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Flash-Point Prediction for Binary Partially Miscible Aqueous-Organic Mixtures

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ABSTRACT

Flash point is the most important variable used to characterize fire and explosion hazard of liquids. Herein, partially miscible mixtures are presented within the context of liquid-liquid extraction processes and heterogeneous distillation processes. This paper describes development of a model for predicting the flash point of binary partially miscible mixtures of aqueous-organic system. To confirm the predictive efficiency of the derived flash points, the model was verified by comparing the predicted values with the experimental data for the studied mixtures: water + 1-butanol; water + 2-butanol; water + isobutanol; water + 1-pentanol; and, water + octane. Results reveal that immiscibility in the two liquid phases should not be ignored in the prediction of flash point. Overall, the predictive results of this proposed model describe the experimental data well when using the LLE and VLE parameters to estimate sequentially the span of two liquid phases and the flash point, respectively. Potential application for the model concerns the assessment of fire and explosion hazards, and the development of inherently safer designs for chemical processes containing binary partially miscible mixtures of aqueous-organic system.

Keywords: Flash point; Prediction; Partially miscible mixtures; Aqueous-organic solution; Vapor-liquid-liquid equilibrium

1. Introduction

In a given liquid, the flash point is the temperature determined experimentally at which the substance emits sufficient vapor to form a combustible mixture with air (CCPS/AIChE, 1993). The lower the flash-point value, the greater is the fire and explosion hazard (Lees, 1996). Recently, the importance of flash point was dramatically highlighted in Taiwan after a series of explosions of essential oils and after the Shengli event. In the former series of accidents, six blasts occurring from January through August of 2003, left eight people badly burnt. The fire and explosion hazard of liquids, such as essential oils, is primarily characterized by their flash point (Crowl and Louvar, 2002). During the Shengli event waste organic solvents were illegally dumped into the Kaoping River (southern Taiwan), causing serious water pollution in 2000, leading the government to require that large quantities of waste organic solutions must be stored temporarily at various factory sites or industrial park precincts (Liaw *et al*., 2002; Liaw and Chiu, 2003). Waste solutions were also diluted with water to diminish hazard at plants located in the Hsinchu Science-based Industrial Park (Taiwan) (Liaw and Chiu, 2003). However, test results using the Flash Point Analyzer indicated that the flash points of such waste solutions remain low despite dilution with large amounts of water. If detailed flash point variation with composition data for the specified aqueous-organic solution had been available at the time of the Shengli event, this attempted dilution of waste solutions to reduce the associated hazard might not have occurred. Thus, flash-point data knowledge for these mixtures has become increasingly important to ensure the safety of this voluminous storage. In addition to the usage and accumulation of flammable liquids, such as is outlined above, the transportation requirements for these mixtures are primarily related to their flash-point values (DOT, 2004).

In Taiwan, the GHS (Globally Harmonized System of Classification and Labeling of Chemicals) will be implemented in 2008. In the implementation of GHS, the flash point of mixtures is the critical property in the classification of flammable liquids. Unfortunately, flash-point data for a variety of mixtures are scarce in the literature, although composition ranges for specific mixtures used or produced in an industrial process can vary quite substantially. Since the cost of flash-point data derived from test instruments is very expensive in Taiwan (NT$20,000/US$600 per sample), a model for predicting the flash point of a given mixture is useful. Partially miscible mixtures are used in liquid-liquid extraction processes (Kurihara, *et al*., 2002; Matsuda and Ochi, 2004) and heterogeneous distillation processes (Kosuge and Iwakabe, 2005). The flash-point value for a given substance is relative to its vapor pressure (Lees, 1996). As the estimation of

vapor pressure for partially miscible mixtures is different from that for miscible analogues, we infer that flash point behavior for the two mixture types will be different. Thus, a model that allows prediction of the flash point of partially miscible mixtures is urgently required to facilitate evaluation of fire and explosion hazard.

Crowl and Louvar (2002) have suggested a method for the estimation of the flash point of a liquid solution with a single flammable component. However, it was shown to be adequate only when the flammable component composition approaches unity for binary aqueous-organic solutions (Liaw and Chiu, 2003), and it is not applicable to solvent/salt systems, even in a similar composition range (Liaw and Wang, 2007). Introducing activity coefficient models to model the non-ideal behavior of liquids, various models have been proposed recently for predicting the flash point of binary aqueous-organic and solvent/salt systems (Liaw and Chiu, 2003; Liaw and Wang, 2007), with successful verification based on comparison with the experimental data. Previously, Affens and McLaren (1972) first developed a predictive model to determine the flash points of binary hydrocarbon mixtures based on Raoult's law that assumes ideality of the liquid solution. White *et al*., (1997) reduced the Raoult's law based model to a simpler equation by ignoring any dependence of the lower flammable limit on temperature, with little practical application. We have proposed recently a model for predicting the flash point of multi-component mixtures of only flammable compounds (Liaw *et al*., 2004) and verified its worth using experimental data for ternary solutions. This model can be simplified for binary solutions, as proposed previously (Liaw *et al*., 2002), with prediction of flash points verified for both ideal and non-ideal mixtures (Liaw *et al*., 2002, 2003; Liaw and Lin, 2007). Garland and Malcolm (2002) developed a statistical model to predict the flash point of organic acid-water solutions at an Eastman Chemical facility: acetic acid + propionic acid + butyric acid + water. However, it deviated significantly from the experimental measurements for multiple organic-water solutions (Liaw and Chiu, 2006).

Overall, application of the former models (Affens and McLaren, 1972; Crowl and Louvar, 2002; Garland and Malcolm, 2002; White *et al*., 1997) is limited to solutions that can be assumed as ideal within the composition range considered. The new models we have developed take into account the non-ideality of the solution through liquid phase activity coefficients and have been used to predict efficiently the flash point of several miscible mixtures (Liaw *et al*., 2002, 2004; Liaw and Chiu, 2003, 2006; Liaw and Wang, 2007). Non-ideality of the liquid phase is in particular responsible to the occurrence of extreme flash-point behavior such as minimum and maximum flash-point behavior (Catoire and Paulmier, 2006; Liaw *et al*., 2003,

2008; Liaw and Lin, 2007; Vidal *et al*., 2006). This is similar to minimum boiling and maximum-boiling azeotropic behavior in vapor-liquid equilibrium. The conditions for identifying whether a binary mixture is able to exhibit a minimum or maximum flash point behavior were derived previously (Liaw *et al*., 2003; Liaw and Lin, 2007). Vidal *et al*., (2006) used Liaw *et al*.'s model (2002) using COSMO-RS instead of NRTL, Wilson or UNIQUAC equation to estimate the activity coefficient at infinite dilution to predict the minimum flash-point behavior for binary mixtures. For given pressure and temperature conditions at which vapor-liquid equilibrium occur, stronger non-ideality within a mixture may often lead to the partial miscibility of the liquid phase, eventually coupled with the occurrence of a so-called heteroazeotrope. We suspect that similar behavior happens for flash point. The model for predicting the flash point of partially miscible mixtures of binary flammable solvents was proposed by Liaw *et al*. (2008). However, to our knowledge no applicable model has been available for partially miscible mixtures of aqueous-organic system where only one of the two components of the mixture is flammable. In this manuscript, a model for such mixtures is investigated for the partially miscible aqueous-organic solutions: water + 1-butanol, water + 2-butanol, water + isobutanol, water + 1-pentanol and water + octane.

Based upon the definition of flash point (Lees, 1996), it is necessary to estimate the vapor-phase composition of flammable substances from a vapor-liquid equilibrium model in order to predict their flash point. Furthermore, it is acknowledged that partial miscibility occurs because of significant interaction within the non-ideal liquid solution. For such solutions, liquid-phase activity coefficients must be taken into account in the vapor-liquid equilibrium equation by means of thermodynamic models. Among common activity coefficient models, the original Wilson thermodynamic model (Wilson, 1964) is not applicable for evaluating the liquid-phase activity coefficients for mixtures that exhibit a miscibility gap (Poling *et al*., 2001). On the other hand, the NRTL (Renon and Prausnitz, 1968) and UNIQUAC thermodynamic models (Abrams and Prausnitz, 1975) are applicable to both vapor-liquid and liquid-liquid equilibria (Poling *et al*., 2001).

2. Experimental protocol

An HFP 362-Tag Flash Point Analyzer (Walter Herzog GmbH, Germany), which meets the requirement of ASTM D56 (ASTM, 1999) standard, was used to measure the flash points for a variety of aqueous-organic solutions (water + 1-butanol, water + 2-butanol, water + isobutanol, water + 1-pentanol and water +

octane) at different compositions. The basic system configuration of the Tag close cup tester is given in Fig. 1. The apparatus consists of an external cooling system, test cup, heating block, electric igniter, measuring module, thermometer and indicator/operating display. The apparatus incorporates control devices that program the instrument to heat the sample at a specified heating rate within a temperature range close to the expected flash point. The flash point is automatically tested using an igniter at specified temperature test intervals. If the expected flash point is lower than or equal to the change temperature, heating rate-1 is used and the igniter is fired at test interval-1. If the expected flash point is higher, heating rate-2 is adopted and the igniter is fired at test interval-2. The first flash-point test series is initiated at a temperature equivalent to the expected flash point minus the start-test value. If the flash point is not determined when the test temperature exceeds the sum of the expected flash point plus the end-of-test value, the experimental iteration is terminated. The instrument operation is conducted according to the standard ASTM D56 test protocol (ASTM, 1999) using the selected parameters: start test 5 ºC; end of test 20 ºC; heat rate-1 1 ºC/min; heat rate-2 3 ºC/min; change temperature 60 ºC; test interval-1 0.5 ºC; and, test interval-2 1.0 ºC. The liquid mole fraction is determined from mass measured using a Setra digital balance (EL-410D: sensitivity 0.001 g, maximum load 100 g). A magnetic stirrer provides sufficient agitation for the test samples. The prepared mixtures were stirred for 30 minutes before the flash point test. A Milli-Q plus was used for water purification. Isobutanol was HPLC/Spectro-grade reagent (Tedia Co. Inc.; USA); 1-butanol, 1-pentanol and octane were also sourced from Tedia. 2-butanol was purchased from Fisher Scientific International Inc. (USA).

3. Mathematical formulation

3.1 The general model for predicting the flash point of miscible mixtures

The flash point of a flammable liquid is the temperature at which the vapor pressure of the liquid is such that it produces a concentration of vapor in the air that corresponds to its lower flammable limit (LFL) (Lees, 1996). Thus, at the flash point of a liquid solution, Le Chatelier's rule (1891) that describes the lower flammable limit of a gas mixture, is followed:

$$1 = \sum_{i \neq k_l} \frac{y_i}{LFL_i} \tag{1}$$

where y_i is the mole fraction of the flammable substance, i, in the vapor phase, LFL_i is its lower flammable limit, and k_l is the non-flammable components of the mixture.

From the definition of the flash point for a pure substance (Lees, 1996), the LFL

of component i, LFL_i, is expressed in terms of its saturated vapor pressure evaluated at the flash point temperature, $P_{i,fp}^{sat}$:

$$LFL_i = \frac{P_{i,fp}^{sat}}{P} \tag{2}$$

where P is the ambient pressure. The flash point for a substance is generally measured at atmospheric pressure, which is low enough for the gas phase to behave as a perfect gas. Thus, the vapor-phase composition, y_i, can be derived from the vapor-liquid equilibrium (VLE) between a non-ideal liquid and a perfect gas as:

$$y_i = \frac{x_i \gamma_i P_i^{sat}}{P} \tag{3}$$

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

$$1 = \sum_{i \neq k_l} \frac{x_i \gamma_i P_i^{sat}}{P_{i,fp}^{sat}} \tag{4}$$

The saturated vapor pressure variation with temperature for a pure substance, i, can be estimated using the Antoine equation:

$$\log P_i^{sat} = A_i - \frac{B_i}{T + C_i} \tag{5}$$

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

The activity coefficients γ_i in Eq. (4), can be estimated using the thermodynamic model, such as: Wilson (Wilson, 1964), NRTL (Renon and Prausnitz, 1968) or UNIQUAC equations (Abrams and Prausnitz, 1975).

The general flash point prediction model developed for a miscible solution is described using Eqs. (4), (5) and any equation for estimating activity coefficient. The temperature that satisfies these equations is the flash point of a miscible solution (Liaw and Chiu, 2006).

For a binary aqueous-organic solution, the water vapor is non-flammable, thus, Eq. (4) is reduced to:

$$1 = \frac{x_2 \gamma_2 P_2^{sat}}{P_{2,fp}^{sat}} \tag{6}$$

with the flammable component denoted as component 2 and water denoted as component 1.

3.2 The model for partially miscible mixtures of aqueous-organic system

Within the mutual-solubility region of a binary partially miscible aqueous-organic mixture, only one liquid phase is present and the variation of the vapor pressure with liquid-phase composition identical to that for a miscible

mixture. Thus, the flash point in such a region can be evaluated by the method for a binary miscible analogue (Liaw and Chiu, 2003):

$$1 = \frac{x_2 \gamma_2 P_2^{sat}}{P_{2,fp}^{sat}} \tag{6}$$

$$\log P_2^{sat} = A_2 - \frac{B_2}{T + C_2} \tag{7}$$

Liquid-phase activity coefficients γ_i enable to tackle the non-ideal behavior of the liquid phase that results in the partial-miscibility. Vapor phase is assumed to behave as a perfect gas as is usual under low to moderate pressure condition (Van Ness and Abbott, 1982).

Within the partially miscible region of a binary partially miscible mixture, two liquid phases are in equilibrium with their compositions defining a so-called tie line. Since any liquid composition located on this tie-line, in particular the overall composition of both liquid phases in equilibrium, is in equilibrium with a single vapor composition located on the so-called vapor line (Van Ness and Abbott, 1982; Pham and Doherty, 1990), the flash point in this region should keep constant whatever the liquid composition on the liquid-liquid equilibrium tie line.

The compositions between liquid phases in equilibrium can be estimated by the equilibrium equality of the compound fugacities in each phase:

$$(x_i \gamma_i)^{\alpha} = (x_i \gamma_i)^{\beta} \qquad i = 1,2 \tag{8}$$

where α and β designate the two coexisting liquid phases. The activity coefficients γ_i in Eqs. (6) and (8), should be estimated using thermodynamic activity coefficient models adequate for partially miscible mixtures, such as the NRTL (Renon and Prausnitz, 1968) or UNIQUAC equations (Abrams and Prausnitz, 1975); both models are employed in this study (Table 1).

The flash point temperature prediction model developed for a binary partially miscible aqueous-organic solution is described using Eqs. (6) - (8), and any suitable thermodynamic model for estimating liquid-phase activity coefficient. The procedure for evaluating the flash point for binary partially miscible aqueous-organic mixtures is depicted in Fig. 2. It requires knowledge of the pure component flash point temperature and suitable binary interaction parameters used in the activity coefficient model. The two liquid phases region and the flash point in this region are first estimated by Eqs. (6) - (8). Then, the flash point in the mutual-solubility region is calculated using Eqs. (6) - (7). The iterative procedure is analogous to that used for calculating the boiling and dew points of mixtures (Smith and Van Ness, 1975).

4. Results and discussion

4.1 Parameters used in this manuscript

The flash-point model for partially miscible mixtures of one flammable solvent with water was used for water + 1-butanol, water + 2-butanol, water + isobutanol, water + 1-pentanol, and water + octane mixtures. The prediction results were compared with experimental data. The liquid-phase activity coefficients for these five mixtures were estimated using the NRTL (Renon and Prausnitz, 1968) and/or UNIQUAC equations (Abrams and Prausnitz, 1975). The binary interaction parameters of the NRTL/UNIQUAC equations obtained from the LLE data and VLE data were both used in this study, with parameters adopted from the literature (Gmehling *et al*., 1981; Klauck *et al*., 2006; Kosuge and Iwakabe, 2005; Lu *et al*., 2002; Resa *et al*., 2006; Tang *et al*., 1995) (Tables 2, 3). The parameters for relative van der Waals volume (r) and the surface area (q) for the pure components needed for the UNIQUAC equation were obtained from the literature (Poling *et al*., 2001) and are listed in Table 4, along with the Antoine coefficients sourced from the literature (Gmehling *et al*., 1980, 1981).

The flash points for the pure substances used in this study were measured using the Flash Point Analyzer, with these values compared with their literature-derived analogues (Bohnet *et al*., 2007; Fisher Scientific, 2008; Freepatentsonline, 2008; Mallinckrodt Baker, 2008; Merck, 2008; NIOSH, 2008; Oxford University, 2008; Tedia, 2008; Univar USA, 2008) (Table 5). There are between-source differences in the flash-point data for 1-butanol, 2-butanol, isobutanol, 1-pentanol and octane. However, the differences are acceptable except for the value of 1-butanol provided by NIOSH (2008), 2-butanol by Tedia (2008) and 1-pentanol by Fisher (2008). Our experimental flash points for those five substances are close to the literature-derived values (Bohnet *et al*., 2007; Fisher Scientific, 2008; Freepatentsonline, 2008; Mallinckrodt Baker, 2008; Merck, 2008; NIOSH, 2008; Oxford University, 2008; Tedia, 2008; Univar USA, 2008), except for the ones mentioned above with greater difference from other sources (Table 5).

4.2 Flash-point variation of partially miscible mixtures of aqueous-organic system

The flash points of water + 1-butanol were tested over the entire flammable range (Table 6). Fig. 3 indicates that the flash point of this mixture increases smoothly along with the quantity of water in the alcohol-rich region, and increases sharply in the water-rich region, with this observation being consistent with that of miscible aqueous-organic solutions (Liaw and Chiu, 2003, 2006) and with the fact that water is an inert non flammable component. The most significant feature is that the measured value is almost constant in the two liquid phases region, where the

water mole fraction ranges between 0.54 and 0.983 (Table 6, Fig. 3). A constant flash point behavior in the two liquid phase region was also observed in the binary partially miscible mixtures of flammable solvents (Liaw *et al*., 2008). Both the flash point variation behavior in two extreme regions and the constant flash point behavior within the two liquid phases coexisting region were also observed in other partially miscible mixtures of this study, water + 2-butanol, water + isobutanol and water + 1-pentanol, which are displayed in Figs. 4-6.

The constant flash point behavior in the two liquid phases region arises because of the particular behavior enounced above that any composition on a liquid-liquid-vapor equilibrium tie line is in equilibrium with a single vapor composition (Van Ness and Abbott, 1982; Pham and Doherty, 1990). The flash point being a feature of the vapor, it is constant when the composition and temperature of the vapor is also constant.

In contrast to the mixtures mentioned above, the flash points of water + octane is almost constant over the whole test range from 0 to 0.99975 (Fig. 7). That the flash point of water + octane doesn't increase with addition of water is a behavior quite different from that of other aqueous-organic solutions, including miscible mixtures (Liaw and Chiu, 2003, 2006) and partially miscible ones mentioned above. Over inspection of our experimental data (Table 7), octane is almost immiscible to water, a behavior well acquainted in the literature (Mączyński *et al*., 2004). Since water is too lean in the octane-rich region, the flash point value approaches that of octane in such a region. The flash point in the two liquid phase region is constant, and is equivalent to that in the span nearing octane-rich region, which value is close to that of octane as mentioned above. In the water-rich region, the vapor composition of octane is too lean, resulting in the mixture being non-flash. Thus, it exhibits a constant flash point behavior over the entire observable flammable region.

Concerning the two liquid phases region, the measured span of two liquid phases region for water + 1-butanol, which are 0.54 and 0.983 in water mole fraction and its average value of flash point is 43.5 ^{o}C, is close to that adopted from the literature (Góra *et al*., 2006), namely 0.528 and 0.983 at 40 ^{o}C, the literature temperature closest to the average measured flash point value (Table 7). The measured analogue of the other studied mixtures, water + 2-butanol, water + isobutanol, water + 1-pentanol and water + octane, are also close to those adopted from the literature (Góra *et al*., 2006; Mączyński *et al*., 2004; Stephenson and Stuart, 1986) (Table 7).

Predictions using Eqs. (6) - (8) make uses of the binary interaction parameters listed in Tables 2 and 3. Those have been regressed either on LLE data or on VLE

data. It is a common knowledge in thermodynamics that use of LLE parameter for predicting VLE is usually not satisfactory (Vidal, 2003). However, partially miscible aqueous-organic mixture flash point determination is a problem combining LLE and VLE issues: the flash point definition of being "sufficient vapor to become a combustible mixture" is related to VLE (Eqs. (6) and (7)), whereas partial miscibility rather concerns LLE as stressed by Eq. (8).

As expected, the estimated result for the span of two liquid phases by the LLE parameters (Table 2) is superior to that by the VLE parameters (Table 3) for all the studied mixtures except for water + octane with only LLE parameters being available. This occurs irrespective of whether the NRTL or UNIQUAC equation is used to estimate the activity coefficients (Table 7). Table 7 also compares measured invariant flash point average value in the two liquid phase region with the prediction. There are some deviations between the prediction values and measurements when using only LLE or only VLE parameters. Deviation when using LLE parameters is attributed to the poor prediction in VLE related flash point by LLE parameters (Figs. 3-5). The least deviation occurs for water + 1-pentanol and water + octane. Deviation when using VLE parameters is attributed to the poor estimation in the span of the two liquid phase region (Table 7).

Because of the excellent estimation in span of two liquid phases by the LLE parameters and the good prediction of flash point by the VLE parameters, the calculated flash points in the two liquid phases by the VLE parameters with the span of two liquid phases estimated by the LLE parameters are also listed in Table 7 for comparison. The estimated flash point in the span nearing alcohol-rich region is much closer to the measurement than that in the span nearing water-rich region for the studied aqueous-alcohol mixtures. It is attributed to the fact that the slope of flash points vs. composition in the water-rich region is much steeper than that in the alcohol-rich region, with a small deviation in the span nearing former region causes much more deviation in the flash point than that in the span nearing latter region.

Thus, the parameters obtained from LLE data (Table 2) and from VLE data (Table 3) are used to estimate the span of two liquid phase region and the flash point, respectively, if both parameters are available. The estimated span nearing flammable-rich region is then used to calculate the constant flash point in the two liquid phase region by the VLE parameters. Such a simulation is denoted as VLLE in this study.

4.3 Comparison of predicted and measured flash points

The flash points predicted by the proposed model for water + 1-butanol and the corresponding measured values are compared in Fig. 3. Predictions are in good

agreement with the experimental data over the entire flammable range (Fig. 3, lines denoted as VLLE (red and blue lines)), when the NRTL or UNIQUAC is used in conjunction with the equation describing the partial miscibility (Eq. (8)). The predicted flash points without considering partial-miscibility behavior (Eq. (8) is simply not used in this case), by using interaction parameters obtained from LLE or from VLE data to estimate activity coefficients, are also plotted in Fig. 3 (black lines). Such a pseudo-homogeneous liquid flash point curve, whose shape is smooth convex then concave, is quite different from the corresponding experimental data in the two liquid phases. Such shape is characteristic of pseudo-homogeneous model prediction applied to composition span when two liquid phases equilibrium hold (Van Dongen *et al*., 1983). The agreement of the predicted flash points by the proposed model with the measurements and the analogous deviation for the prediction when neglecting partial-miscibility behavior for water + 2-butanol, water + isobutanol, water + 1-pentanol and water + octane are also observed in Figs. 4-7. Table 8 also demonstrates that, in terms of predictive efficiency, the model that considers partial-miscibility behavior is superior to the model that doesn't. Thus, it can be concluded that the property of immiscibility should not be ignored to predict the flash point of partially miscible aqueous-organic solutions.

Table 8 demonstrates that predictions are excellent in the entire flammable range excluding the water-rich region for water + 1-butanol, with the deviations being 0.5 ^{o}C and 0.4 ^{o}C by using NRTL or UNIQUAC equation, respectively, with Kosuge and Iwakabe's VLE parameters (2005). However, there are remarkable deviations between the predictions and measurements in the water-rich region, with deviation of flash point being 11.1 ^{o}C and 7.6 ^{o}C for NRTL and UNIQUAC equation, respectively. This phenomenon of greater deviation in water-rich region was also observed in other miscible aqueous-organic solutions (Liaw and Chiu, 2003, 2006) and other partially miscible aqueous-organic mixtures of this study, water + 2-butanol, water + isobutanol and water + 1-pentanol (Table 8). In the estimation of flash point for a mixture, the Le Chatelier's rule was used to describe the lower flammable limit of the gas phase. The Le Chatelier's rule assumed that the presence of inert has no effect on the lower flammable limit of a mixture. However, the fact is that the presence of inert will affect the lower flammable limit, especially in the high concentration of inert, where the lower flammable limit varying significantly (Michael and Zabetakis, 1965). In the water-rich region, the slope of the flash point vs. composition is the steepest, in accordance with the high inert concentration. Indeed, high flash point temperature is connected to high concentration of inert (water) vapor in the gas phase that in turn increases the flammability limit. This deviation in the water-rich region is the most important for

water + 1-butanol and water + 2-butanol, when using Kosuge and Iwakabe's VLE parameters (2005). Moreover, the predicted flash points are discontinuous in the span nearing water-rich region, and substantially lower than the measurements in the water-rich region for water + 2-butanol (Fig. 4). That indicates that Kosuge and Iwakabe's VLE parameters (2005) cannot estimate the flash point satisfactorily in the water-rich region (Fig. 3,4; Table 8), although their LLE parameters (Kosuge and Iwakabe, 2005) estimate the span of two liquid phases well (Table 7). Explanation of the large deviation in the water-rich region for the mixtures water + 1-butanol and water + 2-butanol lies in the fact that the VLE parameters of the two mixtures used for calculating the activity coefficient were regressed over the alcohol-rich region instead of water-rich region by Kosuge and Iwakabe (2005), resulting in worse prediction in the water-rich region compared to other regions. Predictions using VLE parameters from Gmehling *et al.*, (1981) lead to much smaller deviation in the water-rich region (Table 8). Thus, VLLE simulation were performed by using Kosuge and Iwakabe's LLE parameters (2005) and Gmehling *et al.*'s VLE parameters (1981) for water + 1-butanol and water + 2-butanol (Figs. 3,4 and Table 8). They lead to the best agreement.

It is concluded that, in addition to the deviation induced by the Le Chatelier's rule based model when the inert vapor concentration is high, the predictive efficiency of the proposed model, especially in the water-rich region, depends on the accuracy of the binary interaction parameters. Evidently, a new regression of binary interaction parameters over the entire range of a mixture flash point temperature could reduce the discrepancy between the model and the measurements. However, we intended to show that a model using literature VLE or LLE derived binary interaction parameter could predict with good agreement complex flash point behavior mixtures.

In deriving the flash point prediction model for binary aqueous-organic mixtures with partial miscibility, it was assumed that the liquid phases are in equilibrium. Underlined is the assumption of perfect mixing of the mixture. If that is not the case in real tank conditions, further deviations between the model predictions and the experimental flash point may occur.

5. Conclusion

The immiscible behavior in the two liquid phases should not be ignored in the prediction of flash point for partially miscible mixtures of aqueous-organic system. The model for the flash point prediction of binary partially miscible mixtures of one flammable solvent with water is able to represent well the experimental data over the entire composition range if the binary parameters used in the prediction of the

non-ideal liquid activity coefficients are accurate over the entire composition range. Thus, it appears reasonable to propose that this model is potentially applicable for assessment of fire and explosion hazards in real-world environments and producing inherently safer designs for chemical processes. In application of this proposed model, it is suggested to estimate the span of two liquid phase and the flash point by the LLE and VLE parameters, respectively, and then further use the estimated span, in particular the flammable-rich liquid phase composition, to calculate the constant flash point of the two liquid phases in equilibrium.

Nomenclature

A, B, C =Antoine coefficients

A_{ij} = binary parameter (K)

a_{ij} = parameter in Table 1 (J/mol)

b_{ij} = parameter in Table 1 (J/mol·K)

c_{ij} = parameter in Table 1 (J/mol·K^2)

G = defined in Table 1

g = binary parameters of the NRTL equation, J/mol

l = UNIQUAC parameter, defined in Table 1

LFL = lower flammable limit

P = ambient pressure (kPa)

P_i^{sat} = saturated vapor pressure (kPa)

$P_{i,fp}^{sat}$ = saturated vapor pressure of component, i, at flash point (kPa)

q_i = measure of molecular surface areas

R = gas constant (8.314 J/mol·K)

r_i = measure of molecular van der Waals volume

T = temperature (K)

$T_{i,fp}$ = flash point temperature of pure component, i (K)

u = binary parameters of UNIQUAC equation, J/mol

x = liquid-phase composition

y = vapor-phase composition

z = coordination number

Greek letters

Φ_i = segment fraction

α_{ij} =NRTL parameter

γ = activity coefficient

Λ = defined in Table 1

θ_i = area fraction of component i

τ = defined in Table 1

Subscripts

2LP = two liquid phases

exp. = experimental data

fp = flash point

i = species *i*

pred. = predictive value

Superscripts

α = α phase

β = β phase

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FIGURE LEGENDS

Fig. 1. The basic system configuration of the Tag close cup tester.

Fig. 2. Procedure for evaluation of flash point for partially miscible mixtures of one flammable solvent with water.

Fig. 3. Comparison of predicted flash point and experimental data for water (1) + 1-butanol (2).

Fig. 4. Comparison of predicted flash point and experimental data for water (1) + 2-butanol (2).

Fig. 5. Comparison of predicted flash point and experimental data for water (1) + isobutanol (2).

Fig. 6. Comparison of predicted flash point and experimental data for water (1) + 1-pentanol (2).

Fig. 7. Comparison of predicted flash point and experimental data for water (1) + octane (2).

Table 1. Some models for activity coefficients of partially miscible mixtures using only pure-component and binary parameters

Name	Activity coefficient for component *i*
NRTL	$\ln\gamma_i = \frac{\sum_j^N \tau_{ji} G_{ji} x_j}{\sum_k^N G_{ki} x_k} + \sum_j^N \frac{x_j G_{ij}}{\sum_k^N G_{kj} x_k}\left(\tau_{ij} - \frac{\sum_k^N x_k \tau_{kj} G_{kj}}{\sum_k^N G_{kj} x_k}\right)$ where $\ln G_{ij} = -\alpha_{ij}\tau_{ij}$ $\tau_{ij} = \frac{g_{ij} - g_{jj}}{RT}$ and $A_{ij} = \frac{g_{ij} - g_{jj}}{R} = a_{ij} + b_{ij}T + c_{ij}T^2$
UNIQUAC	$\ln\gamma_i = \ln\frac{\Phi_i}{x_i} + \frac{z}{2} q_i \ln\frac{\theta_i}{\Phi_i} + l_i - \frac{\Phi_i}{x_i}\sum_j^N x_j l_j$ $- q_i \ln(\sum_j^N \theta_j \tau_{ji}) + q_i - q_i \sum_j^N \frac{\theta_j \tau_{ji}}{\sum_k^N \theta_k \tau_{kj}}$ where $\ln\tau_{ij} = -\frac{u_{ij} - u_{jj}}{RT}$ $\Phi_i = \frac{x_i r_i}{\sum_k^N x_k r_k}$ $\theta_i = \frac{x_i q_i}{\sum_k^N x_k q_k}$ $l_i = \frac{z}{2}(r_i - q_i) - (r_i - 1)$ z=10 and $A_{ij} = \frac{u_{ij} - u_{jj}}{R} = a_{ij} + b_{ij}T + c_{ij}T^2$

Table 2. LLE parameters of the NRTL and UNIQUAC equations for the binary systems, water + 1-butanol, water + 2-butanol, water + isobutanol, water + 1-pentanol and water + octane

Model	$A_{12} = a_{12} + b_{12}T + c_{12}T^2$ [a]			$A_{21} = a_{21} + b_{21}T + c_{21}T^2$ [a]			Reference
	a_{12}	b_{12}	c_{12}	a_{21}	b_{21}	c_{21}	
Water (1) + 1-butanol (2)							
NRTL (α_{12}=0.45)	-2610.15	19.4473	-0.0237040	-3884.30	30.3191	-0.0527519	c
UNIQUAC	-1237.85	7.12425	-0.0066927	-4.72337	1.36693	-0.0047593	c
Water (1) + 2-butanol (2)							
NRTL (α_{12}=0.45)	-2744.73	19.1484	-0.0228962	-3871.43	25.0760	-0.0393948	c
UNIQUAC	-1276.11	7.59662	-0.0083095	-145.764	1.46978	-0.0038732	c
Water (1) + isobutanol (2)							
NRTL [b] (α_{12}=0.3)	3.770	0	0	0.025	0	0	d
Water (1) + 1-pentanol (2)							
UNIQUAC	242.413	0	0	90.395	0	0	e
Water (1) + octane (2)							
NRTL (α_{12}=0.2)	-169.718	12.5591	0	4197.06	-7.5243	0	f
UNIQUAC	195.95	0	0	2446.88	0	0	g

[a] NRTL: A_{ij}= (g_{ij}-g_{jj})/R; UNIQUAC: A_{ij}= (u_{ij}-u_{jj})/R

[b] $A_{ij} = \tau_{ij}$

[c] Kosuge and Iwakabe, 2005.

[d] Tang *et al*., 1995.

[e] Resa *et al*., 2006.

[f] Klauck *et al*., 2006.

[g] Lu *et al*., 2002.

Table 3. VLE parameters of the NRTL and UNIQUAC equations for the binary systems, water + 1-butanol, water + 2-butanol, water + isobutanol, water + 1-pentanol and water + octane

Mixtures	NRTL			UNIQUAC		Reference
	A_{12}	A_{21}	α_{12}	A_{12}	A_{21}	
Water (1) + 1-butanol (2)	1344.509	264.002	0.45	245.3347	95.078	b
	1332.336	193.464	0.4056	193.397	129.827	c
Water (1) + 2-butanol (2)	1209.987	241.729	0.45	242.918	50.9657	b
	891.640	133.786	0.4406	116.950	87.753	c
Water (1) + isobutanol (2)	1109.011	114.185	0.3155	142.459	150.949	c
Water (1) + 1-pentanol (2)	1643.518	60.776	0.3309	252.687	77.061	c

[a] NRTL: $A_{ij}= (g_{ij}-g_{jj})/R$; UNIQUAC: $A_{ij}= (u_{ij}-u_{jj})/R$

[b] Kosuge and Iwakabe, 2005.

[c] Gmehling *et al*., 1981

Table 4. Antoine coefficients for solution components, and relative van der Waals volumes (r) and surface areas (q) for the pure components for the UNIQUAC model

Material	Antoine coefficients [a]				Relative van der Waals volumes (r) and surface areas (q)		
	A	B	C	Reference	r	Q	Reference
1-butanol	7.83800	1558.190	-76.119	b	3.4543	3.052	c
2-butanol	7.47429	1314.188	-86.500	b	3.4535	3.048	c
isobutanol	8.53516	1950.940	-35.853	b	3.4535	3.048	c
1-pentanol	7.39824	1435.570	-93.202	b	4.1287	3.592	c
Octane	6.93142	1358.800	-63.145	b	5.8486	4.936	c

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

[b] Gmehling *et al*., 1981.

[c] Poling *et al*., 2001

Table 5. Comparison of flash-point values adopted from the literature with experimentally derived data for some alcohols

Component	Experimental data (°C)	Literature (°C)
1-butanol	36.9 ± 1.4	28.88 [a] 34 [b] 35 [c,d,e] 36 [f] 37 [g]
2-butanol	22.0 ± 1.2	23.88 [a] 24 [b,c] 26 [e] 28.88 [d]
Isobutanol	28.5 ± 0.5	27.77 [a] 28 [b,c,e] 29 [d]
1-pentanol	49.5 ± 0.6	38 [c] 48 [h] 48.33 [d] 49 [b,e] 50 [i]
Octane	14.5 ± 0.7	13 [b,c] 13.33 [a,d] 15 [e]

[a] NIOSH, 2008.
[b] Merck, 2008
[c] Fisher, 2008.
[d] Tedia, 2008.
[e] Oxford University, 2008.
[f] Univar USA, 2008.
[g] Mallinckrodt, 2008.
[h] Freepatentsonline, 2008.
[i] Bohnet *et al*., 2007.

Table 6. Measured flash point for partially miscible mixtures

x_1	water (1) + 1-butanol (2) (^oC)	water (1) + 2-butanol (2) (^oC)	water (1) + isobutanol (2) (^oC)	water (1) + 1-pentanol (2) (^oC)	water (1) + octane (2) (^oC)
0	36.9	22.0	28.5	49.5	14.5
0.000002	-	-	-	-	14.8
0.000004	-	-	-	-	14.8
0.000005	-	-	-	-	14.9
0.000008	-	-	-	-	14.5
0.0005	-	-	-	-	14.8
0.001	-	-	-	-	14.6
0.005	-	-	-	-	14.9
0.01	-	-	-	-	14.6
0.05	-	-	-	-	14.3
0.1	38.3	23.3	30.0	51.1	15.1
0.2	40.3	25.0	31.6	52.6	14.6
0.3	41.6	26.1	32.8	54.4	14.3
0.35	-	-	-	56.0	-
0.37	-	-	-	56.2	-
0.38	-	-	-	55.6	-
0.4	42.1	27.1	33.9	55.7	14.7
0.45	-	-	34.45	-	-
0.46	-	-	34.4	-	-
0.47	-	-	34.9	-	-
0.5	43.1	28.6	34.8	55.7	14.9
0.53	44.0	-	-	-	-
0.54	43.5	-	-	-	-
0.55	44.0	-	-	-	-
0.6	43.2	29.0	33.9	55.8	14.1
0.65	-	29.9	-	-	-
0.67	-	29.4	-	-	-
0.68	-	30.1	-	-	-
0.69	-	30.0	-	-	-
0.7	43.3	29.6	34.5	55.9	14.1
0.8	43.8	29.7	34.0	55.6	14.4
0.9	43.0	29.4	34.0	55.7	14.1
0.95	43.1	29.8	33.9	56.0	13.9

0.97	-	31.9	33.9	56.0	14.2
0.98	43.2	36.1	35.4	55.7	-
0.982	43.7	-	-	-	-
0.983	43.85	-	-	-	-
0.985	44.9	-	-	-	-
0.99	50.7	45.7	45.05	56.1	14.4
0.992	54.2	-	-	-	-
0.993	55.6	51.6	-	-	-
0.994	58.5	-	-	-	-
0.995	63.6	58.6	56.7	56.0	-
0.996	68.1	64.7	61.7	58.7	-
0.997	-	-	66.5	65.5	-
0.998	-	-	-	74.4	-
0.999	-	-	-	-	14.0
0.9995	-	-	-	-	14.1
0.9997	-	-	-	-	14.8
0.99975	-	-	-	-	13.8

Table 7. Comparison of estimated values for equilibrium composition between liquid phases, $x_{1,2LP}$, and its flash point, T_{2LP}, with corresponding experimental data

System		Estimated value				Experimental data		Mutual solubility		
		NRTL		UNIQUAC						
		$x_{1,2LP}$	T_{2LP} (°C)	$x_{1,2LP}$	T_{2LP} (°C)	$x_{1,2LP}$	T_{2LP} (°C)	T (°C)	$x_{1,2LP}$	Lit
water (1) + 1-butanol (2)	LLE	0.541 0.985	41.67	0.531 0.986	45.92	0.54 0.983	43.5	40	0.528 0.9830	g
	VLE [a]	0.603 0.993	44.93 44.08 [c] 38.53 [d]	0.346 0.989	41.97 43.68 [c] 39.31 [d]					
	VLE [b]	0.530 0.991	44.24 44.38 [c] 36.40 [d]	0.348 0.984	41.84 43.32 [c] 39.33 [d]					
water (1) + 2-butanol (2)	LLE	0.673 0.957	31.17	0.666 0.959	32.80	0.67 0.95	29.7	29.9	0.684 0.953	h
	VLE [a]	0.596 0.990	29.32 30.13 [c] 23.88 [d]	0.408 0.986	27.80 29.19 [c] 20.36 [d]					
	VLE [b]	0.665 0.939	30.12 30.17 [c] 31.69 [d]	0.575 0.934	29.68 30.14 [c] 31.47 [d]					
water (1) + isobutanol (2)	LLE	0.463 0.975	35.50	-	-	0.46 0.98	34.1	35.7 36.3	0.469 [e] 0.9807 [f]	g
	VLE	0.392 0.978	33.79 34.43 [c] 32.66 [d]	0.371 0.977	33.69					
water (1) + 1-pentanol (2)	LLE	-	-	0.374 0.994	55.69	0.37 0.995	55.8	50	0.384 0.9962	g
	VLE	0.473 0.996	57.6	0.210 0.993	53.0 55.78 [c] 56.20 [d]					
water (1) + octane (2)	LLE	3.8×10^{-6} 0.999996	14.49	3.2×10^{-6} 0.99996	14.49	4×10^{-6} 0.999999	14.3	20	4.3×10^{-4} 0.9999999	i

[a] based on parameters adopted from Kosuge and Iwakabe, 2005

[b] based on parameters adopted from Gmehling *et al.*, 1981

[c] based on the span nearing flammable-rich region estimated by the LLE parameters

[d] based on the span nearing water-rich region estimated by the LLE parameters
[e] solubility data at 36.3 ^{o}C
[f] solubility data at 35.7 ^{o}C
[g] Góra *et al*., 2006.
[h] Stephenson and Stuart, 1986.
[i] Mączyński *et al,*. 2004.)

Table 8. Average temperature deviation between calculated and experimental flash points, ΔT_{fp} [a], for the studied ternary solutions comparing models

Mixture	Model for partially miscible mixtures		Model ignoring partial miscibility			
	NRTL (VLLE)	UNIQUAC (VLLE)	NRTL [b]		UNIQUAC [b]	
			LLE	VLE	LLE	VLE
water (1) + 1-butanol (2)	3.2 [bd] 11.1 [be] 0.5 [bf]	2.2 [bd] 7.6 [be] 0.4 [bf]	3.3 [d] 2.0 [f]	4.3 [bd] 2.0 [bf]	1.8 [d] 1.7 [f]	4.1 [bd] 2.9 [bf]
	3.0 [cd] 9.8 [ce] 0.7 [cf]	1.0 [cd] 3.0 [ce] 0.4 [cf]	-	4.1 [cd] 2.3 [cf]	-	2.2 [cd] 2.0 [cf]
water (1) + 2-butanol (2)	4.8 [bd] 16.0 [be] 0.3 [bf]	4.2 [bd] 13.9 [be] 0.4 [bf]	1.7 [d] 0.9 [f]	5.1 [bd] 0.8 [bf]	2.2 [d] 2.1 [f]	5.2 [bd] 1.7 [bf]
	1.3 [cd] 3.6 [ce] 0.3 [cf]	1.0 [cd] 2.5 [ce] 0.4 [cf]	-	1.3 [cd] 0.4 [cf]	-	1.0 [cd] 0.4 [cf]
water (1) + isobutanol (2)	0.7 [d] 2.0 [e] 0.3 [f]	-	1.0 [d] 1.0 [f]	1.4 [d] 1.2 [f]	-	1.1 [d] 1.2 [f]
water (1) + 1-pentanol (2)	-	0.8 [d] 3.5 [e] 0.2 [f]	-	3.6 [d] 3.9 [f]	3.9 [d] 4.0 [f]	3.9 [d] 4.0 [f]
water (1) + octane (2)	0.3 [d]	0.3 [d]	17.6 [d]	-	15.4 [d]	-

[a] deviation of flash point: $\Delta T_{fp} = \sum_{N} \left| T_{fp,\exp.} - T_{fp,pred.} \right| / N$

[b] based on VLE parameters adopted from Kosuge and Iwakabe (2005)

[c] based on VLE parameters adopted from Gmehling *et al*. (1981)

[d] ΔT_{fp} over the entire flammable range

[e] ΔT_{fp} for water-rich region

[f] ΔT_{fp} over the entire flammable excluding water-rich region

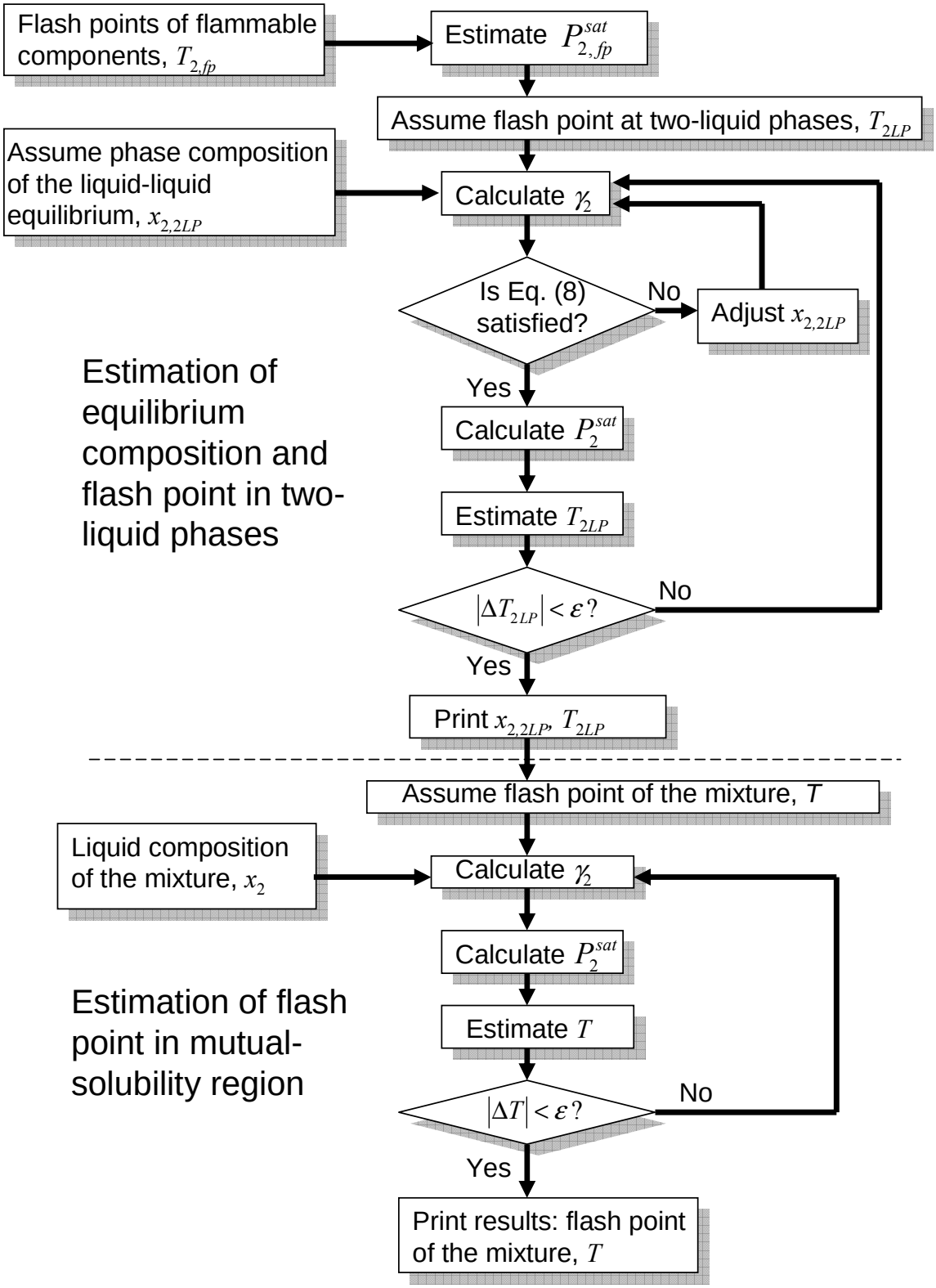
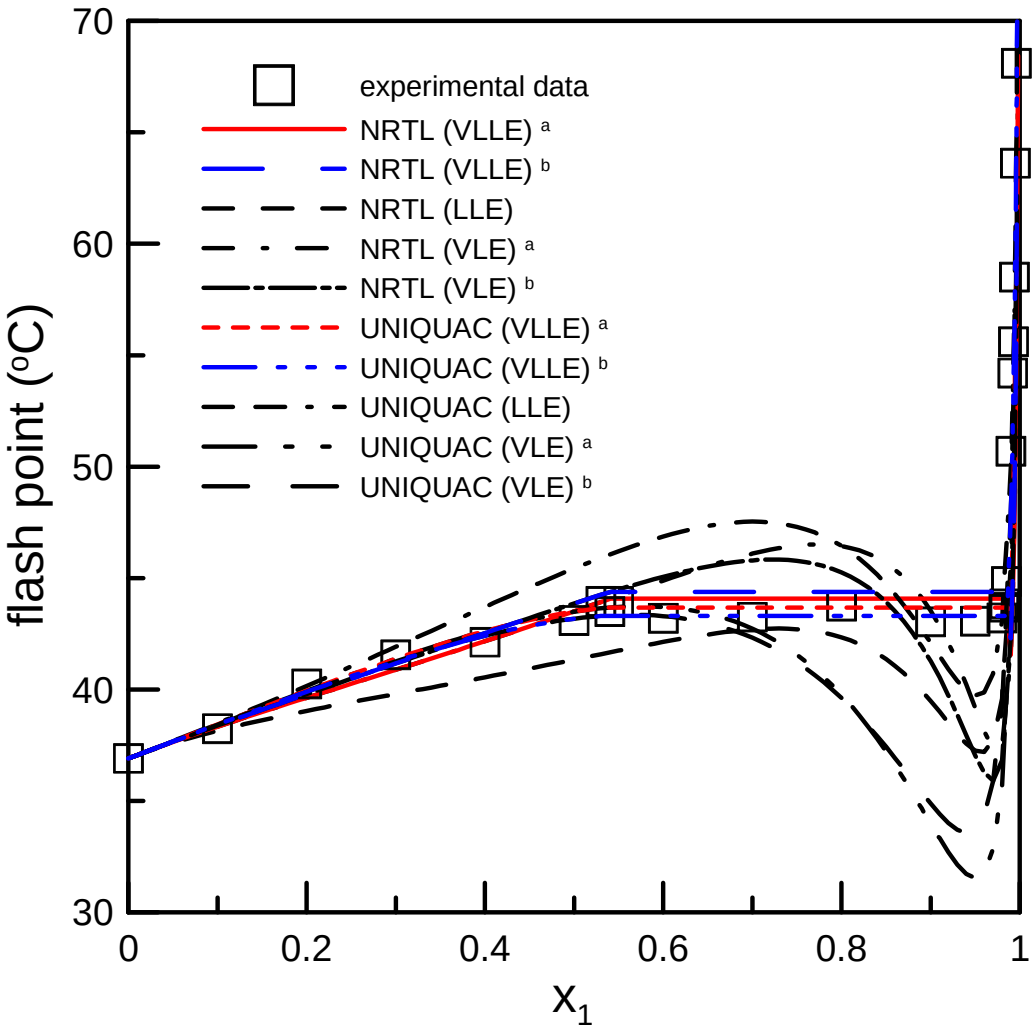
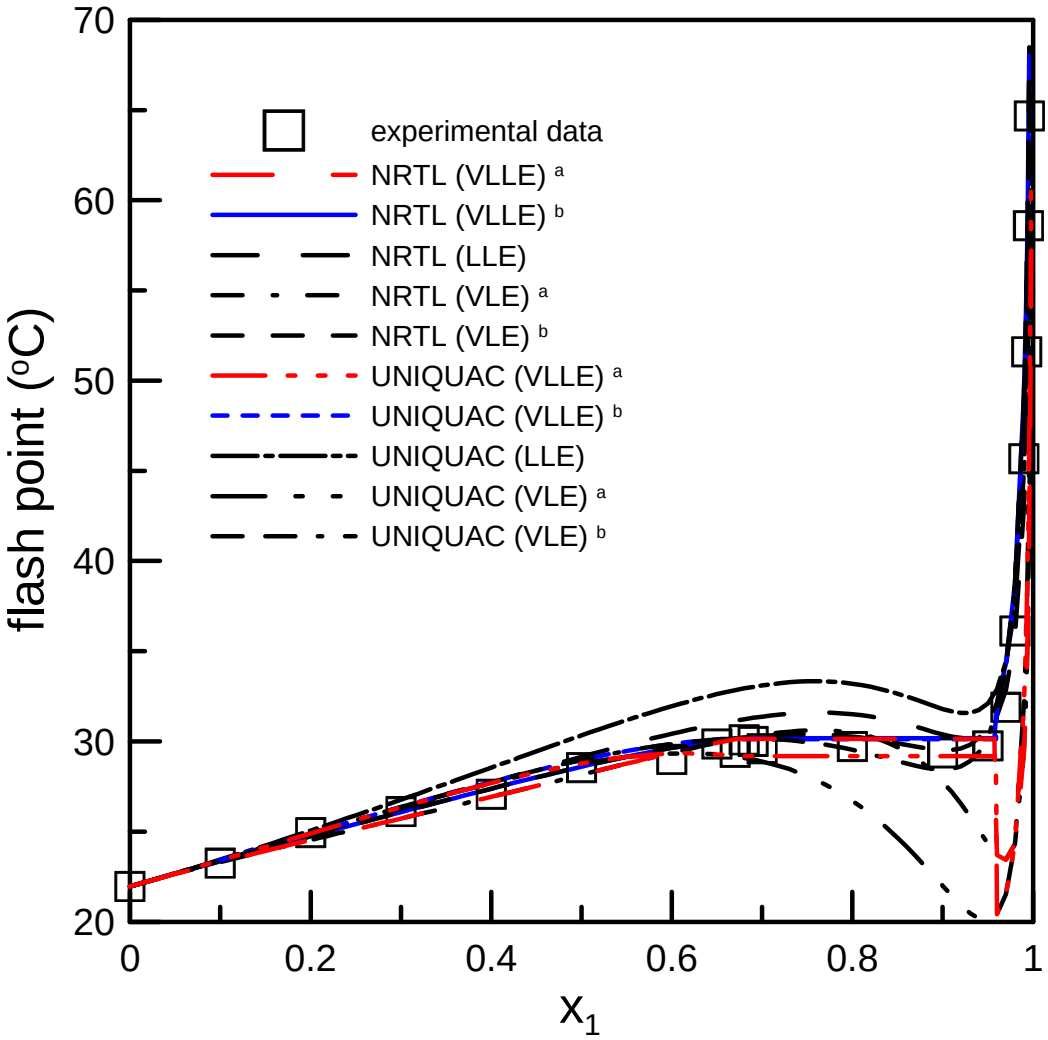


Fig. 2. Procedure for evaluation of flash point for partially miscible mixtures of one flammable solvent with water.



[a] VLE parameters adopted from Kosuge and Iwakabe (2005)
[b] VLE parameters adopted from Gmehling *et al*. (1981)

Fig. 3 Comparison of predicted flash point and experimental data for water (1) + 1-butanol (2).



[a] VLE parameters adopted from Kosuge and Iwakabe (2005)
[b] VLE parameters adopted from Gmehling *et al*. (1981)

Fig. 4. Comparison of predicted flash point and experimental data for water (1) + 2-butanol (2).

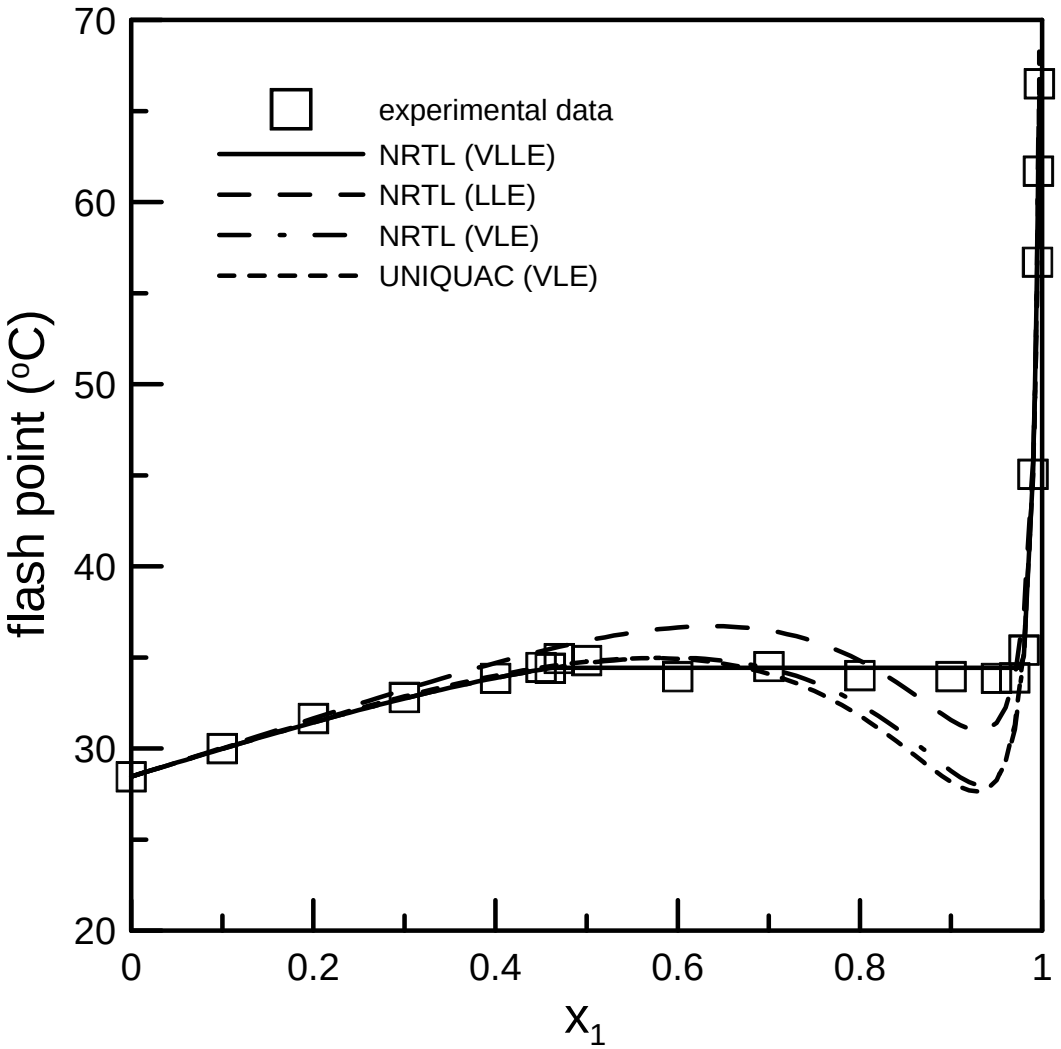


Fig. 5. Comparison of the predicted flash point and experimental data for water (1) + isobutanol (2).

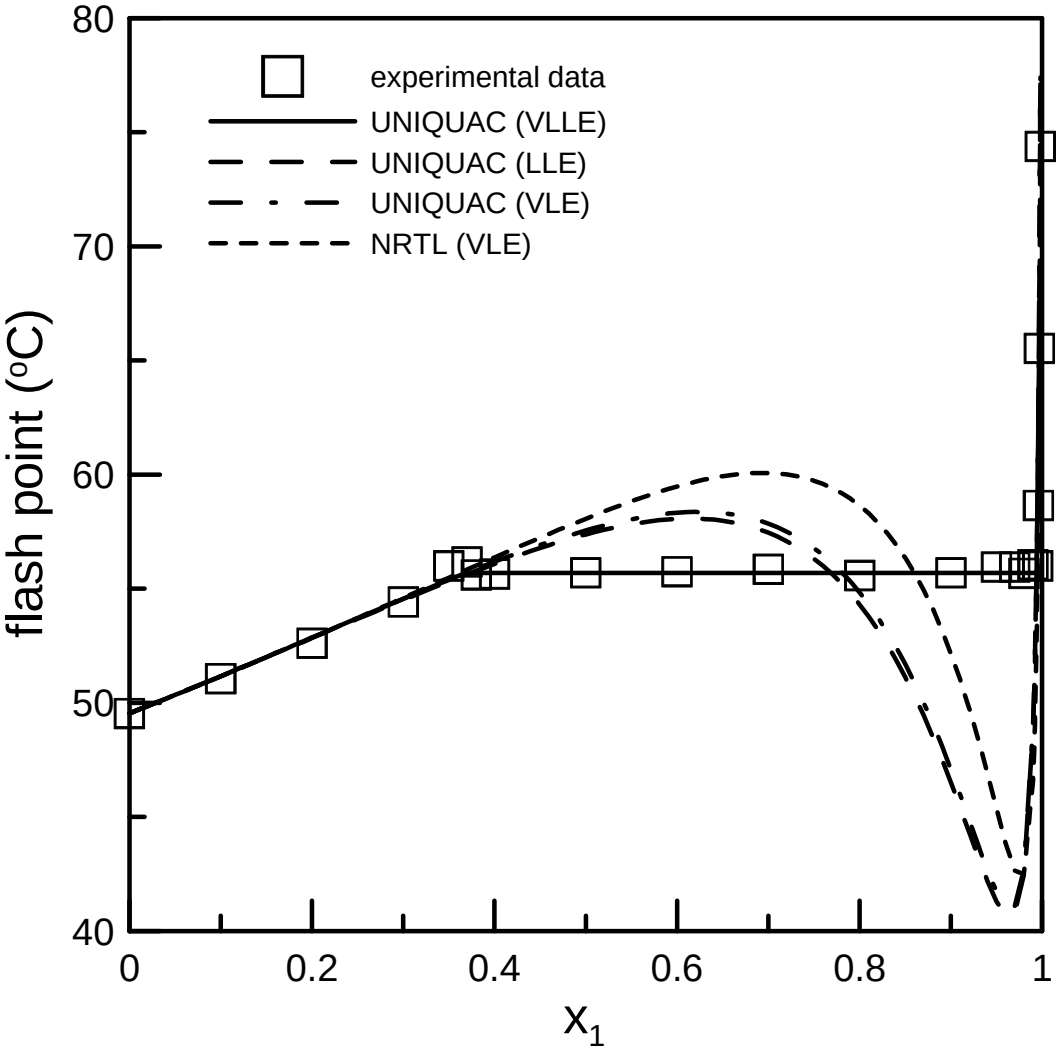


Fig. 6. Comparison of predicted flash point and experimental data for water (1) + 1-pentanol (2).

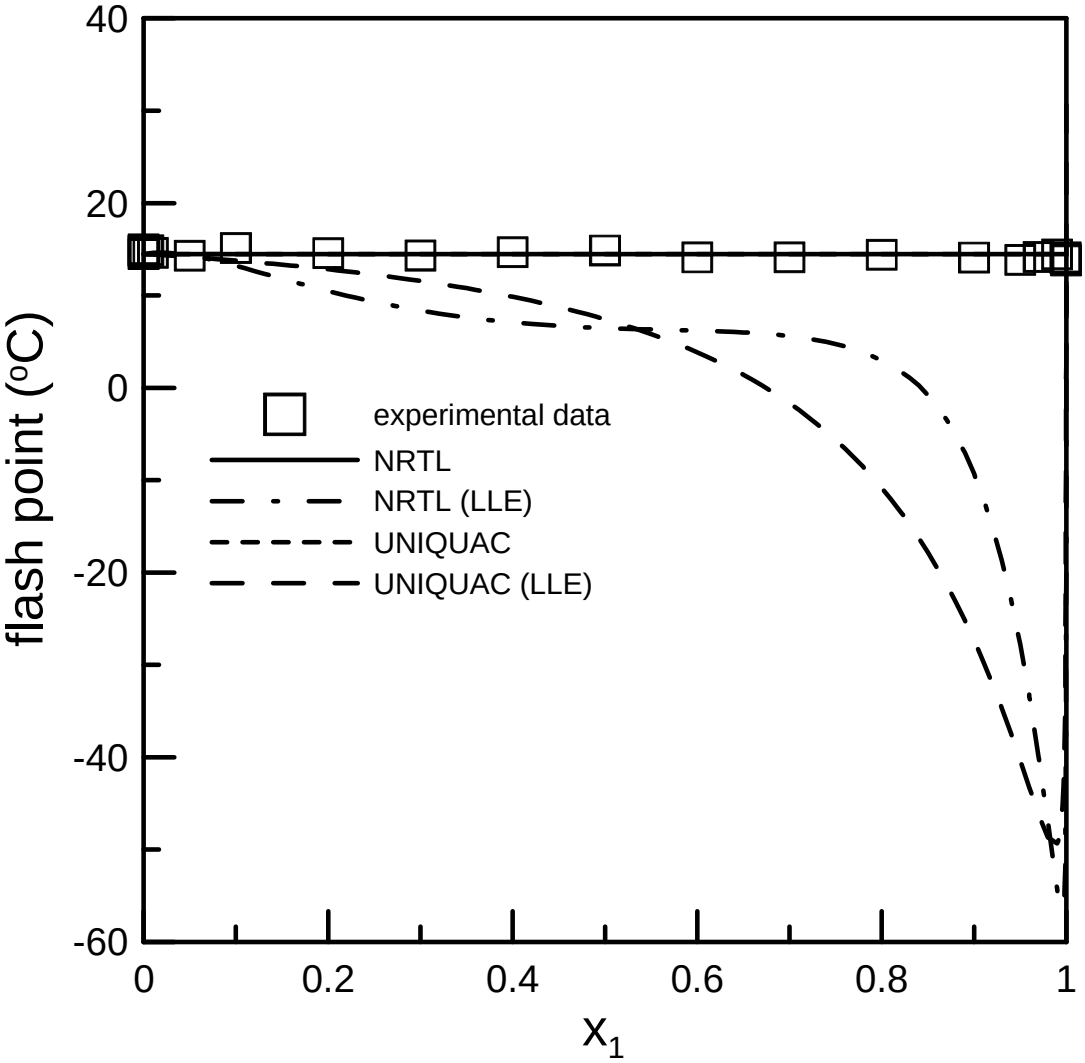


Fig. 7. Comparison of predicted flash point and experimental data for water (1) + octane (2).