

# A general model for predicting the flash point of miscible mixtures

Horng-Jang Liaw<sup>\*</sup>, Yi-Yu Chiu

*Department of Occupational Safety and Health, China Medical University, 91 Hsueh-Shih Rd., Taichung, Taiwan, ROC*

Received 2 March 2005; received in revised form 26 January 2006; accepted 26 January 2006

Available online 18 April 2006

## Abstract

A mathematical model is presented for predicting the flash point of miscible mixtures. This model is reducible and adequate for some specified systems as proposed previously. Except for multiple aqueous-organic solutions, the predictive capability of the reduced form for other miscible mixtures, including binary aqueous-organic solutions and flammables-only analogues, has been verified previously. The model was validated using the ternary aqueous-organic solutions, water + methanol + ethanol/isopropanol. The results of the study confirm that the model predicts the flash points of these solutions by utilizing the flash points of the individual components. Further, if the binary interaction parameters for a ternary aqueous-organic solution are not accessible, a model based upon the binary interaction parameters of the binary solutions may provide a very acceptable means of predicting the flash point for such a ternary solution through comparison of the predicted and experimental data, as demonstrated in this study.

© 2006 Elsevier B.V. All rights reserved.

*Keywords:* Flash point; Prediction; Miscible solution; Aqueous-organic solution

## 1. Introduction

In Taiwan, essential oils have caused a number of explosions, with six blasts leaving eight people badly burnt from January through August of 2003. Essential oils, reputedly antiseptic and helpful for strengthening the immune system, are flammable liquids. The major proportion of most commercialized essential oils is the highly inflammable liquid isopropanol. The fire and explosion hazard for a flammable liquid solution is primarily related to its flash point. In addition, in the Shengli event [1,2] waste organic solvents were illegally dumped into the Kaoping River (southern Taiwan), causing serious water pollution in 2000, leading to the government requirement that large quantities of waste organic solutions must be stored temporarily at various factory sites or industrial park precincts. To ensure the safety of this storage, therefore, flash point data for flammable liquid solutions are important. Around the time of the Shengli event, waste solutions were diluted with water to diminish hazard at plants located in the Hsinchu Science-based Industrial Park (Taiwan) [2]. However, test results using the Flash Point Analyzer indicate 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.

The flash point of a given liquid is the experimentally determined temperature at which such a substance emits sufficient vapor to form a combustible mixture with air [3]. A lower flash point value indicates that a liquid is more hazardous relative to an analogue with a higher value [4]. The flash point data for a pure substance can be obtained from various sources, such as MSDS (Material Safety Data Sheets), the SFPE (Society of Fire Protection Engineers) handbook [5], or the Merck index [6]. Flash point data for a variety of liquid mixtures are scarce in the literature, however. Since the composition ranges for specific materials used or produced in an industrial process can vary quite substantially, a significant amount of time is required to procure satisfactory data using the Flash Point Analyzer. If a model for predicting the flash point of a given solution could be successfully derived, however, the flash point would be predicted relatively easily based on a limited amount of initial basic data.

Crowl and Louvar [7] have suggested that the flash point of a liquid solution with only one flammable component, such as a binary aqueous-organic solution, can be estimated using

<sup>\*</sup> Corresponding author. Tel.: +886 4 22053366x3502; fax: +886 4 22030418.  
E-mail address: hjliaw@mail.cmu.edu.tw (H.-J. Liaw).

## Nomenclature

$A, B, C$	Antoine coefficients
$A_{ij}$	binary parameter
$g$	binary parameters of the NRTL equation (J/mol)
MW	molecular weight (g/mol)
$P_i^{\text{sat}}$	saturated vapor pressure of component $i$ (kPa)
$P_{i,\text{fp}}^{\text{sat}}$	saturated vapor pressure of component, $i$ , at flash point (kPa)
$q$	van der Waals surface area
$R$	gas constant (8.314 J/mol)
$r$	relative van der Waals volume
$T$	temperature (K)
$T_{i,\text{fp}}$	flash point temperature of pure component, $i$ (K)
$u$	binary parameters of UNIQUAC equation (J/mol)
$v^{\text{l}}$	molar volume of liquid ( $\text{m}^3/\text{mol}$ )
$x$	liquid-phase composition

### Greek letters

$\alpha_{ij}$	NRTL parameter
$\gamma$	activity coefficient
$\lambda$	binary parameters of the Wilson equation (J/mol)
$\rho$	density ( $\text{g}/\text{cm}^3$ )

### Subscripts

exp.	experimental data
fp	flash point
$i$	species $i$
pred.	predictive value

Raoult's law. However, our previous study [2] demonstrates that this method is only adequate for a composition range where the composition of the flammable component approaches unity. Therefore, a model for predicting the flash point for a given binary aqueous-organic solution was proposed [2], and prediction of the experimental data successfully verified. Affens and McLaren [8] developed a model to predict the flash points of binary hydrocarbon solutions using Raoult's law. White et al. [9] reduced this model to a simpler equation by ignoring any dependence of the lower flammable limit (LFL) on temperature; these workers then used the derived equation to estimate the flash point of two aviation-fuel mixtures: JP-4/JP-8 and JP-5/JP-8. We have demonstrated that neither the Affens and McLaren's model nor the equation of White et al. is able to effectively predict the measured flash point for a non-ideal solution [1]. Since no model for effectively predicting the flash point of solutions with more than one flammable component has been proposed, especially for non-ideal solutions, it has been suggested that the flash points of these solutions may be determined experimentally using any of the available test methods [3,7]. In our previous study [1], a mathematical model to predict the flash point of binary liquid solutions with two flammable components was proposed, with successful prediction of the experimental results verified for both ideal and non-ideal solutions.

The prediction models for the flash points of liquid solutions referred to above were all developed for binary solutions. A model for predicting the flash point of a multi-component solution comprised of only flammable components has been proposed previously [10] and verified with experimental data for ternary solutions. Garland and Malcolm [11] developed a statistical model to predict the flash point of an organic acid–water solution, acetic acid + propionic acid + butyric acid + water. However, the main assumption of this model, namely the linear relationship between the flash point and the composition of the solution components, appears to deviate from the observation for an aqueous-organic solution, where the flash point is highly non-linear with respect to water composition [2]. Even if Garland and Malcolm's model could roughly predict their finite experimental data, the predictive efficacy of such a model is questionable because it appears to be only adequate over a limited composition range for a given solution. As no model currently exists for flash point-prediction for aqueous-organic solutions with more than one flammable component, such as those often present in many real-world situations such as semiconductor manufacture, there is an urgent need to develop a model for solutions of this type. If a model could be developed which not only predicts the flash points of these solutions but also those of binary aqueous-organic and flammables-only analogues, all the models referred to above would be superseded. The objective of this study, therefore, was to establish such a general model, which is reducible to the analogues proposed previously [1,2,10]. Except for multiple aqueous-organic mixtures, the predictive capability of the reduced form of this general model has been verified. As alcohols, such as methanol, ethanol and isopropanol (IPA), are frequently used for semiconductor manufacture, mixtures of water + methanol + ethanol/isopropanol were selected for investigation.

## 2. Experimental protocol

A Flash Point Analyzer (HFP 362-Tag; Walter Herzog GmbH, Germany) was used to measure the flash point of two ternary aqueous-organic solutions, water + methanol + ethanol/isopropanol, at different compositions. The Flash Point Analyzer incorporates control devices that program the instrument to heat the sample at a specified rate (heating rate) within a temperature range close to the expected flash point. The flash point is automatically tested using an igniter at specified temperature intervals (test interval). If the expected flash point is lower than or equal to the change temperature, which is set to  $60^\circ\text{C}$  according to the standard ASTM D56 method [12], a heating rate of  $1^\circ\text{C}/\text{min}$  is used and the igniter is fired at test interval-1. If the expected flash point is higher, a heating rate of  $3^\circ\text{C}/\text{min}$  is used and the igniter is fired at test interval-2. The first flash point test takes place 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 device's heater cuts out. The Flash Point Analyzer is operated according to a standard test method, namely ASTM D56 [12], with the following

set of selected parameters: start test 5 °C; end of test 20 °C; test interval-1 0.5 °C; test interval-2 1.0 °C. The liquid mole fraction was determined from mass measured using a Setra digital balance (EL-410D: sensitivity 0.001 g, maximum load 100 g). A Milli-Q plus was used for water purification; methanol was HPLC/Spectro Grade (Tedia Co. Inc., USA); isopropanol was verified using an ACS standard (Pharmco Product Inc., USA); and, ethanol (99.5 vol.%) was obtained from NASA enterprises (USA).

### 3. Flash point-prediction model

#### 3.1. Mathematical formulation

At the flash point of a liquid solution, the modified equation of Le Chatelier should be followed [10]:

$$1 = \sum \frac{x_i \gamma_i P_i^{\text{sat}}}{P_{i,\text{fp}}^{\text{sat}}} \quad (1)$$

Essentially, for prediction of the flash point for a liquid solution with certain non-flammable components, it is only necessary to consider the vapor-phase composition of the flammable constituents. Thus, for a multi-component solution with  $M$  non-flammable components, components  $k_l$  ( $l = 1, \dots, M$ ), Eq. (1) is modified:

$$1 = \sum_{i \neq k_l} \frac{x_i \gamma_i P_i^{\text{sat}}}{P_{i,\text{fp}}^{\text{sat}}} \quad (2)$$

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

$$\log P_i^{\text{sat}} = A_i - \frac{B_i}{T + C_i} \quad (3)$$

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

The activity coefficients  $\gamma_i$  in Eq. (2), can be estimated using the Wilson [13], NRTL [14] or UNIQUAC equations [15], with all employed in this study.

The general flash point-prediction model developed for a miscible solution is described using Eqs. (2) and (3) and any equation for estimating activity coefficient. We suggest that the temperature that satisfies these equations is the flash point of a miscible solution.

For a liquid mixture with only flammable components, Eq. (2) is reduced as the one developed previously to describe the flash point for a multi-component flammable solution [10]. This proposed model is also reducible for a binary mixture of flammable liquids as proposed previously [1].

#### 3.2. Reduced form for an aqueous-organic solution

The water vapor in an aqueous-organic solution is non-flammable. Where the other components are all flammable, Eq.

(2) is reduced to:

$$1 = \sum_{i \neq 1} \frac{x_i \gamma_i P_i^{\text{sat}}}{P_{i,\text{fp}}^{\text{sat}}} \quad (4)$$

with the water (vapor) denoted as component 1.

For a binary aqueous-organic solution, Eq. (4) becomes the one for applicable to a binary aqueous-organic solution as developed in our previous work [2].

For a ternary aqueous-organic solution, Eq. (4) reduces to:

$$1 = \frac{x_2 \gamma_2 P_2^{\text{sat}}}{P_{2,\text{fp}}^{\text{sat}}} + \frac{x_3 \gamma_3 P_3^{\text{sat}}}{P_{3,\text{fp}}^{\text{sat}}} \quad (5)$$

Thus, Eqs. (3) and (5) constitute the flash point-prediction model for a ternary aqueous-organic mixture. The temperature derived from the problem solution of the equations is deemed to be the flash point of this ternary aqueous-organic mixture.

In this study, a general flash point-prediction model for a miscible mixture has been derived. This model can be simplified for some specified systems, including mixtures with only flammable components and aqueous-organic solutions. The former reduced form has been verified to predict the experimental data for both binary and ternary mixtures [1,10,16]. The predictive efficacy of the latter analogue for a binary aqueous-organic solution has also been verified for the experimental data for various binary aqueous-organic solutions [2]. If this general model for a miscible mixture can predict the flash point of ternary aqueous-organic solutions, it has the potential for generalization to all miscible mixtures, including aqueous-organic solutions and mixtures with only flammable components. Thus, not only can the models proposed previously [1,2,10] be integrated into one general analogue as proposed in this manuscript, but also the prediction of a mixture's flash point may be extended to more-diverse situations. As part of this study, therefore, the effectiveness of the reduced form of such a general model, simplified for ternary aqueous-organic solutions (as above), was verified for the experimentally derived data.

The procedure for evaluation of the flash point for a ternary aqueous-organic solution is depicted in Fig. 1. The iterative procedure is analogous to that used for calculating the boiling and dew points of mixtures [17].

## 4. Results and discussion

#### 4.1. Parameters used to predict the flash point of ternary aqueous-organic solutions

The model for a ternary aqueous-organic solution was used to predict the flash point of water + methanol + ethanol/isopropanol systems. The results thus obtained were compared with the corresponding experimentally derived data. This study also compared the predictive capability of our proposed model with Garland and Malcolm's statistical analogue [11]. The aqueous solutions of methanol, ethanol and isopropanol are all non-ideal, and the activity coefficients corresponding to the flammable components for such solutions are all greater than unity [18–20]. By contrast, the binary solution of methanol + ethanol behaves

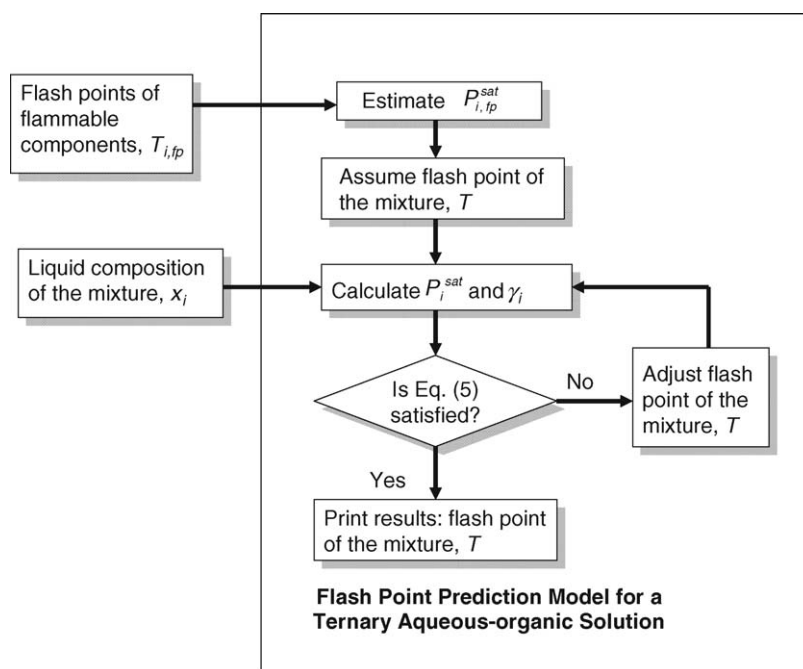


Fig. 1. Procedure for evaluation of flash point for a ternary aqueous-organic solution.

almost like an ideal solution [19]. The liquid-phase activity coefficients for the flammable components of these ternary aqueous-organic solutions were estimated using the Wilson [13], NRTL [14] and UNIQUAC equations [15]. These estimated activity coefficients were subsequently used in this proposed model to predict the corresponding flash points for the ternary aqueous-organic solutions.

The parameters required for our model include the Antoine coefficients for the flammable components and the binary interaction parameters of the Wilson, NRTL or UNIQUAC equations. In addition, it is necessary to input the flash points of the solution components into this model to predict the mixture flash point. The Antoine coefficients were sourced from the literature [21]. The binary interaction parameters of the Wilson, NRTL and UNIQUAC equations for these two mixtures were also derived from the same literature [21]. The values of these binary interaction parameters were obtained by regression of the vapor–liquid equilibrium measurements for the ternary aqueous-organic solutions. The relative van der Waals volume parameter ( $r$ ) and the surface area parameter ( $q$ ) for the pure components needed for the UNIQUAC equation and the corresponding specific volumes necessary for the Wilson equation is listed in Table 1.

The three equations used in this study for estimating the activity coefficients for a multi-component mixture require only binary (i.e., two-body information) interaction constants, and no ternary (or higher) constants appear [22]. This research attempts to compare the predictive efficacy of the model for the ternary aqueous-organic solutions using binary interaction parameters obtained from a ternary or binary system. These binary interaction parameters for binary systems were adopted from different reports (Table 2) [18–21,23].

The flash points of the pure flammable substances used in this study were measured with the Flash Point Analyzer. Table 3 compares the measured values for the solution components with those adopted from the literature. The experiment and literature-derived values of the flash point for ethanol are the same [5,6]. There appear to be slight, but acceptable, deviations between our measurements and the flash points reported for methanol and isopropanol, however. The flash points quoted in the SFPE Handbook [5] and Merck Index [6] were measured using the closed-cup method, although interestingly, the standard test method is not mentioned in either source. It is reported in the former that the results of flash point measurement depends upon the apparatus employed. The measured difference in flash points for methanol and isopropanol between the values applied for this

Table 1

Relative van der Waals volumes ( $r$ ) and surface areas ( $q$ ) for the pure components for the UNIQUAC model, and specific volumes ( $v_i^l$ ) for the pure components for the Wilson model

Component	$v_i^l$ (cm <sup>3</sup> mol <sup>-1</sup> ) <sup>a</sup>	MW [6]	$\rho$ (g cm <sup>-3</sup> )	$r$ [22]	$q$ [22]
Methanol	40.73	32.04	0.7867 [19]	1.4311	1.432
Ethanol	58.68	46.07	0.7851 [19]	2.1055	1.972
Isopropanol	76.53	60.10	0.7853 [18]	2.7791	2.508
Water	18.07	18.02	0.9972 [19]	0.9200	1.400

<sup>a</sup>  $v_i^l = MW_i/\rho_i$ .

Table 2  
Binary interaction parameters of the Wilson, NRTL and UNIQUAC equations for binary systems of water, methanol, ethanol and isopropanol

System	Binary interaction parameter <sup>a</sup>	Wilson	NRTL	UNIQUAC
Methanol (1) + ethanol (2)	$A_{12}$	68.35 [23]	0.0 [19]	-238.94 [23]
	$A_{21}$	-66.46 [23]	0.0 [19]	383.90 [23]
	$\alpha_{12}$	-	0.0 [19]	-
Methanol (1) + isopropanol (2)	$A_{12}$	70.54 [23]	110.50 [23]	-187.48 [23]
	$A_{21}$	-66.79 [23]	-126.32 [23]	280.61 [23]
	$\alpha_{12}$	-	0.3047 [23]	-
Water (1) + methanol (2)	$A_{12}$	908.46 [18]	437.996 [19]	-271.26 [18]
	$A_{21}$	-359.74 [18]	-94.804 [19]	736.01 [18]
	$\alpha_{12}$	-	0.4 [19]	-
Water (1) + ethanol (2)	$A_{12}$	481.44 [20]	633.907 [19]	-109.37 [20]
	$A_{21}$	179.66 [20]	24.862 [19]	299.46 [20]
	$\alpha_{12}$	-	0.4 [19]	-
Water (1) + isopropanol (2)	$A_{12}$	650.35 [18]	814.68 [21]	-41.70 [18]
	$A_{21}$	380.59 [18]	231.98 [21]	283.10 [18]
	$\alpha_{12}$	-	0.5601 [21]	-

<sup>a</sup> Wilson:  $A_{ij} = (\lambda_{ij} - \lambda_{ii})/R$ ; NRTL:  $A_{ij} = (g_{ij} - g_{jj})/R$ ; UNIQUAC:  $A_{ij} = (u_{ij} - u_{jj})/R$ .

Table 3  
Comparison of flash point values adopted from the literature with experimentally derived data for some alcohols<sup>a</sup>

Component	Experimental data (°C)	SFPE (°C) [5]	Merck (°C) [6]
Methanol	10.0 ± 0.4	12	12
Ethanol	13.0 ± 0.3	13	13
Isopropanol	12.9 ± 0.3	12	11.7

<sup>a</sup> Closed-cup test.

work and the corresponding values reported in the two sources above may be attributable to existing differences in the standard test method.

#### 4.2. Comparison of predicted and measured flash points

The measured flash points for the water + methanol + ethanol/isopropanol systems are listed in Table 4 and shown in Figs. 2 and 3. These measurements vary substantially with water composition ( $x_1$ ) in the range,  $0.9 < x_1 < 1$ , however, this variation was modest in the range,  $x_1 \leq 0.9$ . Given the steepness of the slope for flash point versus water composition in the range,  $0.9 < x_1 < 1$ , the number of experimental data points in this range is denser than for other analogous ranges in this study.

The predictive capability of Garland and Malcolm's statistical model [11] was tested. The respective derived best-fit equations for the two systems, water (1) + methanol (2) + ethanol (3) and water (1) + methanol (2) + isopropanol (3), using all the derived experimental data in this study are:

$$T = 6.358 + 43.146x_1 - 1.698x_2 \quad (6)$$

$$T = 7.462 + 34.259x_1 - 0.108x_2 \quad (7)$$

where  $x_1$  and  $x_2$  denoted the respective mole fractions of water and methanol. Fig. 2 compares the predicted flash points from Eq. (6) with the experimental results for water + methanol + ethanol. It is evident that the differences

between the measured and predicted flash points (red surface in Fig. 2) are quite substantial, indicating failure to describe the experimental data. This substantial deviation may be attributed to the observed non-linearity of flash point versus  $x_1$ , which deviates markedly from the linear assumption of the model in question [11]. Table 5 indicates that the flash point deviation for water + methanol + isopropanol is even larger than that for water + methanol + ethanol. Since the measured flash points of the above two mixtures vary modestly for  $x_1 \leq 0.9$ , which is nearly consistent with the linear assumption of Garland and Malcolm's model [11], our experimental data for this range were used to determine the parameters of such a model. The resulting respective equations of Garland and Malcolm for water (1) + methanol (2) + ethanol (3) and water (1) + methanol (2) + isopropanol (3) are:

$$T = 12.214 + 18.937x_1 - 2.776x_2 \quad (8)$$

$$T = 11.969 + 16.393x_1 - 1.308x_2. \quad (9)$$

For water + methanol + ethanol, Fig. 2 depicts the large deviations between the measured and predicted flash points (blue surface) from Eq. (8) for the range  $0.9 < x_1 < 1$ , although the predictions are consistent with the experimental data for  $x_1 \leq 0.9$ . Similar deviation is also observed for water + methanol + isopropanol (Table 5).

The predicted flash points of our general flash point-prediction model, based upon the binary interaction parameters

Table 4  
Measured flash points for water (1) + methanol (2) + ethanol/isopropanol (3)

$x_1$	$x_2$	Measured flash points (°C)		$x_1$	$x_2$	Measured flash points (°C)	
		Water (1) + methanol (2) + ethanol (3)	Water (1) + methanol (2) + isopropanol (3)			Water (1) + methanol (2) + ethanol (3)	Water (1) + methanol (2) + isopropanol (3)
0	0	13.0	12.9	0.6	0.1	22.1	19.5
0	0.1	12.5	12.8	0.6	0.2	21.4	21.5
0	0.2	12.4	12.6	0.6	0.3	20.7	21.6
0	0.3	12.1	12.4	0.6	0.4	24.1	24.1
0	0.4	11.9	12.3	0.7	0	23.0	19.1
0	0.5	11.5	12.0	0.7	0.1	25.1	20.5
0	0.6	11.3	11.6	0.7	0.2	23.5	22.5
0	0.7	11.0	11.5	0.7	0.3	26.0	26.0
0	0.8	10.6	11.1	0.8	0	24.5	20.0
0	0.9	10.4	10.5	0.8	0.1	26.1	24.5
0	1.0	10.0	10.0	0.8	0.2	31.1	31.1
0.1	0	14.5	14.5	0.85	0	26.0	–
0.1	0.1	14.3	14.2	0.9	0	30.0	22.5
0.1	0.2	14.1	14.0	0.9	0.1	43.5	43.5
0.1	0.3	14.0	13.9	0.91	0.01	–	21.9
0.1	0.4	13.5	13.5	0.91	0.02	35.0	22.1
0.1	0.5	13.2	14.2	0.91	0.03	36.1	25.8
0.1	0.6	13.0	13.1	0.91	0.04	37.4	29.5
0.1	0.7	12.5	12.5	0.91	0.05	39.8	31.4
0.1	0.8	12.1	12.0	0.91	0.06	39.5	33.5
0.1	0.9	11.5	11.5	0.91	0.07	42.4	35.3
0.2	0	16.2	15.5	0.91	0.08	45.5	40.5
0.2	0.1	16.0	15.4	0.92	0.06	44.5	–
0.2	0.2	15.5	15.5	0.92	0.07	48.1	–
0.2	0.3	15.3	15.3	0.93	0.05	47.0	–
0.2	0.4	15.1	15.0	0.93	0.06	48.9	–
0.2	0.5	15.0	15.0	0.94	0.04	49.0	–
0.2	0.6	14.5	14.5	0.94	0.05	51.5	–
0.2	0.7	14.1	14.2	0.95	0	41.0	29.0
0.2	0.8	13.0	13.0	0.95	0.01	44.9	–
0.3	0	17.5	16.5	0.95	0.02	47.5	35.1
0.3	0.1	17.3	16.8	0.95	0.03	50.4	39.5
0.3	0.2	17.1	16.5	0.95	0.04	54.5	46.0
0.3	0.3	17.0	16.4	0.95	0.05	58.3	58.3
0.3	0.4	16.5	16.5	0.955	0.045	60.5	60.5
0.3	0.5	16.5	16.4	0.96	0	45.0	33.0
0.3	0.6	15.9	16.1	0.96	0.02	52.1	–
0.3	0.7	15.9	15.9	0.96	0.03	58.5	–
0.4	0	19.0	17.5	0.96	0.04	63.0	63.0
0.4	0.1	18.9	17.5	0.965	0.035	68.1	68.1
0.4	0.2	17.8	18.0	0.97	0	51.0	35.0
0.4	0.3	18.5	18.1	0.97	0.01	54.9	–
0.4	0.4	18.5	17.9	0.97	0.02	62.5	–
0.4	0.5	17.9	17.5	0.97	0.03	70.8	70.8
0.4	0.6	18.2	18.2	0.972	0.028	72.5	72.5
0.5	0	20.5	18.1	0.975	0	53.5	–
0.5	0.1	21.2	18.9	0.98	0	58.5	42.5
0.5	0.2	20.0	19.0	0.98	0.01	68.1	52.1
0.5	0.3	19.5	19.5	0.9875	0	70.0	–
0.5	0.4	19.0	19.5	0.99	0	–	53.1
0.5	0.5	21.2	21.2	0.995	0	–	68.0
0.6	0	21.5	18.5				

of a ternary solution [21], were also compared with the corresponding measured values (Fig. 3 and Table 5). Fig. 3 depicts the predicted flash points for the water + methanol + isopropanol system using different equations to estimate activity coefficients, with each entirely consistent with the experimental data although there are slight differences between them. Table 5

shows that the predictions for water + methanol + ethanol are more in agreement with the experimental data than those for water + methanol + isopropanol over the entire composition range. By contrast, the best results of Garland and Malcolm's model [11] only match the measurements for water composition in the range  $x_1 \leq 0.9$  for these two mixtures (see Fig. 2

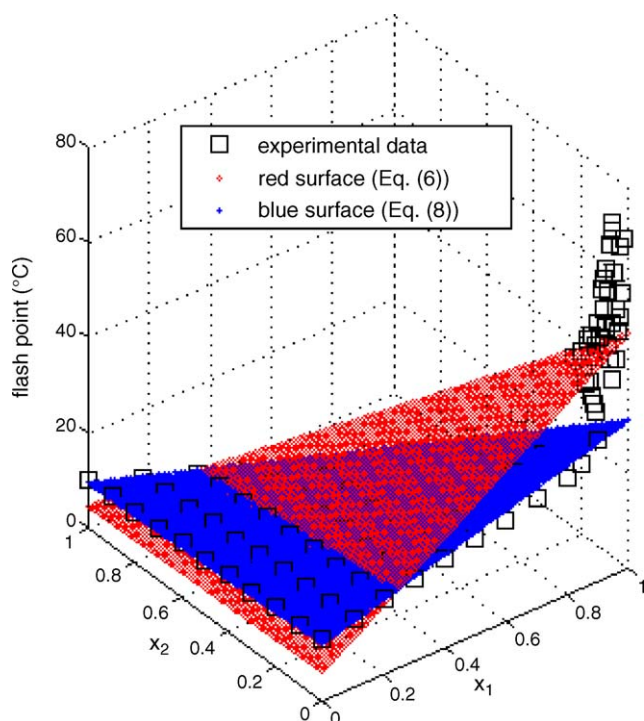


Fig. 2. Comparison of flash point-prediction surfaces based upon Garland and Malcolm's statistical model with experimental data for the water (1) + methanol (2) + ethanol (3) system.

and Table 5). Even where Eqs. (8) and (9) are used to describe flash points for the range  $x_1 \leq 0.9$  (where Garland and Malcolm's model performs best), its predictive capability is markedly lower than that of the proposed model, using any of the tested equations to estimate activity coefficients. It appears reasonable to conclude, therefore, that our model is markedly superior to Garland and Malcolm's paradigm [11] in terms of predictive capability for ternary aqueous-organic solutions.

In addition, the parameters for Garland and Malcolm's model [11] need to be determined using experimental data prior to its application. Essentially, this model just fits the experimental data, rather than predicting the experimental reality. By contrast, the parameters of our flash point-prediction model are simply

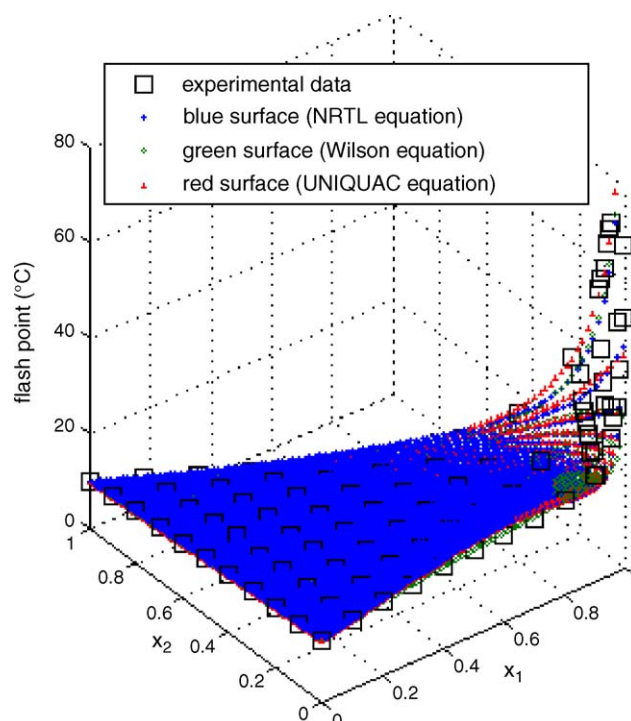


Fig. 3. Comparison of flash point-prediction surfaces based upon binary interaction parameters of a ternary solution with experimental data for the water (1) + methanol (2) + isopropanol (3) system.

basic thermodynamic information that can be sourced from the literature. Thus, the proposed model offers accurate prediction of the measured flash point, rather than curve fitting.

The failure of Garland and Malcolm's model [11] arises from non-linearity in flash point versus  $x_1$ . This non-linearity is attributed to two factors. One is that the mixtures of polar components, as used in this study, exhibit significant interactions between them and thus display strongly non-ideal behavior. The other is that water has no contribution to the vapor pressure of flammables; thus the flash point exhibits highly non-linearity with water composition in the range near pure water [2]. The linear assumption of Garland and Malcolm's model [11] is,

Table 5  
Deviation between calculated and experimental flash points,  $\Delta T_{fp}^a$ , for the studied ternary solutions comparing models

Mixture	Garland and Malcolm		Our flash point-prediction model		
	Eqs. (6) and (7) <sup>b</sup>	Eqs. (8) and (9) <sup>c</sup>	Wilson	NRTL	UNIQUAC
Water + methanol + ethanol	6.08 <sup>d</sup> (5.60 <sup>e</sup> )	6.81 <sup>d</sup> (1.02 <sup>e</sup> )	0.76 <sup>d,f</sup> (0.57) <sup>e,f</sup> 1.87 <sup>d,g</sup> (0.81) <sup>e,g</sup>	0.62 <sup>d,f</sup> (0.53) <sup>e,f</sup> 2.41 <sup>d,g</sup> (0.48) <sup>e,g</sup>	0.70 <sup>d,f</sup> (0.55) <sup>e,f</sup> 0.95 <sup>d,g</sup> (0.77) <sup>e,g</sup>
Water + methanol + isopropanol	7.73 <sup>d</sup> (6.25 <sup>e</sup> )	4.01 <sup>d</sup> (1.65 <sup>e</sup> )	2.55 <sup>d,f</sup> (0.56) <sup>e,f</sup> 1.90 <sup>d,g</sup> (0.95) <sup>e,g</sup>	2.85 <sup>d,f</sup> (0.70) <sup>e,f</sup> 1.82 <sup>d,g</sup> (0.79) <sup>e,g</sup>	1.53 <sup>d,f</sup> (0.56) <sup>e,f</sup> 0.65 <sup>d,g</sup> (0.42) <sup>e,g</sup>

$$^a \text{ Deviation of flash point: } \Delta T_{fp} = \sum_N |T_{fp,exp.} - T_{fp,pred.}| / N.$$

<sup>b</sup> Parameters obtained by fitting with all experimental data.

<sup>c</sup> Parameters obtained by fitting with our experimental data for water composition  $\leq 0.9$ .

<sup>d</sup>  $\Delta T_{fp}$  for  $0 \leq x_1 \leq 1$ .

<sup>e</sup>  $\Delta T_{fp}$  for  $0 \leq x_1 \leq 0.9$ .

<sup>f</sup> Based upon binary parameters of a ternary solution.

<sup>g</sup> Based upon binary parameters of binary solutions.

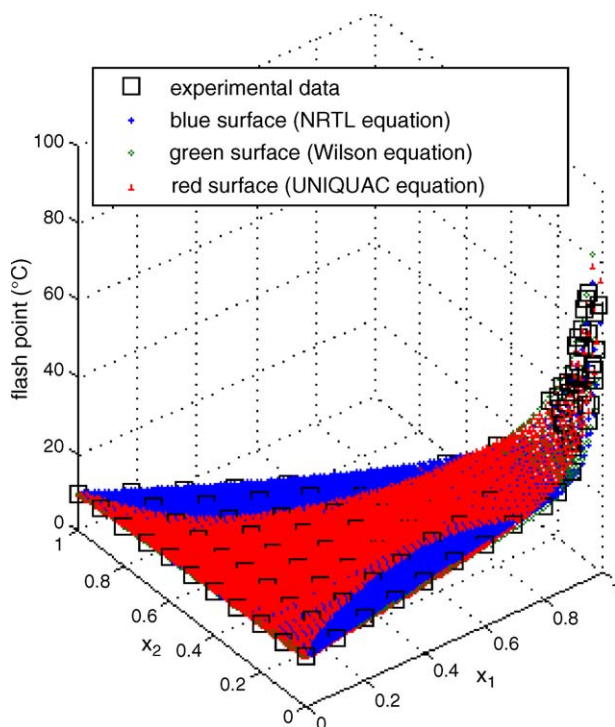


Fig. 4. Comparison of flash point-prediction surfaces based upon binary interaction parameters of binary solutions with experimental data for the water (1) + methanol (2) + ethanol (3) system.

therefore, not only unsuitable for non-ideal solutions but also its model structure is unable to describe the behavior of aqueous solutions. By contrast, our approach does consider non-ideality of the liquid phase and the effect of non-flammables on flash point, and is, thus, intrinsically superior.

#### 4.3. Predictive results when binary interaction parameters of binary solutions are used

The flash points for the two tested ternary solutions were calculated using the binary interaction parameters for binary solutions (Table 2), and the measurements for water + methanol + ethanol were plotted against the corresponding experimental data (Fig. 4). Even where the binary interaction parameters for the NRTL, Wilson and UNIQUAC equations were adopted from different sources, there were only small differences between the predicted flash points using the above equations to estimate activity coefficient (Fig. 4). The predictions are all in good agreement with the experimentally derived data. The predictive capability for the other mixture, water + methanol + isopropanol, is as good as that for water + methanol + ethanol, as demonstrated by the flash point deviation presented in Table 5.

From Table 5, we see that the predictive efficacy of the model based upon the binary interaction parameters of binary solutions is equivalent to the ternary analogue using the water + methanol + isopropanol solution, although the former appears less accurate for water + methanol + ethanol. Regardless, the predictive efficacy of our model, based on the binary interaction parameters of either the binary or ternary solutions,

was far superior to that of Garland and Malcolm [11] for the two tested mixtures. Further, a model based upon the binary interaction parameters of binary solutions may provide a very acceptable means of predicting the flash points for ternary aqueous-organic mixtures if the binary interaction parameters for the ternary solution are not accessible from literature.

It has been reported that aqueous-organic solutions will not flash when the water content is high enough [11], thus, the applicability of the model proposed in this manuscript for aqueous-organic solutions is limited to the composition range where the vapor phase is flammable.

## 5. Conclusion

The statistical model proposed by Garland and Malcolm [11] is not adequate for estimation of the flash point of a ternary aqueous-organic solution where water composition approaches unity. By contrast, our model for miscible mixtures accurately predicts the flash points over the composition range where the mixtures will flash. The failure of Garland and Malcolm's model [11] is a consequence of the fact that this type of model does not consider the non-ideal behavior of mixtures and the model structure can not, therefore, describe the behavior of aqueous solutions. By contrast, our proposed model does consider non-ideality of the liquid phase and the effect of non-flammables on flash point. Further, this derived model is reducible for some specified systems, as proposed previously [1,2,10], including binary aqueous-organic and flammables-only solutions. Thus, this general flash point-prediction model has the potential to accurately calculate the flash points of all miscible solutions, including aqueous-organic systems and mixtures consisting only of flammables. Importantly, these predictions can then be applied to assess fire and explosion hazards in real-world environments and thus produce inherently safer designs for chemical processes.

In this study, predictions based on the binary interaction parameters of binary solutions, instead of a ternary analog, produced good agreement with the experimental data for ternary aqueous-organic solutions. Since the former parameters are relatively easy to access, it appears reasonable to suggest that our proposed flash point-prediction model has the potential for wide application in real-world situations.

## Acknowledgement

The authors would like to thank the National Science Council of the R.O.C. for supporting this study financially under grant #NSC 92-2214-E-039-001.

## References

- [1] H.-J. Liaw, Y.-H. Lee, C.-L. Tang, H.-H. Hsu, J.-H. Liu, A mathematical model for predicting the flash point of binary solutions, *J. Loss Prevent. Proc.* 15 (2002) 429–438.
- [2] H.-J. Liaw, Y.-Y. Chiu, The prediction of the flash point for binary aqueous-organic solutions, *J. Hazard. Mater.* 101 (2003) 83–106.
- [3] CCPS/AIChE, Guidelines for Engineering Design for Process Safety, American Institute of Chemical Engineers, New York, 1993.



- [4] F.P. Lees, *Loss Prevention in the Process Industries*, vol. 1, 2nd ed., Butterworth-Heinemann, Oxford, UK, 1996.
- [5] SFPE, *The SFPE Handbook of Fire Protection Engineering*, 2nd ed., Society of Fire Protection Engineers, Boston, 1995.
- [6] Merck, *The Merck Index*, 12th ed., Merck & Co., NJ, 1996.
- [7] D.A. Crowl, J.F. Louvar, *Chemical Process Safety: Fundamentals with Applications*, Prentice Hall PTR, New Jersey, 2002.
- [8] W.A. Affens, G.W. McLaren, Flammability properties of hydrocarbon solutions in air, *J. Chem. Eng. Data* 17 (1972) 482–488.
- [9] D. White, C.L. Beyler, C. Fulper, J. Leonard, Flame spread on aviation fuels, *Fire Saf. J.* 28 (1997) 1–31.
- [10] H.-J. Liaw, C.-L. Tang, J.-S. Lai, A model for predicting the flash point of ternary flammable solutions of liquid, *Combust. Flame* 138 (2004) 308–319.
- [11] R.W. Garland, M.O. Malcolm, Evaluating vent manifold inerting requirements: flash point modeling for organic acid–water mixtures, *Process Saf. Prog.* 21 (2002) 254–260.
- [12] ASTM D 56, Standard test method for flash point by Tag closed tester, American Society for Testing and Materials, West Conshohocken, PA, 2001.
- [13] G.M. Wilson, Vapor liquid equilibrium. XI. A new expression for the excess free energy of mixing, *J. Am. Chem. Soc.* 86 (1964) 127–130.
- [14] H. Renon, J.M. Prausnitz, Local compositions in thermodynamic excess functions for liquid mixtures, *AIChE J.* 14 (1968) 135–144.
- [15] D.S. Abrams, J.M. Prausnitz, Statistical thermodynamics of liquid mixtures: new expression for the excess Gibbs energy of partly or completely miscible systems, *AIChE J.* 21 (1975) 116–128.
- [16] H.-J. Liaw, T.-P. Lee, J.-S. Tsai, W.-H. Hsiao, M.-H. Chen, T.-T. Hsu, Binary liquid solutions exhibiting minimum flash-point behavior, *J. Loss Prevent. Proc.* 16 (2003) 173–186.
- [17] J.M. Smith, N.C. Van Ness, *Introduction to Chemical Engineering Thermodynamics*, 3rd ed., McGraw-Hill, New York, 1975.
- [18] B. Khalfaoui, A.H. Meniai, R. Borja, Thermodynamics properties of water + normal alcohols and vapor–liquid equilibria for binary systems of methanol or 2-propanol with water, *Fluid Phase Equilib.* 127 (1997) 181–190.
- [19] K. Kurihara, M. Nakamichi, K. Kojima, Isobaric vapor–liquid equilibria for methanol + ethanol + water and the three constituent systems, *J. Chem. Eng. Data* 38 (1993) 446–449.
- [20] A. Arce, J. Martinez-Ageitos, J. Mendoza, A. Soto, Water + ethanol + 2-methoxy-2-methylbutane: properties of mixing at 298.15 K and isobaric vapour–liquid equilibria at 101.32 kPa, *Fluid Phase Equilib.* 141 (1997) 207–220.
- [21] J. Gmehling, U. Onken, W. Arlt, *Vapor–Liquid Equilibrium Data Collection*, vol. 1, DECHEMA, Frankfurt, Germany, 1981, Part 1a.
- [22] R.C. Reid, J.M. Prausnitz, T.K. Sherwood, *The Properties of Gases and Liquids*, 3rd ed., McGraw-Hill, New York, 1977.
- [23] J. Gmehling, U. Onken, *Vapor–Liquid Equilibrium Data Collection*, vol. 1, DECHEMA, Frankfurt, Germany, 1977 (part 2a).