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Combining mixing rules with QSPR models for pure chemicals to predict the flash points of binary organic liquid mixtures

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ABSTRACT

Flash point is a key property of liquids to evaluate the safety of industrial processes. Mixing rules are commonly used to calculate the flash point of liquid mixtures, but they need knowledge of the ones of pure compounds. Theoretical methods notably based on quantitative structure property relationships (QSPR) already exist to predict flash points of pure compounds. So, in this paper, direct combination of these two types of approaches was investigated to achieve predictions even when the flash points of pure compounds were unknown. Three relevant mixing rules and four QSPR models, based on simple constitutional descriptors, were considered. Based on a data set of 284 experimental data of binary mixtures extracted from literature, two reliable combinations were highlighted. The most accurate one reached an error in prediction of only 2.9°C but needed knowledge of the boiling point and Antoine's coefficients of each component of the mixture. A new full-predictive method was in particular proposed with also a low error in prediction (4.4°C), requiring only knowledge of the molecular structure of each pure compound and molar fraction of the mixture. Errors in each predictive method keep quite reasonable against expected accuracies of direct measurements of flash point of binary mixtures.

Keywords: flash point; mixtures; predictive approach; QSPR models

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1. INTRODUCTION

The flash point is the temperature at which the vapor above a flammable liquid ignites in air at atmosphere pressure when an ignition source is applied in specific conditions. [1] This property is a basic indicator of flammability / combustibility hazard of liquids that is also needed for risk assessment of industrial processes and in various regulatory frameworks dedicated to chemicals (for use, storage and transport) [2–4]. If a lot of data exist for pure compounds [5], efforts remain under concern to characterize and anticipate the flammability of mixtures. [6–9]

Numerous studies were carried out to predict the flash points of pure liquid compounds by quantitative structure property relationships (QSPR). [10] This approach is nowadays commonly used to predict the physico-chemical properties of chemical substances properties. [10,11] Among existing models for the flash point, only few of them used only computed molecular descriptors [12–20]. These models are more or less complex by using group contributions [19] and/or quantum chemical descriptors [16,20], based on simple multilinear equations [12,15] or artificial neural networks [16]. The others were based on the correlation of flash point with boiling point [21–23], supporting the general trend that volatile molecules, with low boiling points, present low flash points [22]. Some models used the boiling point alone, like the model of Hshieh et al. [23] or associated with simple structural parameters as proposed by Gharagheizi [24] or Carroll [25]. Recent models also considered the introduction of calculated boiling points, as in the model of Rowley et al. [19].

Some attempts were targeting the development of QSPR models dedicated to liquid mixtures [26] but mixing rules are more commonly used. Indeed, several mixing rules were developed over the years to determine the flash point of mixtures from those of the pure compounds. [27–33] Some of them were empirical, like the method of Wickey [27] who introduced flash point indices (based on the assumption of the additivity of vapor pressures of each constituent at their own flash point). Others, like the one of Affens [28], relied on the search of the temperature at which the concentration in vapor above the liquid surface reached the lower flammability limit of the gas mixture. But these two methods do not take in account intermolecular interactions involved between the different components of the mixture that can have important influence on the liquid-vapor equilibrium and, as a consequence, on the estimation of flash points.

Indeed, a deviation from an ideal mixing behavior (i.e. without significant net intermolecular interaction between compounds) was observed in the flash point profiles of numerous mixtures of organic solvents as a function of concentration. [32] In particular, non-ideal mixtures, exhibiting a strong net attraction between the individual components, can exhibit a flash point higher than the ones of the individual components in a certain range of molar fraction. [34] On the contrary, the others, exhibiting a strong net repulsion between the individual components, within a certain composition range, can exhibit a flash point below the flash points of the individual components. [35] In such cases, considering the lower flash point of the two pure compounds could be hazardous in process safety if it would lead to underestimate the flammability of the mixture.

To overcome such failures, improved mixing rules including intermolecular interactions through activity coefficients were proposed notably by Walsham [29] or Thorne [30]. Various estimation methods can be used to calculate the activity coefficients, based on excess Gibbs energy, such as the methods of Wilson [36], Non-Random Two Liquids [37] (NRTL), UNiVersal QUAsiChemical [38] (UNIQUAC), or UNIQUAC Functional-group Activity-Coefficients [39] (UNIFAC). Liaw *et al.* successfully applied such an approach for various mixtures of flammable compounds [32–34,40,41].

Partial miscibility, i.e. the tendency of the mixture to form separated phases, also influences the flash point of a mixture. Indeed, binary mixtures presenting partial miscibility behaviors present the same flash point within the partial miscibility range of concentrations [42]. In fact, within this range of concentrations, the ratio of respective volumes of the two liquid phases is changed, but not the respective concentrations of each constituent in both liquid phases (in respect to the liquid-liquid equilibria). Indeed, the liquid-liquid-vapor equilibrium (and as a consequence the vapor concentration) keeps unchanged [43]. So, the flash point remains the same. Khalili *et al.* [33] included a procedure, developed by Rachford and Rice [44], to estimate the influence of partial miscibility on the flash point within the algorithm of Liaw [32].

If these approaches proved to reach high reliability [32–34,40,41], their use are bound to the knowledge of the flash points of the individual pure compounds involved in the mixture. To overcome this issue, Saldana *et al.* [26] recently proposed an entirely predictive thermodynamic approach based on a modified Liaw mixing rule, in which three properties of pure compounds (flash point, boiling point and vaporization enthalpy) were calculated from

QSPR models developed using Support Vector Machine (SVM). If this model demonstrated good accuracy with a mean absolute error (MAE) of 3.4°C, the aim of the present study was to simplify this approach by introducing existing linear QSPR models (compared to the more complex SVM models) for the flash point of pure compounds in an existing mixing rule for a large series of organic flammable binary mixtures, targeting at least similar accuracy.

2. MATERIALS AND METHODS

2.1. Experimental data

The measure of flash point (T_{FP}) is apparatus-dependent, leading to different results[45], in particular between closed cup and open cup apparatus. [1] Indeed, in open cups, vapors are exchanged with surrounding, leading in general to higher values than in closed cups (as illustrated in table 1). [1]

For this study, 284 data (given in Supporting Information, table S1) were extracted from the works of Liaw *et al.* [34,42,46–48] for organic binary mixtures of flammable solvents. These measurements were all performed with a same apparatus (HFP 362-Tag, Walter Herzog GmbH, Germany) according to the ASTM D 56 standard [49], which is listed amongst of the standards recommended by the REACH regulation [3].

In this standard, dedicated to liquids exhibiting viscosities lower than 5.5 mm²/s and for flash points lower than 93°C, measurements are carried out with a Tag Closed Cup apparatus. A 50 mL sample is heated at a rate of 1°C/min, if the flash point is expected below 60°C, or 3°C/min, otherwise. Starting from 5°C below the expected flash point, a flame is presented above the surface of the liquid, every 0.5°C of temperature rising if the flash point is expected below 60°C, every 1°C otherwise. The flash point is taken as the temperature at which a first flash is observed. The expected repeatability for this procedure is of 4.3°C and reproducibility is of 5.8°C. [49]

The 284 gathered experimental data covered 22 mixtures, and 21 pure compounds. This database contains Hydrocarbon/Alcohol mixtures (150 data, 7 mixtures) that generally exhibit strong positive deviations from ideality, which corresponds to repulsive net interactions between the components of the mixture. Alcohol/Alcohol (5 mixtures), Alcohol/Ketone (3 mixtures), Hydrocarbon/Hydrocarbon (2 mixtures) combinations, exhibiting more ideal behavior in mixtures, are also significantly represented in the database. The last 5 mixtures are diverse in composition and behavior. Three of these contain esters (2 Alcohol/Ester, 1

Ester/Ester), one is a Ketone/Hydrocarbon mixture, and one is a Heteroaromatic/Alcohol mixture. Finally, among the 22 mixtures of the dataset, 8 follow nearly ideal profiles.

The range of flash points covered by this experimental dataset covers a window from -19.9°C to 112°C, i.e. all categories of flammable liquids in the GHS regulation [2] from extremely and highly flammable liquids (with FP < 23°C) to not classified liquids (with FP > 93°C).

2.2. Mixing rules

A mixing rule is an equation or an algorithm used to predict the property of a mixture from the properties of its individual components. As already explained, several mixing rules were developed by years to estimate the flash point of mixtures. Among them, the mixing rule of Wickey [27] is the simplest one, based on empirical flash point indices. The one of Affens [28] introduced a thermodynamic scheme relying on estimating the temperature at which the concentration in vapor above the liquid surface reached the lower flammability limit of the gas mixture. At last, the mixing rule of Liaw [32] represent the most recent one including the introduction of activity coefficients and of partial miscibility (through the Rachford-Rice Procedure [44]).

a) Mixing rule of Wickey

The Wickey equation [27] was developed to estimate flash points of petroleum blends. This empirical approach relied on the assumption that the vapor pressures of each component at the flash point $P_{satFP,i}$ (called flash point index) contributes linearly to the flash point index of the mixture $P_{satFP,mix}$ [50].

$$P_{satFP,mix} = \sum_i x_i P_{satFP,i} \quad (1)$$

where x_i is the molar fraction of the component i .

The vapor pressures were calculated using the Antoine's relation (in eq. 2).

$$\log P_{sat,i} = A_i - \frac{B_i}{T+C_i} \quad (2)$$

Where $P_{sat,i}$ represents the vapor pressure, T is the temperature and A_i , B_i and C_i are Antoine's coefficients for the component i . An empirical set of Antoine's coefficients was proposed for all petroleum blends: $A_{mix} = 6.1188$, $B_{mix} = 4345.2$ and $C_{mix} = 383$.

Finally, the flash point of the mixture T_{FP} is computed following eq. 3.

$$\frac{B_{mix}}{\log(\sum_{i=1}^n x_i P_{satFP,i}) + A_{mix}} - C_{mix} = T_{FP} (^{\circ}F) \quad (3)$$

A MAE in prediction of 6°F, i.e. 3.3°C, can be estimated from the set of 162 fuel blends tested by Wickey [27]. This equation was also tested by Moghaddam *et al.* [41] for quasi-ideal mixtures (acetic acid/1-pentanol, 1-pentanol/1-hexanol, acetic acid/1-hexanol, acetic acid/cyclohexanone, 1-pentanol/cyclohexanone, acetic acid/1-hexanol/cyclohexanone). If good profiles were obtained for binary mixtures, it was not the case for the ternary mixtures. The same equation was also used by Khalili *et al.* [33] for a quasi-ideal mixture (1-pentanol/cyclohexanone) and for a strongly non-ideal one (1-pentanol/1,2,3,4-tetrahydronaphtalene) with 1.7°C and 6.5°C in MAE, respectively, indicating that, if this equation succeeded for ideal mixtures, it issued to less accurate predictions when mixtures deviated from ideal behaviors.

b) Mixing rule of Affens

The mixing rule of Affens [28] was also developed for predicting the flammability of petroleum blends. The gas mixtures were considered to behave as an ideal gas. The model was based on a combination of the Raoult's law (eq. 4), to estimate the vapor pressures of the gas mixtures, the law of Le Chatelier, to introduce the vapor pressures at flash point (in eq. 5), and the Antoine's relation (eq. 2), to relate vapor pressures to temperatures.

$$P_{sat,mix} = \sum_i x_i P_{sat,i} \quad (4)$$

$$P_{satFP,mix} = \frac{1}{\sum_i \frac{x_i}{P_{satFP,i}}} \quad (5)$$

where $P_{sat,i}$ and $P_{sat,mix}$ are the vapor pressures of component i and of the mixture at a given temperature T and x_i is the molar fraction of the component i .

Finally, the mixing rule of Affens is summarized in eq. 6 where the C coefficient of Antoine's equation for the mixture was arbitrary fixed at $C_{mix} = 230$.

$$\sum_{i=1}^n \frac{x_i 10^{a(1642-\theta_i)}}{(1642-\theta_{mix})} = 1 \quad (6)$$

with:

$$a = -B_i \frac{\theta_i - \theta_m}{\theta_i \theta_m}$$

$$\theta_i = T_{FP,i} + C_i$$

$$\theta_{mix} = T_{FP} + C_{mix}$$

For the 8 hydrocarbon mixtures tested by Affens [28], a MAE of 0.9°C was calculated. This procedure was also tested by Liaw et al. [51] for 55 data on 4 mixtures. It demonstrated it as convenient for ideal mixtures (like n-octane/n-heptane), but not for non-ideal mixtures (like methanol/ethyl acetate and n-octane/1-butanol mixtures), due to the fact that it did not take into account the intermolecular interactions within mixtures. In particular, the Affens mixing rule was unable to predict flash points below the flash point of both components, in the case of n-octane/ethanol mixture. [51]

c) Mixing rule of Liaw

More recently, Liaw *et al.* [32] proposed a computational procedure to use the condition of Wu [31] (in eq. 7) for the prediction the flash point of mixtures.

$$\sum_{i=1}^n \frac{x_i \gamma_i(x, T_{FP}) P_{sat,i}(T_{FP})}{P_{sat,FP,i}} = 1 \quad (7)$$

where γ_i is the activity coefficient of component i at the flash point of the mixture T_{FP} , $P_{sat,i}(T_{FP})$ is the vapor pressure of component i at the mixture flash point T_{FP} , $P_{sat,FP,i}$ is the vapor pressure of component i at its flash point.

This condition of Wu was based on both the Le Chatelier's mixing rule (eq. 5) and the extended Raoult's law that takes into account the interaction between compounds through the activity coefficient γ_i (eq. 8).

$$P_{sat,mix} = \sum_i x_i \gamma_i P_{sat,i} \quad (8)$$

Within the approach of Liaw, the vapor pressures are calculated using the equation of Antoine (already given in eq. 3). Various estimation methods were used by Liaw et al. to calculate the activity coefficients (e.g. NRTL, UNIQUAC, UNIFAC) [48,51]. The Liaw algorithm demonstrated good performances for a large diversity of mixtures including non-linear profiles [48], like ethanol / 1-butanol with a MAE of 0.1°C or octane / ethanol with a MAE of 0.6 °C.

In the present study, the mixing rule of Liaw (summarized in figure 1) was implemented into a C++ program. The coefficients of the Antoine's relation were extracted from the Yaw's database [52] and the UNIFAC [39] method was used to calculate the activity coefficients. This last approach is a group-contribution method arising from the UNIQUAC approach [53], which estimates the activity coefficients from the excess Gibbs energy of the mixture as a

function of the composition. [38] Here, the UNIFAC group-contributions proposed by Gmehling et al. [54,55] were used.

It has to be noticed that, in their work, Saldana et al. [26] adapted this method by calculating the vapor pressures as a function of the boiling point and of the enthalpy of vaporization using the Clausius Clapeyron relation. To avoid the introduction of these experimental properties of the pure compounds, this last option was not chosen in the present study and the Antoine's equation (Eq. 2) was used to calculate the vapor pressure, as in the original works of Liaw.

In addition, to take into account possible partial miscibility, the Rachford-Rice (RR) procedure [44] was here used to calculate the phase fractions of multiphase systems from the liquid-liquid equilibria [56] at each step of the Liaw algorithm. The studied system was considered to form a biphasic liquid if a realistic phase fraction was obtained, i.e. between 0 and 1, and the mixture's flash point was then calculated as the one of the phase presenting the lowest flash point, since such assumption was estimated as relevant by Liaw [57] and Khalili [33]. The studied system was considered to form a biphasic liquid if a realistic phase fraction was obtained, i.e. between 0 and 1, and the mixture's flash point was then calculated as the one of the phase presenting the lowest flash point. Otherwise, the liquid system was considered monophasic. This procedure was already used successfully by Khalili *et al.* [33] for three partially miscible mixtures (1-pentanol/1,2,3,4-tetrahydronaphtalene, cyclohexanone/water and 1-pentanol/water).

2.3. QSPR models for pure compounds

Numerous QSPR models have been developed to predict the flash point of pure organic compounds [58,59]. In this work, four of them were chosen because they use simple equations including the normal boiling point and/or simple structural parameters that can be easily obtained from the 2D-structure of molecules. Moreover, they showed wide applicability domains (including the whole diversity of organic compounds) with a good accuracy (with mean absolute errors in prediction between 2.5°C to 11.7°C).

The first tested model was developed by Hshieh [23] in 1997. It consists in a simple quadratic correlation with the boiling point (T_b).

$$T_{FP}(^{\circ}C) = -54.5377 + 0.5883T_b + 0.00022T_b^2 \quad (11)$$

This correlation was developed for 494 organic and organosilicone derivatives with a MAE of 11.7°C.

In 2010, Rowley [19] developed another model for more than 1000 organic compounds, based on the Clausius-Clapeyron equation [60,61] and a group-contribution term to address the boiling point with an average absolute deviation of 2.84%.

For all compounds but alcohols, the flash point was calculated according to eq. 12. This equation was adapted for alcohols (in eq. 13) by considering that those chemicals present different entropies of vaporization.

$$T_{FP}(^{\circ}C) = \frac{\sum_i n_i g_i - 510.49}{2.13 \ln(8\beta) + 1} + 235.21 \quad (12)$$

$$T_{FP}(^{\circ}C) = \frac{\sum_i n_i g_i - 208.30}{2.40 \ln(8\beta) + 1} + 196.68 \quad (13)$$

where g_i are group contributions, n_i are counts of each group in the molecule and β is a stoichiometric parameter calculated from the chemical formula $C_xH_yO_zN_wS_vX_uSi_t$ using eq. 14.

$$\beta = x + \frac{y-u}{4} + v + t + \frac{z}{2} \quad (14)$$

The third model used was developed by Gharagheizi [24] in 2011 based on a set of 1471 organic compounds from 77 different chemical families (alkanes, alcohols, amines, etc.). It consists in a linear regression with the boiling point to take into account the volatility of chemical compounds, and the number of carbon atoms n_C , as an indicator of the flammable potential of compounds.

$$T_{FP}(^{\circ}C) = -18.44 + 0.8493T_b - 3.723n_C \quad (15)$$

A MAE of 8.1°C was exhibited over the large set of chemical compounds included into the training set of this model.

The last model was developed by Carroll [25] in 2011 based on 1000 organic compounds considering a boiling point number (Y_{BP}) and a flash point number (N_{FP}) that were previously introduced to find correlations with molecular structure [62,63].

$$T_{FP}(K) = N_{FP}^{2/3} + N_{FP}^{1/3} + 31.901 \quad (16)$$

with $N_{FP} = 0.095 + 0.974Y_{BP} + \sum_i n_i g_i$

and $Y_{BP} = \left[\frac{337.38 + \sqrt{113825.2644 + 67.2(-437.88 - T_b)}}{-33.60} \right]^3$

For this model, a high reliability was demonstrated with a MAE of 2.5°C for the 1000 compounds of its training set.

For the present study, all experimental boiling points were extracted from the work of Gharagheizi et al. [24] that collected these data from the DIPPR 801 database. [5]

3. RESULTS AND DISCUSSION

The aim of the present work was to demonstrate the potential offered by the simple combination approach of mixing rules and QSPR models for the flash point of pure chemicals to predict the flash point of mixtures of flammable compounds. After the study of the three mixing rules of Wickey, Affens and Liaw, the combination with the QSPR models of Hshieh, Rowley, Gharagheizi and Carroll was investigated.

3.1 Application of mixing rules

In a first step, the mixing rules of Wickey, Affens and Liaw were applied to predict the 284 flash points of mixtures of the database by using the experimental values of flash points for pure compounds extracted from the work of Gharagheizi et al. [24]

As shown in table 2, the best performances were obtained for the mixing rule of Liaw with a MAE of 0.9°C compared to the ones of Wickey and Affens with MAEs of 7.2°C and 7.4°C, respectively. These results highlighted the importance of taking into account the intermolecular interactions within the liquid phase and the partial miscibility, as actually implemented in the mixing rule of Liaw.

Indeed, for the rules of Wickey and Affens, large differences in errors were observed between the different types of mixtures represented into the dataset. The mixtures following ideal behaviors, i.e. with low interaction between compounds into the liquid phase (characterized by activity coefficients close to 1), exhibited good correlations between experimental and calculated values (with MAE = 0.7°C and 0.6°C for the Wickey and Affens rules, respectively). By contrast, the correlations for non-ideal mixtures were much poorer (with MAE's of 9°C and 10.6°C). For the mixing rule of Liaw, the results were accurate for both the ideal and non-ideal mixtures with MAE in prediction of 0.3°C and 1.4°C, respectively.

For instance, figure 2 represents the 1-butanol/2-butanol mixture which follows an ideal behavior, characterized by UNIFAC activity coefficients close to 1 (e.g., for the 1-butanol and the 2-butanol, of 1.003 and 1.001, respectively, in a 30%/70% mixture, or of 1.001 and 1.002 in a 60%/40% mixture). In this case, the three mixing rules appeared as efficient with MAE of 0.6°C, 0.4°C and 0.3°C for the rules of Wickey, Affens and Liaw, respectively.

It was no more the case for non-ideal mixtures. Figure 3 illustrates the particular case of mixtures presenting a minimum flash point behavior, i.e. for which the flash point of the mixture is lower than those of the individual components at intermediary concentrations. Indeed, the flash points of the n-octane/ethanol mixtures were lower than the flash points of both n-octane (13°C) and ethanol (14.5°C). In this case, only the rule of Liaw offered satisfying predictions with MAE = 0.5°C whereas the rules of Wickey and Affens yielded larger errors (MAE = 6.4°C and 6.2°C, respectively). Six out of the 22 studied mixtures exhibited such minimum flash point profiles.

In particular, it could be noticed that the largest errors in prediction were exhibited for strongly non-ideal mixtures presenting a large difference between the flash points of the two pure compounds, like the ethanol/n-tetradecane mixture profile in figure 4. The most important errors were observed for the lowest molar fractions of ethanol (from 0 to 0.2). At these levels of concentration, the flash point decrease strongly with concentration. So, experimental uncertainty within this range can be estimated as increased since small uncertainty on the composition of the mixture results in an important deviation on the flash point. However, even for ethanol/n-tetradecane from molar fractions of 0 to 0.2, the algorithm of Liaw yielded once again the best results (with MAE = 2.3°C, vs. 24.8°C and 25.6°C for the rules of Wickey and Affens, respectively), due to its ability to take charge of both the non-ideality of the mixture and its partial miscibility for a large part of the profile. Indeed, the Rachford-Rice procedure, based on the UNIFAC activity coefficients, predicted a partial-miscibility range from an ethanol molar fraction range of 0.1 to 0.97, in reasonable agreement with the experimental measurements of Liaw et al. [42], as can be seen in figure 4. So, this mixing rule was selected to be combined with the QSPR models in the second part of the study.

3.2. Combination of a mixing rule and QSPR models

In a second step, a combined approach was proposed consisting in coupling the mixing rule of Liaw, which reached the most accurate predictions, with available QSPR models for the

estimation of the flash points of the pure compounds. Such combination allows the prediction of the flash points of mixtures without knowledge of the flash points of the involved pure compounds.

The flash points of the pure compounds constituting the mixtures of the database were calculated from the four selected QSPR models of Hshieh [23], Rowley [19], Gharagheizi [24] and Carroll [25]. The capabilities in prediction for pure compounds ranged from MAE = 10.2°C for the model of Hshieh to MAE = 3.9°C for the model of Carroll, for the 21 pure compounds of the dataset (as summarized in table 3).

The results obtained with the algorithm of Liaw combined with these four models are shown in table 4. In these combinations, the flash points of the pure compounds were calculated and introduced in the mixing rule of Liaw to predict the 284 flash points of mixtures of the database. The model of Carroll gave the best predictions with a MAE of 2.9°C, followed by the ones of Rowley, Gharagheizi and Hshieh with mean absolute errors of 4.3°C, 7.5°C, and 10.1°C, respectively.

It has to be noticed that the prediction accuracy obtained for mixtures was similar to the one for the pure compounds, thus suggesting that the quality of the predictions was mostly limited by the reliability of the QSPR models. For instance, the errors obtained for each mixture with the combination of the Liaw mixing rule with the model of Carroll were compared in table 5 with the errors obtained for the individual compounds using the model of Carroll. The largest errors obtained for mixtures (in particular those higher than 5°C) corresponded to mixtures for which at least one of the involved compounds presented large errors with the Carroll model. For instance, the predictions for the methanol/n-decane mixture presented a MAE of 5.5°C with the experimental data, while the absolute errors for the pure compounds were of 5.8°C and 9.8°C, respectively. On the opposite, good predictions were obtained when the flash points of the pure compounds were accurately predicted like for the methyl acetate / methyl acrylate mixtures. Indeed, the flash points of each compound were accurately predicted with errors of only 0.9°C and 0.3°C, respectively, and the MAE for the mixtures of these two compounds was of 0.6°C. Similarly, the ethanol/2-butanol mixture was predicted with a MAE of 1.0°C, while the absolute errors for the pure compounds were 1.6°C and 1.1°C, respectively.

It has also to be noticed that the accuracy of the predictions for the pure components also influenced the reproducibility of the shape of the flash point profiles. Indeed, when the flash

points of the pure components were well predicted, the profile was well reproduced. For instance, in figure 5 for the n-Octane/Ethanol mixture, the shape of the profile was well reproduced by the models of Carroll and Rowley whereas the models of Gharagheizi and Hshieh proposed bad shape due to the important error of prediction for pure ethanol.

If the Carroll-Liaw combination led to the best predictions with MAE = 2.9°C (see table 4), the Rowley-Liaw combination was also accurate with a MAE of 4.3°C and presented the advantage of needing no experimental boiling point. But this last combination also needs the knowledge of the Antoine's coefficients within the algorithm of Liaw to determine the vapor pressures. So, to access a full predictive model, averaged Antoine's coefficient values over 700 diverse organic components of the Yaws database [52] ($A_{\text{avg}}=6.8713$, $B_{\text{avg}}=1417.23$ and $C_{\text{avg}}=206.234$) were introduced in the Rowley-Liaw combination. This approach was analogous to the one proposed by Wickey [27], which proposed fixed Antoine coefficients for all petroleum blends. Using this method, no decrease in accuracy was observed with the Rowley's model with a MAE of 4.4°C without requiring the knowledge of the Antoine's coefficients (cf. figure 6). The predictions issued from these two approaches for the 284 flash point of mixtures of the dataset are given in Supporting Information (Table S1).

These two new predictive methods (the Carroll-Liaw and the full predictive Rowley-Liaw combinations) were then assessed on experimental data issued from other sources, i.e. by other laboratories than the one of Liaw. 51 new data were extracted from the works of Hristova et al. [64] and Carareto et al. [8], representing 7 new mixtures and 7 new components (see table S2). The mean absolute errors obtained remained good with MAE of 4.2°C for the mixing rule of Liaw, of 6.0°C for the Carroll-Liaw combination and 4.0°C for the full predictive method. It nevertheless has to be noticed that slightly larger deviations are observed for the mixture of Carareto et al. [8] involving long chain esters (with MAE up to 13.2°C) that are subject to the same failure of the ethanol / tetradecane mixture presented in Figure 4 with a strong deviation to ideality within a small range of concentration (between 0 and 0.05 in molar fraction of ethanol). On the contrary, the flash points of the hydrocarbon mixtures studied by Hristova et al. [64] were well predicted, with MAEs of 1.7°C, 3.5°C and 4.5°C for the Liaw mixing rule, the Carroll / Liaw combination, and the full predictive method, respectively.

At last, the two combined methods demonstrated good performances for the various types of tested mixtures (ideal and non-ideal), as illustrated by different following examples.

For instance, figure 7 illustrates the profile of an ideal mixture, like ethanol/1-butanol. In such ideal mixtures, the net attraction or repulsion between the components is low. This results in a slightly curvy shape in the flash point versus concentration graph, which is characteristic of ideal mixtures (ideal profile). This profile was well reproduced, with MAEs of 2.1°C and 4.5°C for both the Carroll-Liaw combination and the full predictive method, respectively.

Mixtures with positive deviation to ideality (11 mixtures out of 22) were also tested. In such mixtures, compounds have a low affinity. Therefore, there is a net repulsion between the components of the mixtures. When the flash point of both components have similar values and the net repulsion is strong, the mixtures may be characterised by a U-shaped profile of the flash point versus concentration graph. These mixtures are particularly hazardous because they exhibit a flash point below the ones of both pure components. In figure 8, U-shaped profile of the n-octane / iso-propanol mixtures was well reproduced by both of the selected combinations, with MAE's of 3.6°C and 2.5°C for the Carroll-Liaw combination and for the full-predictive model, respectively.

When the flash points of both components are largely different and the net repulsion is strong, the mixtures may be characterized by a L-shaped profile of the flash point versus concentration graph. A mixture of a small amount of the most flammable compound with a great amount of the least flammable one can exhibit a much lower flash point than the one of the least flammable compound. Thus, this type of mixtures also represents a special hazard. Figure 9 (ethanol/n-tetradecane mixture) illustrates that L-shaped profile was correctly represented, with MAE's of 3.1°C and 7.1°C for Carroll-Liaw combination and full-predictive model, respectively.

When the net repulsion is moderate, the profile between the flash point and concentration may follow a quadratic-like curve as illustrated in figure 10 for the methanol / methyl acrylate mixture. In contrast to mixtures characterized by U-shaped and L-shaped profiles, mixtures exhibiting quadratic-like profiles contain miscible components. For methanol / methyl acrylate, it can be seen that both the Carroll / Liaw combination and the full-predictive method offered accurate predictions (with MAE's of 2.4°C and 1.4°C, respectively) and reproduced the quadratic profile.

From the studied database, no profile with strong negative deviation to ideality can be drawn to compare experimental and predicted profiles since at best three points are available for such a mixture. Liaw et al. [34] studied 6 mixtures which exhibited negative deviations to

ideality but data were only provided graphically. For this reason, they were not included in the data set. Nevertheless, these last profiles can be used to assess the capability of the proposed methods on mixtures exhibiting negative deviation to ideality. As shown in table 5, predictions revealed more difficult for these profiles. For instance, a MAE of 14.0°C and 15.5°C is obtained for the p-picoline/phenol mixture for the Carroll-Liaw and the full predictive Rowley-Liaw methods, respectively. Nevertheless, as illustrated in figure 11, both methods shown the negative deviation to ideality but this deviation is lowered due to the absence of important published UNIFAC interaction parameters (for the pyridine-aromatic carbon interaction) for the calculation of liquid-vapor equilibrium in the Liaw algorithm. Besides, the application of the Liaw algorithm on experimental flash points revealed same failure (as illustrated in Figure 11). Moreover, when the UNIFAC interaction parameters are available, the Liaw algorithm succeeds and only the quality of prediction of the QSPR model for the pure compounds guides the reliability of predictions by the combined approaches for the mixtures, as in the case of the phenol / acetophenone mixture (in Figure 12). The best results are obtained for the mixture which is the closest to ideality, i.e. the propanal/2-butanone mixture (with MAEs of 1.3K and 3.3K).

From a general point of view, the performances of the two new predictive methods are in line with the full predictive model of Saldana presenting a MAE of 3.4°C for a similar database size (287 vs. 284 mixtures in our study) notably issued from the same references than the ones used here. To compare these last two methods, it has to be noticed that our new full predictive method requires the implementation of the Liaw algorithm, as done here in a C++ program, in which the only input parameter, the flash points of the pure compounds, is issued from a group-contribution based QSPR model that can be simply used on an excel datasheet. On the contrary, the input parameters of Saldana's model [26] (flash point, heat of vaporization and boiling point of the pure compounds) also require the implementation of the three more complex SVM models.

At last, the prediction errors obtained with the two new models (2.9°C and 4.4°C) were significantly low considering the level of accuracy that can be expected from experimental measurements with reproducibility of 4.3°C under 60°C (and 5.8°C below 60°C) according to the ASTM D56 standard [49]. So, predictions remain into these last levels of confidence.

4. CONCLUSION

In this work, a computational approach was proposed to predict the flash points of binary mixtures of organic liquids by combining existing mixing rules with existing QSPR models for the prediction of the flash points of the pure compounds.

Three mixing rules (developed by Wickey, Affens and Liaw) were compared on an extended set of 284 experimental data for binary mixtures. The mixing rule of Liaw yielded the most accurate predictions (MAE = 0.9°C) using experimental flash points of the pure compounds, due to its capacity to take into account the activity of the components, calculated by the UNIFAC approach.

This mixing rule was combined with four QSPR models to analyze the possibility of using predicted values of flash points for the pure compounds in the case of unavailability of these data. Finally, two new accurate methods are proposed to predict the flash point of liquid mixtures. When experimental boiling points and Antoine's coefficients are available, the Carroll-Liaw combination is the most suitable since it yielded to the best performances with a MAE of 2.9°C (in table 4). If the Antoine's coefficients and/or boiling points are not available, the Rowley-Liaw model using the proposed averaged Antoine's coefficient (full predictive method) values constitutes a reliable alternative (with MAE = 4.4°C), as can be seen in figure 6.

These two approaches allow reliable predictions for the flash point of mixtures when the flash points of individual pure compounds are unknown. In particular, the prediction does not induce significant errors as compared to expectable accuracy of direct measurements of flash points. The full predictive approach can give access to the flash point of mixtures constituted by compounds that are even not synthesized, for instance within a screening process at R&D level.

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NOMENCLATURE

Acronyms

MAE:	Mean Absolute Error
NRTL:	Non-Random Two Liquids
QSPR:	Quantitative Structure-Property Relationship
REACH:	Registration, Evaluation, Authorisation and Restriction of Chemicals
RR:	Rachford-Rice
SVM:	Support Vector Machine
UNIFAC:	UNIQUAC Functional-group Activity-Coefficients
UNIQUAC:	UNIversal QUAsiChemical

Variables

A_i, B_i, C_i :	Antoine's coefficients
g_i :	group contribution
nC :	number of carbon atoms
N_{FP} :	Flash point number
$P_{sat,i}$:	Vapor pressure of the component i
$P_{sat,mix}$:	Vapor pressure of the mixture
$P_{sat,FP,i}$:	Vapor pressure of the component i at its flash point
$P_{sat,FP,mix}$:	Vapor pressure of the mixture at its flash point
T_b :	Boiling point
T_{FP} :	Flash point
$T_{FP,i}$:	Flash Point of component i
$T_{FP,mix}$:	Flash Point of the mixture
x_i :	Mole fraction of the component i in the liquid phase
Y_{BP} :	Boiling point number

Greek letters

γ_i :	Activity coefficient of the component i
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Table 1 – Comparison of open and closed cup flash points for various chemicals (°C) [65]

	closed cup	open cup
toluene	4	7
n-hexanol	45	74
methanol	12	16
ethanol	13	22
formaldehyde (30% in water)	54	93
acetone	-18	-9
acetic acid	40	57
methyl butyl ketone	23	24
aniline	76	91

Table 2 - Performances of the various mixing rules for 284 flash points of liquid mixtures

	All mixtures		Ideal mixtures		Non-ideal mixtures	
	R ²	MAE (°C)	R ²	MAE (°C)	R ²	MAE (°C)
Wickey	0.78	7.2	0.998	0.7	0.73	9.0
Affens	0.71	7.4	0.997	0.6	0.64	10.6
Liaw	0.99	0.9	0.99	0.3	0.98	1.4

Table 3 – Performances of the tested QSPR models for pure compounds

	R ²	MAE (°C)
Hshieh	0.89	10.2
Gharagheizi	0.96	7.0
Rowley	0.97	5.7
Carroll	0.99	3.9

Table 4 – Performances of the various combinations of the algorithm of Liaw with QSPR models

	R ²	MAE (°C)
Hshieh	0.72	10.1
Gharagheizi	0.87	7.5
Rowley (full predictive)	0.91	4.4
Rowley	0.91	4.3
Carroll	0.98	2.9
experimental	0.99	0.9

Table 5 – Mean absolute errors (in °C) for binary mixtures using the two selected combinations

mixtures ^a		Carrol-Liaw			Rowley-Liaw (full predictive)		
compound 1	compound 2	pure compound 1	pure compound 2	mixture	pure compound 1	pure compound 2	mixture
1-Butanol	2-Butanol	3.5	1.1	0.9	0.6	1.9	1.1
Methyl Acetate	Methyl Acrylate	0.9	0.3	0.6	2.0	3.1	2.2
Acetone	n-Decane	0.3	9.8	2.2	2.7	9.6	4.5
iso-Amyl Alcohol	iso-Amyl Acetate	3.4	4.5	4.2	10.9	8.6	10.4
Ethanol	1-Butanol	1.6	3.5	2.1	7.4	0.6	4.5
Ethanol	2-Butanol	1.6	1.1	1.0	7.4	1.9	4.6
Ethanol	n-Tetradecane	1.6	8.9	3.1	7.4	8.8	7.1
Methanol	iso-Octane	5.8	1.4	1.8	10.2	5.7	6.5
Methanol	Acetone	5.8	0.3	1.2	10.2	2.7	3.3
Methanol	Methyl Acrylate	5.8	0.3	2.4	10.2	3.1	1.4
Methanol	n-Decane	5.8	9.8	5.5	10.2	9.6	8.4
Methanol	n-Octane	5.8	4.8	5.1	10.2	4.3	3.6
n-Octane	1-Butanol	4.8	3.5	4.5	4.3	0.6	4.5
n-Octane	2-Butanol	4.8	1.1	3.0	4.3	1.9	2.6
n-Octane	Ethanol	4.8	1.6	3.5	4.3	7.4	1.9
n-Octane	n-Heptane	4.8	2.0	3.0	4.3	1.6	3.3
n-Octane	i-Propanol	4.8	0.6	3.6	4.3	1.3	2.5
^b Cyclohexanol	Phenol	8.6	6.0	16.8	10.8	2.6	10.3
^b Cyclohexanone	Phenol	5.9	10.8	12.3	3.8	2.6	8.6
^b Cyclohexylamine	Cyclohexanol	12.1	8.6	6.4	13.0	6.0	7.1
^b Phenol	Acetophenone	10.8	2.5	8.3	2.6	17.7	8.2
^b p-Picoline	Phenol	4.2	10.8	14.0	8.9	2.6	15.5
^b Propanal	2-Butanone	1.6	0.1	1.3	7.8	1.4	3.3

^a mixtures represented by at least nine data within the database ; ^b mixtures issued from graphics available in ref. 34 not included in the database

Figure 1 – General scheme of the algorithm of Liaw

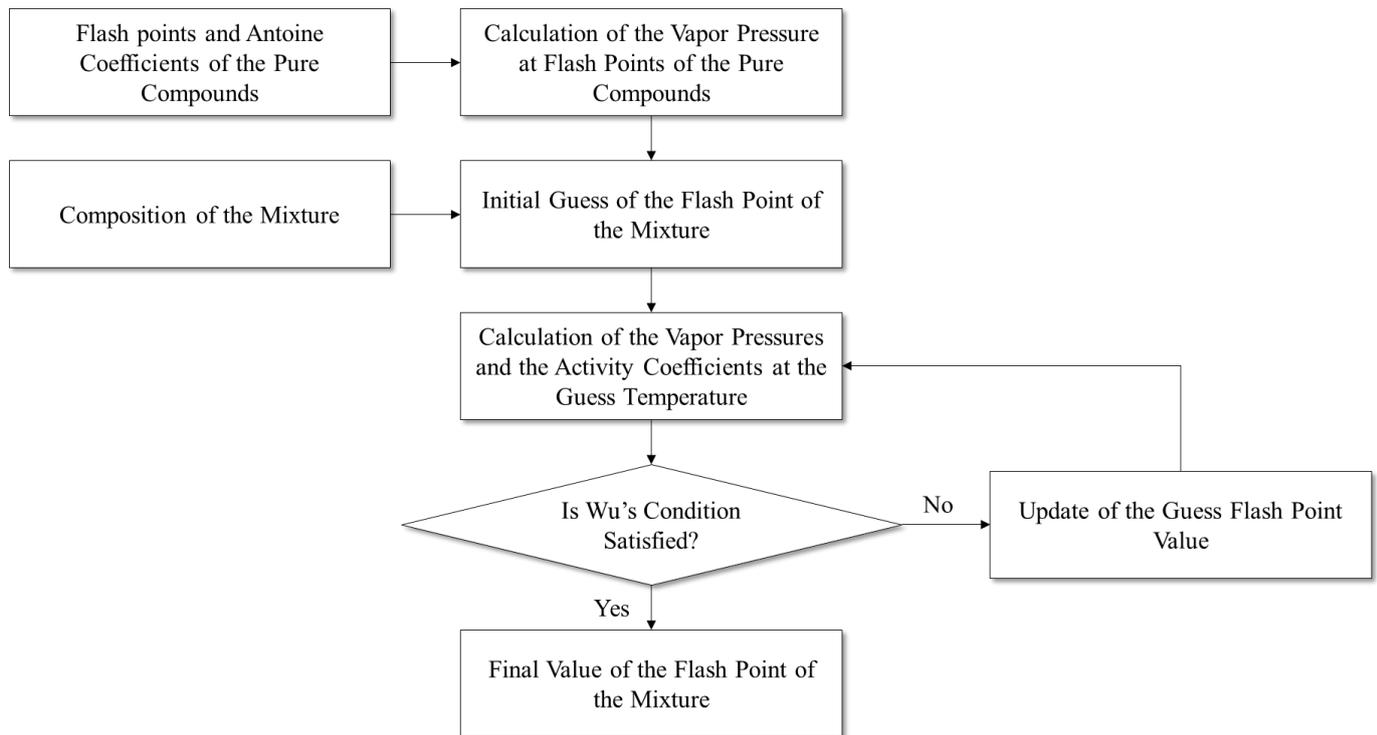


Figure 2 – Application of three mixing rules to the 1-butanol / 2-butanol mixture

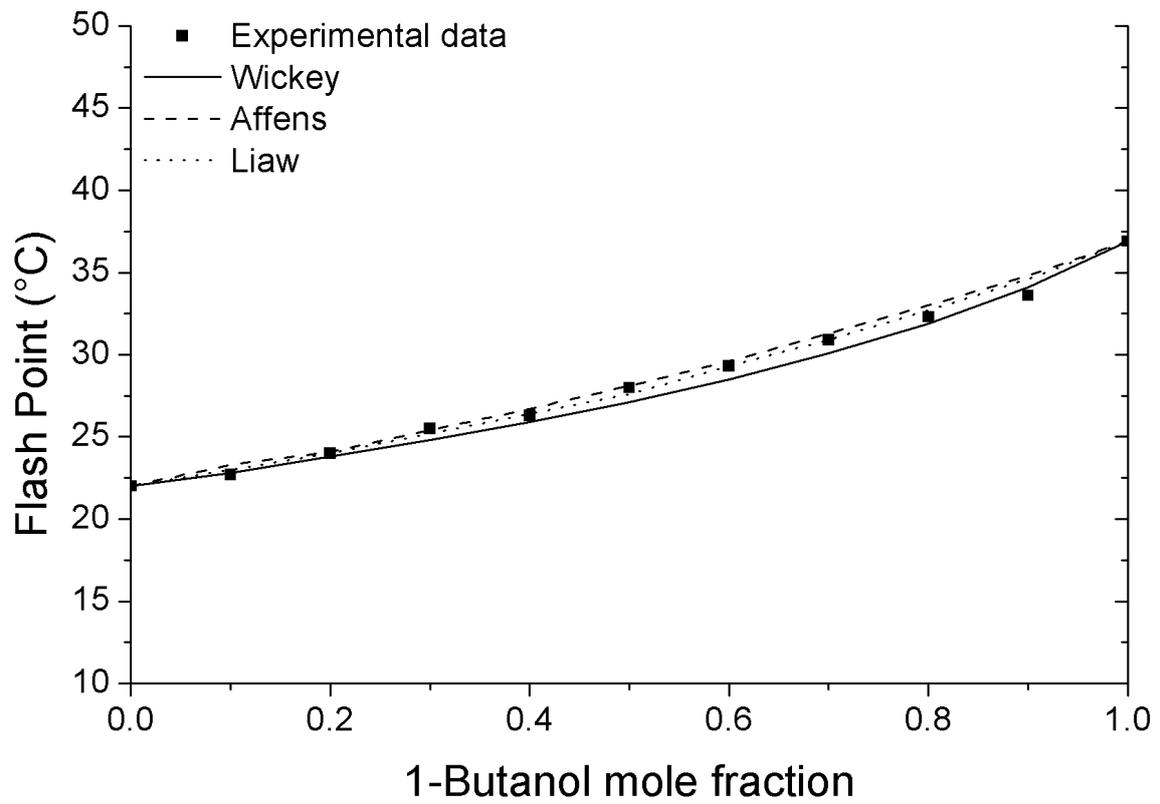


Figure 3 – Application of three mixing rules to the n-octane / ethanol mixture

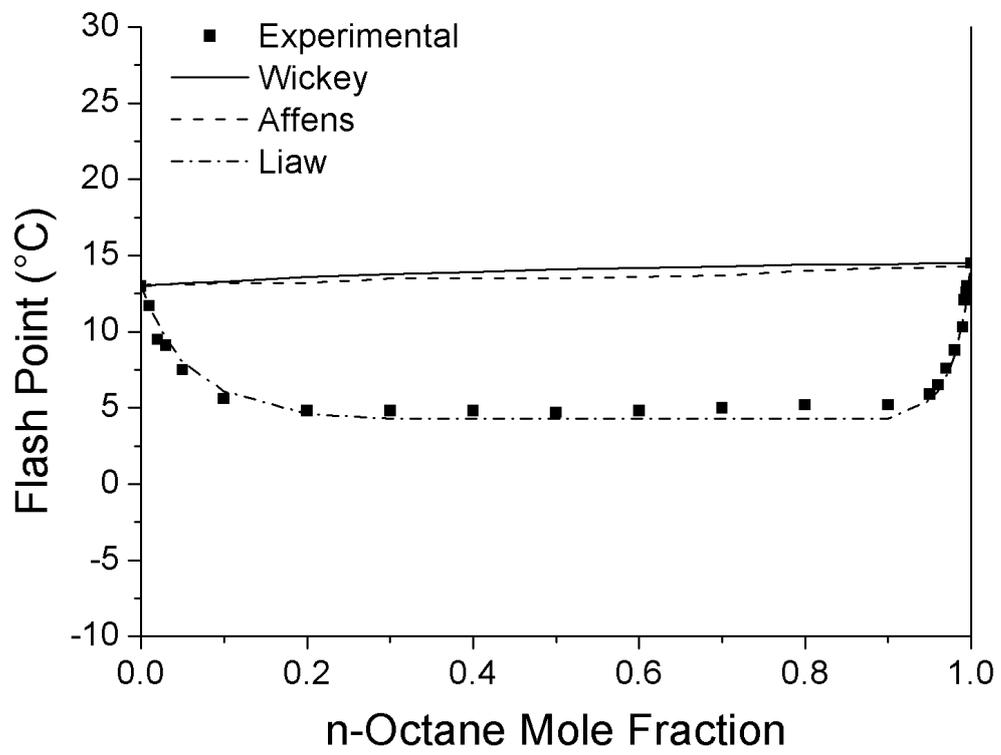


Figure 4 – Application of three mixing rules to the ethanol / n-tetradecane mixture

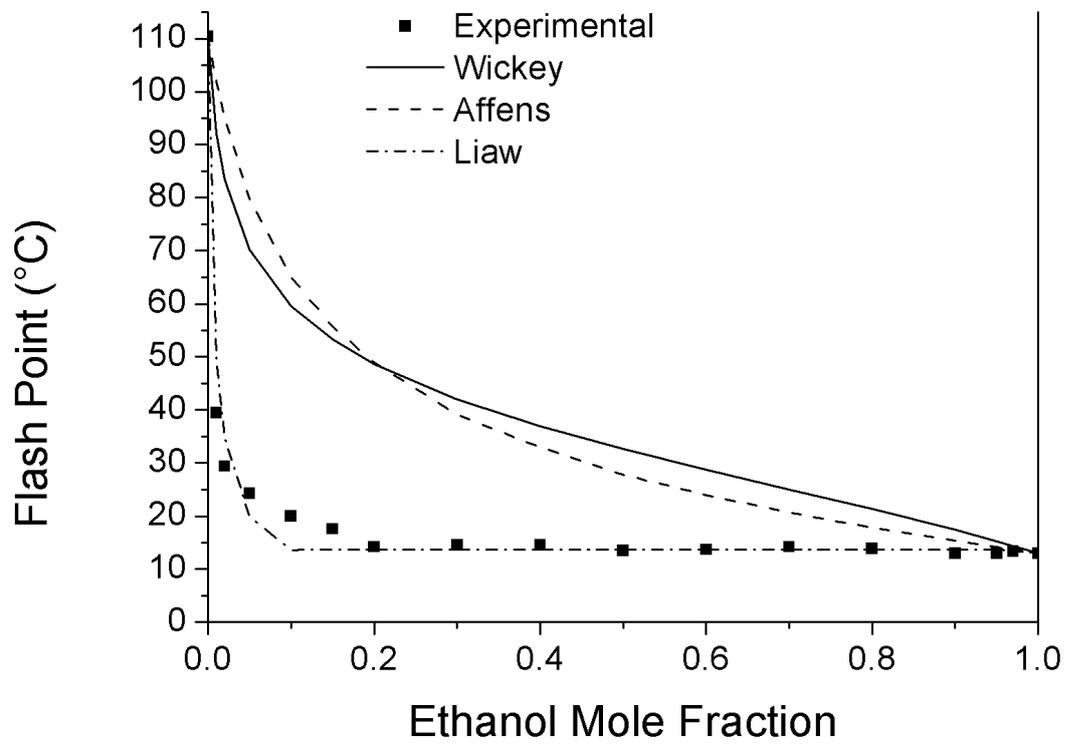


Figure 5 – Application of the various combinations of the mixing rule of Liaw with experimental flash points (No-QSPR) and with calculated ones obtained by the QSPR models of Carroll, Rowley (including the full predictive method), Hshieh and Gharagheizi for the n-octane/ethanol mixtures.

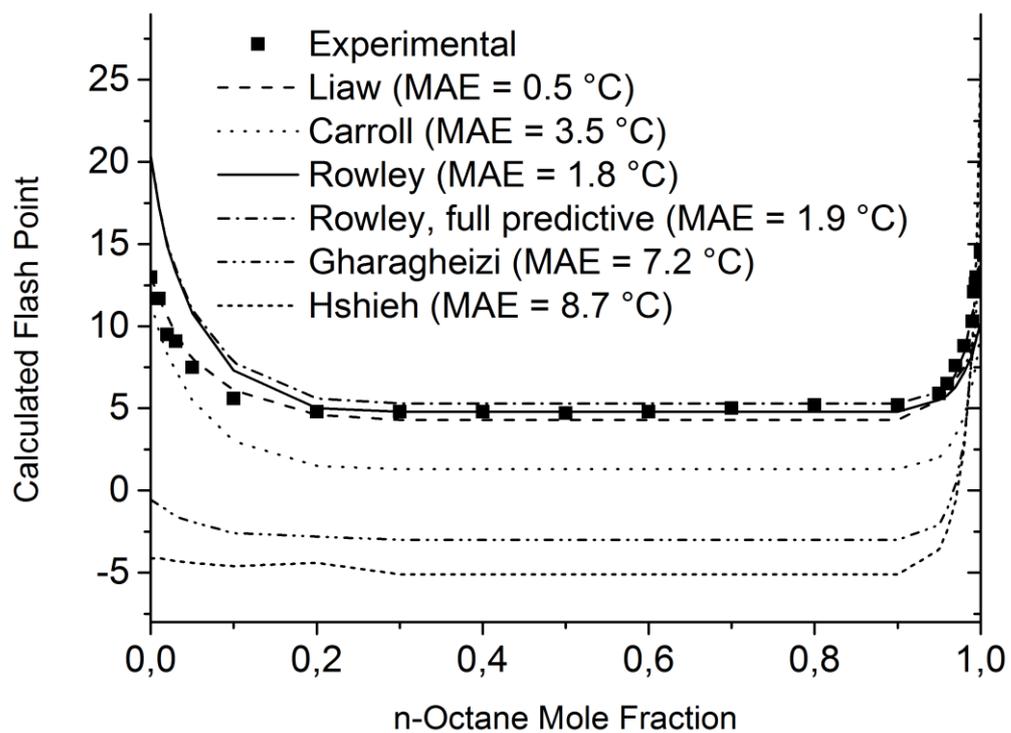


Figure 6 – Experimental vs. calculated experimental flash points of mixtures using the Carroll-Liaw combination and using the full predictive Rowley-Liaw combination. Straight line represents ideal prediction and dash lines limit the reproducibility domain as given by the ASTM D56 standard (i.e. 5.8°C).

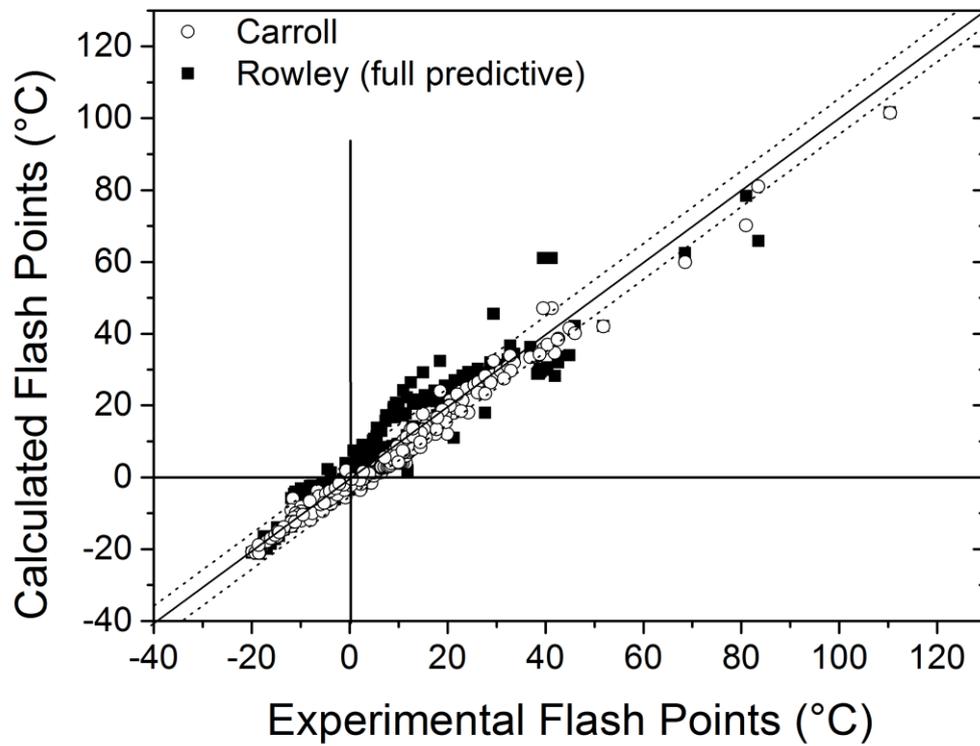


Figure 7 – Application of Carroll-Liaw combination and the full predictive method for the ethanol / 1-butanol mixtures.

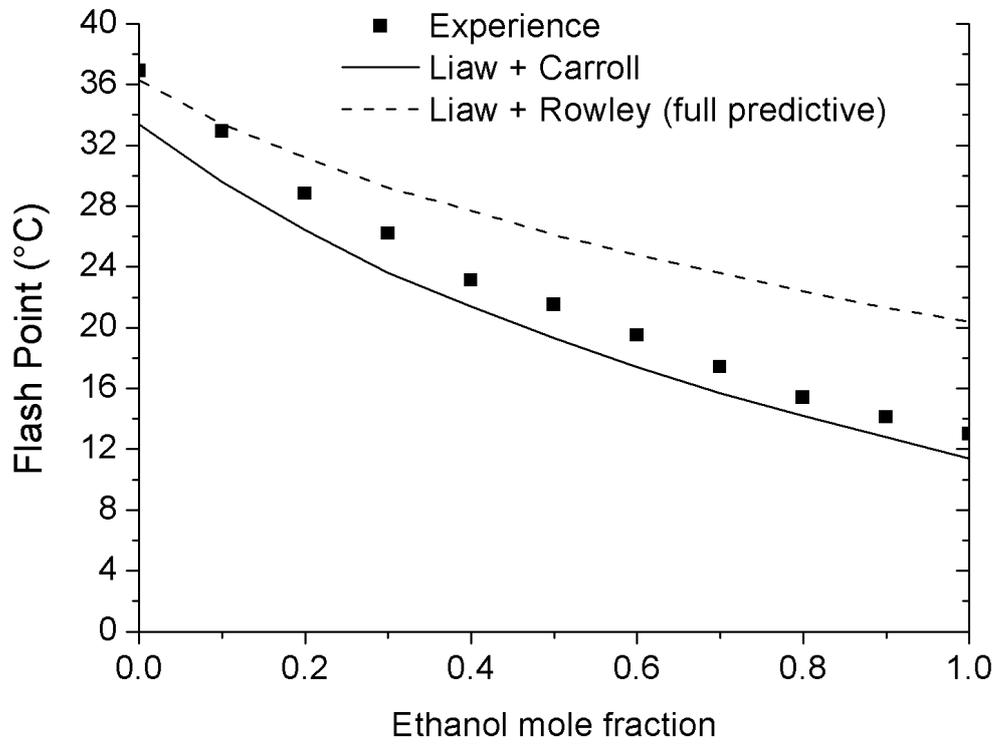


Figure 8 – Application of Carroll-Liaw combination and the full predictive method for the n-octane / iso-propanol mixtures.

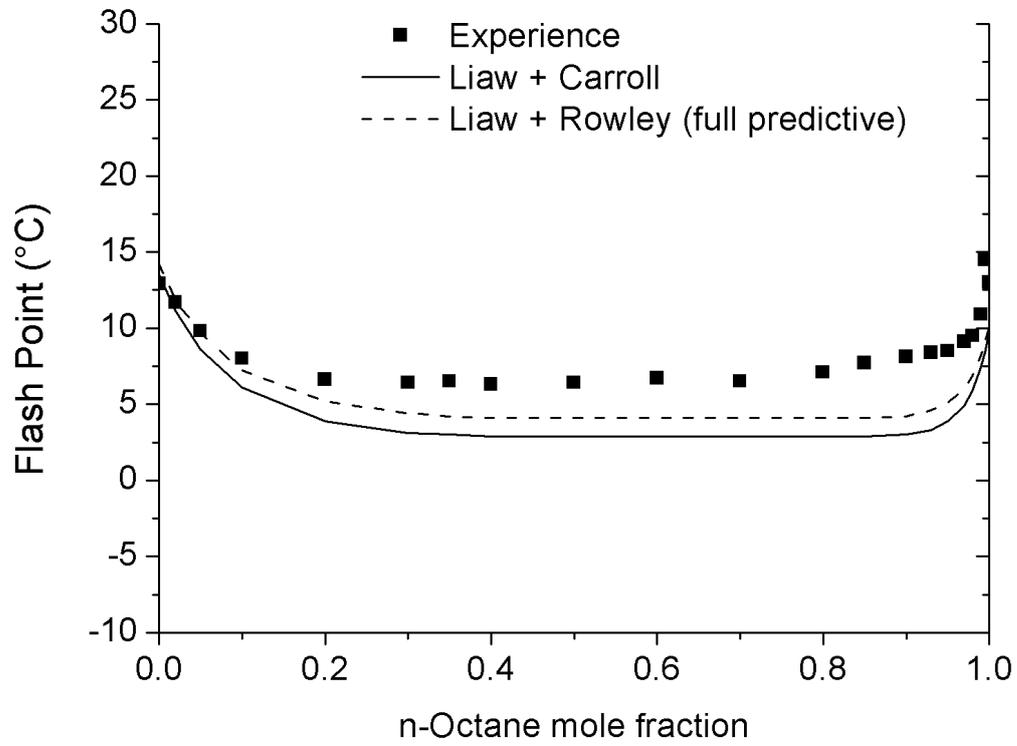


Figure 9 – Application of Carroll-Liaw combination and the full predictive method for the ethanol / n-tetradecane mixtures.

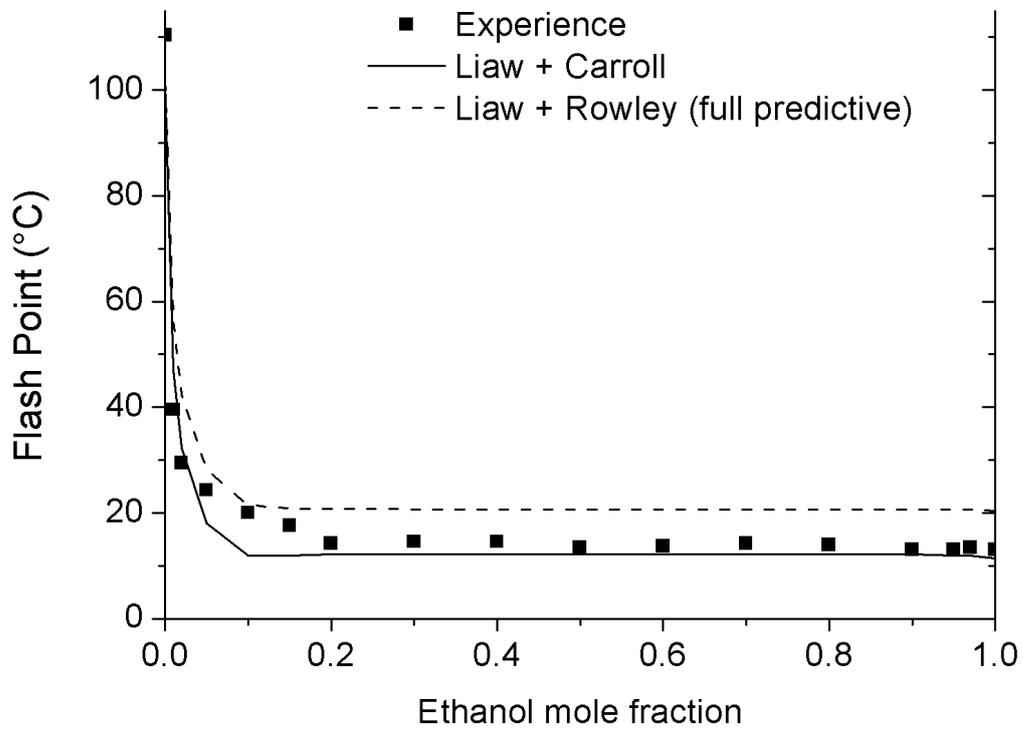


Figure 10 – Application of Carroll-Liaw combination and the full predictive method for the methanol / methyl acrylate mixtures.

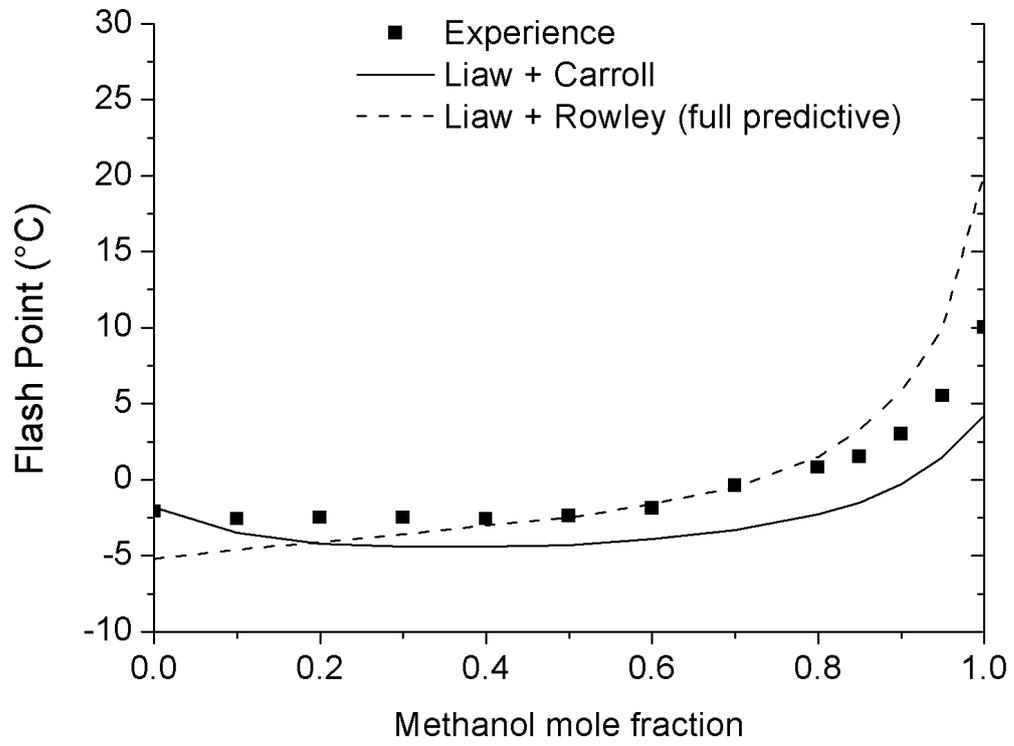


Figure 11 – Application of Liaw mixing rule, Carroll-Liaw combination and the full predictive method for the p-picoline / phenol mixtures.

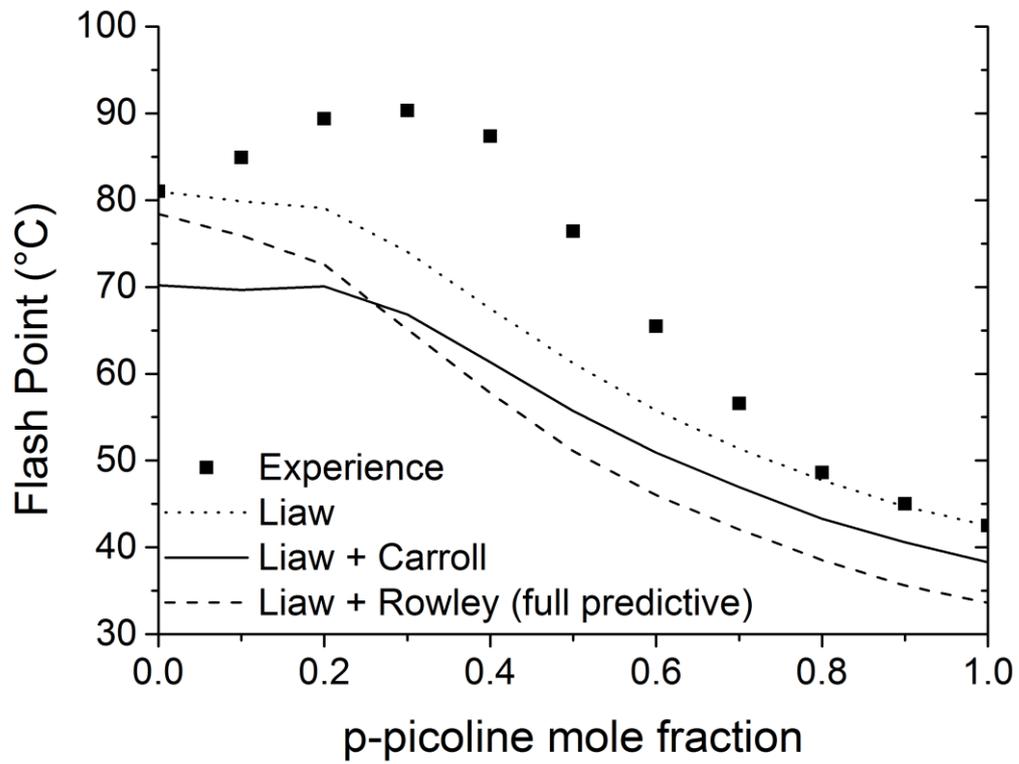


Figure 12 – Application of Liaw mixing rule, Carroll-Liaw combination and the full predictive method for the phenol / acetophenone mixtures.

