



The prediction of the flash point for binary aqueous-organic solutions

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Abstract

A mathematical model, which may be used for predicting the flash point of aqueous-organic solutions, has been proposed and subsequently verified by experimentally-derived data. The results reveal that this model is able to precisely predict the flash point over the entire composition range of binary aqueous-organic solutions by way of utilizing the flash point data pertaining to the flammable component. The derivative of flash point with respect to composition (solution composition effect upon flash point) can be applied to process safety design/operation in order to identify as to whether the dilution of a flammable liquid solution with water is effective in reducing the fire and explosion hazard of the solution at a specified composition. Such a derivative equation was thus derived based upon the flash point prediction model referred to above and then verified by the application of experimentally-derived data.

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1. Introduction

The flash point of a liquid (or solid) is that temperature, as determined under experimental conditions, at which such a substance emits sufficient vapor to form a combustible mixture with air [1]. The flash point is one of the major physical properties used to determine the fire and explosion hazards of liquids [2]. A liquid that exhibits a flash point value below ambient temperature, and which can thus give rise to flammable mixtures under ambient conditions, is generally considered to be more hazardous than one reflecting a higher flash point value [3]. The specific flash point value is generally measured by use of a flash point

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Nomenclature

A, B, C	Antoine coefficients
f	fugacity of pure component (kPa)
g	binary parameters of NRTL equation (J/mol)
G	defined in Table 1
LFL	lower flammable limit
P	ambient pressure (kPa)
P^{sat}	saturated vapor pressure (kPa)
$P_{i,\text{fp}}^{\text{sat}}$	saturated vapor pressure of component i at flash point (kPa)
q_i	measure of molecular surface areas
r_i	measure of molecular van der Waals volumes
R	gas constant (8.314 J/mol)
T	temperature (K)
$T_{i,\text{fp}}$	flash point temperature of pure component i (K)
u	binary parameters of UNIQUAC equation (J/mol)
v^{l}	molar volume of liquid (m^3/mol)
x	liquid-phase composition (mole fraction)
y	vapor-phase composition (mole fraction)
z	coordination number

Greek letters

γ	activity coefficient
θ_i	area fraction of component i
λ	binary parameters of Wilson equation (J/mol)
Λ	defined in Table 1
τ	defined in Table 1
Φ_i	segment fraction
$\hat{\Phi}_i$	fugacity coefficient of species i in solution

Subscripts

fp	flash point
i	species i
m	mixture
1	water
2	flammable component

analyzer. There are two methods for the measurement of the flash point value of a liquid, the closed-cup test and the open-cup test [3]. The open-cup flash point value is, typically, a few degrees greater than the closed-cup flash point value [3].

In 2000, the largest chemical waste handler in Taiwan at that time, Shengli Waste Handler, dumped waste organic solvents into the Kaoping River (southern Taiwan) illegally, causing serious water pollution. As a consequence, the Taiwanese government withdrew the license of Shengli due to their responsibility for such a pollution incident. The revocation of the

license for Shengli led to the necessary collection of a large quantity of waste organic solution which could not be handled legally, such that these waste materials were required to be stored (temporarily) in a variety of factory sites or in the industrial parks precinct. In order to assure the safety of storage of such materials, flash point data corresponding to flammable (or combustible) liquid solutions have clearly become an important issue. During the period of the Shengli event, it had been thought by some people at the plant, located in Hsinchu Science-Based Industrial Park (Taiwan), that the potential hazard constituted by the discarded waste solutions may have been effectively diminished by the dilution of such solutions with water in order to increase the flash point of such waste solutions. In fact, such a notion had been accepted and implemented by some plants as regards waste-solution production and dispersal. By contrast, however, test results elicited by application of the flash point analyzer indicated that the flash point values pertaining to many of the involved waste solutions diluted with a large amount of water were still low. The result of diluting waste solutions with water revealed that not only the flash point of the waste solutions did not necessarily increase as had been expected by operational staff, but also that the quantity of waste solutions so produced increased substantially, which increased the overall waste-handling cost. If detailed flash point variation with composition data for the specified aqueous-organic solution had been available at the time, this specific dilution of the waste solution with water in order to (attempt to) reduce the hazard of such a solution might not have occurred. Detailed flash point data corresponding to various compound solutions appear to be scarce in the literature; even those listed in a variety of material safety data sheets (MSDS) are, typically, only valid for a specific compound composition. If a flash point prediction model for an aqueous-organic solution could be successfully derived, the flash point of various aqueous-organic solutions should be able to be predicted relatively easily using only a small amount of basic data.

Affens and McLaren [4] developed a model in 1972 to predict the flash points of hydrocarbon solutions by application of Raoult's law. In 1997, White et al. [5] reduced Affens and McLaren's model [4] to a simpler equation by ignoring the variation of the lower flammable limit (LFL) with temperature, and used such an equation to estimate the flash point of two aviation fuel mixtures: JP-4/JP-8 and JP-5/JP-8. Unfortunately, however, there would appear to exist some deviation between the experimentally-derived data and their predictive analogues. It was demonstrated in our previous work that Affens and McLaren's model [4] and White et al.'s equation [5] were unable to effectively comprehend the significance of the experimentally-derived data corresponding to the flash point for a non-ideal solution, although they were able to explain those (flash point) data corresponding to an ideal solution [6]. In our previous study [6], a mathematical model developed in order to predict the flash point of binary liquid solutions with two flammable components was proposed, and was verified to be able to be applied in order to successfully predict experimentally-derived data corresponding to ideal solutions and non-ideal solutions.

It has been previously suggested by Crawl and Louvar that the flash point of a liquid solution with only one component which is flammable, such as a binary aqueous-organic solution, is able to be estimated by determining the temperature at which the vapor pressure of the flammable component in the mixture is equal to the pure component vapor pressure at its flash point [2]. These authors used Raoult's law to estimate the vapor-phase composition of the flammable substance. It could be construed that it may be somewhat questionable to

apply the method described by Crowl and Louvar [2] to an aqueous solution, the composition of which is somewhat distinct from the case when the flammable-substance composition is unity. For such a situation it would appear inappropriate to apply Raoult's law to the flammable component of the solution to determine its flash point. It would appear, however, that such a method could be used to describe the flash point variation with a solution's composition for an aqueous solution, the flammable-substance composition of which lies close to unity. For some aqueous-organic solutions, such as alcoholic drinks, the composition of the flammable component differs from unity and thus Raoult's law is not valid for application to the flammable component of such solutions. Thus, for situations such as this, it is necessary to develop a method (model) to predict the flash point of an aqueous-organic solution.

If the variation rate in flash point with composition for an aqueous-organic solution can be predicted accurately, the technique for prediction may be used to identify whether the attempt at hazard control by way of the dilution of the organic solution with water is effective. The composition effect upon flash point for a binary liquid solution comprising two flammable components has been derived earlier, and was based upon a flash point prediction model for binary liquid solutions proposed previously [7]. Since the behavior of flash point variation with composition for a binary aqueous-organic solution appears to be quite different from the analogous behavior of a binary solution with two flammable components, it is necessary to derive a new equation to describe the composition effect upon flash point for an aqueous-organic solution.

The main objective of this research was to establish a flash point prediction model that was able to be successfully used to predict the flash point of binary aqueous-organic solutions. In addition, an equation to describe the composition effect upon flash point for a binary aqueous-organic solution is also proposed. Such a model was developed based upon the theory of vapor-liquid equilibrium (VLE) and such an equation was derived based upon the application of the referred model. Both the model and the equation were subsequently verified by using the experimental data provided by the closed-cup test method. Since alcohols, such as methanol and isopropanol (IPA), are used frequently for semiconductor manufacture, and since alcoholic mixed drinks may be the universal drinks in daily life in some parts of the world, some aqueous solutions of various alcohols were selected for investigation in this study.

2. Experimental details

The flash point analyzer, HFP 362-Tag, manufactured by Walter Herzog GmbH (Germany) was used to measure the flash point of aqueous-organic solutions of varying different compositions as tested. The flash point analyzer incorporates control devices to program the instrument to heat the sample at a specified rate (heat rate) to within a temperature range close to the expected flash point, after which the vapor pressure is automatically tested with the igniter at specified temperature intervals (test interval). The first time that the solution flash point is tested is at a temperature equivalent to the expected flash point minus the start test value. The flash point analyzer's heater cuts out as soon as the testing temperature exceeds the sum of the expected flash point plus the end-of-test value, if the flash point is

not determined. The flash point analyzer is operated according to the standard test method, ASTM D56 [8] with the following set of selected parameters: start of test, 5 K; end of test, 20 K; test interval 1, 0.5 K; test interval 2, 1.0 K; heat rate 1, 1 K/min; and heat rate 2, 3 K/min.

Water was purified using a Milli-Q plus system. Methanol was an HPLC/Spectro-grade reagent, supplied by the Tedia Co. Inc. (USA). Isopropanol was verified by an ACS Standard and purchased from Pharmco Product Inc. (USA). Ethanol (99.5 vol.%) was obtained from NASA Enterprises (USA), and *n*-propanol purchased from J.T. Baker (USA).

3. Model for predicting the flash point of binary aqueous-organic solutions

3.1. Mathematical formulation

From the definition of flash point [3], the flash point of a flammable liquid is defined as that temperature at which the vapor pressure of the specified liquid is such as to produce a concentration of vapor in the air that corresponds to the lower flammable limit. In the vapor phase of a binary aqueous-organic solution, water vapor is not a flammable vapor but an inert one; thus, it is only necessary to consider the vapor-phase composition of the flammable component for the prediction of the flash point for an aqueous-organic solution. It has been previously reported in the literature that the lower flammable limit of a gas is almost the same in oxygen as it is in air [3]; hence, it is assumed for this study that the lower flammable (solution) limit of a flammable component is invariant regardless of the presence of any inert gas for the condition of there being present a sufficient quantity of oxygen for combustion. Expanding the definition of flash point for a pure substance [3] referred to above to that for a binary aqueous-organic solution under the assumption of a constant LFL for the flammable component, the flash point of a binary aqueous-organic solution is that temperature at which the vapor-phase composition of the flammable component is equivalent to its lower flammable limit in air. Therefore, the composition of the flammable component, which is denoted as component 2, in the vapor phase is expressed as follows when the temperature of an aqueous-organic solution lies at its flash point:

$$y_2 = \text{LFL}_2 \quad (1)$$

where LFL_2 is the lower flammable limit of pure flammable substance 2. In this paper, the flammable component of a binary aqueous-organic solution is denoted as component 2, and water (vapor) is denoted as component 1. From the definition of flash point [3], the LFL of a pure flammable (or combustible) liquid 2 (LFL_2) is expressed relative to its saturated vapor pressure at flash point ($P_{2,\text{fp}}^{\text{sat}}$) as:

$$\text{LFL}_i = \frac{P_{i,\text{fp}}^{\text{sat}}}{P} \quad (2)$$

where P is the ambient pressure. Under the ideal gas assumption, the composition of the flammable substance 2 in the vapor phase (y_2) can be derived from the vapor–liquid

equilibrium [6]:

$$y_2 = \frac{x_2 \gamma_2 P_2^{\text{sat}}}{P} \quad (3)$$

Substituting Eqs. (2) and (3) into Eq. (1) results in:

$$P_2^{\text{sat}} = \frac{P_{2,\text{fp}}^{\text{sat}}}{x_2 \gamma_2} \quad (4)$$

The Antoine equation, which describes the saturated vapor pressure variation with temperature for a pure substance i , may be used to estimate the temperature needed to produce a specified vapor pressure, i.e.:

$$\log P_i^{\text{sat}} = A_i - \frac{B_i}{T + C_i} \quad (5)$$

The vapor pressure of the pure flammable component 2 at its flash point $P_{2,\text{fp}}^{\text{sat}}$, as presented in Eq. (4), can be estimated by substituting $T_{2,\text{fp}}$, the flash point of such a flammable component, into the Antoine equation.

The activity coefficient γ_2 , which is presented in Eq. (4), can be estimated by the use of several equations, such as the Wilson equation [9], the NRTL equation [10], or the UNIQUAC equation [11], such equations being listed in Table 1.

The Wilson equation [9] contains only two adjustable parameters, the number of such parameters being less than is the case for the NRTL equation [10], which contains three parameters, and further, the Wilson equation is mathematically simpler than the UNIQUAC equation [11]. The Wilson equation, however, is not applicable to a mixture, which exhibits a miscibility gap [12]. Unlike Wilson's equation, the NRTL and UNIQUAC equations are applicable to both vapor–liquid and liquid–liquid equilibria [12]. Whilst the UNIQUAC equation is mathematically more complex than the NRTL equation, it does feature only two parameters and these parameters often exhibit a smaller dependence upon temperature than those of the NRTL and Wilson equations [12].

The flash point prediction model developed for a binary aqueous-organic solution is described using Eqs. (4) and (5) and the equations listed in Table 1. That temperature, which satisfies all these equations, is deemed, by us, to constitute the flash point of the aqueous-organic solution.

3.2. Reduced model under an ideal-solution assumption

For an ideal solution, the activity coefficient of the liquid phase for any component is equal to unity, and the flash point prediction model for an aqueous-organic solution may be reduced to a simpler form. Under this condition, Eq. (4) was able to be reduced to:

$$P_2^{\text{sat}} = \frac{P_{2,\text{fp}}^{\text{sat}}}{x_2} \quad (6)$$

Taking the logarithm on both sides of the equation results in:

$$\log P_2^{\text{sat}} = \log P_{2,\text{fp}}^{\text{sat}} - \log x_2 \quad (7)$$

Table 1
Some models for activity coefficients and their associated composition and temperature effect for binary systems

Wilson equation

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2 \left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2} \right)$$

$$\ln \gamma_2 = -\ln(x_2 + \Lambda_{21}x_1) - x_1 \left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2} \right)$$

$$\text{where } \Lambda_{ij} = \frac{v_j^1}{v_i^1} \exp \left(-\frac{\lambda_{ij} - \lambda_{ii}}{RT} \right)$$

$$\left(\frac{\partial \gamma_2}{\partial x_1} \right)_T = \gamma_2 \left\{ -\frac{1 - \Lambda_{21}}{x_2 - \Lambda_{21}x_1} - \left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2} \right) + x_1 \left[-\frac{\Lambda_{12}}{(x_1 + \Lambda_{12}x_2)^2} (1 - \Lambda_{12}) + \frac{\Lambda_{21}}{(\Lambda_{21}x_1 + x_2)^2} (\Lambda_{21} - 1) \right] \right\}$$

$$\left(\frac{\partial \gamma_2}{\partial T} \right)_{x_1} = \gamma_2 \left\{ -\frac{x_1}{x_2 + \Lambda_{12}x_1} \frac{d\Lambda_{21}}{dT} - x_1 \left[\frac{1}{x_1 + \Lambda_{12}x_2} \frac{d\Lambda_{12}}{dT} - \frac{\Lambda_{12}}{(x_1 + \Lambda_{12}x_2)^2} x_2 \frac{d\Lambda_{12}}{dT} - \frac{1}{\Lambda_{21}x_1 + x_2} \frac{d\Lambda_{21}}{dT} + \frac{\Lambda_{21}}{(\Lambda_{12}x_1 + x_2)^2} x_1 \frac{d\Lambda_{12}}{dT} \right] \right\}$$

NRTL equation

$$\ln \gamma_1 = x_2^2 \left[\tau_{21} \left(\frac{G_{21}}{x_1 + x_2 G_{21}} \right)^2 + \frac{\tau_{12} G_{12}}{(x_2 + x_1 G_{12})^2} \right]$$

$$\ln \gamma_2 = x_1^2 \left[\tau_{12} \left(\frac{G_{12}}{x_2 + x_1 G_{12}} \right)^2 + \frac{\tau_{21} G_{21}}{(x_1 + x_2 G_{21})^2} \right]$$

$$\text{where } \tau_{12} = \frac{g_{12} - g_{22}}{RT}, \tau_{21} = \frac{g_{21} - g_{11}}{RT}, \ln G_{12} = -\alpha_{12} \tau_{12}, \ln G_{21} = -\alpha_{12} \tau_{21}$$

$$\left(\frac{\partial \gamma_2}{\partial x_1} \right)_T = \gamma_2 \left\{ 2x_1 \left[\tau_{12} \left(\frac{G_{12}}{x_2 + x_1 G_{12}} \right)^2 + \frac{\tau_{21} G_{21}}{(x_1 + x_2 G_{21})^2} \right] + x_1^2 \left[2\tau_{12} \frac{G_{12}^2}{(x_2 + x_1 G_{12})^3} (1 - G_{12}) - \frac{2\tau_{21} G_{21}}{(x_1 + x_2 G_{21})^3} (1 - G_{21}) \right] \right\}$$

$$\begin{aligned} \left(\frac{\partial \gamma_2}{\partial T} \right)_{x_1} = & x_1^2 \gamma_2 \left[\left(\frac{G_{12}}{x_2 + x_1 G_{12}} \right)^2 \frac{d\tau_{12}}{dT} + 2\tau_{12} \left(\frac{G_{12}}{x_2 + x_1 G_{12}} \right) \left(\frac{1}{x_2 + x_1 G_{12}} \frac{dG_{12}}{dT} - \frac{G_{12}}{(x_2 + x_1 G_{12})^2} x_1 \frac{dG_{12}}{dT} \right) \right. \\ & \left. + \frac{1}{(x_1 + x_2 G_{21})^2} \left(G_{21} \frac{d\tau_{21}}{dT} + \tau_{21} \frac{dG_{21}}{dT} \right) - \frac{2\tau_{21} G_{21}}{(x_1 + x_2 G_{21})^3} x_2 \frac{dG_{21}}{dT} \right] \end{aligned}$$

Table 1 (Continued)

UNIQUAC equation

$$\ln \gamma_i = \ln \frac{\Phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\Phi_i} + \Phi_j \left(l_i - \frac{r_i}{r_j} l_j \right) - q_i \ln(\theta_i + \theta_j \tau_{ji}) + \theta_j q_i \left(\frac{\tau_{ji}}{\theta_i + \theta_j \tau_{ji}} - \frac{\tau_{ij}}{\theta_j + \theta_i \tau_{ij}} \right)$$

$$\text{where } i = 1 \text{ and } j = 2, \text{ or } i = 2 \text{ and } j = 1, \ln \tau_{ij} = -\frac{u_{ij} - u_{ji}}{RT}, \Phi_i = \frac{x_i r_i}{x_i r_i + x_j r_j}, \theta_i = \frac{x_i q_i}{x_i q_i + x_j q_j}, l_i = \frac{z}{2}(r_i - q_i) - (r_i - 1), z = 0$$

$$\left(\frac{\partial \gamma_2}{\partial x_1} \right)_T = \gamma_2 \left\{ \frac{1}{\Phi_2} \frac{d\Phi_2}{dx_1} + \frac{1}{x_2} + \frac{z}{2} q_2 \left(\frac{1}{\theta_2} \frac{d\theta_2}{dx_1} - \frac{1}{\Phi_2} \frac{d\Phi_2}{dx_1} \right) + \left(l_2 - \frac{r_2}{r_1} l_1 \right) \frac{d\Phi_1}{dx_1} - \frac{q_2}{\theta_2 + \theta_1 \tau_{12}} \left(\frac{d\theta_2}{dx_1} + \tau_{12} \frac{d\theta_1}{dx_1} \right) \right. \\ \left. + q_2 \frac{d\theta_1}{dx_1} \left(\frac{\tau_{12}}{\theta + \theta_1 \tau_{12}} - \frac{\tau_{21}}{\theta_1 + \theta_2 \tau_{21}} \right) + \theta_1 q_2 \left[\frac{\tau_{21}}{(\theta_1 + \theta_2 \tau_{21})^2} \left(\frac{d\theta_1}{dx_1} + \tau_{21} \frac{d\theta_2}{dx_1} \right) - \frac{\tau_{12}}{(\theta_2 + \theta_1 \tau_{12})^2} \left(\frac{d\theta_2}{dx_1} + \tau_{12} \frac{d\theta_1}{dx_1} \right) \right] \right\}$$

$$\left(\frac{\partial \gamma_2}{\partial T} \right)_{x_1} = \gamma_2 \left\{ -\frac{q_2 \theta_1}{\theta_2 + \theta_1 \tau_{12}} \frac{d\tau_{12}}{dT} + \theta_1 q_2 \left[\frac{\theta_2}{(\theta_2 + \theta_1 \tau_{12})^2} \frac{d\tau_{12}}{dT} - \frac{\theta_1}{(\theta_1 + \theta_2 \tau_{21})^2} \frac{d\tau_{12}}{dT} \right] \right\}$$

$$\text{where } \frac{d\Phi_1}{dx_1} = \frac{r_1 r_2}{(x_1 r_1 + x_2 r_2)^2}, \frac{d\Phi_2}{dx_1} = -\frac{r_1 r_2}{(x_1 r_1 + x_2 r_2)^2}, \frac{d\theta_1}{dx_1} = \frac{q_1 q_2}{(x_1 q_1 + x_2 q_2)^2}, \frac{d\theta_2}{dx_1} = -\frac{q_1 q_2}{(x_1 q_1 + x_2 q_2)^2}, \frac{d\tau_{12}}{dT} = \tau_{12} \frac{u_{12} - u_{22}}{RT^2}, \frac{d\tau_{21}}{dT} = \tau_{21} \frac{u_{21} - u_{11}}{RT^2}$$

Substituting the Antoine equation into the above equation to estimate P_2^{sat} and $P_{2,\text{fp}}^{\text{sat}}$ results in:

$$T = \frac{B_2}{(B_2/(T_{2,\text{fp}} + C_2)) + \log x_2} - C_2 \quad (8)$$

Therefore, the flash point of a binary aqueous-organic solution under an ideal-solution assumption can be estimated using Eq. (8). The estimation of the flash point for a binary aqueous-organic solution by the use of the reduced model under an ideal-solution assumption, Eq. (8), is virtually equivalent to the method described by Crowl and Louvar [2], which uses Eq. (6) and a graph of the vapor pressure versus temperature to estimate the flash point of a binary aqueous-organic solution. Our technique would appear to be simpler.

4. Composition effect upon flash point for a binary aqueous-organic solution

4.1. General formulation

At the flash point for a liquid solution based upon the closed-cup test method, the vapor phase will be in equilibrium with the liquid phase for any component in the mixture. Thus, the composition of the flammable component for a binary aqueous-organic solution in the vapor phase (y_2) will obey the vapor–liquid equilibrium relationship [6] given in Eq. (3).

Differentiating Eq. (3) with respect to x_1 at constant temperature results in:

$$\left(\frac{\partial y_2}{\partial x_1}\right)_T = \frac{P_2^{\text{sat}}}{P} \left(-\gamma_2 + x_2 \left(\frac{\partial \gamma_2}{\partial x_1}\right)_T\right) \quad (9)$$

The following relationship, the sum of mole fractions, was used when deriving the above equation:

$$x_1 + x_2 = 1$$

Differentiating Eq. (3) with respect to T at constant x_1 results in:

$$\left(\frac{\partial y_2}{\partial T}\right)_{x_1} = \frac{x_2}{P} \left(\gamma_2 \frac{dP_2^{\text{sat}}}{dT} + P_2^{\text{sat}} \left(\frac{\partial \gamma_2}{\partial T}\right)_{x_1}\right) \quad (10)$$

As mentioned in Section 3.1, at the flash point of a binary aqueous-organic solution, the vapor phase composition of the flammable component is assumed to be equal to the LFL of this pure flammable substance. The vapor phase composition of the flammable component (y_2) remains constant, this value being equivalent to LFL_2 , when the flash point of a binary aqueous-organic solution varies with composition. Further, the composition effect upon the flash point for a binary aqueous-organic solution is expressed as $(\partial T/\partial x_1)_{y_2}$, and the subscript y_2 indicates that y_2 is held constant. The equation for this derivative of flash point with respect to solution composition, $(\partial T/\partial x_1)_{y_2}$, can be derived by application of the

triple-product relationship:

$$\begin{aligned} \left(\frac{\partial T}{\partial x_1}\right)_{y_2} &= -\frac{(\partial y_2/\partial x_1)_T}{(\partial y_2/\partial T)_{x_1}} = -\frac{(P_2^{\text{sat}}/P)(-\gamma_2 + x_2(\partial\gamma_2/\partial x_1)_T)}{(x_2/P)(\gamma_2(dP_2^{\text{sat}}/dT) + P_2^{\text{sat}}(\partial\gamma_2/\partial T)_{x_1})} \\ &= -\frac{P_2^{\text{sat}}(-\gamma_2 + x_2(\partial\gamma_2/\partial x_1)_T)}{x_2(\gamma_2(dP_2^{\text{sat}}/dT) + P_2^{\text{sat}}(\partial\gamma_2/\partial T)_{x_1})} \end{aligned} \quad (11)$$

The Antoine equation for the flammable substance, which is denoted as “component 2”, is described as:

$$\log P_2^{\text{sat}} = A_2 - \frac{B_2}{T + C_2}$$

The derivative of saturated vapor pressure with respect to T for component 2 is expressed as:

$$\frac{1}{P_2^{\text{sat}}} \frac{dP_2^{\text{sat}}}{dT} = \frac{B_2/(T + C_2)^2}{\log(e)} \quad (12)$$

or

$$\frac{dP_2^{\text{sat}}}{dT} = \frac{B_2 P_2^{\text{sat}}/(T + C_2)^2}{\log(e)} \quad (13)$$

The formulae associated with the partial derivatives of γ_2 with respect to x_1 at constant T and with respect to T at constant x_1 depend upon the particular equation used to estimate the liquid-phase activity coefficient. These partial derivative formulae for the Wilson equation [9] and the NRTL equation [10] were derived in previous work [7], and those corresponding to the UNIQUAC equation [11] are derived in this paper, all of these derivative formulae being listed in Table 1.

Therefore, the composition effect upon flash point for a binary aqueous-organic solution can be estimated by the application of Eqs. (5), (11) and (13) together with the equations for estimating the liquid-phase activity coefficient for the flammable component of the solution and the derivatives of γ_2 with respect to x_1 or T , $(\partial\gamma_2/\partial x_1)_T$ and $(\partial\gamma_2/\partial T)_{x_1}$, as listed in Table 1.

4.2. Composition effect upon flash point for a binary aqueous-organic solution under an ideal-solution assumption

For an ideal solution, the value of the activity coefficient corresponding to the (solution) flammable component which is denoted as component 2, is independent of solution composition and temperature, and is equal to unity, i.e.:

$$\begin{aligned} \gamma_2 &= 1 \\ \left(\frac{\partial\gamma_2}{\partial x_1}\right)_T &= 0 \\ \left(\frac{\partial\gamma_2}{\partial T}\right)_{x_1} &= 0 \end{aligned}$$

Thus, Eq. (11) becomes reducible to:

$$\left(\frac{\partial T}{\partial x_1}\right)_{y_2} = \frac{P_2^{\text{sat}}}{x_2(dP_2^{\text{sat}}/dT)} \quad (14)$$

Substituting Eq. (13) into the above equation results in:

$$\left(\frac{\partial T}{\partial x_1}\right)_{y_2} = \frac{(T + C_2)^2}{B_2 x_2} \log(e) \quad (15)$$

Therefore, the composition effect upon flash point for a binary aqueous-organic solution under an ideal-solution assumption can be estimated using Eq. (15) for a given solution composition.

5. Results and discussion

5.1. The parameters used in this paper

In this study, the flash point prediction model for a binary aqueous-organic solution proposed in Section 3.1 and the reduced model under an ideal-solution assumption derived in Section 3.2, which is equivalent to Crowl and Louvar's method [2], were used to predict the flash point of the following binary aqueous solutions: water + methanol, water + ethanol, water + *n*-propanol and water + isopropanol. The prediction results so obtained were compared with the corresponding experimentally-derived data. These aqueous solutions are all non-ideal solutions, and the activity coefficients corresponding to the flammable components for all such solutions are all greater than unity [13–16]. The liquid-phase activity coefficients corresponding to the flammable components of these aqueous solutions were all estimated by use of three different equations, namely the NRTL equation [10], the Wilson equation [9] and the UNIQUAC equation [11]. These activity coefficients were subsequently used in the flash point prediction model for a binary aqueous-organic solution in order to predict the corresponding flash point variation curves. Further, the results of the flash point variation curves, based upon different activity coefficient equations, were compared with the corresponding experimentally-derived data. The parameters pertaining to the flash point prediction model for a binary aqueous-organic solution include the Antoine coefficients, the parameters pertaining to certain equations necessary to estimate the activity coefficients corresponding to the flammable components of these aqueous solutions, such as the Wilson, NRTL, and/or UNIQUAC equations, and the flash point of the relevant pure flammable component. The Antoine coefficients for these species were adopted from the literature [12,17–19] and are listed in Table 2. The relevant parameters for the equations to estimate the activity coefficients as abstracted from different literature sources pertaining to the same equations were used in this flash point prediction model to predict the appropriate flash point variation curves for the particular aqueous solution concerned. Following this, the results so obtained were compared with the corresponding experimentally-derived data. The various parameters that were relevant to the Wilson, NRTL and UNIQUAC equations for the aqueous solutions used in this study were abstracted from the relevant literature

Table 2
Antoine coefficients for the involved components

Material	A	B	C	Reference
Methanol ^a	7.20519	1581.993	−33.289	[17]
Ethanol ^a	7.24222	1595.811	−46.702	[18]
<i>n</i> -Propanol ^b	17.5439	3166.38	−80.15	[12]
2-Propanol ^c	7.56634	1366.142	−75.030	[18]
Water ^a	7.23255	1750.286	−38.000	[19]

$$^a \log(P/\text{kPa}) = A - B/[(T/K) + C].$$

$$^b \log(P/\text{mmHg}) = A - B/[(T/K) + C].$$

$$^c \ln(P/\text{mmHg}) = A - B/[(T/K) + C].$$

[13–15,20–24], and are listed in Table 3. The relative van der Waals volume parameter (r) and the surface area parameter (q) for the pure components needed for the application of the UNIQUAC equation to our system were also obtained from the relevant literature [12], and are listed in Table 4. This table also lists the specific volume values corresponding to some solution components, which were used to estimate the relevant parameter values for the Wilson equation, with the relevant formulae used for this purpose being listed in Table 1.

Table 3
Parameters corresponding to the NRTL, Wilson and UNIQUAC equations for experimental binary systems

System	Parameters ^a			Reference
	A_{12}	A_{21}	α_{12}	
NRTL equation				
Water (1) + methanol (2)	487.79	−214.15	0.1	[20]
Water (1) + methanol (2)	164.56	168.31	0.3	[13]
Water (1) + ethanol (2)	523.84	3.17	0.3	[21]
Water (1) + ethanol (2)	633.91	24.86	0.4	[14]
Water (1) + <i>n</i> -propanol (2)	865.41	77.33	0.3772	[15]
Water (1) + isopropanol (2)	869.00	352.79	0.45	[13]
Wilson equation				
Water (1) + methanol (2)	304.16	98.02	−	[20]
Water (1) + methanol (2)	908.46	−359.74	−	[13]
Water (1) + ethanol (2)	481.44	179.66	−	[21]
Water (1) + <i>n</i> -propanol (2)	597.523	527.50	−	[22]
Water (1) + isopropanol (2)	380.59	650.35	−	[13]
UNIQUAC equation				
Water (1) + methanol (2)	180.22	−117.34	−	[20]
Water (1) + methanol (2)	−271.26	736.01	−	[13]
Water (1) + ethanol (2)	−109.37	299.46	−	[21]
Water (1) + <i>n</i> -propanol (2)	200.64	9.58	−	[23]
Water (1) + isopropanol (2)	32.45	164.90	−	[24]
Water (1) + isopropanol (2)	−41.7	283.10	−	[13]

^a NRTL equation: $A_{12} = (g_{12} - g_{22})/R$, $A_{21} = (g_{21} - g_{11})/R$; Wilson equation: $A_{12} = (\lambda_{12} - \lambda_{11})/R$, $A_{21} = (\lambda_{21} - \lambda_{22})/R$; UNIQUAC equation: $A_{12} = (u_{12} - u_{22})/R$, $A_{21} = (u_{21} - u_{11})/R$.

Table 4

The relative van der Waals volumes (r) and surface areas (q) for the pure components for the UNIQUAC model and the specific volume (v_i^l) for the pure components for the Wilson model

Component	v_i^l (cm ³ /mol) ^a	MW [26]	ρ (g/cm ³)	r [12]	q [12]
Methanol	40.73	32.04	0.7867 [14]	1.4311	1.432
Ethanol	58.68	46.07	0.7851 [14]	2.1055	1.972
<i>n</i> -Propanol	75.09	60.10	0.80034 [15]	2.7799	2.512
Isopropanol	76.53	60.10	0.7853 [13]	2.7791	2.508
Water	18.07	18.02	0.9972 [14]	0.9200	1.400

$$^a v_i^l = MW_i/\rho_i.$$

The flash point values of the pure flammable substances used in this study were obtained by way of testing with the flash point analyzer. Table 5 compares the experimentally-derived data for flash point for some alcohols with the analogous values adopted from the literature listed alongside. The value of the flash point for *n*-propanol adopted from Society of Fire Protection Engineers (SFPE) Handbook [25] and the Merck Index [26] (15 and 22 °C, respectively) clearly appear to be quite different. The corresponding value provided by the chemical supplier of the *n*-propanol used herein, J.T. Baker, is 23 °C, which appears to be quite similar to that value adopted by Merck [26]. This study's experimentally-derived analogue is 21.5 °C, which appears to be very close to the value listed in Merck [26] as also that provided by J.T. Baker. The experimentally-derived value of the flash point for ethanol is the same as that figure adopted from various literature sources [25,26], although there did appear to exist some slight deviation between our experimentally-derived data and the analogous value reported for methanol and isopropanol in the literature [25,26]. The flash point values quoted from SFPE and Merck are obtained by a closed-cup method [25,26], although interestingly, the standard test method is not mentioned in SFPE [25] or Merck [26]. The perceived difference in flash point data for methanol and isopropanol as regards the values applied for this work and the corresponding values reported in the SFPE Handbook [25] and the Merck Index [26] might be attributable to existing differences in the "standard test method" or may be due to the presence of impurities in the sample used.

Eq. (11), which was derived in Section 4.1 in order to predict the composition effect upon flash point for a binary aqueous solution, was used to predict the composition effect upon the respective flash point for the aqueous solutions referred to above in this section,

Table 5

Comparison of flash point values adopted from the literature with experimentally-derived data for some alcohols^a

Component	Experimental data (°C)	SFPE (°C) [25]	Merck (°C) [26]
Methanol	10.0	12	12
Ethanol	13.0	13	13
<i>n</i> -Propanol	21.5	15	22
Isopropanol	13.0	12	11.7

^a Closed-cup test.

the prediction results here being compared with the corresponding experimentally-derived data. For the effective prediction of the composition effect upon a solution's flash point by use of Eq. (11), the liquid-phase activity coefficients for methanol and ethanol were estimated by use of the NRTL equation [10], those for *n*-propanol were estimated by use of the Wilson equation [9], and those analogous coefficients corresponding to isopropanol were estimated by use of the UNIQUAC equation [11]. The equation used to estimate the activity coefficients for each of these referred to aqueous solutions in this simulation was selected randomly. The experimentally-derived data corresponding to an analysis of the composition effect upon the flash point (the derivative of flash point with respect to solution composition) were obtained by rearranging the experimentally-derived data corresponding to solution flash point versus composition using central-difference approximation.

5.2. The flash point variation of binary aqueous-organic solutions

The flash points of differing concentration aqueous methanol solutions covering the entire composition range of methanol in water were tested herein. The results were plotted against the predictive curves from the flash point prediction model for a binary aqueous-organic

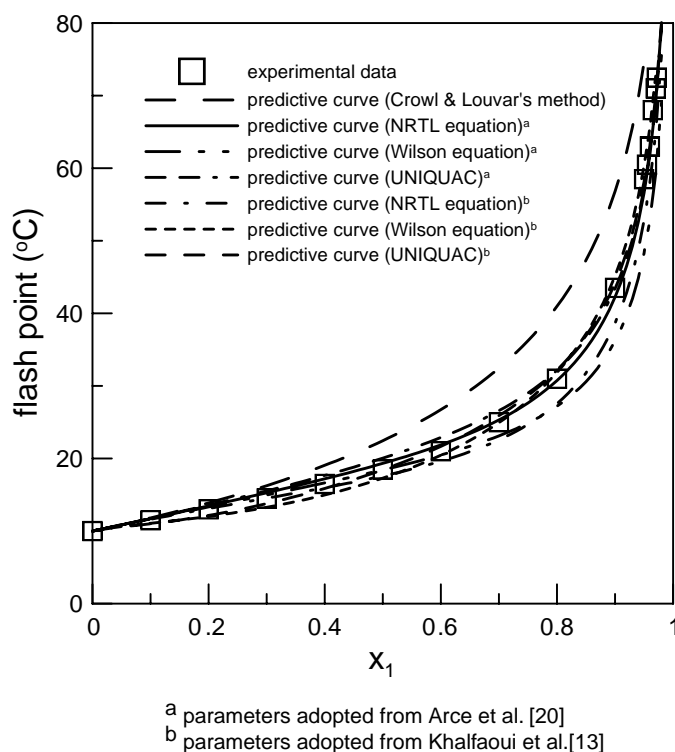


Fig. 1. Comparison of the flash point prediction curves with experimental data for a water (1) + methanol (2) solution.

solution using different equations for estimating the activity coefficients of the curves depicted in Fig. 1. The other (predictive) curve being suggested by application of Eq. (8), which is virtually equivalent to Crowl and Louvar's method [2], is also plotted in Fig. 1. It can be clearly seen that the predictive values for the flash point simulation based upon Crowl and Louvar's method [2], which are described by Eq. (8), are somewhat larger than the corresponding experimentally-derived data for the composition of an aqueous solution of methanol apart from the case when the water concentration is zero, although the method is able to predict the experimentally-derived analogues successfully for such a solution when the composition of water in the solution approaches zero. By contrast, although there are differences between the predicted values of flash point for the predictive curves, when using the NRTL, Wilson or UNIQUAC equations to estimate activity coefficients, the experimentally-derived results appear to be in much better agreement with such predictive curves than is the case for the analogous curve based upon Crowl and Louvar's method [2]. In particular, the predictive curve arrived at using the NRTL equation with parameters adopted from Arce et al.'s study [20], and which was intended to predict the activity coefficient, is in best agreement with the experimental data. It is demonstrated here, that the flash point prediction model proposed in this paper is able to successfully predict the flash

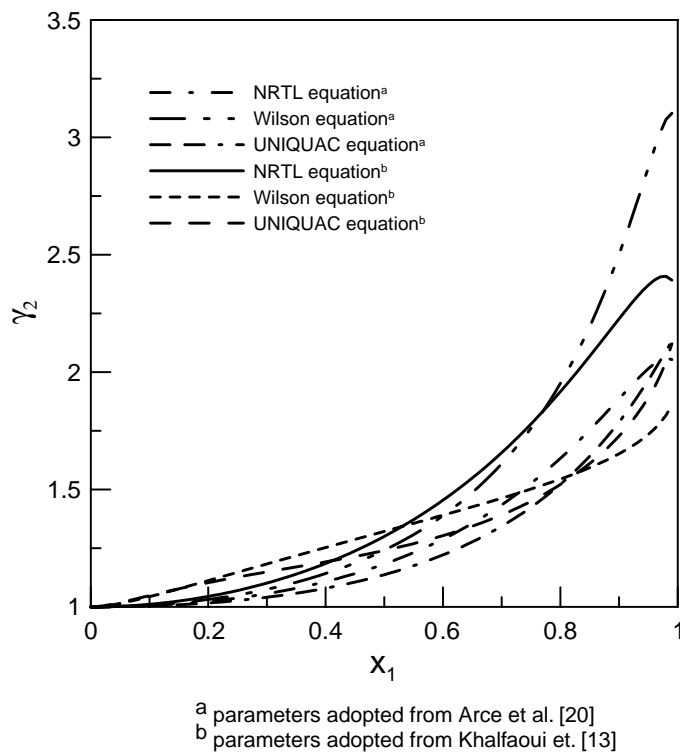


Fig. 2. Activity coefficient–liquid composition diagram for a water (1) + methanol (2) solution at its flash point conditions.

point variation of a binary aqueous-organic solution, such as a methanol aqueous solution. The estimated activity coefficients of methanol for a water + methanol system based upon the NRTL, Wilson and UNIQUAC equations with the necessary relevant parameters being adopted from different sources, as displayed in Fig. 2, all appear to be larger than unity. It is revealed from our study that the deviation of our experimentally-derived data from the predictive curve proffered by Crowl and Louvar's method [2] arises from the fact that the behavior of this aqueous-organic solution reveals a positive deviation from that of an ideal solution, with such behavior resulting in a reduction of the solution's flash point from the predicted analogue for an ideal solution. The application of Raoult's law for the flammable component of the solution, which is the main assumption of Crowl and Louvar's method [2], is even valid for a composition range for water approaching zero. Further, such behavior results in good agreement between the experimentally-derived data for the flash point and the predictive curve based upon such a method over such a composition range.

In addition to the predictive results for the aqueous solution of methanol, the flash point prediction model for a binary aqueous-organic solution was also used to predict the flash point variations for other aqueous solutions, including water + ethanol, water + *n*-propanol and water + isopropanol, as reflected by a comparison of the predictive results with the experimentally-derived data, such results being displayed in Figs. 3–5. The flash point prediction model for a binary aqueous-organic solution used herein is able to predict the experimentally-derived data for water + ethanol and water + *n*-propanol solutions no matter

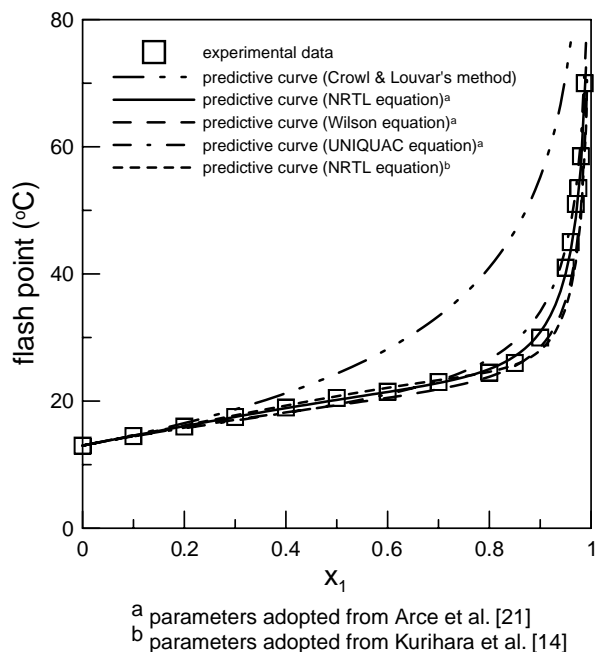


Fig. 3. Comparison of the flash point prediction curves with experimental data for a water (1) + ethanol (2) solution.

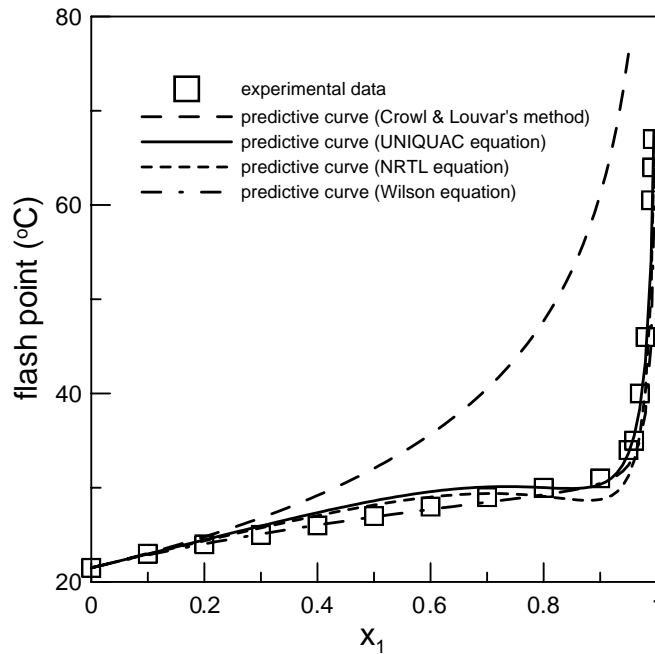


Fig. 4. Comparison of the flash point prediction curves with experimental data for a water (1) + *n*-propanol (2) solution.

whether the procedure involved the use of the NRTL, Wilson or UNIQUAC equations to estimate the relevant activity coefficients. The predictive results of the flash point prediction model for a binary aqueous-organic solution using the UNIQUAC equation with parameters adopted from two different sources, Khalfaoui et al. [13] and Wolf and Schlunder [24], to predict the activity coefficients for isopropanol, are in excellent agreement with the respective experimentally-derived analogues for an isopropanol aqueous solution. The analogous results for an isopropanol aqueous solution using the Wilson equation to estimate the activity coefficients of isopropanol are also consistent with the experimentally-derived data. The analogous predictive curves derived using the NRTL equation, however, the parameters for which were abstracted from Khalfaoui et al. [13], and used to predict the relevant activity coefficients for isopropanol, do deviate from the experimentally-derived analogues for the solution composition ranges with a water composition of around 0.9. For the parameter value estimation process for the equations used to describe the activity coefficients, the values of the parameters, which give a global minimum of one objective function, are deemed to be the parameters of the equations. Due to the presence of multiple solutions and the complexity of the equation employed, it becomes difficult to provide a guarantee of obtaining the global solution for the parameters necessary for the activity coefficient equations as applied to the phase equilibrium problem [27]. Therefore, this deviation between the predictive curve and the corresponding experimental data for an isopropanol aqueous

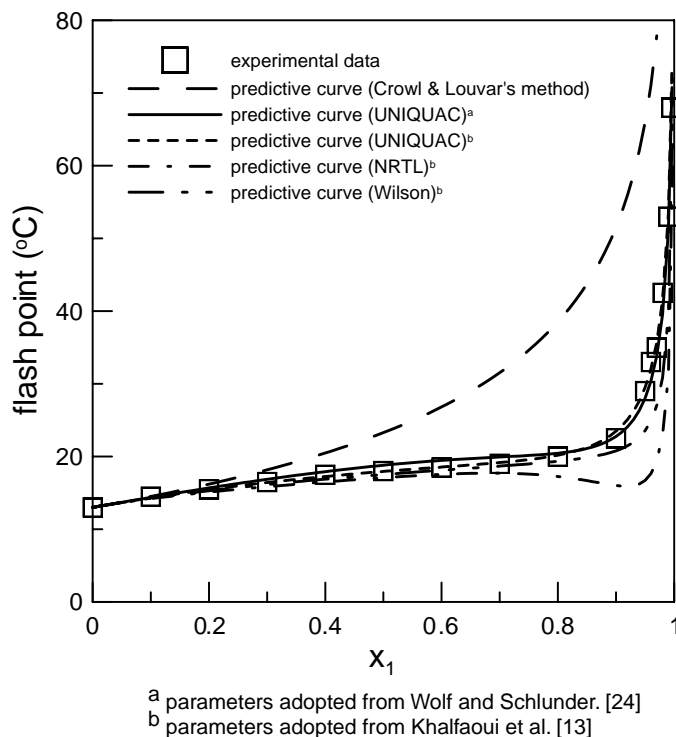


Fig. 5. Comparison of the flash point prediction curves with experimental data for a water (1) + isopropanol (2) solution.

solution may be attributable to the notion that the values of the parameters necessary for the NRTL equation, as determined by the optimization method by Khalfaoui et al. [13], are not the appropriate global optimal values but merely local optimal values.

In summary, the prediction results of the flash point prediction model proposed in this paper either based upon the NRTL, the Wilson or the UNIQUAC equation appear to agree well with the experimentally-derived data for flash point corresponding to an aqueous-organic solution. Further, such a prediction model may provide a very acceptable means of predicting such flash point data points. The relative precision of the model's prediction results depends upon the relative accuracy of the selected parameter values for such equations used to estimate the activity coefficients.

As was the case for the methanol aqueous solution referred to above, the predictive curves based upon Crowl and Louvar's method [2] were unable to satisfactorily equate with the experimentally-derived data corresponding to the other study-included aqueous solutions, namely: water + ethanol, water + *n*-propanol, and water + isopropanol (Figs. 3–5). The reason for this (apparently) substantial deviation between the experimentally-derived data and the predictive curves based upon Crowl and Louvar's method [2] is the same as that which would apply to a system of water + methanol. Essentially, Raoult's law is unable to

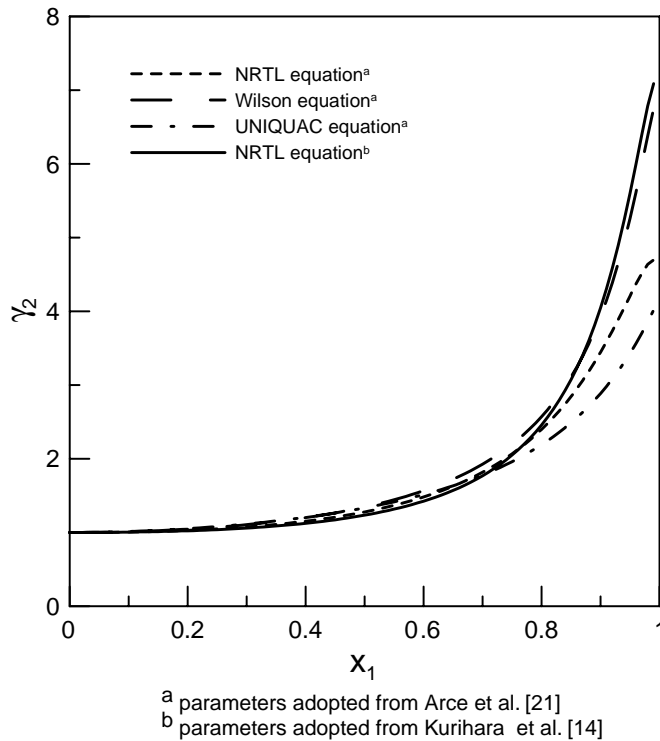


Fig. 6. Activity coefficient–liquid composition diagram for a water (1) + ethanol (2) solution at its flash point conditions.

effectively describe the behavior of a non-ideal solution, such as water + ethanol, water + *n*-propanol and water + isopropanol. This result is illustrated in Figs. 6–8, respectively, where the estimated activity coefficients of the flammable components for these solutions are demonstrated to deviate notably from unity. Figs. 2 and 6–8 reveal that the activity coefficients for ethanol, *n*-propanol and isopropanol in their tested aqueous solutions are (numerically) larger than those for methanol in an aqueous solution. Such an observation indicates that the behavior of the aqueous solutions for ethanol, *n*-propanol and isopropanol do deviate more substantially from an ideal solution than do those of a methanol aqueous solution. Further, such behavior as reflected in Figs. 3–5 also suggests that the deviation between the predictive curves of Crowl and Louvar's method [2], which was based upon an ideal-solution assumption, and experimentally-derived data are more substantial for water + ethanol, water + *n*-propanol and water + isopropanol than is the case for water + methanol. This observation is especially substantial for the water + *n*-propanol system, the predictive curve for which, based upon Crowl and Louvar's method [2], indicates that the flash point of such a system increases to 60 °C if the *n*-propanol composition is diluted to 10% (water composition is 90%). By comparison, however, the experimentally-derived data reveals that the flash point of the solution is still quite low at such a composition, namely, 28 °C. There

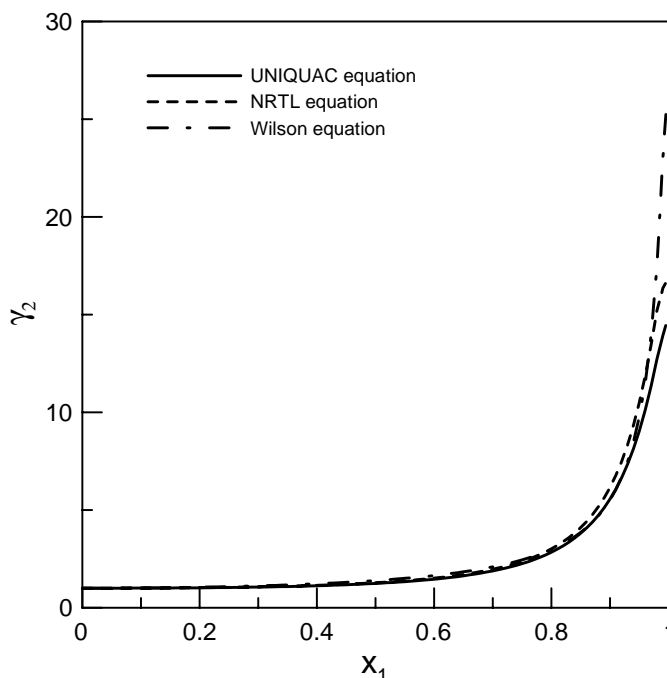


Fig. 7. Activity coefficient–liquid composition diagram for a water (1) + *n*-propanol (2) solution at its flash point conditions.

appears to exist significant deviation between the experimentally-derived data and the flash point predictive curves based upon the method described by Crowl and Louvar [2], for the composition of a binary solution of an alcohol and water, the water concentration of which is other than zero. Thus, it can be concluded that the method selected to predict the flash point of an aqueous-organic solution, as described by Crowl and Louvar [2], is limited to a solution for which the concentration of water remains close to zero, i.e. a situation where the application of Raoult's law is valid for the flammable component. The more-powerful model, the flash point prediction model for a binary aqueous-organic solution as proposed in this paper, is thus necessary for accurately predicting the flash point behavior of a binary aqueous-organic solution at all concentrations.

In deriving the flash point prediction model for a binary aqueous-organic solution, it was assumed that the liquid phase and the vapor phase for an aqueous solution are in equilibrium. The estimation of the flash point using the flash point prediction model for a binary aqueous-organic solution is only adequate for the data determined by the closed-cup test method, such a condition being presumed under the assumption of a vapor–liquid equilibrium. Further, for such an estimation of flash point, it may not be appropriate to apply such a model to the data obtained from the open-cup test method, under which situation the operating conditions deviate from the assumption of an existing vapor–liquid equilibrium and presume the existence of a vapor-concentration gradient.

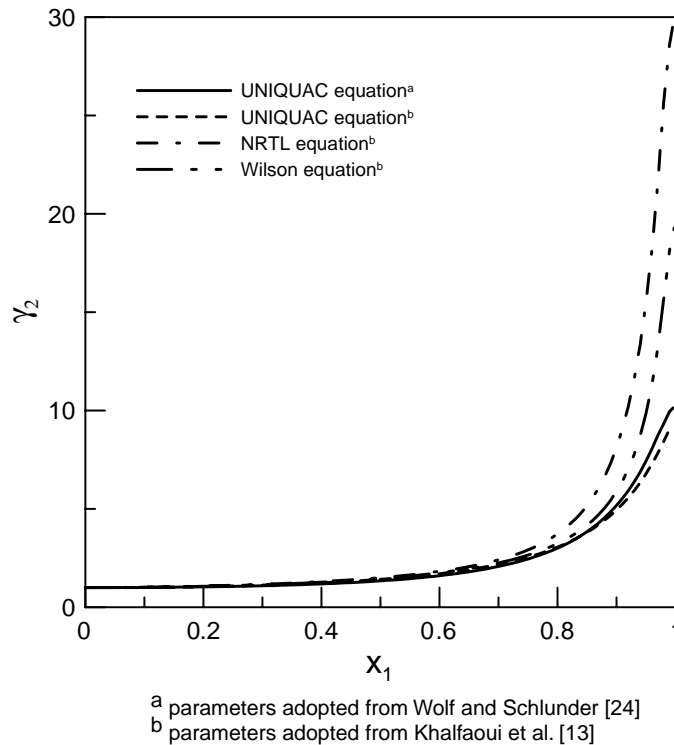


Fig. 8. Activity coefficient–liquid composition diagram for a water (1) + isopropanol (2) solution at its flash point conditions.

5.3. Comparison of the composition effect upon flash point for the predictive curves versus experimentally-derived data

A comparison of the predictive curves for the composition effect upon the flash point of a binary aqueous-organic solution as predicted by Eq. (11) with experimentally-derived data, is displayed in Fig. 9. The other predictive curves, based upon the assumption of an ideal solution, as predicted by the application of Eq. (15), which is the reduced form of Eq. (11) for an ideal solution, are also plotted in Fig. 9. It can be readily seen from Fig. 9 that the predictive curves for the composition effect upon (solution) flash point based upon an ideal-solution assumption, Eq. (15), are all numerically larger than the experimentally-derived data for these four aqueous solutions: water + methanol, water + ethanol, water + *n*-propanol and water + isopropanol. Such predictive results may encourage people to mistakenly believe that the dilution of a flammable solution with water is able to increase the flash point of such a solution, and thus effectively reduce the potential hazard of subsequent fire and explosion. The experimentally-derived data, however, do not support such a conclusion. The deviation between the predictive curve based upon Eq. (15) and experimentally-derived analogues is more notable for both the aqueous solutions of *n*-propanol and isopropanol. The predicted

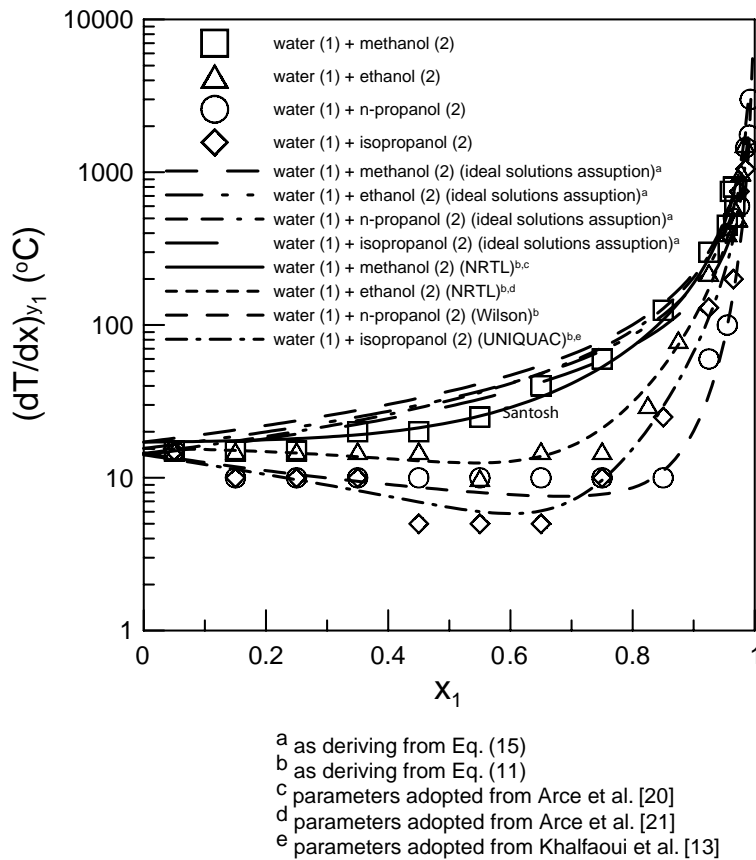


Fig. 9. Comparison of the predicted composition effect upon flash point and the experimentally-derived data.

value of the composition effect upon flash point would appear to be more than 10 times larger than the experimentally-derived data for an *n*-propanol aqueous solution at $x_1 = 0.9$. This deviation of the experimentally-derived data from the predictive curve based upon Eq. (15) may be attributed to the non-ideality of the solutions referred to above. This result is referred to in Figs. 2 and 6–8 in which the estimated activity coefficients for these solutions were demonstrated to deviate notably from unity. By contrast, the predictive curves for the composition effect upon (solution) flash point based upon Eq. (11) are in good agreement with the analogous experimentally-derived data. From such a result it may be concluded that Eq. (11) can effectively describe the experimentally-derived data corresponding to the composition effect upon the flash point for a binary aqueous-organic solution.

It is revealed in Fig. 9 that the dimension of the composition effect upon flash point for the aqueous solutions used in this study is relatively small, such determined values all being less than 20 °C, for the solution composition range featuring a high concentration of the flammable component. By contrast, the dimension of such a composition effect upon

flash point appears to only become particularly notable for low concentration ranges of the flammable component. Thus, it is apparent that to attempt to reduce the fire and explosion hazard posed by a flammable solution by diluting such a solution with water is, typically, only effective for an already-dilute aqueous-organic solution.

6. Conclusion

The method described by Crowl and Louvar [2] can only be effectively used to estimate the flash point of a binary aqueous-organic solution for which the composition range of water approaches zero (the composition of the flammable component close to unity), and it is not adequate to apply such a method to the composition of such a solution when the concentration of water in such a solution lies outside such a composition range. By contrast, the flash point prediction model for a binary aqueous-organic solution proposed in this paper is able to accurately predict the flash point for a binary aqueous-organic solution as revealed by a comparison between predicted and experimentally-derived data. The prediction results of this model can thus be applied to incorporate inherently safer designs for various laboratory and commercial chemical processes, such as the determination of the safe-storage conditions for various aqueous-organic solutions. The experimentally-derived data for a variety of binary aqueous-organic solutions have demonstrated that the paper-presented equations derived above may be used to accurately estimate the composition effect upon flash point for a binary aqueous-organic solution. The composition effect upon flash point derived in this paper can be used for the analysis of the sensitivity of flash point variation for a flammable solution diluted with water. Such a result can be applied in the process safety design/operation in order to identify if the dilution of a flammable liquid with water is effective at reducing the fire/explosion hazard of the solution at a specified composition.

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