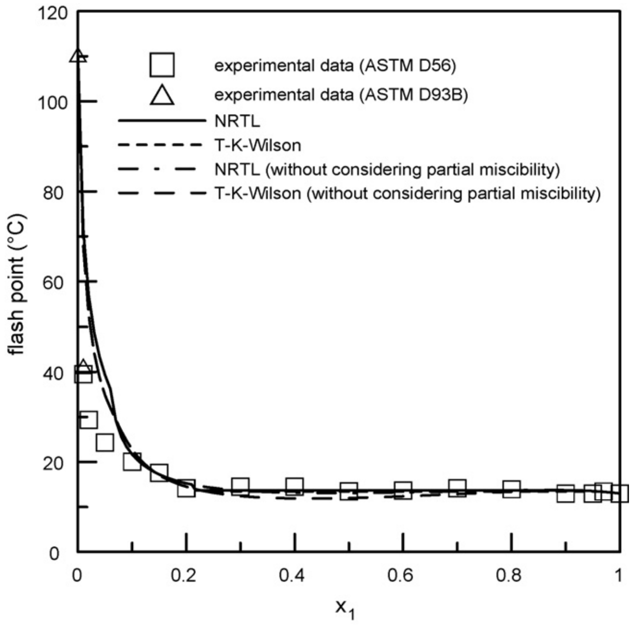

Fig. 6. Comparison of predicted flash point and experimental data for ethanol (1) + tetradecane (2).

Table 8
Comparison of estimated values for equilibrium composition between liquid phases, $x_{1,2\mathrm{LP}}$, and its flash point, $T_{2\mathrm{LP}}$, with corresponding experimental data

system	Estimated value				Experimental data	
	NRTL		T–K–Wilson		$x_{1,2\mathrm{LP}}$	$T_{2\mathrm{LP}}$ (°C)
	$x_{1,2\mathrm{LP}}$	$T_{2\mathrm{LP}}$ (°C)	$x_{1,2\mathrm{LP}}$	$T_{2\mathrm{LP}}$ (°C)		
Methanol (1) + octane (2)	0.057 0.966	1.94	0.064 0.965	1.88	0.06 0.97	2.12
Methanol (1) + decane (2)	0.040 0.982	9.33	0.037 0.988	9.23	0.05 0.98	10.23
Acetone (1) + decane (2)	0.130 0.989	−18.50	–	–	0.12 0.95	−17.78
Methanol (1) + 2,2,4-trimethylpentane (2)	0.191 0.973	−10.42	0.386 0.928	−9.16	0.20 0.97	−10.41
Ethanol (1) + tetradecane (2)	0.217 0.930	13.67	0.237 0.958	13.45	0.20 0.95	13.82

The experimental flash points for ethanol + tetradecane, as tested by the ASTM D56 and the ASTM D93B standard methods are all displayed in Fig. 6. The difference between flash-point values derived using the two standard methods is slight and acceptable (Fig. 6 and Table 6 for ethanol composition equal to 0.01). The small difference between the values measured using ASTM D56 and ASTM D93B is also observed in the reported measurements of pure decane flash point [22,23] (Table 5). The experimental and predicted values for ethanol + tetradecane (Fig. 6) are in good agreement in the two liquid phases, irrespective of whether the NRTL or T–K–Wilson thermodynamic model is used to estimate the relevant activity coefficients. However, the predictive curves do deviate from the experimental data in the ethanol-lean phase. The lack of predictive accuracy in this region is considered the reason that the LLE data used by Matsuda and Ochi to estimate the parameter values used for the NRTL or T–K–Wilson thermodynamic model are mostly in the ethanol-rich region [8].

Comparing the predictive efficiency of the NRTL or T–K–Wilson thermodynamic model, Table 7 demonstrates that predictions are better in the two liquid phases than over the entire composition range for methanol + octane, acetone + decane and ethanol + tetradecane. However, there are not significant difference in predictive efficacy between the two ranges for methanol + decane and methanol + 2,2,4-trimethylpentane (Table 7). The observation for the former three mixtures is attributed to the fact that the binary parameters used for calculating the activity coefficient were regressed from LLE data sets, resulting in better prediction in the two liquid phases compared to other regions. Overall, the predictive results are acceptable, although there may be greater deviation outside the two liquid phases when using the binary interaction parameters estimated from the LLE data. In vapor–liquid equilibrium calculations, it has also been observed that using binary parameters regressed on LLE data sets may not represent as well VLE experimental data as models with binary parameters regressed on VLE data.

Table 8 compares experimental span and invariant flash-point average value of the two liquid phases region and predictions with the NRTL or T–K–Wilson thermodynamic models for the methanol + octane, methanol + decane, acetone + decane, methanol + 2,2,4-trimethylpentane and ethanol + tetradecane mixtures. Agreement is remarkable for the methanol + octane mixture with a two liquid phase methanol composition ranging experimentally from 0.06 and 0.97 and with an experimental invariant flash-point average value of 2.12 °C (Fig. 2, Table 8) NRTL (respectively T–K–Wilson) predicts [0.057–0.966] (respectively [0.064–0.965]) and 1.94 °C (respectively 1.88 °C) (Table 8). As hinted by the figures, agreement is also good for the other mixtures, with better prediction for the NRTL model over the T–K–Wilson model in particular for the methanol + 2,2,4-trimethylpentane mixture (Table 8).

The flash points for the five studied partially miscible mixtures decrease remarkably after addition of a small quantity of a low-flash-point liquid to a relatively high-flash-point analogue.

Table 9
Values of $\gamma_i^\infty P_i^{\mathrm{sat}}|_{T_{j,\mathrm{fp}}}/P_{i,\mathrm{fp}}^{\mathrm{sat}}$ for different binary solutions

system	$\gamma_1^\infty P_1^{sat}\|_{T_{2,fp}}/P_{1,fp}^{sat}$		$\gamma_2^\infty P_2^{sat}\|_{T_{1,fp}}/P_{2,fp}^{sat}$	
	NRTL	T–K–Wilson	NRTL	T–K–Wilson
Methanol (1) + octane (2)	24.3931	39.8223	22.0796	26.9269
Methanol (1) + decane (2)	143.3447	114.0020	4.93052	6.2316
Acetone (1) + decane (2)	275.9230	–	0.375489	–
2,2,4-Trimethylpentane (1) + Methanol (2)	52.12461	73.0221	3.061445	2.2447
Ethanol (1) + tetradecane (2)	357.1958	393.6342	0.012414	0.0177

This phenomenon is most remarkable when ethanol is added to tetradecane, with flash point decreasing from 110.4 to 29.4 °C when the mole fraction of ethanol is increased to 0.02.

Both predicted values of $\gamma_1^\infty P_1^{\text{sat}}|_{T_{2,\text{fp}}}/P_{1,\text{fp}}^{\text{sat}}$ and $\gamma_2^\infty P_2^{\text{sat}}|_{T_{1,\text{fp}}}/P_{2,\text{fp}}^{\text{sat}}$ for methanol + octane, 2,2,4-trimethylpentane + methanol and methanol + decane are greater than unity (Table 9). Such behavior was considered a sufficient condition for a mixture to form a minimum flash point solution [13], and the former two mixtures do exhibit a flash point of the mixture below the pure-substance flash points.

The value of $\gamma_2^\infty P_2^{\text{sat}}|_{T_{1,\text{fp}}}/P_{2,\text{fp}}^{\text{sat}}$ for the former mixture is much greater than those for the latter two, thus the minimum flash point behavior of methanol + octane is much remarkable than those of the other two mixtures [13]. For the mixture of methanol (1) + decane (2), methanol is the relatively low-flash-point substance and the two liquid phase region extends close to pure methanol. The variation of the flash point with composition in the alcohol-rich single liquid phase region is small and occurs in a narrow region (x_1 from 0.98 to 1.0). So, for this particular mixture, the flash point value in the two liquid phases is close to that of the lowest boiling pure substance.

Acetone + decane and ethanol + tetradecane mixture behave similarly and the flash point value in the two liquid phases is also close to that of the lowest boiling pure substance. For mixtures exhibiting such behavior with close minimum mixture flash point and low-flash-point pure substance, there might be some uncertainty to evaluate the existence of the minimum flash point values. In that case, the model shows is usefulness as it gives a definite answer to the existence of a minimum flash point via the computation of the $\gamma_1^\infty P_1^{\text{sat}}|_{T_{2,\text{fp}}}/P_{1,\text{fp}}^{\text{sat}}$ and $\gamma_2^\infty P_2^{\text{sat}}|_{T_{1,\text{fp}}}/P_{2,\text{fp}}^{\text{sat}}$ values and of its numerical value.

5. Conclusion

Existence of minimum flash point solution for partially miscible mixtures has been shown experimentally for two different mixtures. The model including activity coefficient for the flash point prediction of binary partially miscible mixtures of flammable solvents is able to represent well the experimental data over the entire composition range, provided that equation for the liquid–liquid equilibrium is considered. Thus, it appears reasonable to propose that this model is potentially applicable for assessment of fire and explosion hazards in real-world environments and producing inherently safer designs for chemical processes.

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