

Flash-Point Measurements and Modeling for Ternary Partially Miscible Aqueous–Organic Mixtures

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Flash point is the most important variable used to characterize the fire and explosion hazard of liquids. This paper presents the first partially miscible aqueous–organic mixtures flash-point measurements and modeling for the ternary type-I mixtures, water + ethanol + 1-butanol and water + ethanol + 2-butanol, and the type-II mixture, water + 1-butanol + 2-butanol. Results reveal that the flash points are constant in each tie line. Handling the nonideality of the liquid phase through the use of activity coefficient models, the general flash-point model of Liaw et al. extended to partially miscible mixtures predicts the experimental data well when using literature liquid–liquid equilibria (LLE) and the vapor–liquid equilibria (VLE) activity coefficient model binary parameters to estimate sequentially the span and flash point in each tie line and the flash point in the mutual solubility region, respectively. The constant flash-point behavior in a tie line is also observed and predicted, in agreement with the vapor–liquid–liquid equilibrium (VLLE) tie line property that a single vapor is in equilibrium with all liquid composition on a tie line. For the aqueous–organic mixtures here studied, a deviation between prediction and measurements is observed, arising from the failure of the constant lower flammable limit assumption in the mutual solubility inert-rich region. Potential application for the model concerns the assessment of fire and explosion hazards and the development of inherently safer designs for chemical processes containing partially miscible aqueous–organic mixtures.

Introduction

The fire and explosion hazard of liquids is primarily characterized by their flash point.¹ The flash point is the temperature determined experimentally at which a liquid emits sufficient vapor to form a combustible mixture with air.² Recently, the importance of flash point in the usage and storage of combustible and flammable liquid mixtures was dramatically highlighted in Taiwan after a series of explosions of essential oils and the Shengli event.^{3–5} In addition, combustible and flammable liquids are major hazardous materials both involved in chemical transportation and responsible for most road tanker accidents.⁶ The requirements of transportation for combustible and flammable liquids are primarily related to their flash-point values.⁷

The United Nations encouraged the worldwide implementation of the GHS (Globally Harmonized System of Classification and Labeling of Chemicals) in 2008, and within it, the flash point of mixtures is the critical property in the classification of flammable liquids. Unfortunately, mixture flash-point data are scarce, which may explain the decision of the EC (European community) CLP (Classification, Labeling, and Packaging) to delay the classification of mixtures until 2015.⁸ The flash points of partially miscible mixtures are the least studied despite their use in the liquid–liquid extraction processes^{9,10} and heterogeneous distillation processes¹¹ encountered in many chemical

plants. A review of the literature revealed that the only published data available for partially miscible mixtures are those reported in our previous studies.^{12–15}

Since the cost of deriving flash-point data from test instruments is very high, NT\$20 000/US\$600 per sample in Taiwan, several alternative models for predicting the flash points of different types of mixtures have been proposed, especially for miscible mixtures.^{1,3–5,16–23} Models based on the assumption of ideal solutions^{1,16–18} show limitations when applied to nonideal mixtures, which are the most frequent ones. Models taking into account the nonideality of the solution through liquid-phase activity coefficients have a wider application range and predicted efficiently the flash point of miscible mixtures.^{3–5,19,20,22,23}

Nonideality of the liquid phase is in particular responsible for the occurrence of extreme flash-point behavior such as minimum and maximum flash-point behavior,^{21,24–27} with strong implications on the fire and explosion hazard assessment for the concerned mixtures. The extreme behavior was set in parallel with minimum-boiling and maximum-boiling azeotropic behavior in vapor–liquid equilibrium. In vapor–liquid equilibrium, stronger nonideality with positive deviation from ideality within a mixture may often result in the partial miscibility of the liquid phase, eventually coupled with the occurrence of a so-called heteroazeotrope. An analogous partial miscibility behavior was observed for the flash points of binary partially miscible mixtures of flammable solvents¹² or of aqueous–organic mixtures¹³ and for ternary partially miscible mixtures of flammable solvents.¹⁴ In all three studies, a model handling the nonideality of the solution, testing for partial

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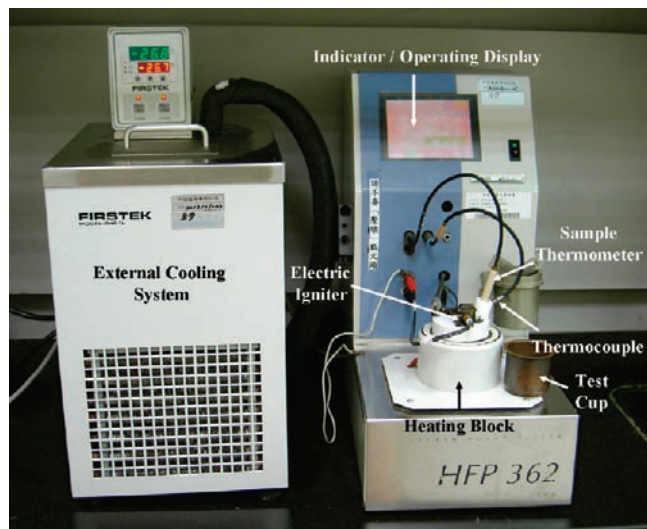


Figure 1. Basic system configuration of the Tag close cup tester.

miscibility span, and computing the flash point was successfully used in a predictive manner, using literature binary interaction parameters. In this manuscript, we extend its use for multicomponent partially miscible aqueous–organic mixtures and validate it on the data of ternary partially miscible solutions: water + ethanol + 1-butanol, water + ethanol + 2-butanol, and water + 1-butanol + 2-butanol.

Experimental Protocol

An HFP 362-Tag Flash Point Analyzer (Walter Herzog GmbH, Germany), which meets the requirement of ASTM D56 standard,²⁸ was used to measure the flash points for three ternary mixtures (water + ethanol + 1-butanol, water + ethanol + 2-butanol, and water + 1-butanol + 2-butanol) at different compositions. The basic system configuration of the Tag close cup tester is given in Figure 1. The apparatus consists of an external cooling system, test cup, heating block, electric igniter, sample thermometer, thermocouple (sensor for fire detection), and indicator/operating display. The apparatus incorporates control devices that program the instrument to heat the sample at a specified rate within a temperature range close to the expected flash point. The literature data and the estimated one under ideality assumption were used as the expected flash point for pure substance and mixture, respectively. The flash point is automatically tested using an igniter at specified temperature test intervals. The values of expected flash point and change temperature determine which test interval is used. 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. In the standard method, the change temperature is laid down by the standard and cannot be changed. 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 was conducted according to the standard ASTM D56 test protocol²⁸ using the following parameters: start test 5 K; end of test 20 K; heat rate-1, 1 K·min⁻¹; heat rate-2, 3 K·min⁻¹; change temperature 60 °C; test interval-1, 0.5 K; and, test interval-2, 1.0 K. The liquid mole fraction was estimated from

the mass divided by molecular weight, with the mass measuring by a Setra digital balance (EL-410D: sensitivity 0.001 g, maximum load 100 g). A magnetic stirrer provided sufficient agitation for the test samples. The prepared mixtures were stirred for 30 min before the flash-point test. A Milli-Q plus was used for water purification. Ethanol (99.5 vol %) was purchased from NASA enterprises (USA). 1-Butanol (99.8 vol %) was obtained from J.T. Baker. 2-Butanol (99.0 %) was sourced from Panreac (Spain).

Mathematical Formulation

Flash-Point Equations for Partially Miscible Aqueous–Organic Mixtures. Upon the basis of the definition of flash point,²⁹ it is necessary to estimate the vapor-phase composition of flammable substances from a vapor–liquid equilibrium equation to predict their flash point. Furthermore, for partially miscible mixtures, liquid–liquid equilibrium must be solved to check the ability of the liquid phase to demix. Nonideality of the liquid solution must be taken into account, as it is a major cause of demixtion. This is done by considering liquid-phase activity coefficient thermodynamic models.³⁰ NRTL³¹ and UNIQUAC thermodynamic models³² are applicable to both vapor–liquid and liquid–liquid equilibria, unlike the Wilson model³³ which cannot be used for liquid–liquid equilibrium.³⁰

Within the mutual-solubility region, only one liquid phase is present, and the variation of the partial pressure of each component with liquid-phase composition is identical to that for a miscible aqueous–organic mixture. Thus, the flash point in such a region can be evaluated by the method for a multicomponent *i* miscible

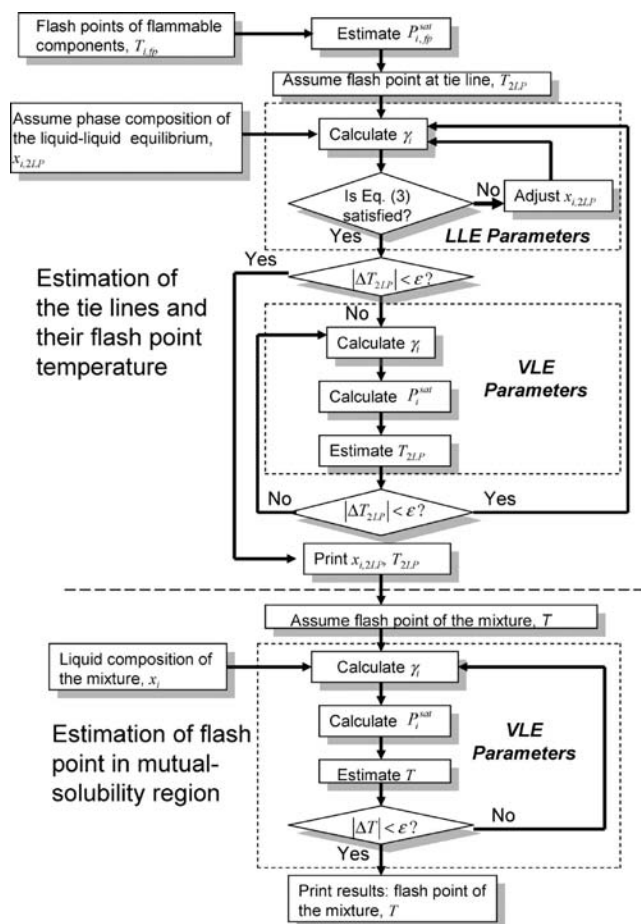


Figure 2. Procedure for evaluation of flash point for ternary partially miscible aqueous–organic mixtures.

Table 1. LLE Parameters for the Binary Solutions of Water, Ethanol, and 1-Butanol/2-Butanol^{38 a}

mixture	model	$A_{12} = a_{12} + b_{12}T + c_{12}T^2/J \cdot \text{mol}^{-1} b$			$A_{21} = a_{21} + b_{21}T + c_{21}T^2/J \cdot \text{mol}^{-1} b$		
		a_{12}	b_{12}	c_{12}	a_{21}	b_{21}	c_{21}
		$J \cdot \text{mol}^{-1}$	$J \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$	$J \cdot \text{mol}^{-1} \cdot \text{K}^{-2}$	$J \cdot \text{mol}^{-1}$	$J \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$	$J \cdot \text{mol}^{-1} \cdot \text{K}^{-2}$
Water + Ethanol + 1-Butanol							
water (1) + ethanol (2)	NRTL ($\alpha_{12} = 0.45$)	4471.10	0	0	8240.27	0	0
water (1) + 1-butanol (2)	NRTL ($\alpha_{12} = 0.45$)	-21700.79	161.685	-0.197075	-32294.07	252.073	-0.438579
	UNIQUAC	-10291.48	59.231	-0.055643	-39.27	11.365	-0.039569
ethanol (1) + 1-butanol (2)	NRTL ($\alpha_{12} = 0.45$)	-1594.56	0	0	4098.58	0	0
Water + Ethanol + 2-Butanol							
water (1) + ethanol (2)	NRTL ($\alpha_{12} = 0.45$)	-326.93	0	0	1299.54	0	0
water (1) + 2-butanol (2)	NRTL ($\alpha_{12} = 0.45$)	-22819.69	159.200	-0.190359	-32187.07	208.482	-0.327528
	UNIQUAC	-10609.58	63.158	-0.069085	-1211.88	12.220	-0.032202
ethanol (1) + 2-butanol (2)	NRTL ($\alpha_{12} = 0.45$)	-1968.94	0	0	-779.42	0	0

^a LLE parameters for partially miscible binary pairs were determined from binary solubility data, and the analogues for others were determined from ternary VLE data. ^b NRTL: $A_{ij} = g_{ij} - g_{ji}$. UNIQUAC: $A_{ij} = u_{ij} - u_{ji}$.

Table 2. VLE Parameters Determined from Binary VLE Data

mixtures	NRTL			UNIQUAC		ref
	$g_{12} - g_{22}$	$g_{21} - g_{11}$	α_{12}	$u_{12} - u_{22}$	$u_{21} - u_{11}$	
	$J \cdot \text{mol}^{-1}$	$J \cdot \text{mol}^{-1}$		$J \cdot \text{mol}^{-1}$	$J \cdot \text{mol}^{-1}$	
water (1) + 1-butanol (2)	11077.04	1608.46	0.4056	1607.90	1079.38	39
water (1) + 2-butanol (2)	7413.10	1112.30	0.4406	972.32	729.58	39
water (1) + ethanol (2)	5085.97	392.75	0.4500	—	—	38
ethanol (1) + 1-butanol (2)	316.53	-273.87	0.3038	—	—	38
ethanol (1) + 2-butanol (2)	-2184.17	3143.17	0.2835	—	—	38
1-butanol (1) + 2-butanol (2)	2316.60	-1418.39	0.3388	1452.38	-1016.24	40

analogue⁵ that for a ternary mixture with a nonflammable aqueous phase taken as component 1 becomes

$$1 = \sum_{i \neq 1} \frac{x_i \gamma_i P_i^{\text{sat}}}{P_{i,\text{fp}}^{\text{sat}}} = \frac{x_2 \gamma_2 P_2^{\text{sat}}}{P_{2,\text{fp}}^{\text{sat}}} + \frac{x_3 \gamma_3 P_3^{\text{sat}}}{P_{3,\text{fp}}^{\text{sat}}} \quad (1)$$

$$\log P_i^{\text{sat}} = A_i - \frac{B_i}{T + C_i} \quad (2)$$

$P_{i,\text{fp}}^{\text{sat}}$, the vapor pressure of the pure flammable component, i , at its flash point, $T_{i,\text{fp}}$, can be estimated using the Antoine equation (eq 2). Liquid-phase activity coefficients γ_i are evaluated using an activity coefficient model, like NRTL or UNIQUAC. Vapor phase is assumed to behave as a perfect gas as is usual under low to moderate pressure conditions.³⁴

Within the partially miscible region, two liquid phases are in equilibrium with compositions defining a so-called tie line. A property of vapor–liquid–liquid equilibrium is that any liquid composition located on this tie line, in particular, the composition of both liquid phases in equilibrium, is in equilibrium with a single vapor composition located on the so-called vapor line.^{34,35} As the flash point is related to the vapor composition, it should keep constant whatever the liquid composition on the liquid–liquid equilibrium tie line. For a binary mixture, a single tie line exists, and the flash point is constant for the whole composition range within the partial miscibility region.^{12,13} For a ternary mixture, several tie lines lead to several flash-point values within the partial miscibility region.¹⁴ For two liquid phases in equilibrium in which the reference fugacity is the same, the equilibrium compositions can be estimated by the equilibrium equality of the compound fugacities in each phase, and such an equality is reducible as

$$(x_i \gamma_i)^\alpha = (x_i \gamma_i)^\beta \quad i = 1, \dots, N \quad (3)$$

where α and β refer to the two coexisting liquid phases.

The flash point within each tie line can be calculated by substituting into eqs 1 and 2 the estimated value of equilibrium composition estimated by eq 3 by an iterative procedure described in Figure 2 analogous to that used for calculating the boiling and dew points of mixtures.³⁶

Use of Binary Parameters. Use of existing binary parameters in the activity coefficient models makes the aforementioned model predictive. Since the binary interaction parameters of NRTL and UNIQUAC models are accessible for the studied mixtures, the two models were used in this study. However, the flash point mixes the LLE equation (eq 3) and the flash-

Table 3. Antoine Coefficients and Relative van der Waals Volumes (r) and Surface Areas (q)

material	Antoine coefficients ^{39 a}			relative van der Waals volumes (r) and surface areas (q) ³⁰	
	A	B	C	r	q
1-butanol	6.96280	1558.190	-76.119	3.4543	3.052
2-butanol	6.59909	1314.188	-86.500	3.4535	3.048
ethanol	4.46155	1648.220	-42.232	2.1055	1.972
water	—	—	—	0.9200	1.400

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

Table 4. Comparison of Flash-Point Values Adopted from the Literature, $t_{\text{fp,lit}}$, with Experimentally Derived Data, $t_{\text{fp,exp}}$

component	$t_{\text{fp,exp}}/^\circ\text{C}^a$	$t_{\text{fp,lit}}/^\circ\text{C}$
ethanol	13.0 ± 0.6	$13^{41,42}$
1-butanol	36.9 ± 2.8	28.88^{43} 34^{41} 35^{44-46} 36^{47} 37^{48}
2-butanol	22.0 ± 2.4	23.88^{43} $24^{41,44}$ 26^{46} 28.88^{45}

^a The uncertainty is represented by the value of double standard deviation.

Table 5. Measured Flash Point within the Mutual Solubility Region for Water (1) + Ethanol (2) + 1-Butanol (3)

x_1	x_2	t_{fp} °C	x_1	x_2	t_{fp} °C
0.000	0.000	36.9	0.500	0.000	43.1
0.000	0.100	32.9	0.500	0.020	42.7
0.000	0.200	28.8	0.500	0.100	37.4
0.000	0.300	26.2	0.500	0.200	32.1
0.000	0.400	23.1	0.500	0.300	28.1
0.000	0.500	21.5	0.500	0.400	24.5
0.000	0.600	19.5	0.500	0.500	20.5
0.000	0.700	17.4	0.524	0.014	43.9
0.000	0.800	15.4	0.530	0.000	44.0
0.000	0.900	14.1	0.550	0.030	42.5
0.000	1.000	13.0	0.550	0.060	40.9
0.100	0.000	38.3	0.590	0.050	41.0
0.100	0.100	33.4	0.600	0.100	38.1
0.100	0.200	30.2	0.600	0.200	31.9
0.100	0.300	27.5	0.600	0.300	26.5
0.100	0.400	24.1	0.600	0.400	21.5
0.100	0.500	22.3	0.650	0.090	38.1
0.100	0.600	19.9	0.660	0.090	38.2
0.100	0.700	18.1	0.700	0.100	37.2
0.100	0.800	16.0	0.700	0.200	30.0
0.100	0.900	14.5	0.700	0.300	23.0
0.200	0.000	40.3	0.730	0.100	36.8
0.200	0.100	35.2	0.800	0.100	35.0
0.200	0.200	31.4	0.800	0.200	24.5
0.200	0.300	27.3	0.850	0.150	26.0
0.200	0.400	24.8	0.900	0.070	33.1
0.200	0.500	22.3	0.900	0.100	30.0
0.200	0.600	20.7	0.950	0.030	35.4
0.200	0.700	18.4	0.950	0.050	41.0
0.200	0.800	16.0	0.960	0.040	45.0
0.300	0.000	41.6	0.966	0.016	41.9
0.300	0.100	35.3	0.970	0.020	43.4
0.300	0.200	31.8	0.970	0.030	51.0
0.300	0.300	28.1	0.975	0.025	53.5
0.300	0.400	25.5	0.980	0.003	44.3
0.300	0.500	22.8	0.980	0.020	58.5
0.300	0.600	20.0	0.985	0.000	44.9
0.300	0.700	17.5	0.988	0.012	70.0
0.400	0.000	42.1	0.990	0.000	50.7
0.400	0.100	37.0	0.992	0.000	54.2
0.400	0.200	32.3	0.993	0.000	55.6
0.400	0.300	28.6	0.994	0.000	58.5
0.400	0.400	25.2	0.995	0.000	63.6
0.400	0.500	21.7	0.996	0.000	68.1
0.400	0.600	19.0			

Table 6. Measured Flash Point within the Two Liquid Phase Region for Water (1) + Ethanol (2) + 1-Butanol (3)

x_1	x_2	t_{fp} °C	x_1	x_2	t_{fp} °C
0.540	0.000	44.4	0.807	0.073	37.4
0.547	0.014	43.1	0.825	0.068	37.3
0.550	0.000	44.5	0.830	0.052	39.2
0.562	0.012	43.8	0.843	0.063	37.8
0.600	0.000	44.1	0.862	0.059	37.8
0.616	0.053	41.5	0.876	0.006	43.7
0.633	0.050	40.8	0.880	0.042	39.6
0.647	0.050	41.1	0.880	0.054	37.5
0.667	0.010	43.4	0.882	0.024	41.7
0.700	0.000	44.7	0.883	0.054	37.5
0.705	0.078	39.1	0.900	0.000	44.1
0.712	0.076	39.0	0.928	0.004	43.4
0.726	0.041	41.5	0.930	0.032	39.4
0.729	0.072	39.5	0.940	0.031	39.4
0.771	0.008	43.7	0.950	0.000	44.8
0.778	0.082	37.2	0.959	0.004	43.7
0.781	0.062	39.1	0.960	0.016	41.3
0.788	0.080	37.0	0.980	0.000	44.2
0.800	0.000	43.8	0.982	0.000	44.3
0.804	0.033	40.9	0.983	0.000	43.9

Table 7. Measured Flash Point within the Mutual Solubility Region for Water (1) + Ethanol (2) + 2-Butanol (3)

x_1	x_2	t_{fp} °C	x_1	x_2	t_{fp} °C
0.000	0.000	22.0	0.600	0.100	27.4
0.000	0.100	20.6	0.600	0.200	26.4
0.000	0.200	20.4	0.600	0.300	24.2
0.000	0.300	18.7	0.600	0.400	21.5
0.000	0.400	18.4	0.630	0.01	30.0
0.000	0.500	17.2	0.650	0.000	29.9
0.000	0.600	15.8	0.660	0.030	29.4
0.000	0.700	15.6	0.690	0.040	29.2
0.000	0.800	14.9	0.699	0.011	30.5
0.000	0.900	14.2	0.700	0.100	28.4
0.000	1.000	13.0	0.700	0.200	26.5
0.100	0.000	23.3	0.700	0.300	23.0
0.100	0.100	22.0	0.719	0.010	29.6
0.100	0.200	20.5	0.719	0.018	30.6
0.100	0.300	20.3	0.720	0.030	29.9
0.100	0.400	19.7	0.721	0.010	29.5
0.100	0.500	18.1	0.741	0.017	30.5
0.100	0.600	17.7	0.741	0.024	30.0
0.100	0.700	16.8	0.750	0.024	30.2
0.100	0.800	15.6	0.750	0.050	29.6
0.100	0.900	14.5	0.752	0.021	29.6
0.200	0.000	25.0	0.760	0.028	29.9
0.200	0.100	23.7	0.760	0.217	25.3
0.200	0.200	22.2	0.765	0.023	30.8
0.200	0.300	21.4	0.770	0.050	29.8
0.200	0.400	20.0	0.781	0.027	30.1
0.200	0.500	18.9	0.787	0.026	30.3
0.200	0.600	17.7	0.792	0.026	30.8
0.200	0.700	17.5	0.800	0.100	28.5
0.200	0.800	16.0	0.800	0.200	24.5
0.300	0.000	26.1	0.802	0.026	30.0
0.300	0.100	24.7	0.840	0.022	30.8
0.300	0.200	23.4	0.850	0.05	29.8
0.300	0.300	22.3	0.850	0.150	26.0
0.300	0.400	21.2	0.900	0.100	30.0
0.300	0.500	20.1	0.901	0.014	29.4
0.300	0.600	19.3	0.901	0.085	30.3
0.300	0.700	17.5	0.907	0.014	29.8
0.390	0.010	26.8	0.911	0.013	29.8
0.400	0.000	27.1	0.913	0.015	30.3
0.400	0.100	25.8	0.920	0.015	30.4
0.400	0.200	24.4	0.921	0.012	30.7
0.400	0.300	23.1	0.929	0.008	30.4
0.400	0.400	21.8	0.930	0.012	30.6
0.400	0.500	19.9	0.940	0.008	29.1
0.400	0.600	19.0	0.948	0.004	29.0
0.420	0.010	27.9	0.950	0.050	41.0
0.450	0.010	27.9	0.960	0.040	45.0
0.460	0.010	28.5	0.970	0.000	31.9
0.490	0.010	28.7	0.970	0.030	51.0
0.500	0.000	28.6	0.975	0.025	53.5
0.500	0.100	27.0	0.980	0.000	36.1
0.500	0.200	26.0	0.980	0.020	58.5
0.500	0.300	23.6	0.988	0.012	70.0
0.500	0.400	22.2	0.990	0.000	45.7
0.500	0.500	20.5	0.993	0.000	51.6
0.560	0.010	28.4	0.995	0.000	58.6
0.600	0.000	29.0	0.996	0.000	64.7

point equation based on VLE calculation (eq 1). Ideally, the same set of parameters should be used for eqs 1 and 3, which is possible if a VLLE data regressed parameter exists, which is rare. On the other hand, it is acknowledged that the binary parameter regressed on LLE data is not suitable for predicting VLE data.³⁷ Thus we validated in a former study¹⁴ the iterative procedure described in Figure 2: The flash point in the mutual solubility region was estimated by the VLE parameters. For the partially miscible region, LLE parameters are used in eq 3 to estimate the tie line equilibrium liquid compositions, and the relevant flash point is computed using, first, VLE parameters to ensure no discontinuity in the calculated flash-point surface

Table 8. Measured Flash Point within the Two Liquid Phase Region for Water (1) + Ethanol (2) + 2-Butanol (3)

x_1	x_2	t_{fp} °C	x_1	x_2	t_{fp} °C
0.670	0.000	29.4	0.836	0.019	29.8
0.680	0.000	30.1	0.883	0.015	30.0
0.690	0.000	30.0	0.885	0.011	30.1
0.700	0.000	29.6	0.886	0.005	30.1
0.726	0.009	30.0	0.892	0.014	30.0
0.763	0.016	29.6	0.900	0.000	29.4
0.775	0.017	29.9	0.918	0.004	29.8
0.790	0.022	30.0	0.923	0.005	30.3
0.800	0.000	29.7	0.936	0.004	30.2
0.813	0.020	30.0	0.950	0.000	29.8
0.822	0.007	30.1	0.950	0.004	30.5
0.830	0.014	29.8			

and, second, the liquid–liquid equilibrium composition approaching the lower boiling pure component. This is the so-called VLLE model in this study.

Results and Discussion

Parameters Used in This Manuscript. The flash-point model for ternary partially miscible aqueous–organic mixtures was used for water + ethanol + 1-butanol, water + ethanol + 2-butanol, and water + 1-butanol + 2-butanol mixtures and validated against the corresponding experimental data. Liquid-phase activity coefficients were estimated by using the NRTL³¹ and UNIQUAC equations.³² Binary interaction parameters obtained from either the LLE or VLE data are used in this study, with parameters adopted from the literature^{38–40} (Tables 1 and 2). The parameters for relative van der Waals volume (r) and the surface area (q) for the pure components needed in the UNIQUAC equation (also obtained from the literature³⁰) are listed in Table 3 along with the Antoine coefficients sourced from the literature.³⁹

Pure Component Flash Points. The flash points for the pure substances used in this study were measured using the Flash Point Analyzer and compared to literature data^{41–48} (Table 4). Some of the literature data were tested by the closed-cup method,^{41,42,48} and others did not mention the test method; however, the latter data seem to be tested by the closed-cup method from the reported values. Our experimental flash point for ethanol was identical to the literature-derived values.^{41,42} The measured flash points for 1-butanol and 2-butanol were close to the literature-derived values,^{41,43–48} except that there were between-source differences in the flash-point data for 1-butanol and 2-butanol. However, these differences were acceptable except for the value of 1-butanol provided by NIOSH⁴³ and 2-butanol by Tedia.⁴⁵

Flash-Point Variation for Binary Pairs of the Studied Ternary Mixtures. Experimental flash-point data for the ternary mixtures of water + ethanol + 1-butanol, water + ethanol + 2-butanol, and water + 1-butanol + 2-butanol covering their flammable composition ranges were listed in Tables 5 to 10. The average value of standard deviation of these data is around 0.8 °C, and the maximum one is 1.6 °C.

Water + ethanol, ethanol + 1-butanol, ethanol + 2-butanol, and 1-butanol + 2-butanol are miscible binary pairs at their flash-point temperature. However, water + 1-butanol and water + 2-butanol are partially miscible ones.

Figures 3 and 4 and Table 11 compare measured and predicted flash points, based upon literature binary parameters as listed in Tables 1 and 2. Predictions are in good agreement with the experimental data over the flammable composition range, when the NRTL and UNIQUAC equations with Gme-

Table 9. Measured Flash Point within the Mutual Solubility Region for Water (1) + 1-Butanol (2) + 2-Butanol (3)

x_1	x_2	t_{fp} °C	x_1	x_2	t_{fp} °C
0.000	0.000	22.0	0.400	0.200	31.4
0.000	0.100	22.7	0.400	0.300	33.1
0.000	0.200	24.0	0.400	0.400	35.1
0.000	0.300	25.5	0.400	0.500	38.2
0.000	0.400	26.3	0.400	0.600	42.1
0.000	0.500	28.0	0.500	0.000	28.6
0.000	0.600	29.3	0.500	0.100	30.6
0.000	0.700	30.9	0.500	0.200	32.6
0.000	0.800	32.3	0.500	0.300	35.7
0.000	0.900	33.6	0.500	0.400	38.6
0.000	1.000	36.9	0.500	0.500	43.1
0.100	0.000	23.3	0.530	0.470	44.0
0.100	0.100	24.5	0.560	0.177	34.8
0.100	0.200	26.0	0.577	0.247	36.4
0.100	0.300	26.8	0.600	0.000	29.0
0.100	0.400	28.6	0.600	0.100	31.9
0.100	0.500	30.0	0.600	0.200	35.3
0.100	0.600	31.7	0.640	0.030	31.5
0.100	0.700	33.4	0.650	0.000	29.9
0.100	0.800	35.1	0.960	0.003	31.5
0.100	0.900	38.3	0.967	0.001	32.8
0.200	0.000	25.0	0.970	0.000	31.9
0.200	0.100	26.1	0.971	0.005	37.4
0.200	0.200	27.1	0.977	0.006	38.8
0.200	0.300	29.1	0.980	0.000	36.1
0.200	0.400	30.9	0.980	0.010	37.7
0.200	0.500	32.5	0.981	0.002	37.5
0.200	0.600	34.4	0.982	0.008	39.0
0.200	0.700	36.9	0.985	0.015	44.9
0.200	0.800	40.3	0.990	0.000	45.7
0.300	0.000	26.1	0.990	0.010	50.7
0.300	0.100	27.5	0.992	0.008	54.2
0.300	0.200	28.9	0.993	0.000	51.6
0.300	0.300	31.2	0.993	0.001	52.5
0.300	0.400	33.1	0.993	0.007	55.6
0.300	0.500	35.3	0.994	0.006	58.5
0.300	0.600	37.3	0.995	0.000	58.6
0.300	0.700	41.6	0.995	0.005	63.6
0.400	0.000	27.1	0.996	0.000	64.7
0.400	0.100	29.1	0.996	0.004	68.1

Table 10. Measured Flash Point within the Two Liquid Phase Region for Water (1) + 1-Butanol (2) + 2-Butanol (3)

x_1	x_2	t_{fp} °C	x_1	x_2	t_{fp} °C
0.538	0.363	39.9	0.779	0.172	39.3
0.540	0.460	44.4	0.791	0.121	36.8
0.550	0.360	39.9	0.799	0.079	34.5
0.550	0.450	44.5	0.800	0.000	29.7
0.577	0.170	34.2	0.800	0.200	43.8
0.579	0.331	39.3	0.806	0.045	32.3
0.580	0.250	37.1	0.812	0.016	30.9
0.594	0.163	34.1	0.880	0.093	39.4
0.600	0.400	44.1	0.883	0.066	36.9
0.606	0.230	37.0	0.885	0.025	32.5
0.611	0.156	34.3	0.885	0.044	34.8
0.615	0.091	32.7	0.886	0.009	31.1
0.628	0.149	33.9	0.900	0.000	29.4
0.647	0.083	32.8	0.900	0.100	44.1
0.663	0.030	31.6	0.950	0.000	29.8
0.670	0.000	29.4	0.950	0.050	44.8
0.679	0.252	39.4	0.954	0.003	30.8
0.680	0.000	30.1	0.957	0.022	36.3
0.690	0.000	30.0	0.965	0.006	33.1
0.698	0.176	36.4	0.970	0.009	34.7
0.700	0.000	29.6	0.975	0.012	36.8
0.700	0.300	44.7	0.980	0.014	39.4
0.714	0.114	34.0	0.980	0.020	44.2
0.726	0.064	32.4	0.982	0.018	44.3
0.738	0.023	31.1	0.983	0.017	43.9

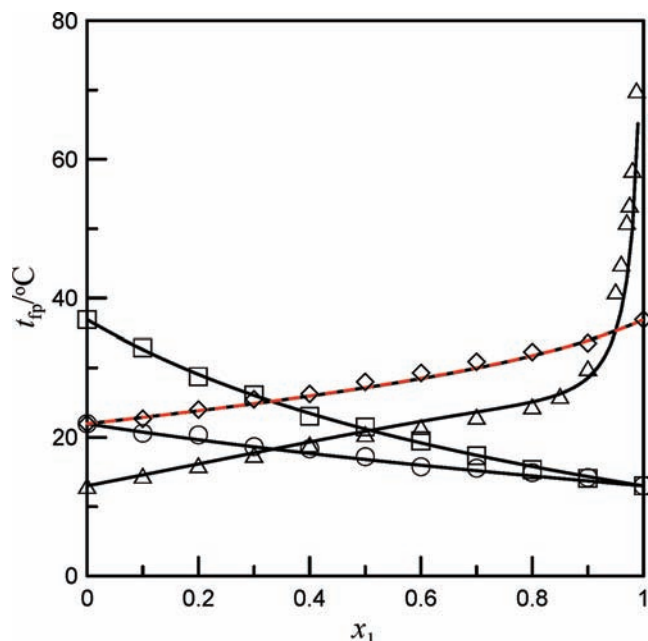


Figure 3. Comparison of predicted flash point and experimental data for miscible binary pairs of studied ternary mixtures. —, prediction by the NRTL equation; red - - -, prediction by the UNIQUAC equation; □, ethanol (1) + 1-butanol (2); ○, ethanol (1) + 2-butanol (2); ◇, 1-butanol (1) + 2-butanol (2); △, water (1) + ethanol (2).

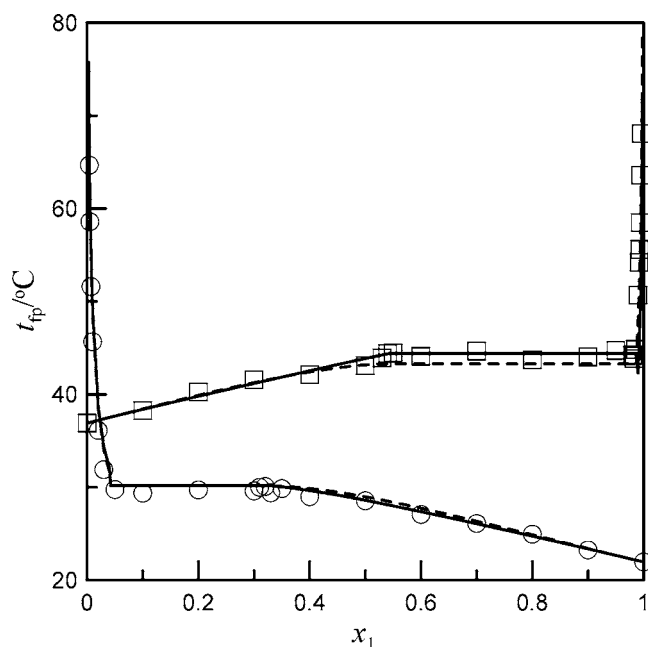


Figure 4. Comparison of predicted flash point and experimental data for water + 1-butanol and water + 2-butanol. —, prediction by the NRTL equation; - - -, prediction by the UNIQUAC equation; □, water (1) + 1-butanol (2); ○, water (1) + 2-butanol (2).

hling et al.'s VLE parameters⁴⁰ are used for the miscible binary mixtures 1-butanol + 2-butanol and with Kosuge and Iwakabe's VLE ones³⁸ are used for the other binary miscible mixtures water + ethanol, ethanol + 1-butanol, and ethanol + 2-butanol (Figure 3).

Table 11 also shows the excellent predictions for the flammable mixtures ethanol + 1-butanol, ethanol + 2-butanol, and 1-butanol + 2-butanol. However, for aqueous-flammable mixtures, remarkable deviations occur: For water + ethanol, predictions are excellent for $x_{\text{water}} < 0.9$, with the deviations being

Table 11. Deviation between Calculated and Experimental Flash Points, ΔT_{fp}^a , for the Studied Binary Pairs and Ternary Solutions Comparing Models

mixture	NRTL		UNIQUAC	
	VLE $\Delta T_{\text{fp}}/\text{K}$	VLLE $\Delta T_{\text{fp}}/\text{K}$	VLE $\Delta T_{\text{fp}}/\text{K}$	VLLE $\Delta T_{\text{fp}}/\text{K}$
ethanol + 1-butanol	0.22	—	—	—
ethanol + 2-butanol	0.32	—	—	—
1-butanol + 2-butanol	0.44	—	0.43	—
water + ethanol	2.94 ^b 7.52 ^c 0.44 ^d	—	—	—
water + 1-butanol	—	2.68 ^b 9.75 ^e 0.32 ^f	—	1.28 ^b 2.96 ^e 0.72 ^f
water + 2-butanol	—	1.25 ^b 3.57 ^e 0.32 ^f	—	1.00 ^b 2.53 ^e 0.38 ^f
water + ethanol + 1-butanol	—	1.26 ^b 6.90 ^g 0.46 ^h	—	—
water + ethanol + 2-butanol	—	0.81 ^b 4.86 ^g 0.35 ^h	—	—
water + 1-butanol + 2-butanol	—	1.01 ^b 4.54 ^e 0.37 ^f	—	1.00 ^b 3.71 ^e 0.41 ^f

^a Deviation of flash point: $\Delta T_{\text{fp}} = \sum N T_{\text{fp,exp.}} - T_{\text{fp,pred.}}/N$. ^b ΔT_{fp} over the entire flammable range. ^c ΔT_{fp} for $x_{\text{water}} \geq 0.9$. ^d ΔT_{fp} for $x_{\text{water}} < 0.9$. ^e ΔT_{fp} for the water-rich region. ^f ΔT_{fp} over the entire flammable excluding water-rich region. ^g ΔT_{fp} for mutual solubility region of water-rich with $x_{\text{water}} \geq 0.9$. ^h ΔT_{fp} over the entire flammable excluding mutual solubility region of water-rich with $x_{\text{water}} \geq 0.9$.

Table 12. Comparison of Estimated Values for Equilibrium Composition between Liquid Phases, $x_{1,2\text{LP}}$, and Its Flash Point, $t_{2\text{LP}}$, with Corresponding Experimental Data

system	estimated value				experimental data	
	NRTL		UNIQUAC		$x_{1,2\text{LP}}$	$t_{2\text{LP}}/\text{°C}$
water (1) + 1-butanol (2)	0.542 ^a 0.986 ^a 0.541 ^b 0.985 ^b	44.40 ^a 44.38 ^b	0.526 ^a 0.987 ^a 0.531 ^b 0.986 ^b	43.29 ^a 43.32 ^b	0.540 0.983	44.2 ± 0.7
water (1) + 2-butanol (2)	0.674 ^a 0.958 ^a 0.673 ^b 0.957 ^b	30.18 ^a 30.17 ^b	0.669 ^a 0.958 ^a 0.666 ^b 0.959 ^b	30.14 ^a 29.68 ^b	0.670 0.950	29.7 ± 0.5

^a This study. ^b Previous study.¹³ ^c The uncertainty is represented by the value of double standard deviation.

0.44 °C. For $x_{\text{water}} \geq 0.9$, the deviation of flash point is 7.52 °C. This phenomenon of greater deviation in high water composition region was also observed in other miscible aqueous–organic solutions^{4,5} and other partially miscible aqueous–organic mixtures¹³ and can be explained by the model failure to consider the effect of inert concentration on the lower flammable limit of a mixture.⁴⁹ In the estimation of flash point for a mixture, eq 1 uses the Le Chatelier's rule⁵⁰ that assumes that an inert substance such as water has no effect on the lower flammable limit of a mixture. The same trend is observed for the other binary and ternary aqueous–organic mixtures in this study (Table 11).

Regarding the liquid–liquid equilibrium span and related flash point of the binary mixtures water + 1-butanol and water + 2-butanol, Table 12 shows predictions in this study, and experimental data agree very well, whether the NRTL or UNIQUAC equation is used, and are in agreement with the former study.¹³

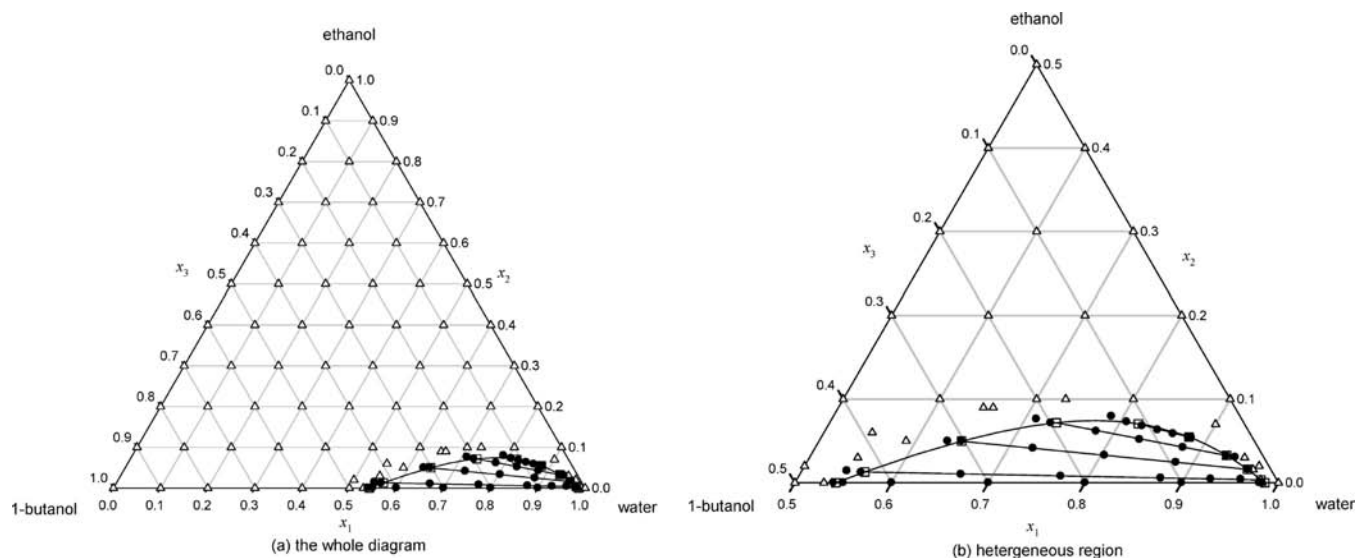


Figure 5. Binodal curves of water (1) + ethanol (2) + 1-butanol (3). ●, partially miscible; Δ, miscible; □–□, tie line.

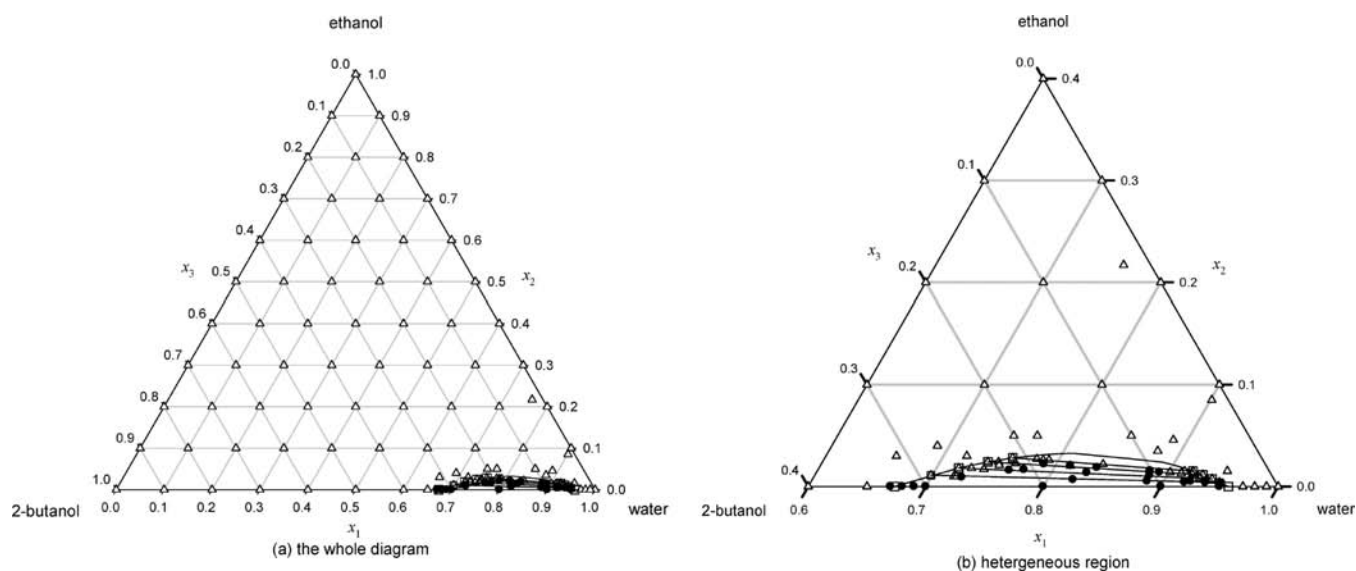


Figure 6. Binodal curves of water (1) + ethanol (2) + 2-butanol (3). ●, partially miscible; Δ, miscible; □–□, tie line.

Table 13. Comparison of Predicted Flash-Point Values, $t_{fp,pred}$, in the Estimated Tie Lines with Corresponding Experimental Data, $t_{fp,exp}$, for Water (1) + Ethanol (2) + 1-Butanol (3)

no. of tie line	prediction			measurement		
	span of tie line		$t_{fp,pred}$	span of tie line		$t_{fp,exp}$
	x_1	x_3	$^{\circ}\text{C}$	x_1	x_3	$^{\circ}\text{C}^a$
#1	0.9859	0.0141	44.40	0.983	0.017	44.2 ± 0.7
	0.5425	0.4575		0.540	0.460	
#2	0.9800	0.0166	43.76	0.959	0.037	43.5 ± 0.5
	0.5658	0.4213		0.547	0.439	
#3	0.9600	0.0240	41.66	0.960	0.024	41.3 ± 0.7
	0.6474	0.3029		0.616	0.331	
#4	0.9300	0.0373	39.52	0.940	0.030	39.3 ± 0.4
	0.7344	0.1938		0.705	0.217	
#5	0.8800	0.0653	37.49	0.883	0.063	37.4 ± 0.6
	0.8200	0.1095		0.778	0.140	

^a The uncertainty is represented by the value of double standard deviation.

Table 14. Comparison of Predicted Flash-Point Values, $t_{fp,pred}$, in the Estimated Tie Lines with Corresponding Experimental Data, $t_{fp,exp}$, for Water (1) + Ethanol (2) + 2-Butanol (3)

no. of tie line	prediction			measurement		
	span of tie line		$t_{fp,pred}$	span of tie line		$t_{fp,exp}$
	x_1	x_3	$^{\circ}\text{C}$	x_1	x_3	$^{\circ}\text{C}^a$
#1	0.9576	0.0424	30.18	0.95	0.05	29.7 ± 0.5
	0.6736	0.3264		0.67	0.03	
#2	0.9480	0.0480	30.12	0.923	0.072	30.1 ± 0.5
	0.6988	0.2901		0.726	0.265	
#3	0.9400	0.0525	30.08	0.936	0.060	29.9 ± 0.4
	0.7190	0.2629		0.763	0.221	
#4	0.9300	0.0585	30.03	0.892	0.094	30.0 ± 0.2
	0.7409	0.2350		0.790	0.188	

^a The uncertainty is represented by the value of double standard deviation.

Two Liquid Phase Region of Ternary Mixtures. By analogy with common liquid–liquid equilibrium ternary diagram clas-

sification, the water + ethanol + 1-butanol and water + ethanol + 2-butanol mixtures exhibit a single partially miscible binary mixture, and both are type-I mixtures (see Figures 5 and 6).

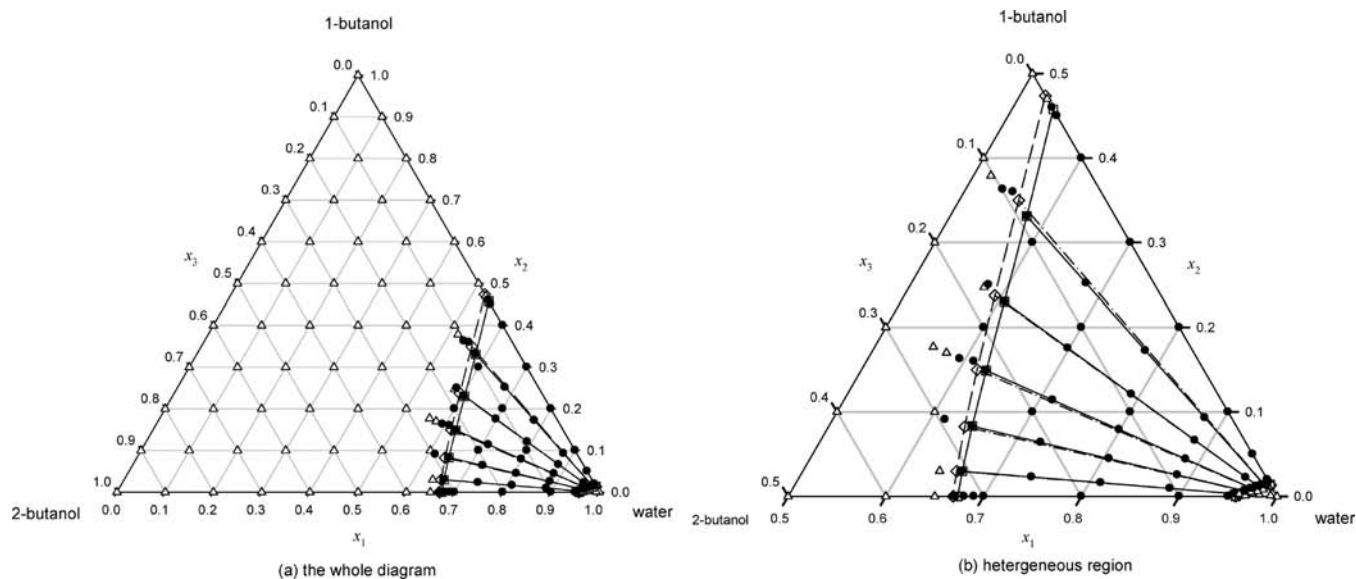


Figure 7. Binodal curves of water (1) + 1-butanol (2) + 2-butanol (3). ●, partially miscible; Δ, miscible; □-□, NRTL; ◇-◇, UNIQUAC.

Table 15. Comparison of Predicted Flash-Point Values, $t_{fp,pred}$, in the Estimated Tie Lines with Corresponding Experimental Data, $t_{fp,exp}$, for Water (1) + 1-Butanol (2) + 2-Butanol (3)

no. of tie line	activity coefficient model	prediction		measurement			
		span of tie line		$t_{fp,pred}$	span of tie line		$t_{fp,exp}$
		x_1	x_3	°C	x_1	x_3	°C ^a
#1	NRTL	0.9576	0.0424	30.18	0.95	0.05	29.7 ± 0.5
		0.6736	0.3264		0.67	0.03	
#1	UNIQUAC	0.9575	0.0425	30.14	0.6689	0.3311	
		0.6689	0.3311		0.663	0.307	
#2	NRTL	0.9600	0.0374	31.24	0.954	0.043	31.1 ± 0.6
		0.6633	0.3070		0.663	0.307	
#2	UNIQUAC	0.9610	0.0366	31.03	0.6576	0.3127	
		0.6576	0.3127		0.6395	0.2781	
#3	NRTL	0.9650	0.0288	32.74	0.965	0.029	32.6 ± 0.6
		0.6468	0.2700		0.615	0.294	
#3	UNIQUAC	0.9660	0.0283	32.54	0.6395	0.2781	
		0.6395	0.2781		0.6183	0.2317	
#4	NRTL	0.9700	0.0207	34.58	0.970	0.021	34.3 ± 0.6
		0.6282	0.2229		0.577	0.253	
#4	UNIQUAC	0.9710	0.0203	34.40	0.6183	0.2317	
		0.6183	0.2317		0.5928	0.1700	
#5	NRTL	0.9750	0.0132	36.90	0.975	0.013	36.8 ± 0.6
		0.6061	0.1637		0.58	0.17	
#5	UNIQUAC	0.9760	0.0128	36.74	0.5928	0.1700	
		0.5928	0.1700		0.5610	0.0892	
#6	NRTL	0.9800	0.0063	39.95	0.980	0.006	39.5 ± 0.6
		0.5785	0.0902		0.538	0.099	
#6	UNIQUAC	0.9810	0.0058	39.77	0.5610	0.0892	
		0.5610	0.0892		0.5425	0.000	
#7	NRTL	0.9859	0.0000	44.40	0.983	0.000	44.2 ± 0.7
		0.5425	0.0000		0.540	0.000	
#7	UNIQUAC	0.9869	0.0000	43.29	0.5263	0.0000	
		0.5263	0.0000				

^a The uncertainty is represented by the value of double standard deviation.

One notices that the NRTL-based predicted regions of the water + ethanol + 1-butanol mixture and of the water + ethanol + 2-butanol mixture are slightly less and larger than the measurements, respectively. However, they are both very close to the corresponding measurements (Figures 5 and 6 and Tables 13 and 14).

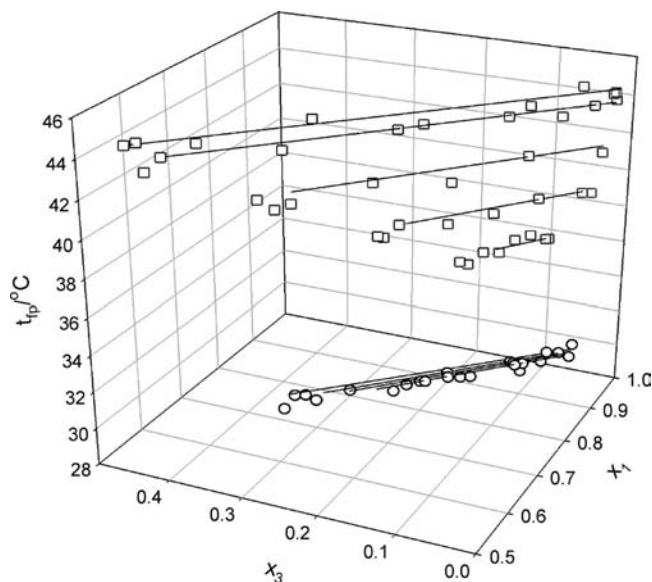


Figure 8. Comparison of predicted flash points in the tie lines with experimental data for water + ethanol + 1-butanol/2-butanol. □, water (1) + ethanol (2) + 1-butanol (3); ○, water (1) + ethanol (2) + 2-butanol (3); —, NRTL.

For water + 1-butanol + 2-butanol, a type-II mixture with two partially miscible binary mixtures, Figure 7 shows LLE predictions for several tie-lines with either NRTL or UNIQUAC parameter sets. Both equations predict well the tie line slopes, but not with the same extend length, which are both slightly less than the measurement (Figure 7 and Table 15).

Tie Line Flash Point within the Two Liquid Phase Region of Ternary Mixtures. According to the theory, flash point on a given tie line should be constant. However, only chance would enable us to guess beforehand the compositions in equilibrium on the same tie line and record then a constant flash point. Therefore, we use the model to predict tie line compositions and flash point and afterward measure flash point based on the predicted composition.

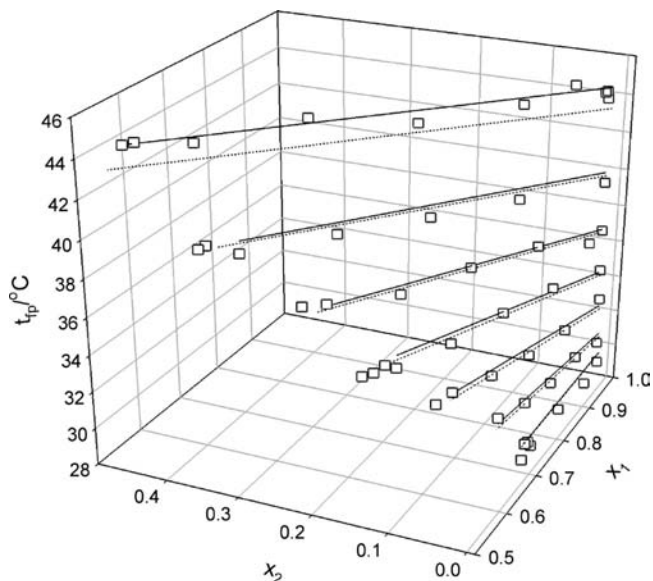


Figure 9. Comparison of predicted flash points in the tie lines with experimental data for water (1) + 1-butanol (2) + 2-butanol (3). □, experimental data; —, NRTL; ---, UNIQUAC.

Predictions and subsequent measures are displayed in Figures 8 and 9 and recorded in Tables 13 to 15 for water + ethanol + 1-butanol, water + ethanol + 2-butanol, and water + 1-butanol + 2-butanol mixtures.

The constant flash-point behavior is predicted by the model as expected. The measurements done after the predictions are almost collinear and constant on Figures 8 and 9, as confirmed by the moderate standard deviation in average flash point reported in Tables 13 to 15 for each tie line. The average measured flash point also agrees with the constant predicted flash-point value. The estimated tie lines have a slope similar to the measured ones, although the extend lengths are slightly different (Figures 5 to 7, Tables 13 to 15). A special observation is that the average flash points for the tie lines listed in Table 14 are almost identical for water + ethanol + 2-butanol, and this can be attributed to that the two liquid phase region of such

a mixture is very small resulting in each tie line being very close (Figures 6 and 8).

Flash Points for Ternary Mixtures over the Entire Composition Range. At first, Kosuge and Iwakabe's VLE parameters regressed on the ternary compositions of water + ethanol + 1-butanol and water + ethanol + 2-butanol³⁸ were used to predict the flash point. However, computation diverged. It was concluded in our previous studies that a model based upon the binary parameters of binary solutions may reasonably predict flash point for ternary miscible solutions,^{5,19} and the parameters listed in Table 2 were used. Results are displayed in Figures 10 to 12, and the average deviation between measurements and predicted flash points is listed in Table 11.

Figures 10 and 11 depict the measured and the NRTL-based predicted flash points for the water + ethanol + 1-butanol and water + ethanol + 2-butanol mixtures, and Figure 12 displays the measured and either NRTL-based or UNIQUAC-based prediction flash point for the water + 1-butanol + 2-butanol mixture.

As in the case of binary aqueous–organic solutions mentioned above, the agreement is excellent over the entire flammable range except near the water-rich mutual solubility region (Table 11). Again, this can be attributed to the failure of the constant lower flammable limit assumption in the mutual solubility water-rich region. Overall, the predictions are consistent with the experimental data, as confirmed by the low average deviation reported in Table 11.

In deriving the flash-point prediction model for ternary partially miscible aqueous–organic mixtures, 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.

In this study, the binary parameters regressed on binary solutions were used in the flash-point prediction of ternary solution, and the predictions gave good agreement with the measurements. However, it is not guaranteed that the use of binary parameters regressed on binary solutions is better than the analogue regressed on ternary solutions when

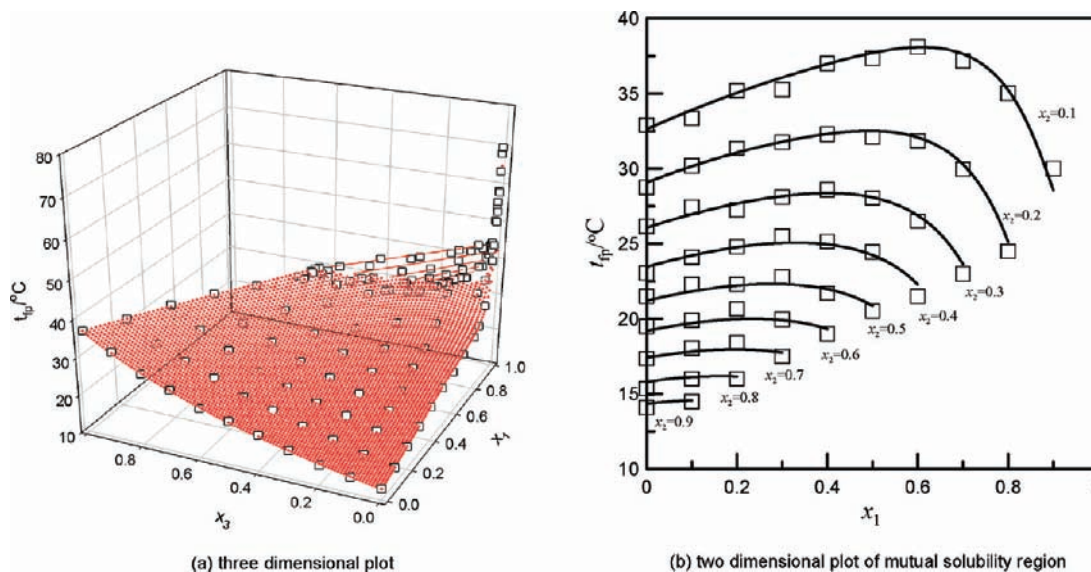


Figure 10. Comparison of predicted flash point and experimental data for water (1) + ethanol (2) + 1-butanol (3). □, experimental data; red ●, mutual solubility region; red —, tie lines.

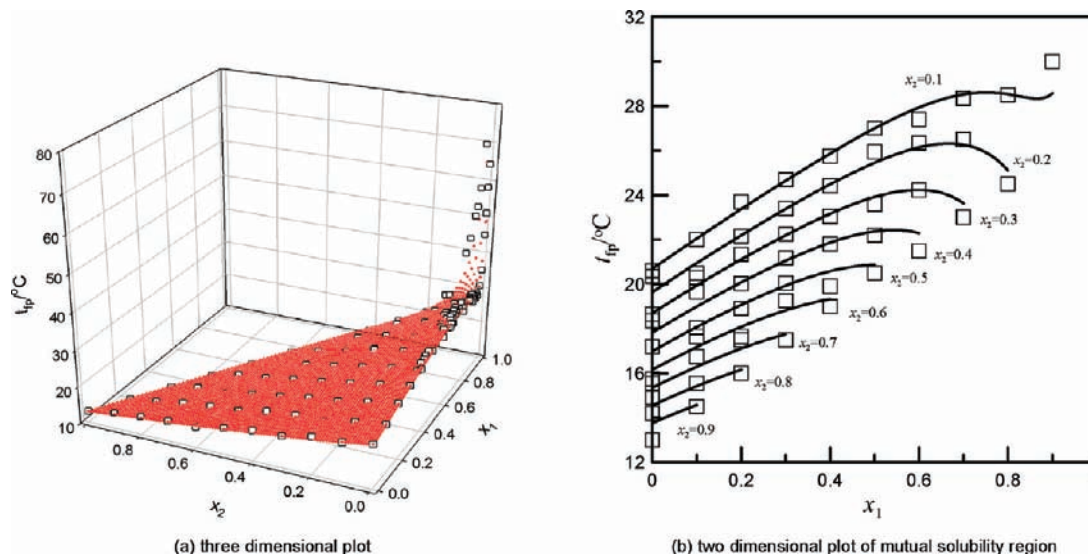


Figure 11. Comparison of predicted flash point and experimental data for water (1) + ethanol (2) + 2-butanol (3). \square , experimental data; red \bullet , mutual solubility region; red $-$, tie lines.

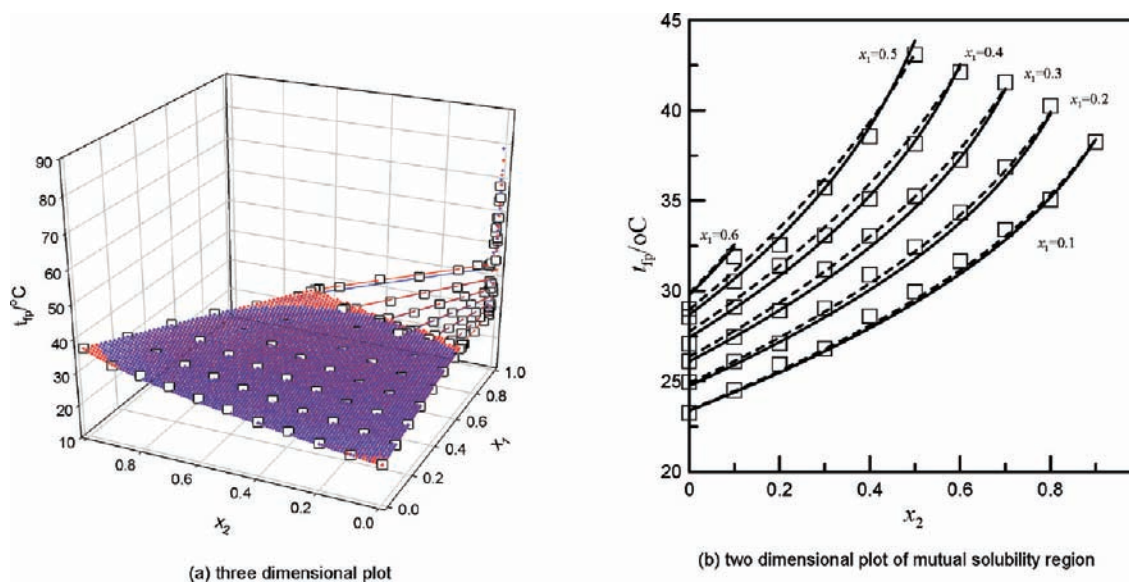


Figure 12. Comparison of predicted flash point and experimental data for water (1) + 1-butanol (2) + 2-butanol (3). (a) \square , experimental data; red \bullet , NRTL (mutual solubility region); red $-$, NRTL (tie lines); blue \bullet , UNIQUAC (mutual solubility region); blue $-$, UNIQUAC (tie lines). (b) \square , experimental data; $-$, NRTL; $- -$, UNIQUAC.

predicting flash point of ternary solutions. The predictive capability of the proposed model depends on the quality of the parameters.

Conclusion

The paper presents the first measurements of flash point for ternary partially miscible aqueous–organic mixtures. The flash-point model of Liaw et al. accounting for the nonideality of the liquid phase in such mixtures and considering the liquid–liquid equilibrium is able to predict satisfactorily the experimental data, using binary interaction parameters from the literature. In particular, it is able to predict the constant flash-point behavior on any liquid–liquid tie line within the two liquid phase region, which is a property of partially miscible mixtures. For the aqueous–organic mixtures here studied, a deviation between prediction and measurements

is observed, arising from the failure of the constant lower flammable limit assumption in the mutual solubility inert-rich region.

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