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Full Length Article

Minimum flash point behavior of ternary solutions with three minimum flash point binary constituents

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ABSTRACT

The fire and explosion hazards for a mixture demonstrating minimum flash point behavior (MinFPB) are greater than for those of its individual components. Studies of MinFPB for ternary solutions are extremely rare, although such solutions are frequently encountered in real processes. A new type of MinFPB for ternary mixtures with three binary constituents showing MinFPB is reported in this study. This new type of MinFPB was observed in methyl butyrate + ethanol + octane and propyl acetate + ethanol + octane. The minimum flash point value for the two studied mixtures is not only lower than that of the individual components but was also lower than the minimum ones of the three constituent binary mixtures. Such an observation has not formerly been reported. This finding has implications for fuel design, hazard assessment, process safety design, and process safety operation.

1. Introduction

A series of fire and explosion (F&E) accidents attributed to the leakage of flammable gases or liquids occurred in the middle Taiwan from 2010 to 2012 [1]. The F&E hazards of a liquid are mainly determined by its flash point value [2]. The Shengli event in 2000 and the six explosions involving essential oils in 2003 in Taiwan highlight the importance of flash point in the storage and use of flammable liquids [3–5]. The flash point value as well as the initial boiling point are critical in determining the safety requirements for transportation of combustible or flammable liquids [6]. For liquid fuels, the safety of production, ignition, storage, and transportation are associated with flash point values. Frequently, organic compounds are added to fuels to improve the combustion performance; one such example is the addition of alcohol to biodiesel-diesel mixtures [7]. From the view-point of safety, the fuel blend's flash point is the basis to control the composition of the additives in the fuel. Thus, the flash point behavior of a fuel blend is applicable in fuel design.

The flash point of a liquid is the lowest temperature at which it emits sufficient vapor that when mixed with air, it is ignitable [2,8]. Additionally, the flash point of certain mixtures, for example, butanol + mineral spirits is lower than that of its individual components; this behavior is called minimum flash point behavior (MinFPB), which was first reported by Ellis [9]. Later, the same behavior was observed for a mixture of isobutanol + toluene [10]. Unfortunately, this finding of MinFPB was not taken seriously until the successful prediction of MinFPB for ethanol + octane was reported in 2002 [3]. After this, the MinFPB began to be frequently discussed in the literature. Mixtures showing MinFPB have greater F&E hazards than their individual components because their flash points within a particular composition range are lower than those of their individual constituents. The cause of the MinFPB is that more molecules escaping into the gas phase reduce the flash point value due to the strong repulsive interaction in solutions for highly positive non-ideal solutions [11]. Thus, the MinFPB is frequently observed in partially miscible mixtures made up of flammable compounds [1,12–16]. In addition to the previously mentioned mixtures, MinFPB is also observed at least in miscible mixtures of ethylbenzene + *n*-propanol, methanol + methyl acrylate, decane + propanol, octane + propanol or isopropanol or 2-butanol, isopropanol + toluene, and butanol + p-xylene [17–23].

In real situations, mixtures with multiple components are more applicable more often than binary mixtures, and most liquid fuels are mixtures made up of multiple components. Notwithstanding the above, research on MinFPB has almost exclusively focused on binary mixtures. A literature review has revealed that our previous two studies seem to be the only ones to discuss the MinFPB of ternary miscible solutions [18,21]. Two MinFPB types of ternary miscible solutions are reported in one of these two studies [21] describing single and two minimum flash point binary solution(s). Using the studied mixtures of the two types of MinFPB, the minimum flash point was located in the binary constituent solutions; specifically, a flash point lower than the minimum flashpoint of the binary constituents was not observed. If a ternary solution with a minimum flash point lower than those of its binary constituent solutions exists, its F&E hazards would be greater than those of its binary

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Nomenclature

A, B, C	Antoine coefficients
N	number of measurements
P_i^{sat}	saturated vapor pressure (kPa)
$P_{i,fp}^{sat}$	component i's vapor pressure at its flash point (kPa)
T	temperature (K)
x	molar fraction of liquid phase

Greek letters

ΔT_{fp}	flash point deviation
γ	activity coefficient

Subscripts

exp	experimental data
pred	predictive value

constituent solutions. In this situation, only an understanding of the MinFPB of binary mixtures is not enough. Furthermore, ternary mixtures with three minimum flash point binary constituents have never been reported. If it is possible for the minimum flash point value of such a ternary mixture to be less than those of its binary constituents, studies of the MinFPB of such ternary mixtures becomes essential.

Because we did not find any ternary mixtures with three minimum flash point binary solutions, the MinFPB of such ternary mixtures was not discussed in the previous report [21]. A model that adequately describes the flash points of multi-component mixtures can be used to help find the ternary mixtures with three minimum flash point binary constituents, analysis of their MinFPB, and in estimating their F&E hazards. Models based on the assumption of ideality [2,24–26] are not adequate for describing MinFPB because high non-ideality exists in solutions showing MinFPB. The models that describe the MinFPB must consider the solution's non-ideality. Our proposed general flash point prediction model for miscible solutions was verified for describing the flash point of ideal and non-ideal mixtures [5]. This model is reducible to the models for binary and ternary mixtures regardless of the existence of non-flammable components [3–5,27]. Phoon et al. indicated that our proposed model is the most commonly used model and more reliable than other models and recommended the use of our model in the application of real situation [28]. Liu and Liu stated that our models are the only ones that can forecast whether a mixture will exhibit the MinFPB or maximum flash point behavior, correctly [29]. The proposed model has also been applied in formulated chemical-based product design [30] and estimation of fuel flash points [31–36].

In the application of the non-ideal model to calculate mixtures' flash points, a model describing the activity coefficient is necessary. The binary interaction parameters of the activity coefficient models frequently used, such as UNIQUAC [37], Wilson [38], and NRTL [39], were regressed against the experimental data. Unfortunately, these parameters for the mixtures of interest are often unavailable. In contrast, the UNIFAC-type models do not require the experimental binary interaction parameters, and these parameters are accessible from a database. In a previous study, the general flash point prediction model [5] based on the UNIFAC-Dortmund 93 [40,41] and original UNIFAC [42,43] models was validated systematically. The model describes the flash points of the mixtures well, including those for ideal, minimum/maximum flash point solutions, and aqueous–organic solutions [44]. Moghaddam et al. [45] concluded that the prediction capability of our general model [5] is superior to other models studied, including those of Catoire et al. [46] and Wickey and Chittenden [47], when applying the UNIFAC model, after verification with one ternary and six binary mixtures of flammable solvents.

The goals of the current study were to discover the ternary mixtures with three minimum flash point binary constituents and to investigate the MinFPB of such mixtures, including verifying whether or not the minimum flash point is less than those of their binary constituents.

2. Methods and materials

2.1. Experiment

The flash points of studied mixtures were measured in a flash point analyzer (HFP 362-Tag, Walter Herzog GmbH, Germany). The instrument was designed to meet the ASTM D56 standard [48] and operate using a closed-cup method. The analyzer was operated according to ASTM D56 guidelines [48], with the detailed parameter settings and operation as described in previous studies [1,3–5,14–18,21,44]. The composition of the tested samples was determined from the mass measured with an OHAUS digital balance (PA214C: repeatability, 0.1 mg; capacity, 210 g). Before testing, a magnetic stirrer was used to stir the samples for 30 min.

Ethanol (99.9%) was sourced from J.T. Baker (Selangor Darul Ehsan, Malaysia), methyl butyrate (99%) was obtained from Sigma-Aldrich (St. Louis, MO, USA), octane (99%), from Panreac (Barcelona, Spain), and propyl acetate (99%), from Alfa Aesar (Heysham, England).

2.2. General model for miscible mixtures to predict their flash points

The general model for estimating the miscible mixtures' flash points is made up of the modified Le Chatelier equation, the Antoine equation, and either model can be used to estimate liquid phase activity coefficients [5]. This general model is reducible as follows for flammable solutions:

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

$$\log P_i^{sat} = A_i - \frac{B_i}{T + C_i} \tag{2}$$

where $P_{i,fp}^{sat}$ is component i's vapor pressure at its flash point. In this study, the activity coefficients, γ_i, were evaluated using the UNIFAC-type model.

The temperatures from the solutions of Eqs. (1) and (2), and the activity coefficient model are the mixtures' flash point.

3. Results and discussion

3.1. Necessary parameters for simulation

Because of the good prediction capability of flash points obtained by combining the UNIFAC-Dortmund and original UNIFAC models [44,45], the general model mentioned above based on the two UNIFAC-type models was applied to search for the ternary mixtures with three minimum flash point binary constituents and to analyze the MinFPB of the ternary mixtures and their binary constituents. The interaction parameters of the UNIFAC groups, group volume, and surface area were obtained from the literature [43,49]. The Antoine coefficients were sourced from Poling et al. [50].

The flash points of methyl butyrate and propyl acetate were measured, and those of ethanol and octane were obtained from a previous study [44]. Table 1 indicates that the measured flash point for methyl