



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



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ABSTRACT

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.

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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

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