

STRAIGHTFORWARD DIMENSIONLESS EXPERIMENTAL FORMULAE FOR FLASH POINT OF BINARY MIXTURES OF TWO FLAMMABLE COMPONENTS

by

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Dimensionless experimental formulae based on a rational reciprocal function for correlation of flashpoint data of binary mixtures of two flammable components have been developed. The formulae are based on data obtained from flash-point experiments. The proposed approach requires only two coefficients, molar fraction of components and flashpoint temperatures of the pure flammable components to be known in advance. Literature data were used for formulae verification and validation obtained results indicate that accuracy is comparable and to some extent better than that of conventional flash point prediction models. Dimensional analysis and scaling of data have been performed in order to define the correct construction of the equation fitting flash-point data in dimensionless form using the independent variables suggested by Catoire. Stefan number relevant flash-point of a single compound or a blend has been defined.

Key words: flashpoint, binary mixtures, two flammable components, reciprocal functions, data correlation, dimensional analysis, Stefan number

Introduction

Flashpoint of liquids

The flash points (FP) of flammable liquids are of uttermost importance for risk estimation in fire scenarios as well as for storage, usage and transport of flammable substances. The FP is defined as the “lowest temperature under ambient conditions (corrected to 101.3 kPa) at which the vapors of a specimen ignite by application of an external ignition source [1]). Even though the FP are almost constant characteristics of materials, the published values vary due to differences in both the method as well as the testing devices used (*i. e.* closed-cup or open-cup methods) [2]. The more reliable closed cup FP predictions [3-7] use iterative calculations, for instance, based on the Antoine equation [8], and the Le Chatelier’s rule helped by either Dalton’s or Raoult’s laws for ideal solutions or their corrected versions when the solutions deviate from the perfect ones [9].

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The FP data of chemicals are readily available in literature, but useful dimensionless formulae correlating data obtained from experiments are highly needed. To be precise, this statement addresses the main drawback of the existing relationships in dimensional forms leading to ambiguities, dimensional pre-factors and exponents, dimensional non-homogeneity and last but not least those relationships are incorrectly constructed. This problem and the author's standpoint are especially developed in discussion.

Aim

The present work addresses correlations of experimental data obtained from either open or closed cup tests. The goal of this report is to show: how the experimental data can be correlated from a uniform point a view through non-dimensionalization, and how the proposed reciprocal functions can be derived directly from the behavior of dimensionless plots of the experimental data.

Therefore, the work addresses a post processing step following the experimental determination of FP data. The tests were performed with literature data due to two main reasons:

- to avoid any doubts about the correctness of the experimental data used, and
- to demonstrate the approach through simple examples.

Dimensional analysis and scaling are used to demonstrate how the correct construction of data fitting equations should be developed. The example was performed on the basis of the equation suggested by Catoire *et al.* [6, 10] that finally resulted in a decaying function well-represented by the reciprocal one used in this work.

Experimental formulae for FP data the currents status and problem formulation

Before explaining the guiding idea of the new approach the next section state the scientific problem in FP data correlations which inspired the authors to undertake this research. Numerous FP experimental data are published in scientific literature; while most of that data incorporate either experimental or systematic errors (see the scope of such equations and data in ref. 6). Commonly, a 3rd order polynomial correlations for FP is used to fit particular sets of experimental data (tab. 1), where the independent variable is the mole fraction of the flammable component, for aqueous solutions, for example. The polynomial expressions could be of different orders, either quadratic or cubic or higher but general rule in choosing the order of polynomial doesn't exist. A cubic relationship with 4 coefficients, for instance, is inherently affected by the uncertainty in the experiments and the regression [11].

The extant approach, briefly mentioned above, treats the data in dimensional form by polynomial expressions *without any rule in choosing the order of approximation*. Commonly, the rule "as much as higher order of the chosen polynomial expression provides better approximation" does not seems sound and generate enormous number of dimensional coefficients without any physical meaning. To be precise in this judgment, consider the case of 3rd or 5th order polynomial expressions of the flash point data for hypothetic flammable mixture, simply expressed as:

$$T_{FP}(x) = A_0 + A_1x + A_2x^2 + A_3x^3 + A_4x^4 + A_5x^5 \quad (1)$$

where x is the molar fraction and A_1 to A_5 are coefficients derived by regressions in eq. (1); A_1 to A_5 are dimensional coefficients with dimensions such A_2 [$1/^\circ\text{C}^2$] or A_2 [$1/^\circ\text{C}^5$] which are com-

pletely physically inconsistent. Moreover, the orders of magnitudes of each member on RHS of eq. (1) are quite different. The dimensional form of the expressions does not allow estimating the significance of the coefficients generated by such approximations. The literature is plenty of similar empirically generated formulae (see the examples provided in this work) and unfortunately no right approach in data correlation has been developed yet.

Table 1. FP approximations developed for binary mixtures

Mixture	Reciprocal approximation	
n-decane (1)-n-dodecane (2) $\max T_{FP(x=1)} = 344.15 \text{ K}_{(2)}$ Exp. data from [6] Correlation (T_{FP} in °C): $T_{FP} = 16.841 x_1^2 - 43.523x_1 + 72.049$	RA ₁	$y = (1.003 + 0.085x_1)^{-1}, R^2 = 0.961, \chi^2 = 0.0002$
	RA _M	$y = 0.999 (1 + 0.085x_1)^{-1}, R^2 = 0.9969, \chi^2 = 0.00002$
	RA _S	$y = (1 + 0.0865x_1)^{-1}, R^2 = 0.9609, \chi^2 = 0.0003$
	FH function	$y = (1.0 + 0.0812x_1^{0.542})^{-1}, R^2 = 0.9698, \chi^2 = 1.0118 \cdot 10^{-4}$
n-octane (1)-n-heptane (2) $\max T_{FP(x=1)} = 288.15 \text{ K}_{(1)}$ Exp. data from [6] Correlation (T_{fp} in °C): $T_{FP} = 8.9394 x_1^2 - 10.088x_1 + 4.0455$ $R^2 = 0.9781, T_{FP}$ in °C	RA ₁	$y = (1.004 + 0.0716x_2)^{-1}, R^2 = 0.9864, \chi^2 = 7.332 \cdot 10^{-6}$
	RA _M	$y = 0.996 (1 + 0.0713x_2)^{-1}, R^2 = 0.9864, \chi^2 = 7.332 \cdot 10^{-6}$
	RA _S	$y = (1 + 0.0994x_2)^{-1}, R^2 = 0.9987, \chi^2 = 7.886 \cdot 10^{-7}$
	FH function	$y = (1.0 + 0.078x_2^{0.693})^{-1}, R^2 = 0.995, \chi^2 = 7.03 \cdot 10^{-6}$
chlorobenzene (1)-aniline (2) $\max T_{FP(x=1)} = 343.15 \text{ K}_{(2)}$ Exp. data from [7]	RA ₁	$y = (1.012 + 0.135x_1)^{-1}, R^2 = 0.9616, \chi^2 = 5.856 \cdot 10^{-5}$
	RA _M	$y = 0.987 (1 + 0.133x_1)^{-1}, R^2 = 0.9616, \chi^2 = 5.271 \cdot 10^{-4}$
	RA _S	$y = (1 + 0.154x_1)^{-1}, R^2 = 0.9361, \chi^2 = 9.748 \cdot 10^{-5}$
	FH function	$y = (1.0 + 0.133x_1^{0.469})^{-1}, R^2 = 0.9698, \chi^2 = 2.457 \cdot 10^{-5}$
methyl acetate (1)-methyl-acrylate (2) $\max T_{FP(x=1)} = 271.05 \text{ K}_{(2)}$ Exp. data from [12]	RA ₁	$y = (0.999 + 0.0492x_1)^{-1}, R^2 = 0.989, \chi^2 = 2.675 \cdot 10^{-6}$
	RA _M	$y = 1.0 (1 + 0.049x_1)^{-1}, R^2 = 0.989, \chi^2 = 2.675 \cdot 10^{-6}$
	RA _S	$y = (1 + 0.049x_1)^{-1}, R^2 = 0.990, \chi^2 = 2.407 \cdot 10^{-6}$
	FH function	$y = (1.0 + 0.046x_1^{0.723})^{-1}, R^2 = 0.9698, \chi^2 = 2.457 \cdot 10^{-5}$
ethanol (1)- 1-butanol (2) $\max T_{FP(x=1)} = 308.15 \text{ K}_{(2)}$ Exp. data from [12]	RA ₁	$y = (1.003 + 0.078x_1)^{-1}, R^2 = 0.9791, \chi^2 = 1.230 \cdot 10^{-5}$
	RA _M	$y = 1.0 (1 + 0.078x_1)^{-1}, R^2 = 0.9791, \chi^2 = 1.230 \cdot 10^{-5}$
	RA _S	$y = (1 + 0.841x_1)^{-1}, R^2 = 0.975, \chi^2 = 1.470 \cdot 10^{-5}$
	FH function	$y = (1.0 + 0.078x_1^{0.748})^{-1}, R^2 = 0.9788, \chi^2 = 9.841 \cdot 10^{-6}$
cyclohexylamine (1)- cyclohexanol (2) $\max T_{FP(x=1)} = 341.15 \text{ K}_{(2)}$ Exp. data from [13]	RA ₁	$y = (1.009 + 0.136x_1)^{-1}, R^2 = 0.9652, \chi^2 = 5.390 \cdot 10^{-5}$
	RA _M	$y = 0.990 (1 + 0.134x_1)^{-1}, R^2 = 0.9652, \chi^2 = 5.390 \cdot 10^{-5}$
	RA _S	$y = (1 + 0.149x_1)^{-1}, R^2 = 0.9538, \chi^2 = 7.172 \cdot 10^{-5}$
	FH function	$y = (1.0 + 0.133x_1^{0.575})^{-1}, R^2 = 0.9788, \chi^2 = 9.834 \cdot 10^{-6}$

Method

Initial steps

The present work addresses some major issues in data correlations allowing creating common rules among them:

- All the data are presented in Kelvin [K] rather than in Celsius [°C] thus avoiding problems with those mixtures having flashpoint below 0 °C. The outcome of this is that all data are positive.
- All the data are preliminary normalized by maximum of FP of components from mixture the main outcome of this approach is that all data are presented in the dimensionless square [1, 1], which indicates that the scaled dependent variable (the mixture FP) varies in the range [0, 1]. The same stands for the independent parameter (the mole fraction). The non-dimensionalization of the FP data and dimensionless formulae have never been applied before even though this is the common rule in data treatment widely applied in mechanics, fluid flow, mass transfer, *etc.*

The dimensionless forms allow estimating the order of magnitudes of the coefficients in formulae and the rational order of magnitude of approximation. This approach does not limit the choice of the function used to correlate the data. This is explicitly demonstrated in the present work by simultaneous use of different versions of the reciprocal function and polynomial expressions.

The formulae should be useful, allowing good approximations by using minimum numerical data (coefficients) to be known preliminarily which is very important in creation of practical documents such as handbooks and datasheets of particular mixtures, sub-program in large computer codes, *etc.*

Correlation method by examples

The main function used to correlate the data in the present work is the reciprocal function $y = 1 / (a + bx_1 + c_1x_2)$. The choice is natural since after non-dimensionalization of the experimental data through the step described in preceding subsection, all plots (see the figures with experimental data) become decaying and closed by the dimensionless square [1, 1]. Moreover, the reciprocal function has just a few unknown coefficients that have to determine using the conventional regression methods. Exactly, that property offers the advantage as opposed to conventional polynomial approximation approach (where the coefficients and more importantly order of the polynomial has to be estimated by trial and error procedures). In the following text, we will explain the approach on the example of one flammable component and will continue applying it to two flammable components. Additionally, in the section *Alternatives to the reciprocal function* different reciprocal functions will be tested to correlation of the dimensionless data.

One flammable component

The method was conceived with data about FP of water-alcohol mixtures [14] using the relationship based on following reciprocal function:

$$y = \frac{1}{a + bx}, \quad y = \frac{T_{FP}}{T_{FP(x=1)}} \quad (2)$$

where y is the scaled (dimensionless) FP temperature of given flammable mixture and x – the molar fraction of the alcohol. In eq. (1), a and b are coefficient that have to determined via fitting to experimental data.

The approach requires an initial normalization of the experimental mixture FP data by T_{FP} of the pure flammable component as it described in point 1 (see the subsection *Initial steps*). Moreover, we have $a + b \approx 1$ because if $x \rightarrow 1$, we have $y \rightarrow 1$. The main advantage of the initial normalization and the use of the reciprocal function are:

- The data correlated are normalized and all of them prior the regression analysis have order of magnitude of unity, *i. e.* $y \sim O(1)$ as it was formulated above.
- The right-hand side of eq. (1) varies within the range $[0, 1]$. Therefore, both sides of eq. (1) have equal order of magnitudes of order of unity $O(1)$ which is the primary requirement in data correlation and scaling. Unfortunately, the exiting literature, as already mentioned, provides correlations in dimensional form, where this basic requirement for data correlation is not satisfied (see further the discussion section for general comments).

Two flammable components: correlations by reciprocal functions

Additionally, the proposed approach can be used for approximation of FP data of binary non-aqueous mixtures of two flammable components. In that case the scaled (dimensionless) FP temperature of mixture is:

$$y = \frac{1}{a + bx_1 + c_1x_2} \quad (3)$$

The molar fractions x_1 and x_2 of the two components satisfy the condition ($x_1 + x_2 = 1$). In eq. (3) a , b , and c , are coefficient that have to determined via fitting to experimental data. Additionally, in eq. (3) the right-hand side is dimensionless, *i. e.* $y = T_{FP(\text{mixture})}/\max T_{FP(x=1)}$ where $\max T_{FP(x=1)} = \max(T_{FP(x_1=1)}, T_{FP(x_2=1)})$ is the higher FP exhibited of each the components at $x = 1$. Then, the general rules for correct data correlations are:

In eq. (3), x_1 is the molar fraction of the component with the lower $T_{FP(x=1)}$ (high-volatile component), while x_2 is that of the component with the higher one (low-volatile component). With this concept, eq. (3) can be simplified as:

$$y = \frac{1}{a + bx_1 + c(1 - x_1)} \Rightarrow \frac{1}{(a + c) + (b - c)x_1} \Rightarrow \frac{1}{m + nx_1} \quad (4a, b, c)$$

or *vice versa*

$$y = \frac{1}{a + bx_1 + c(1 - x_1)} \Rightarrow \frac{1}{a + b(1 - x_2) + cx_2} \Rightarrow \frac{1}{p + qx_2} \quad (5a, b, c)$$

The concept can be simply exemplified by mixture of n-decane (1)/n-dodecane (2) discussed further in this work (tab. 2) and exhibiting and $T_{FP}(x_1 = 1, x_2 = 0) = 319.15$ K and $T_{FP}(x_1 = 0, x_2 = 1) = 344.15$ K. Then, $\max T_{FP(x=1)} = 344.15$ corresponding to $x_1 = 0, x_2 = 1$ and the correlation (3) reads $y = T_{FP(\text{mixture})}/T_{FP(x_1=1)} = f(x_1)$, *i. e.* expressed by eq. (4c). In contrast, the example with n-octane (1)-n-heptane (2) (see tab. 1) shows that $T_{FP}(x_1 = 1, x_2 = 0) = 288.15$ K (n-octane), while $T_{FP}(x_1 = 0, x_2 = 1) = 269.15$ K (n-heptane) then following the rule we get $\max T_{FP(x=1)} = 288.15$ K and the correlations is $y = T_{FP(\text{mixture})}/\max T_{FP(x_1=1)} = f(x_2)$.

Table 2. Mixture flash points of n-decane(1)-n-dodecane(2)

Experimental data		Thermodynamic- -based model predictions		Approximations (present work) $\Delta = (T_{\text{predicted}} - T_{\text{experimental}})$					
x_1	T_{FP} [K] (exp)	T_{FP} [K] (Ideal)	Δ_{IE} [K]	T_{FP} [K] appr. (RA ₁)	Δ_{RA_1} [K]	T_{FP} [K] appr. (RA _M)	Δ_{RA_M} [K]	T_{FP} [K] appr. (RA _S)	Δ_{RA_S} [K]
1.0	319.15	319.15	0	316.31	2.84	316.87	2.28	316.75	2.4
0.9	319.65	320.55	0.9	318.81	0.84	319.37	0.28	319.29	0.36
0.8	320.95	322.05	1.1	321.33	-0.38	321.92	-0.97	321.88	-0.93
0.7	322.65	323.75	1.1	323.91	-1.26	324.5	-1.85	324.50	-1.85
0.6	324.15	325.65	1.5	326.52	-2.37	327.12	-2.97	327.17	-3.02
0.5	326.65	327.75	1.1	329.17	-2.52	329.79	-3.14	329.88	-3.23
0.4	331.65	330.15	-1.5	331.87	-0.22	332.5	-0.85	332.64	-0.99
0.3	334.35	332.85	-1.5	334.61	-0.26	335.26	-0.91	335.44	-1.09
0.2	338.15	336.05	-2.1	337.40	0.75	338.06	0.09	338.30	-0.15
0.1	341.15	339.75	-1.4	340.24	0.91	340.91	0.24	341.20	-0.05
0.0	344.15	344.15	0	343.12	1.03	343.81	0.34	344.15	0

Exp. data from [6]; I – ideal (Raoult's law) [8]

Alternatives to the reciprocal function

The data normalization of the initial data *does not restrict the methodology to the reciprocal function only*, even though the dominating examples in this work stress the attention on it. Following the dominating case in the literature and the rules drawn above it is possible to create correlations as polynomials of different orders, namely, as an example:

$$y = \frac{T_{\text{FP(mixture)}}}{\max T_{\text{FP}(x_i=1)}} = f(x_1) = p_0 + p_1 x_1 + p_2 x_1^2 + p_3 x_1^3 \quad (6)$$

In this case all the coefficients p_i are dimensionless that enables to estimate the order of magnitude of each of them, as well as to estimate the reasonable order of the approximating polynomials.

The target of the proposed approach

In order to demonstrate the merits of the proposed approach, only the FP data for binary mixtures showing normal behavior were used (*i. e.* the mixture FP is neither higher nor lower than those exhibited by the pure components) were used. Additionally, some examples of mixtures exhibiting strong concave behavior due to partial immiscibility of components were tested. Mixtures with extrema (maxima or minima) in the FP [13-16] are beyond the scope of

the present work even though the general approach in data scaling through initial non-dimensionalization is also valid, but such mixtures form a special group requiring more refined approach in the choice of the correlating functions. Therefore, the correlations developed in this work by reciprocal functions are limited to binary mixtures with concave behaviour of the curve fitting FP experimental data.

Versions of the reciprocal function

The reciprocal function (see eqs. (2), 4(c), and 5(c)) has two versions which will be also explored, namely:

– *modified reciprocal approximation* (RA_M)

$$y_M = \frac{a_M}{1 + b_M x} \quad (7)$$

– *simplified reciprocal* (RA_S)

$$y_S = \frac{1}{1 + b_S x} \quad (8)$$

– *Farazdaghi-Harris function*

$$y = \frac{1}{a + b x^c} \quad (9)$$

The Farazdaghi-Harris (FH) function [17] is commonly classified among the power-law function but looking at the similarity with the reciprocal function we will explore its suitability to correlate FP data.

Numerical experiments

Reciprocal function approximations

The numerical experiments were performed with a set of binary mixtures exhibiting both ideal and no-ideal behaviour. Moreover, parallel to the reciprocal formulae, polynomial approximation up to the 5th order were performed. The equations developed by all numerical tests are summarized in tab.1. In addition, tab. 2-5 provide data about the accuracy of data fitting compared to both experimental data and predictions by thermodynamic models. The mixtures presented in these tables are practically ideal because the components are of one and the same homological series. An addition, graphical presentation are shown in fig.1. Even though the plots provide a visual information of the behavior of the approximation function the exact information about the errors can be taken from the tabulated data.

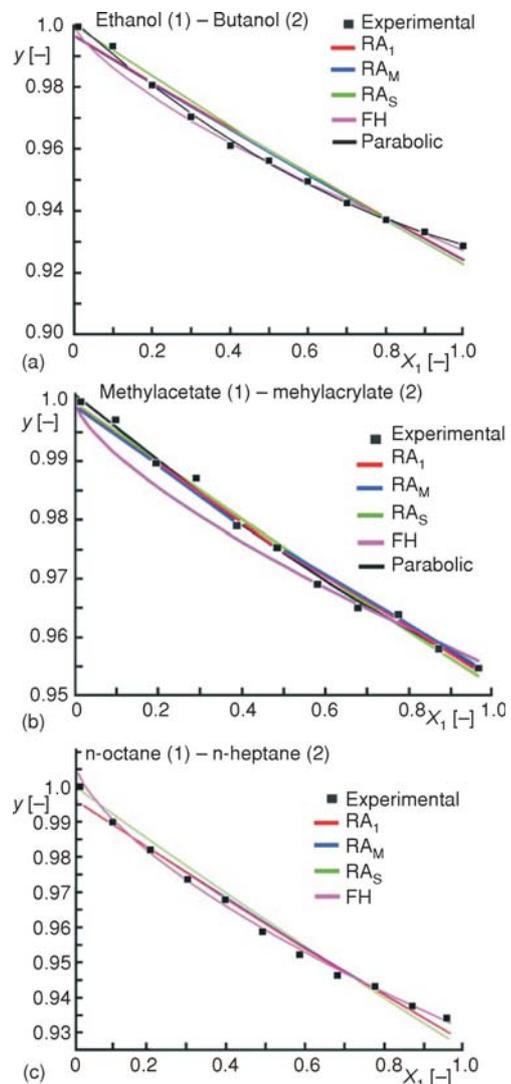


Figure 1. Graphical tests of binary mixture FP correlation by reciprocal functions (for color image see journal web site)

Table 3. Mixture FP of chlorobenzene (1)-aniline(2)

Experimental data		Thermodynamic- -based model predictions		Approximations (present work) $\Delta = (T_{\text{predicted}} - T_{\text{experimental}})$					
x_1	T_{FP} [K] (exp)	T_{FP} [K] (Ideal)	Δ_{IE} [K]	T_{FP} [K] appr. (RA_1)	Δ_{RA_1} [K]	T_{FP} [K] appr. (RA_M)	Δ_{RA_M} [K]	T_{FP} [K] appr. (RA_S)	Δ_{RA_S} [K]
1.0	301.15	301.15	0.0	299.17	1.98	298.93	2.22	297.36	3.79
0.9	304.95	302.95	-2.0	302.73	2.22	302.48	2.47	301.38	3.57
0.8	305.65	304.95	-0.7	306.38	-0.73	306.12	-0.47	305.51	0.14
0.7	308.15	307.15	-1.0	310.12	-1.97	309.84	-1.69	309.76	-1.61
0.6	310.75	309.75	-1.0	313.95	-3.2	313.66	-2.91	314.12	-3.37
0.5	315.85	312.75	-3.1	317.88	-2.03	317.57	-1.72	318.62	-2.77
0.4	321.85	316.35	-5.5	321.90	-0.05	321.58	-0.27	323.24	-1.39
0.3	328.15	320.75	-7.4	326.03	2.12	325.69	2.46	328.00	0.15
0.2	327.95	325.15	1.6	330.27	-2.32	329.91	-1.96	332.9	-4.95
0.1	331.65	333.35	1.7	334.62	-2.97	334.24	-2.59	337.95	-6.3
0.0	343.15	343.15	0.0	339.08	4.07	338.69	4.46	343.15	0

Exp. data from [7]; I – ideal (Raoult's law) [8]

Table 4. Mixture FP of methylacetate (1)-methyl acrylate(2)

Experimental data		Thermodynamic- -based model predictions		Approximations (present work) $\Delta = (T_{\text{predicted}} - T_{\text{experimental}})$					
x_1	T_{FP} [K] (exp)	T_{FP} [K] (Ideal)	Δ_{IE} [K]	T_{FP} [K] appr. (RA_1)	Δ_{RA_1} [K]	T_{FP} [K] appr. (RA_M)	Δ_{RA_M} [K]	T_{FP} [K] appr. (RA_S)	Δ_{RA_S} [K]
1.0	258.75	258.75	0.0	258.59	0.16	258.34	0.41	258.34	0.41
0.9	259.65	259.65	0.0	259.81	-0.16	259.56	0.09	259.56	0.09
0.8	261.25	260.60	0.65	261.04	0.21	260.78	0.47	260.78	0.47
0.7	261.55	261.62	-0.07	262.28	-0.73	262.03	-0.48	262.03	-0.48
0.6	262.65	262.70	-0.05	263.53	-0.88	263.28	-0.63	263.28	-0.63
0.5	264.35	263.85	0.50	264.80	-0.45	264.54	-0.19	264.54	-0.19
0.4	265.35	265.08	0.27	266.08	-0.73	265.82	-0.47	265.82	-0.47
0.3	267.55	266.40	1.15	267.37	0.18	267.12	0.43	267.12	0.43
0.2	268.25	267.83	0.42	268.67	-0.42	268.41	-0.16	268.41	-0.16
0.1	270.25	269.37	0.88	269.99	0.26	269.72	0.53	269.72	0.53
0.0	271.05	271.05	0.0	271.32	-0.27	271.05	0	271.05	0

Exp. data from [16]; I – ideal (Raoult's law) [8]

Table 5. Mixture FP of ethanol(1)-1-butanol(2)

Experimental data		Thermodynamic-based model predictions		Approximations (present work) $\Delta = (T_{\text{predicted}} - T_{\text{experimental}})$					
x_1	T_{FP} [K] (exp)	T_{FP} [K] (Ideal)	Δ_{IE} [K]	T_{FP} [K] appr. (RA_1)	Δ_{RA_1} [K]	T_{FP} [K] appr. (RA_M)	Δ_{RA_M} [K]	T_{FP} [K] appr. (RA_S)	Δ_{RA_S} [K]
1.0	286.15	286.15	0.0	285.06	1.09	285.85	0.3	284.24	1.91
0.9	287.55	287.00	0.55	287.13	0.42	287.94	-0.39	286.47	1.08
0.8	288.75	287.95	0.8	289.23	-0.48	290.05	-1.3	288.72	0.03
0.7	290.45	289.02	1.43	291.37	-0.92	292.20	-1.75	291.02	-0.57
0.6	292.65	290.24	2.41	293.53	-0.88	294.37	-1.72	293.35	-0.7
0.5	294.65	291.66	2.99	295.73	-1.08	296.58	-1.93	295.71	-1.06
0.4	296.15	293.36	2.79	297.96	-1.81	298.83	-2.68	298.12	-1.97
0.3	299.05	295.43	3.62	300.22	-1.17	301.10	-2.05	300.57	-1.52
0.2	302.15	298.12	4.03	302.52	-0.37	303.42	-1.27	303.05	-0.9
0.1	306.05	301.87	4.18	304.86	1.19	305.76	0.29	305.58	0.47
0.0	308.15	308.15	0.0	307.23	0.92	308.15	0	308.15	0

Exp. data from [16]; I – ideal (Raoult's law) [8]

The FH function: Performance in the convex curves approximation

The best performance of the FH approximation in the previous example can be successfully extended to mixture exhibiting partial immiscibility at low molar concentrations resulting in convex FP data plots, fig. 2. The attempt to use polynomial approximations, fig. 2(b)

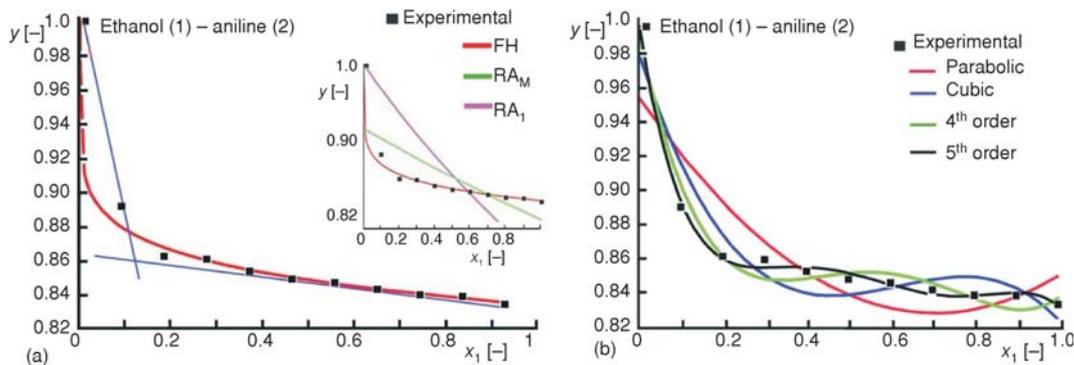


Figure 2. Examples of convex plots successfully approximated by the FH function (a) and polynomials (b) (for color image see journal web site)

reveals the same accuracy with polynomial of 4th and 5th orders. These data are summarized in tab. 6 where the FH approximation exhibits the best accuracy among the other versions of the reciprocal function. Moreover, the convex plot indicates two approximation by straight lines at low ($x_1 < 0.1$) and high ($x_1 > 0.2$) molar fractions. This relays to problems in approximation of flashpoint data of mixtures, which is beyond the scope of the present work.

Polynomial approximations

The suggested and tested reciprocal function, both simplified ones and FH, demonstrate adequate approximation with acceptable errors and minimized number of coefficients, and parameters required. In contrasts, the polynomial approximations either in dimensional forms (see tab. 1) or dimensionless one (see eq. 6) can attain the same level of accuracy at 4th or 5th order of approximation (tab. 6). To be precise, the dimensionless polynomial correlations provide $y \rightarrow 1$ at $x \rightarrow 0$; the accuracy increases with increase in the order of the polynomial expression?, *i. e.* for example of about -4.4% for the parabola and about -0.1% in the case of the 5th approximation. The same order of accuracy can be attained by the reciprocal function: about -0.2% for RA_M and about -0.1% for FH approximation. In this context, some comments on the polynomial approximations are briefly outlined in the next discussion section.

Table 6. Examples of polynomial dimensionless approximations of FP data compared to dimensionless approximations by reciprocal function conceived in the present work

Ethanol (a)-aniline (2), $\max T_{FP(x=1)} = 343.15 \text{ K}_{(2)}$, Exp. data from [7]		
Polynomial approximations ($x = x_1$)	Reciprocal approximations	
Parabola $y = 0.956 - 0.358x + 0.254x^2$	RA ₁	$y = (1.003 + 0.085x_1)^{-1}$; $R^2 = 0.961$; $\chi^2 = 0.0002$
Cubic $y = 0.981 - 0.776x + 1.332x^2 - 0.712x^3$	RA _M	$y = 0.992 (1 + 0.135x_1)^{-1}$ $R^2 = 0.513$; $\chi^2 = 0.0011$
4 th order $y = 0.994 - 1.206x + 3.255x^2 - 4.237x^3 + 1.762x^4$	RA _S	$y = (1 + 0.308x_2)^{-1}$, $R^2 = 0.197$, $\chi^2 = 0.0027$
5 th order $y = 0.999 - 1.594x + 6.719x^2 - 13.237x^3 + 12.066x^4 - 4.121x^5$	FH function	$y = (0.999 + 0.196x_1^{0.156})^{-1}$, $R^2 = 0.9698$; $\chi^2 = 2.457 \times 10^{-5}$

Discussion

Why we wrote this article?

The ideas suggested in this article demonstrate how to construct the dimensionless correlation of FP temperature of binary mixtures of two flammable components. The stand-points expressed by the authors were discussed at large with many colleagues and the manuscript was reviewed about nine times; in all case the comments of the referee were in quite different directions but never on the fact that something new appears in data correlations of FP data. We especially stress the attention on the number of reviews through which the text passed since two major obstacles in explaining the idea were met, namely:

- Why the data should be made dimensionless before scaling (data correlation)?
- Why we have to suggest a new correlation based on experimental data when the equation of Catoire *et al.*[6, 10] (see below) fits the data quite well?

The answer to the first question is straightforward. The data undergoing scaling should be of equal order of magnitude [18, 19]. Making the temperature dimensionless we get $y = T_{FP}/T_{FP(x=1)}$ which is order of magnitude of 1, that is $0 < y \leq 1$. At the same time the molar fraction, the independent variable, is dimensionless and vary from 0 to 1, therefore it satisfy the basic condition to be the same order of magnitude as the dependent variable $y = T_{FP}/T_{FP(x=1)}$. Hence, the data ready to be scaled are correctly designed. Further, the coefficients in the established correlations are dimensionless that makes them homogeneous. The dimensional homogeneity of any equation is mandatory. This point will be explained by using the equation of Catoire *et al.* [10], see eq. 10(a), which in fact is inhomogeneous.

The answer of the second questions will be demonstrated by an analysis of the equation developed by Catoire [6, 10], for both pure compound and mixtures, namely:

$$T_{FP} = 1.477T_b^{0.79686} (\Delta H_{vap}^0)^{0.168845} n^{-0.05948} \quad (10a)$$

Equation (10a) relates the FP temperature T_{FP} to the normal boiling point T_b , the standard enthalpy of vaporization ΔH_{vap}^0 at 298.15 K in kJ/mol and the total number of carbon atoms n in the molecule (the mixture). When the standard enthalpy of vaporization ΔH_{vap}^0 is difficult to be determined, a simplified equation was developed:

$$T_{FP} = 0.3544T_b^{1.14711} n^{-0.07677} \quad (10b)$$

In fact, the correlation of the T_{FP} to the normal boiling point T_b is an old idea and used in many empirical correlations referred by [6, 10].

First of all, we focus the attention on the dimensional homogeneity of these relationships. The LSD of eq. (10a) is in Kelvin while the product $T_b^{0.79686} (\Delta H_{vap}^0)^{0.168845}$ require the coefficient 1.477 to has a dimension [molkJ⁻¹] that from any point of view make eq. (10a) improperly designed as relationship. In the sense of equation homogeneity the simplified version eq. (10b) satisfies the basic condition and the coefficient 0.3544 is dimensionless. Moreover, both expressions are misbalanced as order of magnitudes because for most of case considered by Catoire *et al.* [6, 17] the value of T_{FP} is around 100 °C that in Kelvin mean and order of magnitude $O(10^3)$. The RHS of (10a) is a product of $T_b \sim O(10^3)$ and $\Delta H_{vap}^0 \sim O(10^5)$ that implies that (10a) is disbalanced because it correlates quantities of different order of magnitudes and the basic rule of data scaling is violated. When the suggested construct of eq. (10a) is subjected to estimation of the coefficient and the powers through fitting to either experimental or calculated values of T_b and ΔH_{vap}^0 , the procedure to minimize the quadratic error of approximation leads to the values estimated by Catoire *et al.* [6, 10]. This equations is assumed by many authors as a generalized relationship since it was established by fitting data of moreover 600 compounds, but the main drawback is the with scattering of predicted data around the experimental ones. Besides, it is not a generalized relations because it is simple regression using data from either experiments or thermodynamic calculations; the coefficient and the exponents are established by data fitting, the same as approach as that used in the present work.

The simplified version of eq. (10b) satisfies the aforementioned conditions of dimensional homogeneity and balanced ordered of magnitude, but the principle drawback is the omitted enthalpy of vaporization ΔH_{vap}^0 . The omission of ΔH_{vap}^0 means neglecting a very important physical phenomenon is determination of the FP temperature, as it will be discussed next.

The construct of the dimensionless relationship: how it should be done

Now, we will demonstrate how the correlation about the FP data should be constructed. For this reason we will use only the variables used in eq. (10a), *i. e.* $T_{FP} \sim (T_b, \Delta H_{vap}^0, n)$. Therefore, we use the same basis as Catoire *et al.* [6, 10] but a different strategy in data analysis and interpretation of the functional relationship will be developed, that finally leads to the reciprocal functions used in the examples demonstrated in this article.

In the physical situation of FP determination there is an amount of liquid with open surface subjected to vaporization. The amount of vapors above the interface depends on the absolute temperature T and pressure P . The main variable is the mixture composition (expressed through the molar fraction of either the low-volatile component or vice versa) because it determines the partial pressure of vapors, the boiling point and the enthalpy of vaporization. This is well-known fact, exactly exemplified by Catoire *et al.* [6, 10] in case when T_b and ΔH_{vap}^0 are determined by thermodynamic relationships.

Since, the liquid should be heated towards conditions enabling vaporization and production a minimum vapor concentration enough to produce a flash by energy supplied by an external source, the sensible heat is $C_p(T_b - T_0)$ while latent heat is represented by the enthalpy of vaporization ΔH_{vap}^0 . The ratio of these heats defines the dimensionless Stefan number (Ste) [20, 21] in case of a liquid surface undergoing combustion, namely:

$$\text{Ste} = \frac{C_p(T_b - T_0)}{\Delta H_{vap}^0} \quad (11)$$

Both the nominator and the denominator of the Ste depend on the mixture composition, *i. e.* on the molar fractions (represented by x_1 or x_2). Hence, at normal pressure conditions, the Ste is a function of the molar concentrations of the component only. In the case considered here, it is more convenient to use the inverse definition of the Ste related to the FP calculations, namely:

$$\text{Ste}_{FP} = \frac{\Delta H_{vap}^0}{C_p(T_b - T_0)} \quad (12)$$

Since the denominator Ste_{FP} of includes a reference temperature some problems would emerge to define a common value of T_0 for all compounds and mixtures. Because of that, neglecting T_0 , without loss of homogeneity the Ste related to the flashpoint Ste_{FP} can be expressed as:

$$\text{Ste}_{FP}^b = \frac{\Delta H_{vap}^0}{C_p T_b} = \frac{\Delta H_{vap}^0}{C_p} \frac{1}{T_b} \quad (13a,b)$$

The second form of Ste_{FP}^b , eq. (13b), shows that the normal boiling point T_b is a characteristic temperature scale for a given compound or mixture when the FP temperature is considered. The subscript *b* indicates that the normal boiling temperature is used as temperature scale. Therefore, following the rules of data scaling we have a construct showing how the correlation should be done, namely:

$$\left(\frac{T_{FP}}{T_b} \right) \sim f(\text{Ste}_{FP}^b) \Rightarrow \varphi(x) \quad (14)$$

The LHS of eq. (14) is order of magnitude $T_{FP}/T_b \sim (1)$. The order of magnitude of Ste_{FP}^b is also $\text{Ste}_{FP}^b \sim O(1)$ because both C_p and ΔH_{vap}^0 have almost equal order of magnitudes.

However, in both sides of eq. (14) there are terms depending on T_b (it is a function of the molar fractions) that should be avoided. If the FP temperatures of the pure compounds forming a given mixture are known, then without loss of generality the relation (14) can be expressed as a function of the molar concentration of the high-volatility component, namely:

$$y = \left(\frac{T_{FP(\text{mixture})}}{\max T_{FP(x=1)}} \right) f(\text{Ste}_{FP}^b) \Rightarrow \varphi(x_h) \quad (15)$$

The temperature scale $\max T_{FP(x=1)}$ in eq. (15) is the FP temperature of the pure component with the low volatility (subscript L that is $x = 1$ implies $x_L = 1$ and $x_h = 0$). From this construct, the relationship $y \sim f(\text{Ste}_{FP}^b) \Rightarrow \varphi(x_h)$ is a decaying function in the square $y [1, 0]$ and $x_h [0, 1]$. Therefore, all rules and conditions of proper data scaling are satisfied. In this context, the decaying behaviour of the chosen reciprocal function is physically reasonable. Otherwise, if the correlation is performed as $y = \varphi(x_L)$ using the molar fraction of low-volatility component, the function $y = T_{FP(\text{mixture})}/T_{FP(x_L=1)}$ is growing, that violates the rules of scaling since $y \geq 1$ and the upper limit is not defined. This, in fact, was done in the examples provided by Catoire *et al.* [6, 10].

Moreover, if the number of carbon atoms in the molecule (or in the mixture) have to be taken into account, following the idea of Catoire *et al.* [6, 10], since n is dimensionless, the general construct becomes:

$$y = \left(\frac{T_{FP(\text{mixture})}}{\max T_{FP(x=1)}} \right) \sim f(\text{Ste}_{FP}^b, n) \Rightarrow \varphi_1(x_h) \quad (16)$$

Because $n = n(x_L, x_h)$ the decaying function $y \sim \varphi_1(x_h)$ is natural if the correlation is made as it is demonstrated by Catoire *et al.* [10]. We have to mention that the inclusion of the total number of the carbon atoms in the set of dimensionless variables by Catoire *et al.* [10] is a voluntary step not related to thermodynamic analysis used in the development of the scaling relationship. It comes from another idea in flashpoint temperature data correlations [12] regarding the chemical structures of the compounds (mixtures) (see comments in ref. 10, section 5).

The rules of scaling require the depended dimensionless variable to be a function of a product of powers of the independent variables [18, 19], namely:

$$y = M(\text{Ste}_{FP}^b)^{m_1} n^{m_2} \quad (17)$$

The pre-factor M and powers m_1 and m_2 in eq. (17) have to be determined by fitting either experimental data or predicted values of T_b , C_p , and ΔH_{vap}^0 defining Ste_{FP}^b . Therefore, looking again at eq. (10b) we may say that it is incorrect irrespective to its dimensional homogeneity, because the physical process of vaporization represented by ΔH_{vap}^0 is neglected.

Let us now consider the order of magnitudes of Ste_{FP}^b . With a simplifying assumption that the heat capacity does C_p not vary significantly with variation in the composition (in case of mixtures) we get that the ratio $(\Delta H_{\text{vap}}^0/T_b)$ does not vary in a broad range. To exemplify this standpoint, we refer to the data provided by Catoire *et al.* in [6] about n-octane/n-heptane blend (tab. 1 in the original work). These data show that the normal boiling point varies from $100.25^\circ\text{C}_{(x_{n\text{-octane}}=0.1)}$ to $100.25^\circ\text{C}_{(x_{n\text{-octane}}=0.8)}$ with respective values of ΔH_{vap}^0 : ΔH_{vap}^0 36.87 kJ/mol_($x_{n\text{-octane}}=0.1$) and $\Delta H_{\text{vap}}^0 = 39.47$ kJ/mol_($x_{n\text{-octane}}=0.8$). Under these circumstances, the value of $(\Delta H_{\text{vap}}^0/T_b)$ varies from 0.367 kJ/molK_($x_{n\text{-octane}}=0.1$) to 0.333 kJ/molK_($x_{n\text{-octane}}=0.1$). Therefore, we may suggest that $\text{Ste}_{FP}^b \approx \text{const}$ for a given blend. Then, the main contribution to T_{FP} through variation in the mixture content comes through the total number of carbon atoms which is a function of the molar fraction as it demonstrated; and used for calculations by Catoire *et al.*

[6, 10]. Hence, the only term resulting to a sensible effect on T_{FP} is that accounting the total number of the carbon atoms. The scaling estimates show that $T_{FP} \sim 1/n^{m_2}$, that is a hyperbolic decaying function. It is worth noting to mention that Catoire *et al.* [6, 10] especially used the term $1/n^{m_2}$ to get reliable expression (see in ref. 12, section 8.1, the comments about equation 4a), which was impossible when only ΔH_{vap}^0 and T_b were taken into account.

In the correlation (10a) where T_{FP} is correlated to a product of powers $(T_b)^{d_1} (\Delta H_{vap}^0)^{d_2}$ there is an overestimation of the contribution of the molar fraction, since both $T_b \sim T_b(x)$ and $\Delta H_{vap}^0 = \Delta H_{vap}^0(x)$. Treatment of data in this way yields an almost parabolic relationship $T_{FP} \sim T_{FP}(x^2)$ as it is demonstrated by [6, 12] for blends non-exhibiting maxima. In the specific case of n-octane / n-heptane blend used as example here, the plot (fig. 1 in ref. 10) is parabolic at low n-octane molar fractions (< 0.4) and approaches a linear behaviour beyond this limit. For n-decane/n-dodecane mixtures (fig. 2 in ref. 6) the decaying behaviour of the relationship $T_{FP} \sim T_{FP}(x)$ is clearly demonstrated because the plot is done with the molar fraction of the high-volatility component (n-decane), *i. e.*, $x = x_h$, exhibiting the lower T_{FP} as a pure compound. This plot confirms the analysis done in this work.

The analysis done in this section shows that the relationship $T_{FP} \sim T_{FP}(x)$, with independent variable represented by the molar fraction of the high-volatile component, should be a decaying function. The choice of the decaying function should be a power-law as it suggested by the scaling analysis, polynomial or by the reciprocal function conceived in this work. The reciprocal function and the non-dimensional polynomials developed in this work has an advantage since at $x_h \rightarrow 0$ we have that $y_h \rightarrow 0$ is physically adequate.

Fitting experimental or predicted data with such scaling relationship the accuracy of the developed equations strongly depends on the scattering of the initial data points. As the number of compounds (or blends) providing data for scaling increases the scattering of the data point around the estimated relationship increases, too. This is well demonstrated by Catoire *et al.* [10] where linear relationships were estimated for clouds of data points leading to large discrepancies between experimental and predicted values of T_{FP} . In accordance with these authors the mean absolute deviation is about 2.9 °C while the maximum absolute error was established about 7-10 °C. In this context, it is a matter of argument what to be used for data scaling: large number of data fitted by a single equation and with large errors or limited data (to close groups of compounds or blends) fitted with acceptable accuracy.

The analysis done in the *discussion* section demonstrates that the scaling under circumstances imposed by the set of independent variable suggested by [17], *i. e.* T_b , ΔH_{vap}^0 , and n is decaying if the proper non-dimensionalization is performed and the scaling is to the molar fraction of the high-volatile component x_h , as it was done with all numerical examples employing dimensionless reciprocal function or polynomials. The scaling analysis developed is only the initial step towards unified data treatment and relationships and for correlating or prediction of flash point temperatures.

Some comments on the polynomial approximations

Some problems emerging in application of polynomial expressions would be briefly outlined, because they are commonly used in FP data correlation and, probably some readers could see conflict with the ideas developed in this work.

- The polynomial expressions contain too many coefficients and undefined order of approximation assuring the desired accuracy of approximation. The latter yields in doubtful results and hinder the physical analysis. Moreover, the published so far literature

data [5, 6, 10, 12-14, 16, 17] are in dimensional forms and the coefficients have different dimensions depending of the order of the terms if dimensional data are correlated, which is highly unacceptable, physical irrelevant and does not permit a comparative analyzes.

- The polynomial approximations do not refer to the physical meaning of the data at issue when they are performed in dimensional form. As it was already mentioned, when $x_1 \rightarrow 0$, the predicted result should approach the FP temperature for $x_2 \rightarrow 1$. Simple tests with polynomial approximations, summarized from the literature (see tab. 1 for example) are not encouraging due to the aforementioned reasons.
- The data normalization and the development of dimensionless polynomial expressions avoid most of the drawbacks of the polynomial expressions but the problem of the desired order of approximation still remains and is a matter of choice without well-defined criteria. The reciprocal function in its various versions provide more reliable answer to the problem by limiting the number of the coefficients and slightly changing the type of the function; which in fact does not affect too much the accuracy of the approximation.

Conclusions

The approach conceived in this work includes two basic steps:

- Initial normalization of the FP data provided by either thermodynamic simulations or physical tests. This step refers to an initial presentation of all data about $T_{\text{FP(mixture)}}$ are in Kelvin as a general rule, which allows the general approach to be applied even in cases when the $T_{\text{FP(mixture)}} < 0$ °C. Next, the normalization of the data, $y = T_{\text{FP(mixture)}} / \max T_{\text{FP(x=1)}}$ satisfies the basic rule in data approximation, *i. e.* all data should be or order of unity $O(1)$.
- Analysis of the suitable approximation relationship stressing the attention of the features of the basic reciprocal function (and modifications) in comparison with polynomials (both dimensional and dimensionless versions) of different orders. The numerical experiments performed with published data indicate the simplicity of the reciprocal function with accuracy comparable to that assured by 4th and 5th order polynomial approximations.
- The final choice of the approximate function is a matter of argument since such a discussion never has been opened in the literature where the dominating expressions are dimensional polynomials. The users can employ either reciprocal functions or polynomial but the initial normalization of the data is mandatory since it allows the developed formulae to be compared easily. Besides, the unified expressions allow extracting more information and cross-related relations than that provided by dimensional correlations. In this context, the present article suggests an algorithm in data treatment with rules allowing more readable presentation of flash point data of binary mixtures. The rules imposed by the initial data normalization are not restricted to the examples used in this work but are widely applicable to other flashpoint data exhibiting deviations from the ideal solution behavior.
- This work, beyond the initial normalization step in data treatment, suggests for the first time the use of the reciprocal function and its versions for correlation of FP data of flammable mixtures, with a reasonable accuracy attainable by 4th and 5th orders polynomials as commonly used approximations.
- The scale analysis and the correct construct of dimensionless relationship resulting in a decaying function fitting experimental data was performed with the same independent variables as those used by Catoire *et al.* [6, 10]. This analysis reveals a misconstruction of this equation (see eq. 10a) and defines a dimensionless Stefan number relevant the flashpoints of blends. In this context, it is worthy to mention that despite the misconstruction of eq. (10a)

its use in a regression analysis resulted in the established pre-factor and exponents. However, this is a result of data approximation due to data fitting, but not a result of prediction procedures.

Nomenclature

A_0, A_1	– dimensional coefficients in eq. 1 with dimensions of ion, depending of the order of the term
a	– dimensionless coefficient in eq. 2, eq. 3, and eq. 4
b	– dimensionless coefficient in eq. 2, eq. 3, and eq. 4
m, n	– dimensionless coefficients in eq. 4
p, q	– dimensionless coefficients in eq. 5
p_0, p_1, \dots	– dimensionless coefficients in eq. 6
R^2	– residual variance, (see tab. 1 and all other tables in this work), [–]
T_{FP}	– flash point temperature, [K]
$T_{FP(x=1)}$	– flash point temperature of the pure flammable component, [°C]
x	– mol fraction of a given component of the mixture, [–]
x_1	– mol fraction of the of the water, [–]
x_2	– mol fraction of the flammable component, [–]
y	– dimensionless FP defined by eq. 2 and eq. 3, ($= T_{FP}/T_{FP(x=1.0)}$), [–]

Greek symbols

Δ	– error in data correlation, [$= (T_{\text{predicted}} - T_{\text{experimental}})$]
Δ_{RA_1}	– error of the basic reciprocal function (eq. 3), [K]
Δ_{RA_M}	– error of the modified reciprocal function (eq. 7), [K]
Δ_{RA_S}	– error of the simplified reciprocal function (eq. 7), [K]
Δ_{IE}	– error of the method based on the Rault's law (ideal solutions), [°C]
χ	– the Pearson's Chi-square, [–]

Subscripts

FP	– flash point
i	– ideal (Rault's law)
R	– reciprocal
RA_1	– basic reciprocal function
RA_M	– modified reciprocal function
RA_S	– simplified reciprocal function

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