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On the relation between azeotropic behavior and minimum / maximum flash point occurrences in binary mixtures of flammable compounds

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A B S T R A C T

The flash point temperature and the boiling temperature of a mixture are related by the fact that both can be modeled based on vapor-liquid equilibrium (VLE) of each component. It has been suggested in the literature that there might exist a concomitance between azeotropic behavior and minimum/maximum flash point temperature for binary mixtures. In order to verify this statement, we derive new temperature dependent functions that relate the conditions valid for azeotropic behavior and those valid for minimum/maximum flash point behavior. Analysis of experimental data and predicted results allowed us to propose a heuristic to forecast extremum flash point based on the sole knowledge of azeotropic data and boiling and flash point temperatures differences. Extremum flash point might occur when both components are flammable and when the gap between the flash point temperatures of individual components (ΔT_{fp}) is of the same order or smaller than the boiling temperature gap (ΔT_b). Hence, we contribute to the assessment of the fire and explosion hazards in binary mixtures eventually presenting a minimum flash point behavior.

Keywords:

Flash point
Vapor liquid equilibrium
Azeotrope
Azeotropic conditions
Minimum flash point behavior

1. Introduction

The study of flash point temperature of mixtures plays an important role for the safety in the chemical processes. Several accidents due to fire and explosions [1–3] highlight the importance of an accurate description of the flash point temperature in liquids, including pure compounds and mixtures.

One of the major concerns in these studies is to forecast a minimum flash point mixture, in which the flash point over a composition range is less than those of its components. This kind of behavior is quite dangerous, since the mixture becomes more hazardous than its pure components. And it is not rare to see mixtures presenting such characteristic, especially when it comes to binary combustible mixtures. Previous works [4–13] reported nearly 15 of them to date, as n-octane + ethanol, methanol + methyl acrylate, ethylbenzene + n-propanol, etc.

Since the flash point data available for binary mixtures is quite

scarce, and the experiments to get these data take some time [13], it would be important to find an easy way to predict minimum flash point in binary mixtures. This kind of behavior is associated with the positive (negative in the case of maximum flash point mixtures) deviation from an ideal solution behavior [4,13].

Many different methods have been previously proposed to compute the flash point of different types of mixtures. The developed methods first concerned flammable miscible mixtures [14] and were later extended for miscible mixtures with flammable and non-flammable compounds [6,13]. Finally, a model has been developed taking into account partially miscible mixtures [7,15–17]. Wickey and Chittenden used the flash point indices of stocks to calculate the flash point of petroleum blends [18]. Affens and McLaren developed a model to estimate the flash point of mixtures based on the Raoult's law and Le Chatelier's rule [19,20]. White et al. reduced Affens and McLaren's model by ignoring temperature effect on LFL to estimate the flash point of aviation fuels [21]. Catoire et al. extended their developed empirical equation of estimating pure compounds' flash point to estimate the flash point of mixtures [22]. Gmehling and Rasmussen were the first ones to estimate the flash point by taking into account non-ideality

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Nomenclature

T_{fp}	Flash point temperature
ΔT_{fp}	Flash point temperature gap ($ T_{1,fp} - T_{2,fp} $)
T_b	Boiling temperature
ΔT_b	Boiling temperature gap ($ T_{1,b} - T_{2,b} $)
LFL	Lower flammability limit
y_i	Molar fraction of compound i in the vapor phase
x_i	Molar fraction of compound i in the liquid phase
γ_i	Activity coefficient of compound i
P_i^{sat}	Saturation vapor pressure of compound i for a given temperature
$P_{i,fp}^{sat}$	Saturation vapor pressure of compound i at its flash point temperature
MinFP	Minimum flash point
MaxFP	Maximum flash point
MinBP	Minimum boiling point
MaxBP	Maximum boiling point
MinFPB	Minimum flash point behavior

[14]. The general flash point prediction model for miscible mixtures developed by the authors [6] was reducible for the ones of binary mixtures, either with water or not [4,5]. All the models mentioned were developed for miscible mixtures of flammable solvents, which are relevant to the scope of this study. All these methods, excluding Wickey and Chittenden's and Catoire et al.'s models, consider vapor-liquid equilibrium (VLE) for all components and we keep this hypothesis here with some nuances explained later. Do notice however that non-equilibrium conditions (such as not stirring in the liquid phase) can affect flash point behavior [8]. Nonetheless, this effect has been observed only in partially miscible systems, and such systems are out of the scope of this study.

Such a VLE based approach is similar to the one used to describe distillation curves and boiling temperature surfaces. And since the azeotropic behavior (minimum and maximum) is also associated with deviations from ideal behavior [23,24], a relation between both azeotropes and extremum (minimum/maximum) flash point behaviors has been suggested in previous works [13,25] for several mixtures, such as phenol + cyclohexanone, n-octane + 2-propanol, etc.

In this article we explore that concomitance more systematically. The paper is organized as follows: after recalling the flash-point prediction model (section 2), two T -dependent functions are derived relating both extremum azeotropic and flash point behaviors (Section 3). By studying these functions together with the available data for binary mixtures flash point, we propose an empirical criterion to predict extremum flash point without further computation (Section 4). Such criterion is based solely on the knowledge of pure component data and azeotropic behavior. Section 5 reports experimental materials and methods. The criterion is tested over almost all the available flash point mixture data (Section 6). Finally, we use this criterion to forecast the flash point behavior of two mixtures. The results are then compared with our experimental data, in order to evaluate the performance and limits of the heuristics.

2. Flash-point prediction model

The model used in this manuscript to predict flash point temperatures of flammable mixtures is based on Le Chatelier's rule (1891), which can be written as [20,26].

$$LFL_{mix} = \frac{1}{\sum_i^N \frac{z_i}{LFL_i}} \quad (1)$$

where LFL_{mix} is the lower flammability limit of the mixture in volume percent, z_i is the molar fraction of component i in the vapor phase (considering only the combustible species) and LFL_i is the lower flammability limit of pure component i , also in volume percent. Equation (1) can be rewritten as follows:

$$\sum_i^N \frac{y_i}{LFL_i} = 1 \quad (2)$$

where y_i is the molar fraction of compound i in vapor phase considering all species in equilibrium.

We precise that strictly speaking the flash point phenomena requires air in the vapor phase and one usually neglects its presence in the liquid phase. This consideration is enough to characterize a non-equilibrium condition for the whole system, since the chemical potentials of the air are not the same in both phases. Even so, we assume that near "vapor-liquid equilibrium" conditions hold for all the other components i . Hence, they are considered to have the same chemical potential in both phases and we can rewrite equation (2) as:

$$\sum_i \frac{x_i \gamma_i(\underline{x}, T) P_i^{sat}(T)}{P_{i,fp}^{sat}} = 1 \quad (3)$$

where x_i is the molar fraction of component i in the liquid phase, γ_i is its activity coefficient, $P_i^{sat}(T)$ is the saturation pressure at temperature T and $\underline{x}$ is the vector of molar fractions in the liquid phase.

Equation (3) is known as Liaw's equation. It can be modified in the case of the presence of a non-flammable compound (as water, for example). In this case one can ignore non-flammable components in equation (3) and rewrite it as:

$$\sum_{i \neq k} \frac{x_i \gamma_i(\underline{x}, T) P_i^{sat}(T)}{P_{i,fp}^{sat}} = 1 \quad (4)$$

where k refers to the non-flammable compounds in the mixture [6].

A more detailed review on flash point prediction models for pure components and mixtures is available in Vidal et al. [27] and Liu and Liu [28].

Several models are available to estimate the activity coefficient in eqs. (3) and (4), such as UNIFAC, UNIFAC Dortmund 93, NRTL, Wilson, UNIQUAC, etc. Once we choose the model, it is possible to compute the flash point temperature at a given composition by solving recursively for T equation (3) or (4) [13]. An assessment on the main activity coefficient models, including their limitations, is available in Kontogeorgis and Folas [29].

3. Sufficient conditions for extremum behavior in binary mixtures

3.1. The condition for minimum/maximum azeotrope

An azeotropic behavior occurs in a VLE diagram when a mixture's composition in the liquid phase is the same as the one in the vapor phase for a given pressure and temperature.

For a binary mixture, the azeotropic point has to satisfy:

$$x_1 = y_1 ; x_2 = y_2 \quad (5)$$

This condition can also be presented in terms of the distribution

coefficient $K_i = y_i/x_i$. Equation (5) is now written as:

$$K_1 = 1 ; K_2 = 1 \quad (6)$$

We can see from the above definition of the distribution coefficient that K_i is not defined when $x_i = y_i = 0$. However, at the limit $x_i \rightarrow 0$ for isobaric distillation:

$$\lim_{x_i \rightarrow 0} \frac{y_i}{x_i} = \lim_{x_i \rightarrow 0} \frac{x_i \gamma_i P_i^{sat}}{P x_i} \Rightarrow \Rightarrow K_i|_{x_i=0} = \frac{\gamma_i^\infty P_i^{sat}|_{T_{j,b}}}{P} \quad (7)$$

where γ_i^∞ represents the activity coefficient of i at an infinite dilution in j , and $T_{j,b}$ is the boiling temperature of component j .

By using the distribution coefficient, it is possible to write sufficient conditions to forecast an isobaric azeotrope in binary mixtures. These well-known conditions are [23,24].

$$K_1|_{x_1=0} > 1 ; K_2|_{x_1=1} > 1 \text{ (minimum azeotrope)} \quad (8)$$

$$K_1|_{x_1=0} < 1 ; K_2|_{x_1=1} < 1 \text{ (maximum azeotrope)} \quad (9)$$

The Fig. 1 below, extracted from Kiva et al., 2003 [30], describes graphically the conditions presented above.

In the above Figure, the horizontal axis represents the molar fraction of component 1 in the liquid phase. Plots (1), (1'), (2) and (2') concern mixtures that do not show azeotropic behavior, as eq. (6) is never valid. The graphics (3'), and (4') represent maximum azeotrope mixtures, as predicted by equation (9). Also, plots (3) and (4) represent minimum azeotropes predicted by equation (8). One can see from plot number (5) that equations (8) and (9) fail to forecast double azeotropes. However, this kind of behavior is quite rare and has been reported for the hexafluorobenzene + benzene mixture [31,32] and a few others (see Fig. 1).

3.2. The condition for minimum/maximum flash point

A sufficient condition for minimum/maximum flash points in binary mixtures has been proposed and verified with experimental data in previous works [33,34]. A minimum flash point occurs if flash point temperature decreases in the vicinity of $x_1 = 0$ and increases near $x_1 = 1$ (see Fig. 2). Inversely, a maximum flash point occurs when the temperature increases around $x_1 = 0$ and decreases near $x_1 = 1$.

Using $\left. \frac{dT}{dx_1} \right|_{x_1=0} < 0$ (resp. > 0) and $\left. \frac{dT}{dx_1} \right|_{x_1=1} > 0$ (resp. < 0), Liaw et al. [33,34] derived the following expressions, based on Liaw's model [4], as sufficient conditions for minimum (resp. maximum) flash point mixtures:

$$\frac{\gamma_1^\infty P_1^{sat}|_{T_{2,fp}}}{P_{1,fp}^{sat}} > 1 ; \frac{\gamma_2^\infty P_2^{sat}|_{T_{1,fp}}}{P_{2,fp}^{sat}} > 1 \text{ (minimum fp)} \quad (10)$$

$$\frac{\gamma_1^\infty P_1^{sat}|_{T_{2,fp}}}{P_{1,fp}^{sat}} < 1 ; \frac{\gamma_2^\infty P_2^{sat}|_{T_{1,fp}}}{P_{2,fp}^{sat}} < 1 \text{ (maximum fp)} \quad (11)$$

According to literature, Liaw's model, which was used in deriving above sufficient condition, is more reliable than other vapor-pressure-based models [35], and is the only one to predict the occurrence of minimum/maximum flash point behavior of mixtures correctly [28].

The above criteria is as reliable as the thermodynamic model

and data used to describe the mixture. In other words, wrong predictions coming from eqs. (10) and (11) may be related to: (i) inaccuracy of the activity coefficient model regarding the target mixture; (ii) poor estimation of the saturation pressures, due for example to a short temperature-domain of validity of the Antoine coefficients; (iii) inaccurate data for individual flash point temperatures.

Equations (10) and (11) for flash point extrema are quite similar to equations (8) and (9) for azeotropes. Indeed, by rewriting (8) and (9) in terms of γ and P^{sat} (using eq. (7)), we get:

$$\frac{\gamma_1^\infty P_1^{sat}|_{T_{2,b}}}{P} > 1 ; \frac{\gamma_2^\infty P_2^{sat}|_{T_{1,b}}}{P} > 1 \text{ (minimum bp)} \quad (12)$$

$$\frac{\gamma_1^\infty P_1^{sat}|_{T_{2,b}}}{P} < 1 ; \frac{\gamma_2^\infty P_2^{sat}|_{T_{1,b}}}{P} < 1 \text{ (maximum bp)} \quad (13)$$

Notice the fp or b subscript differences to identify quickly the equations corresponding to flash point or boiling point extremum behavior in this paper.

4. Mathematical formulation – the equations associating both conditions

The similarity between the conditions to form azeotropes (eqs. (12) and (13)) and minimum/maximum flash points (eqs. (10) and (11)) is remarkable. Indeed, it is possible to rewrite these conditions in terms of the same functions. Let us define two new functions, f_1 and f_2 , as follows:

$$f_1(T) = \frac{\gamma_1^\infty(T) P_1^{sat}(T)}{P_{1,fp}^{sat}} ; f_2(T) = \frac{\gamma_2^\infty(T) P_2^{sat}(T)}{P_{2,fp}^{sat}} \quad (14)$$

By substitution in equations (10)–(13), it is now possible to rewrite them in terms of f_1 and f_2 applied either at $T = T_{i,b}$ or at $T = T_{i,fp}$, as follows:

$$f_1|_{T_{2,b}} > \frac{P}{P_{1,fp}^{sat}} ; f_2|_{T_{1,b}} > \frac{P}{P_{2,fp}^{sat}} \text{ (minimum bp)} \quad (15)$$

$$f_1|_{T_{2,b}} < \frac{P}{P_{1,fp}^{sat}} ; f_2|_{T_{1,b}} < \frac{P}{P_{2,fp}^{sat}} \text{ (maximum bp)} \quad (16)$$

$$f_1|_{T_{2,fp}} > 1 ; f_2|_{T_{1,fp}} > 1 \text{ (minimum fp)} \quad (17)$$

$$f_1|_{T_{2,fp}} < 1 ; f_2|_{T_{1,fp}} < 1 \text{ (maximum fp)} \quad (18)$$

The relation between an azeotropic behavior and an extremum flash point behavior can be better understood by studying equations (15)–(18).

5. Materials and methods

5.1. Pure compounds data

Flash point and boiling point of each individual component, as well as its Antoine coefficients (for calculating the vapor pressure in f_1 and f_2 expressions), were extracted from different sources in order to plot f_1 and f_2 , as indicated in Table 1.

For each mixture, it was verified if the UNIFAC Dortmund 93 model predicts satisfactorily the azeotropic behavior reported in the literature (see Table 3). Other activity coefficient models could be used and they might better predict experimental data with the

Fig. 1. Distribution coefficients. (reprinted with permission from Fig. 30 in Kiva et al., 2003 [30]. Copyright 2003 Elsevier.)

Fig. 2. Minimum flash point behavior for methyl acrylate (1) + methanol (2), reprinted with permission from Fig. 3 in Liaw et al., 2003 [33]. Copyright 2003 Elsevier.

help of binary interaction parameters. Our current choice of a predictive model suits the heuristics we would like to establish.

5.2. Flash point measurement

The flash point of binary mixtures were measured by the flash point analyzer, HFP 362-Tag, which was made by Walter Herzog GmbH, Germany, and meets the requirement of ASTM D56 [42]. The

operation of the instrument was according to ASTM D56, which is a close cup method. The detailed operational parameters were described in previous studies [3–8,15,16,25,33,43]. The flash point value of each composition was the average one, measured more than ten times.

Acetone (99.5%), heptane (99%), ethanol (99.9%) and ethyl acetate (99.9%) were purchased from J.T. Baker (USA). Octane (99%) and decane (99%) were from Applichem Panreac (Germany) and Alfa Aesar (USA), respectively.

6. Results and discussion

6.1. Application of the thermodynamic criterion for three different mixtures

The plots of f_1 and f_2 for different mixtures are shown in appendix A. They were made by using the group contribution method UNIFAC Dortmund 93 for calculation of the activity coefficients within the software environment offered by *Simulis Thermodynamics*[®] in Excel [44].

For the sake of illustration, let us study a few examples. Fig. 3 shows the functions f_1 and f_2 drawn for five different mixtures.

We know from available sources [4,13,33,45] that mixture n-octane + ethanol in Fig. 3a presents both minimum azeotropic and minimum flash point behavior. We explain now how to infer it from the plot in Fig. 3a.

First, we remark the intersection between f_1 (—♦—) and the vertical $T_{2,b}$ line (—♦—). This point corresponds to $f_1|_{T_{2,b}}$, and it is located above the dotted line $\frac{P}{P_{sat}^{1,jp}}$ (.....). Hence one can conclude that $f_1|_{T_{2,b}} > \frac{P}{P_{sat}^{1,jp}}$, and so the first condition for azeotrope in equation (15) is satisfied. Analogously, the intersection between f_2 (—▲—) and the vertical $T_{1,b}$ line (—♦—) above the horizontal dashed line (-----) corresponds to the condition $f_2|_{T_{1,b}} > \frac{P}{P_{sat}^{2,jp}}$. And so, since both conditions in eq. (15) are satisfied, one can conclude that this mixture

Table 1
Data of pure compounds.

Compound	Flash point T _{fp}	Antoine coef. ^{a,b}	Boiling point T _{bp} ^c
n-octane	14.5 °C [13]	A = 96.084 B = -7900.2 C = -11.003 D = 7.1802E-6 E = 2	125.68 °C
ethanol	13 °C [13]	A = 73.304 B = -7122.3 C = -7.1424 D = 2.8853E-6 E = 2	78.29 °C
2-butanol	22 °C [13]	A = 105.64 B = -9401.9 C = -11.641 D = 1.2635E-6 E = 6	99.55 °C
2-propanol	12.9 °C [13]	A = 76.43 B = -7607 C = -7.4086 D = 4.3986E-18 E = 6	82.26 °C
1-butanol	36.9 °C [13]	A = 107.09 B = -9914.7 C = -11.768 D = 1.0925E-17 E = 6	117.66 °C
methanol	10 °C [13]	A = 82.718 B = -6904.5 C = -8.8622 D = 7.4664E-6 E = 2	64.7 °C
methyl acrylate	-2.1 °C [13]	A = 107.69 B = -7027.2 C = -13.916 D = -0.015185 E = 1	80.2 °C
3-methyl-1-butanol	44.9 °C [13]	A = 107.02 B = -10237 C = -11.695 D = 6.8003E-18 E = 6	131.2 °C
isopentyl acetate	38.8 °C [13]	A = 99.558 B = -8876.8 C = -11.075 D = 2.4723E-17 E = 6	142 °C
acetone	-18.6 °C [7]	A = 69.006 B = -5599.6 C = -7.0985 D = 6.2237E-6 E = 2	56.29 °C
methyl acetate	-14.4 °C [13]	A = 61.267 B = -5618.6 C = -5.6473 D = 2.108E-17 E = 6	56.94 °C
n-heptane	-5.2 °C [13]	A = 87.829 B = -6996.4 C = -9.8802 D = 7.2099E-6 E = 2	98.43 °C
phenol	81 °C [34]	A = 95.444 B = -10113 C = -10.09 D = 6.7603E-18 E = 6	181.84 °C
acetophenone	83.5 °C [34]	A = 64.239 B = -8173.9 C = -5.7673 D = 2.6743E-18 E = 6	202.11 °C
cyclohexanone	46 °C [34]	A = 85.424 B = -7944.4 C = -9.2862	155.43 °C

(continued on next page)

Table 1 (continued)

Compound	Flash point T _{fp}	Antoine coef. ^{a,b}	Boiling point T _{bp} ^c
cyclohexanol	68.5 °C [34]	D = 4.9957E-6 E = 2 A = 189.19 B = -14337 C = -24.148 D = 1.074E-5 E = 2	160.85 °C
1-propanol	21.5 °C [5]	A = 94.126 B = -8604.8 C = -10.11 D = 3.1334E-6 E = 2	97.2 °C
ethyl hexanoate	57.55 °C [36]	A = 16.675 B = 3399 C = -80.95	166 °C [37]
ethyl laurate	126.85 °C [36]	A = 10.9743 B = 1392.1779 C = -258.9533	269 °C [37]
ethyl tetradecanoate	150.85 °C [36]	A = 12.1979 B = 1847.2703 C = -259.4646	295 °C [37]
ethyl palmitate	160.85 °C [36]	A = 15.7216 B = 3690.0998 C = -194.6189	378 °C [37]
ethyl oleate	153.85 °C [36]	A = 14.0085 B = 2724.21 C = -252.243	331.52 °C [37]
ethyl linoleate	155.85 °C [36]	A = 20.543 B = 6837 C = -111.8136	319.16 °C [37]
toluene	5.56 °C [14]	A = 76.945 B = -6729.8 C = -8.179 D = 5.3017E-6 E = 2	110.63 °C
4-methylpyridine	42.5 °C [34]	A = 90.839 B = -8013.6 C = -10.096 D = 5.7026E-6 E = 2	145.35 °C
cyclohexylamine	28 °C [34]	A = 149.08 B = -9336.7 C = -20.524 D = 0.021378 E = 1	134.5 °C
propanal	-26 °C [34]	A = 80.581 B = -5896.1 C = -8.9301 D = 8.2236E-6 E = 2	48 °C
methyl ethyl ketone	-6 °C [34]	A = 72.698 B = -6143.6 C = -7.5779 D = 5.6476E-6 E = 2	79.64 °C
propionic acid	56.6 °C [10]	A = 54.552 B = -7149.4 C = -4.2769 D = 1.1843E-18 E = 6	141.17 °C
p-xylene	25 °C [10]	A = 88.72 B = -7741.2 C = -9.8693 D = 6.077E-6 E = 2	138.36 °C
n-decane	46 °C [37]	A = 112.73 B = -9749.6 C = -13.245 D = 7.1266E-6 E = 2	174.155 °C
n-dodecane	71 °C [37]	A = 137.47 B = -11976 C = -16.698 D = 8.0906E-6 E = 2	216.323 °C

Table 1 (continued)

Compound	Flash point T_{fp}	Antoine coef. ^{a,b}	Boiling point T_{bp} ^c
1-pentanol	51 °C [38]	A = 162.64 B = -12413 C = -20.383 D = 1.0482E-5 E = 2	137.7 °C
1,2,3,4-tetrahydronaphtalene	72.5 °C [12]	A = 137.23 B = -10620 C = -17.908 D = 0.014506 E = 1	207.62 °C
acetic acid	40.5 °C [38]	A = 53.27 B = -6304.5 C = -4.2985 D = 8.8865E-18 E = 6	117.9 °C
1-hexanol	64 °C [38]	A = 125.08 B = -11692 C = -14.258 D = 1.1102E-17 E = 6	157.4 °C
cyclohexane	-18 °C [37]	A = 51.087 B = -5226.4 C = -4.2278 D = 9.7554E-18 E = 6	80.72 °C
m-xylene	25 °C [37]	A = 85.099 B = -7615.9 C = -9.3072 D = 5.5643E-6 E = 2	139.12 °C
2-methyl-1-propanol	28 °C [37]	A = 121.78 B = -10504 C = -13.921 D = 1.6898E-17 E = 6	107.66 °C

^a Formulation with five parameters: $\ln(P^{sat}) = A + \frac{B}{T} + C \ln(T) + DT^E$, with pressure P^{sat} in Pa and temperature T in Kelvins and parameters from DIPPR [39].

^b Formulation with three parameters: Antoine's law: $\ln(P^{sat}) = A - \frac{B}{T-C}$, with pressure P^{sat} in mmHg and temperature T in Kelvins and parameters from Silva et al., 2011 [40] except for ethyl hexanoate from Ref. [41]. N.B.: for Silva et al., 2011 [40], Antoine coefficients do not fit well for all temperature range.

^c From DIPPR [39] except when another reference is given.

will present a minimum azeotrope.

Now for the minimum flash point behavior. The intersection between f_1 and the vertical line $T_{2,fp}$ (---) takes place above the ordinate equals 1 line. This results in $f_1|_{T_{2,fp}} > 1$. Similarly, since f_2 crosses the $T_{1,fp}$ line (—) above the ordinate equals 1 line, we conclude that $f_2|_{T_{1,fp}} > 1$. Hence, the model forecasts a minimum flash point behavior.

But how could the minimum flash point be inferred in a simpler way? The answer relies in both azeotropic behavior and a short gap between flash point temperatures.

Mixtures presenting a minimum azeotropic behavior have positive interactions in the liquid phase ($\gamma_1 > 1$; $\gamma_2 > 1$). If we suppose that these positive interactions will be maintained at the vicinity of the flash point temperature of the pure components, we can write from equations (14), (18) and (19):

$$f_1|_{T_{1,fp}} = \frac{\gamma_1^\infty(T = T_{1,fp})P_1^{sat}(T = T_{1,fp})}{P_{1,fp}^{sat}} = \gamma_1^\infty|_{T_{1,fp}} > 1 \quad (19)$$

$$f_2|_{T_{2,fp}} = \frac{\gamma_2^\infty(T = T_{2,fp})P_2^{sat}(T = T_{2,fp})}{P_{2,fp}^{sat}} = \gamma_2^\infty|_{T_{2,fp}} > 1 \quad (20)$$

A careful check at the subscript shows that this is not equivalent to equation (17) criterion and does not yet proves a minimum flash

point behavior.

Assuming that $T_{2,fp} < T_{1,fp}$, and since both f_1 and f_2 are strictly increasing functions, $f_2|_{T_{2,fp}} > 1$ implies $f_2|_{T_{1,fp}} > 1$. Hence, the criterion in eq. (17) concerning both $f_1|_{T_{2,fp}} > 1$ and $f_2|_{T_{1,fp}} > 1$ can be reduced to $f_1|_{T_{2,fp}} > 1$.

Then, supposing that the gap $|T_{2,fp} - T_{1,fp}|$ is quite small (as in the mixture shown in Fig. 3a), one can roughly state that f_1 will have similar values at $T = T_{2,fp}$ and at $T = T_{1,fp}$ (see Fig. 3a). Therefore, excluding particular cases where $f_1|_{T_{1,fp}} \approx 1$:

$$f_1|_{T_{2,fp}} \approx f_1|_{T_{1,fp}} > 1$$

So, we conclude that the mixture satisfies the reduced eq. (17) and so presents a minimum flash point.

Table 2
Possible combinations of azeotropic and extreme flash point behaviors.

Possible combinations	Corresponding figure
MinBP and MinFP	3a
MinBP and non-extreme flash point	3b
MaxBP and MaxFP	3c
MaxBP and non-extreme flash point	—
Non-azeotropic and MinFP	3d
Non-azeotropic and non-extreme flash point	3e
Non-azeotropic and MaxFP	—

Table 3
Relation between azeotropes and minimum/maximum flash point behavior. Refs. 48–53.

	n-octane / ethanol	n-octane / 2-butanol	n-octane / 2-propanol	n-octane / 1- butanol	methanol / methyl acrylate	2-propanol / Toluene	1-butanol / p-xylene	2-methyl-1-propanol / toluene	1-propanol / n-octane	methanol / acetone	methanol / methyl acetate	1-pentanol / cyclohexanone
A Exp. MinBP	T ^[45]	T ^[48]	T ^[45]	T ^[45]	T ^[45]	T ^[45]	T ^[45]	T ^[45]	T ^[45]	T ^[45]	T ^[45]	F ^[45]
B Exp. MinFP	T ^[4,13]	T ^[5,13]	T ^[13,43]	T ^[4,13]	T ^[4,13]	T ^[10]	T ^[10]	T ^[9]	T ^[11]	F ^[13,46]	F ^[4,14]	T ^[12]
is $A \stackrel{?}{\equiv} B$	T	T	T	T	T	T	T	T	T	F	F	F
Pred. MinBP eq. 15	T	T	T	T	T	T	T	T	T	T	T	F
Pred. MinFP eq. 17	T	T	T	T	T	T	T	T	T	F	F	T
ΔT_{fp}	1.5	7.5	1.6	22.4	12.1	7.3	11.9	22.4	7	28.6	24.4	6
ΔT_b	47.4	26.1	43.4	8	15.5	28.4	20.7	3	28.5	8.4	7.8	17.6
$\frac{\Delta T_{fp}}{\Delta T_b}$	0.032	0.287	0.037	2.793	0.781	0.259	0.575	7.556	0.246	3.401	3.144	0.341
	1-pentanol / 1,2,3,4-tetrahydronaphthalene	1-propanol / n-decane	3-methyl-1-butanol / isopentyl acetate	phenol / acetophenone	phenol / cyclohexanol	4-methylpyridine / phenol	phenol / cyclohexanone	acetic acid / 1-pentanol	acetic acid / cyclohexanone	p- xylene / m-xylene ^d	1-hexanol / cyclohexanone	
A Exp. MinBP	F ^c	F ^[45]	F ^[45]	-	-	-	-	F ^c	F ^c	F ^[45]	F ^[45]	
B Exp. MinFP	T ^[12]	T ^[11]	T ^[5,13]	-	-	-	-	F ^{[38],†}	F ^{[38],†}	F [†]	F ^[38]	
is $A \stackrel{?}{\equiv} B$	F	F	F	-	-	-	-	T	T	T	T	
Pred. MinBP eq. 15	F	F	F	-	-	-	-	F	F	F	F	
Pred. MinFP eq. 17	T	T	T	-	-	-	-	T	T	T	F	
C Exp. MaxBP	-	-	-	T ^[45]	T ^[45]	T ^[45]	T ^[45]	F ^c	F ^c	F ^[45]	F ^[45]	
D Exp. MaxFP	-	-	-	T ^[13,24]	T ^[13,34]	T ^[34]	T ^[13,34]	F ^{[38],†}	F ^{[38],†}	F [†]	F ^[38]	
is $C \stackrel{?}{\equiv} D$	-	-	-	T	T	T	T	T	T	T	T	
Pred. MaxBP eq. 16	-	-	-	T	T	T	T	F	F	F	F	
Pred. MaxFP eq. 18	-	-	-	T	T	T	F	F	F	F	F	
ΔT_{fp}	21.5	24.5	6.1	2.5	12.5	38.5	36	10.5	4.5	0.0e	19	
ΔT_b	69.8	77	10.8	20.3	21	36.5	26.4	19.9	37.5	0.8	2	
$\frac{\Delta T_{fp}}{\Delta T_b}$	0.308	0.318	0.565	0.123	0.596	1.055	1.363	0.528	0.12	0	9.5	

	ethanol / acetone	n-octane / n-heptane	n-octane / n-decane	ethanol / 1-butanol	methyl acetate / methyl acrylate	ethanol / ethyl hexanoate	ethanol / ethyl laureate	ethanol / ethyl tetradecanoate	ethanol / ethyl palmitate	ethanol / ethyl oleate	ethanol / ethyl linoleate	cyclohexylamine / cyclohexanol
A Exp. MinBP	F ^[45]	F ^[45]	F ^[45]	F ^[45]	F ^[49]	F ^[41]	F ^c	F ^c	F ^[50]	F ^c	F ^c	F ^[45]
B Exp. MinFP	F ^[13,46]	F ^[13]	(T ^{[11],f}) F [†]	F ^[13]	F ^[5,13]	F ^[36]	F ^[36]	F ^[36]	F ^[36]	F ^[36]	F ^[36]	F ^[34]
is $A \stackrel{?}{\equiv} B$	T	T	T	T	T	T	T	T	T	T	T	T
Pred. MinBP eq. 15	F	F	F	F	F	F	F	F	F	F	F	F
Pred. MinFP eq. 17	F	F	F	F	F	F	F	F	F	F	F	F
C Exp. MaxBP	F ^[45]	F ^[45]	F ^[45]	F ^[45]	F ^[49]	F ^[41]	F ^c	F ^c	F ^[50]	F ^c	F ^c	F ^[45]
D Exp. MaxFP	F ^[13,46]	F ^[13]	F [†]	F ^[13]	F ^[5,13]	F ^[36]	F ^[36]	F ^[36]	F ^[36]	F ^[36]	F ^[36]	F ^[34]
is $C \stackrel{?}{\equiv} D$	T	T	T	T	T	T	T	T	T	T	T	T
Pred. MaxBP eq. 16	F	F	F	F	F	F	F	F	F	F	F	F
Pred. MaxFP eq. 18	F	F	F	F	F	F	F	F	F	F	F	F
ΔT_{fp}	31.6	19.7	31.5	23.9	12.3	44.6	113.9	137.9	147.9	140.9	142.9	40.5
ΔT_b	22	27.3	48.5	39.4	23.3	87.7	190.7	216.7	299.7	253.2	240.9	26.4
$\frac{\Delta T_{fp}}{\Delta T_b}$	1.436	0.723	0.65	0.607	0.529	0.508	0.597	0.636	0.493	0.556	0.593	1.537

	propanal / methyl ethyl ketone	1-butanol / propionic acid	methyl ethyl ketone / Toluene	n-decane / n-dodecane	1-pentanol / 1-hexanol	acetic acid / 1-hexanol	cyclohexane / cyclohexanone	cyclohexane / cyclohexanol	cyclohexanol / cyclohexanone	cyclohexanone / p-xylene ^b
A Exp. MinBP	F ^[45]	F ^[45]	F ^[45]	F ^[45]	F ^c	F ^[52]	F ^[45]	F ^[45]	F ^[45]	F ^[53]
B Exp. MinFP	F ^[34]	F ^[10]	F ^[10]	F ^[51]	F ^[38]	F ^[38]	F ^[9]	F ^[9]	F ^[9]	F ^[9]
is $A \stackrel{?}{\equiv} B$	T	T	T	T	T	T	T	T	T	T
Pred. MinBP eq. 15	F	F	F	F	F	F	F	F	F	F
Pred. MinFP eq. 17	F	F	F	F	F	F	F	F	F	F
C Exp. MaxBP	F ^[45]	F ^[45]	F ^[45]	F ^[45]	F ^c	F ^[52]	F ^[45]	F ^[45]	F ^[45]	F ^[53]
D Exp. MaxFP	F ^[34]	F ^[10]	F ^[10]	F ^[51]	F ^[38]	F ^[38]	F ^[9]	F ^[9]	F ^[9]	F ^[9]
is $C \stackrel{?}{\equiv} D$	T	T	T	T	T	T	T	T	T	T
Pred. MaxBP eq. 16	F	F	F	F	F	F	F	F	F	F
Pred. MaxFP eq. 18	F	F	F	F	F	F	F	F	F	F
ΔT_{fp}	20	19.7	11.6	25	13	23.5	63	86.5	23.5	20
ΔT_b	31.6	23.5	31	42.2	19.6	39.5	74.7	80.1	5.4	17.1
$\frac{\Delta T_{fp}}{\Delta T_b}$	0.632	0.838	0.373	0.593	0.663	0.595	0.843	1.079	4.351	1.169

^a VLE in reference [52] is available for $P = 90\text{ kPa}$

^b VLE in reference [53] is available for $P = 98.67\text{ kPa}$

^c No VLE data available at atmospheric pressure; results predicted with UNIFAC Dortmund model

^d Predictions based on Wilson model

^e Experimental flash point from sources in Table 1 is the same $\pm 1\text{ }^\circ\text{C}$ for both xylenes.

^f Questionable data in contradiction with our new measurements (see text below)

[†] Experimental data first published here

A second example is hereafter analyzed, concerning the methanol-acetone mixture (Fig. 3b) with a significantly larger gap $|T_{2,fp} - T_{1,fp}|$. This mixture exhibits a minimum azeotropic behavior [45] without presenting a minimum flash point [13,46].

One can see in Fig. 3b that the conditions are met for a minimum azeotrope (f_1 intersecting the $T_{2,b}$ line above the $P/P_{1,fp}$ line and f_2 intersecting $T_{1,b}$ line above $P/P_{2,fp}$ line). However, the conditions for minimum flash point are not met as $f_1|_{T_{2,fp}}$ is smaller than unity. A possible explanation relies on the large gap $|T_{2,fp} - T_{1,fp}|$, which is equal to 28.8 °C in this case. As in the example from Fig. 3, one can state for the methanol + acetone mixture:

$$f_1|_{T_{1,fp}} > 1$$

$$f_2|_{T_{2,fp}} > 1$$

As mentioned above, since $T_{2,fp} < T_{1,fp}$ and both f_1 and f_2 are strictly increasing functions, $f_2|_{T_{2,fp}} > 1$ implies $f_2|_{T_{1,fp}} > 1$. And so criterion in eq. (17) is again reduced to: $f_1|_{T_{2,fp}} > 1$.

However, since the gap between both flash point temperatures is high, f_1 (which values more than 1 at $T_{1,fp}$) decreases from right to left, and eventually will become smaller than 1 before crossing the $T_{2,fp}$ line. So there is no minimum flash point behavior.

A third example is discussed next, for the phenol-acetophenone mixture (Fig. 3c). This mixture is reported to present a maximum azeotropic point [45] and a maximum flash point [13,34] as well. And one can conclude both by analyzing the plot. Indeed, f_1 intersecting $T_{2,b}$ line below the $P/P_{1,fp}$ line and f_2 intersecting $T_{1,b}$ line below the $P/P_{2,fp}$ line are signs of maximum azeotrope.

Besides, one can also see from the plot that both conditions from eq. (18) are met, which implies a maximum flash point behavior. We can transpose the reasoning made for the n-octane – ethanol mixture to prove the extremum flash point behavior:

Maximum azeotropes are due to a negative deviation from ideality, characterized by $\gamma_1 < 1$ and $\gamma_2 < 1$. Assuming that this behavior is also present at the vicinities of the flash point temperatures of each component, one can write:

$$f_1|_{T_{1,fp}} = \frac{\gamma_1^\infty(T = T_{1,fp}) P_1^{\text{sat}}(T = T_{1,fp})}{P_{1,fp}^{\text{sat}}} = \gamma_1^\infty|_{T_{1,fp}} < 1$$

$$f_2|_{T_{2,fp}} = \frac{\gamma_2^\infty(T = T_{2,fp}) P_2^{\text{sat}}(T = T_{2,fp})}{P_{2,fp}^{\text{sat}}} = \gamma_2^\infty|_{T_{2,fp}} < 1$$

Again, since $T_{1,fp} < T_{2,fp}$ and both f_1 and f_2 are strictly increasing functions, $f_2|_{T_{2,fp}} < 1$ implies $f_2|_{T_{1,fp}} < 1$. Hence, the criterion in eq. (18) becomes: $f_1|_{T_{2,fp}} < 1$.

In our example, the gap between flash point temperatures of the pure components is quite small, so that we can state excluding particular cases where $f_1|_{T_{1,fp}} \approx 1$ (see Fig. 5):

$$f_1|_{T_{2,fp}} \approx f_1|_{T_{1,fp}} < 1$$

Here again we see the role of the small ΔT_{fp} gap on the flash point behavior of the mixture. The two remaining mixtures in Fig. 3 (1-pentanol + cyclohexanone and n-decane + n-dodecane) correspond to a non-azeotropic mixture presenting a MinFPB and a non-azeotropic mixture without an extreme flash point behavior, respectively. Table 2 summarizes the different configurations of f_1

and f_2 according to mixture behaviors.

Note that Table 2 does not have corresponding figures for two cases: MaxBP + non-extreme flash point and non-azeotropic + MaxFP. Such combinations might exist, but they are not observed in any of the 45 mixtures selected in this study (Table 3).

6.2. Analysis of literature data and proposal of a heuristic to forecast flash point extreme behavior

From the prediction of extremum behaviors by f_1 and f_2 , together with the available data for flash point and VLE diagrams in the literature, we have compiled Table 3. This table gathers results for 45 binary mixtures. The presence of azeotropes/extremum flash point regards isobaric evaluations at atmospheric pressure. All the predictions have been made based on UNIFAC Dortmund 93 model, except for the mixture of p-xylene + m-xylene, F, where Wilson model has been applied to represent that special mixture where both components have the same boiling point.

Lines A, B, C, D, ΔT_{fp} and ΔT_b report experimental observations and data. Lines “eq. (15)” and “eq. (16)” relative to predicted Min. (or Max) Boiling point, indicate whether functions f_1 and f_2 predict a minimum (maximum) azeotrope. If they do so, the field’s value is T (True). If they do not, then it is F (False). Lines “eq. (17)” and “eq. (18)” are similar to lines “eq. (15)” and “eq. (16)” but relative to flash point.

The line (“is $A \stackrel{?}{=} B$ ”) is True (T) when the mixture presents both a minimum azeotrope and a minimum flash point, or when it does not present neither a minimum azeotrope nor a minimum flash point. The same reasoning has been used for the field “is $C \stackrel{?}{=} D$ ” in with respect to maximum temperature behavior. If our assumption is valid (and so minima or maxima for boiling point and flash point are related), lines “is $A \stackrel{?}{=} B$ ” and “is $C \stackrel{?}{=} D$ ” should *a priori* be a True (T) value. When the mixture presents one minimum behavior without presenting the other (as in the case of methanol + acetone, 1-pentanol + cyclohexanone, etc.), its value is False (F) and the cell is colored in red.

The light yellow colored fields with bold font in lines “eq. (17)” and “eq. (18)” indicate that our model gives a wrong prediction of the Min. (or Max) flash point occurrence, as for the mixture phenol + cyclohexanone. The model with f_1 and f_2 works fine but there are four cases of wrong extreme flash point prediction highlighted: phenol + cyclohexanone (maximum FP not predicted), acetic acid + 1-pentanol, acetic acid + cyclohexanone and p-xylene + m-xylene (no extremum FP reported but the model predicts one). Let’s examine them.

The behavior of the mixture p-xylene + m-xylene has been predicted using the Wilson model instead of UNIFAC Dortmund 93, with parameters taken from Kato et al. [47]. A group contribution model such as UNIFAC is not suggested for this case since both compounds are described with the same organic groups and group interactions. As shown in Table 3, an extreme flash point was predicted using eq. (10) with Wilson model for the mixture p-xylene + m-xylene, with the individual flash point temperatures considered at first equal for both xylenes (Table 1). However, a closer analysis shows that the predicted minimum flash point temperature is only 0.03 °C lower than the individual flash point temperatures. Such a marginal difference might be attributed to the slight non-ideality predicted by the model in the mixture but it remains questionable. Therefore, since no experimental flash point data of p-xylene + m-xylene were reported in literature from our literature review, new experimental data tested in this study are displayed in Fig. 4. First, they do not exhibit any extreme flash point

Fig. 3. f_1 and f_2 plotted for different mixtures.

Fig. 4. Experimental flash point data for p-xylene + m-xylene with predictions based on Wilson model (dashed line) and UNIFAC Dortmund model (solid line).

behavior and we may update lines B and D in Table 3. Second, the pure component p-xylene and m-xylene FP measurements in the literature [10] (Table 1) report a value of 25 °C where we have measured 28.5 °C and 29.2 °C for p-xylene and m-xylene respectively. With these new values, the Wilson and UNIFAC-Dortmund models shown in Fig. 4 predicts no extremum flash point, and Wilson-based prediction also demonstrated nearly ideality for p-xylene + m-xylene.

For the mixtures acetic acid + 1-pentanol and acetic acid + cyclohexanone, the UNIFAC Dortmund 93 model fails to predict the non-extremum flash point behavior. Indeed, it predicts a strong positive deviation from ideal behavior for both mixtures, while the experimental data in Moghaddam et al., 2012 [38]

indicates a negative deviation. If we switch to the original UNIFAC model, we still predict a positive deviation for these mixtures but much smaller, and we do not forecast extreme flash point behavior, as shown in the Figures below. This shows the limit of the model with f_1 and f_2 that is used with a predictive activity coefficient model which extrapolation power is not absolute. One possible reason for the differences between the experimental data and the predictions is the strong association of acetic acid that takes place in the vapor phase. This phenomenon has been verified experimentally over a wide range of temperature encompassing the flash point range measured [54]. It can be described by the chemical theory by considering either dimerization only or higher order association schemes detailed in Ref. [54]. It indicates that the vapor phase deviates from its ideal behavior, and thus eqs. (3) and (4), which rely upon this hypothesis, are no longer valid. Inclusion of the dimerization is out of the present contribution.

The plots in Fig. 5 have been generated based on the Antoine coefficients available in Poling et al., 2001 [55]. The individual flash point temperatures were taken from Table 1.

Finally, the UNIFAC Dortmund 93 model fails to predict the maximum flash point behavior for the mixture phenol + cyclohexanone. This model actually predicts the mixture as being barely to exhibit MaxFPB. But, the maximum flash point can be correctly forecasted if we switch to other activity coefficient models like NRTL, Wilson or UNIQUAC [34].

From the above discussion regarding the three mixtures in Figs. 4 and 5, it is evident that predictions of extreme flash point behavior are sensitive to the individual flash point data and the activity coefficient model chosen. In order to minimize inaccuracies, the selection of the source of individual flash point data should be made carefully. Because of repeatability and reproducibility, the measured values of flash point will be different and it is suggested to take the average value. As exemplified by the xylenes mixture, it is suggested to re-test the flash point values if the flash point gap between components is small, such as less than 1 °C.

As for the activity coefficient model, models using parameters fitted on experimental VLE data should be prioritized to group-contribution methods, likely to be used when no VLE data is available. Even so, the use of the group-contribution UNIFAC Dortmund 93 model is justified in this work because we dealt with

Fig. 5. Predicted flash point temperatures using UNIFAC and UNIFAC Dortmund 93 models. Experimental data from Moghaddam et al. (2012) [38].

Fig. 6. Experimental flash point data for octane + decane.

a large number of binary mixtures and the group-contribution method made it possible to use the same model for all the mixtures.

Noorollahy et al.'s data [11] indicated that the mixture n-octane + n-decane presents a minimum flash point behavior. However, the fact that two linear hydrocarbons present such deviation from ideality surprised the authors. Therefore, the flash point data of n-octane + n-decane were re-tested. Our experimental data and the prediction curve indicated that n-octane + n-decane did not exhibit minimum flash point behavior (Fig. 6).

The fields " ΔT_{fp} " and " ΔT_b " are the absolute differences between the pure component flash point temperatures $|T_{1,fp} - T_{2,fp}|$ and the pure component boiling point temperatures $|T_{1,b} - T_{2,b}|$, respectively.

From the example in Fig. 3a, we concluded that it should be sufficient for a minimum azeotrope mixture to exhibit a small flash point gap (ΔT_{fp}) in order to guarantee a minimum flash point behavior. But how small should be this gap? Table 3 provides an answer.

The flash point gap in the mixture 1-hexanol + cyclohexanone is slightly smaller (19 °C) if compared with the n-octane + 1-butanol flash point gap (22.4 °C). Both mixtures present a minimum azeotrope. However, the second mixture presents a minimum flash point behavior, while the first one does not. To explain it, we must take into account the boiling point gap (ΔT_b) of the components, 2 °C and 8 °C, respectively.

It has been noticed that the higher is the boiling point gap, the more unlikely is for a mixture to present an azeotropic behavior [56]. Indeed, mixtures with large ΔT_b have to present very strong positive deviations from ideal mixtures in order to exhibit azeotropes. But the stronger this deviation, the more likely is that the mixture will present minimum flash point behavior, even for large ΔT_{fp} . In other words, azeotropic mixtures with large enough boiling point gaps may present minimum flash point behavior even if the flash point gaps are large.

This suggests that, instead of creating a criterion based solely on ΔT_{fp} , we should seek for one based on the ratio $\Delta T_{fp}/\Delta T_b$ (last line in Table 3). Looking again to Table 3, one can see that the three

minimum azeotropes mixtures not presenting a minimum flash point (methanol + acetone, methanol + methyl acetate and 1-hexanol + cyclohexanone) have a ratio $\Delta T_{fp}/\Delta T_b$ higher than 3. This fact reinforces the authors' idea and drives the reasoning towards an empirical criterion based on $\Delta T_{fp}/\Delta T_b$ to guarantee an extremum flash point behavior based on the azeotropic behavior.

Now, one should be careful to drive conclusion for mixtures presenting very small flash point and boiling point temperature gaps ($\Delta T_{fp} \approx 0$ and $\Delta T_b \approx 0$) since experimental errors might be of the same order or higher than the gaps themselves. This could greatly affect the computation of the ratio $\frac{\Delta T_{fp}}{\Delta T_b}$, and perhaps driving the user to a wrong conclusion.

Note that mixture 2-methyl-1-propanol + toluene is a minimum azeotrope with a large $\Delta T_{fp}/\Delta T_b$ ratio (7.556). However, experiments show this mixture presents minimum flash point behavior. Thus, it is not guaranteed that azeotropic mixtures with large $\Delta T_{fp}/\Delta T_b$ will be free from extremum flash point behavior. It seems that a large value of $\Delta T_{fp}/\Delta T_b$ is a necessary, but not sufficient, condition for a minimum azeotrope not to exhibit MinFPB.

The next question to be answered is: when a non-azeotropic mixture will present minimum flash point behavior?

We know that for a mixture to present minimum flash point, it has to have a positive deviation from ideality. However, mixtures with positive deviation from ideality shall not present azeotropic behavior if their boiling point gap is too large. So a mixture with positive deviation and high boiling point gap relative to its flash point gap (conversely a small $\Delta T_{fp}/\Delta T_b$) could present minimum flash point without presenting an azeotropic behavior. Again, the ratio $\Delta T_{fp}/\Delta T_b$ seems to be a good criterion for study.

Non-azeotropic mixtures presenting small $\Delta T_{fp}/\Delta T_b$ ratio should be experimentally tested for flash point. We cannot affirm that these mixtures will not present extremum flash point behavior, as we can see from 1-pentanol + cyclohexanone ($\frac{\Delta T_{fp}}{\Delta T_b} = 0.341$), 1-pentanol + 1,2,3,4-tetrahydronaphthalene ($\frac{\Delta T_{fp}}{\Delta T_b} = 0.308$) and 1-propanol + n-decane ($\frac{\Delta T_{fp}}{\Delta T_b} = 0.318$).

Finally, all maximum azeotropes showed in Table 3 present a maximum flash point behavior and vice-versa. The ratio between flash point and boiling point gaps for these mixtures are comprised between 0.123 and 1.325, reinforcing the idea that azeotropes with small $\Delta T_{fp}/\Delta T_b$ ratios will present extremum flash point behavior.

This said, a first empirical criterion to forecast extremum flash point behaviors is proposed here. It is based on flash point and boiling point temperature gaps, and on the azeotropic data of the mixture (Fig. 7).

6.3. Forecasting flash point behavior from heuristic: verification and limits

To confirm this criterion, we tried to forecast the flash point behavior for two different mixtures: ethyl acetate + ethanol and acetone + n-heptane. The two mixtures present minimum azeotropes. The ratios $\frac{\Delta T_{fp}}{\Delta T_b}$ value, respectively, 17.0 and 0.3 (flash points and boiling points taken from Alfa Aesar [34] database). Hence, we expect that acetone + n-heptane (small ratio) will present minimum flash point behavior, while the mixture ethyl acetate + ethanol might not do so.

The experimental flash point diagrams for these two mixtures are presented below:

Fig. 7. Heuristic for inferring extreme flash point behavior from azeotropic behavior in binary mixtures.

Fig. 8. Experimental flash point diagram for the mixture ethanol + ethyl acetate.

Fig. 9. Experimental flash point diagram for the mixture acetone + n-heptane.

In Figs. 8 and 9 the solid lines correspond to the UNIFAC Dortmund model, while the dashed lines correspond to the original UNIFAC model. The white squares represent the experimental data. Our empirical model predicts correctly the minimum flash point behavior for the acetone + n-heptane mixture. For the other mixture, the empirical criterion is not conclusive $\left(\frac{\Delta T_{fp}}{\Delta T_{eb}} > 1\right)$, and so we cannot be sure about a minimum flash point behavior.

The experiments seem to indicate that the mixture ethanol + ethyl acetate (Fig. 8) presents a slight minimum flash point. However, due to the experimental error, the data is not conclusive. This mixture could as well be one barely to exhibit MinFPB.

7. Conclusion

After gathering most of the data available in the literature for flash point of 45 binary mixtures, and comparing them with azeotropic data available for these mixtures, we can infer a concomitance between minimum/maximum flash point and minimum/maximum azeotropic behavior, at least for binary mixtures. This relation could be better understood by using the new T -dependent functions f_1 and f_2 as defined in equation (14). Indeed, f_1

and f_2 could be used to reformulate the known conditions of extremum flash point and boiling point occurrence, as done in eq. (15)–(18).

We can also state that, in general, azeotropic mixtures presenting small $\frac{\Delta T_{fp}}{\Delta T_b}$ ratios likely present minimum/maximum flash point behavior. Besides, non-azeotropic mixtures with small $\frac{\Delta T_{fp}}{\Delta T_b}$ ratios might present minimum/maximum flash point and therefore should be further tested experimentally. A limitation was found for mixtures with acetic acid, and reason may come from the well known vapor association, which is not taken into account in the model.

A first empirical criterion has been proposed to forecast extremum flash point behaviors, based solely on flash point and boiling point temperature gaps, and on the azeotropic data of the mixture. However, more data on flash point of binary mixtures is necessary to validate it more precisely.

In any case, if a suitable thermodynamic model is valid for the mixture, a thermodynamic calculation can be used to check flash point extreme behavior.

Appendix A

Fig. A1. f_1 and f_2 plotted for mixtures in Table 3.

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