Flash Point for Ternary Partially Miscible Mixtures of Flammable Solvents

Horng-Jang Liaw,*,[†] Vincent Gerbaud,[‡] and Chao-Yang Chiu[†]

Department of Occupational Safety and Health, China Medical University, Taichung, Taiwan, R.O.C., and Université de Toulouse, LGC (Laboratoire de Génie Chimique), CNRS, INP, UPS, 5 allées Emile Monso, F-31029 Toulouse cedex 4, France

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 the development of a model for predicting the flash point of multiple partially miscible mixtures of flammable solvents. The validation of the model is done by comparing the predicted values with the experimental data for the ternary mixture with one partially miscible binary pair, methanol + toluene + 2,2,4-trimethylpentane, and the one with two analogous pairs, methanol + acetone + decane. Results reveal that the flash points are almost constant in each tie line that is inherently a vapor phase property. Liquid immiscibility could lead to mixture flash point lower than or equal to that of the lowest boiling pure compound, increasing the fire and explosion hazard. Use of activity coefficient models like UNIQUAC and NRTL is needed to describe the nonideal behavior of the liquid phase. Overall, the model describes the experimental data well when using the VLLE and the 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. 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 mixtures of flammable solvents.

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,[1] with a lower flash-point value indicating relatively greater fire and explosion hazard.[2] Recently, the importance of flash point was dramatically highlighted in Taiwan after a series of explosions of essential oils and 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.[3] The Shengli event subsequently resulted in the temporary storage of large quantities of waste organic solutions at various factory sites and industrial park precincts.[4,5] Thus, flash-point data knowledge for these mixtures has become increasingly important to ensure the safety of this voluminous storage. In addition, flammable liquids are the major hazardous material involved in chemical transportation, and hazardous materials responsible for road tanker accidents are flammable liquids mostly and more than 60 %.[6] A recent famous accident involved a gasoline tanker that crashed and burst into flames near the San Francisco−Oakland Bay Bridge in April 29, 2007, creating such an intense heat that a stretch of highway melted and collapsed. The requirements of transportation for these materials are primarily related to their flash-point values.[7]

In Taiwan, the GHS (Globally Harmonized System of Classification and Labeling of Chemicals) was 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 the least studied mixtures regarding their flash point, although they are used in liquid−liquid extraction processes[8,9] and heterogeneous distillation processes[10] encountered in many chemical plants. The flash-point value for a given substance is relative to its vapor pressure.[2] As the estimation of the vapor pressure for partially miscible mixtures is quite different from that for miscible analogues, we infer that flash-point behavior for the two mixture types will be quite different.

Crowl and Louvar[3] have suggested a method for the estimation of the flash point for 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,[5] and it is not applicable to solvent/salt systems, even in a similar composition range.[11] Introducing activity coefficient models to model the nonideal behavior of liquids, various models have been proposed recently for predicting the flash point of binary aqueous−organic and solvent/salt systems[5,11] with successful verification based on comparison with the experimental data. Previously, Affens and McLaren[12] have developed a predictive model to determine the flash points of binary hydrocarbon mixtures based on Raoult's law. White et al.[13] have reduced this model to a simpler equation by ignoring any dependence of the lower flammable limit on temperature. A model for predicting the flash point of multicomponent mixtures of only flammable compounds was also proposed and verified using experimental data for ternary

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* Corresponding author. Department of Occupational Safety and Health, China Medical University, 91 Hsueh-Shih Rd., Taichung, Taiwan. Tel.: 886-4-22053366, ext. 6209. Fax: 886-4-22030418. E-mail: hjliaw@mail.cmu.edu.tw.
[†] China Medical University.
[‡] Université de Toulouse.

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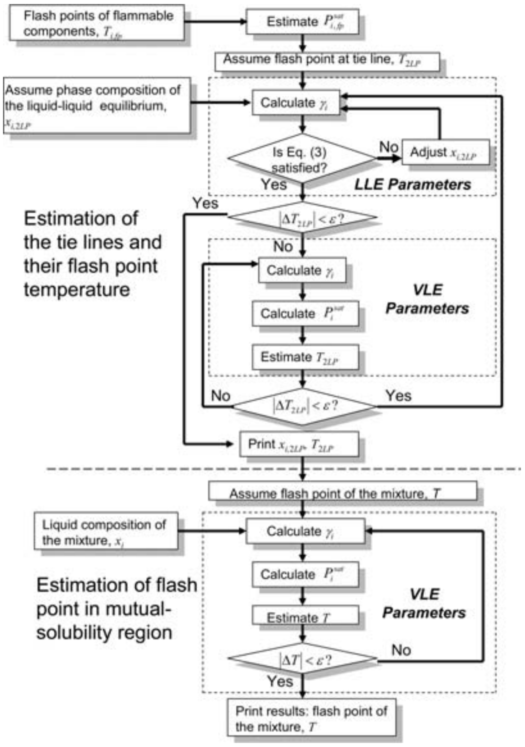


Figure 1. Procedure for evaluation of flash point for ternary partially miscible mixtures of flammable solvents.

solutions.[14] This model can be simplified for binary solutions, as proposed previously,[4] with prediction of flash points verified for both ideal and nonideal mixtures.[4,15,16] Garland and Malcolm[17] developed a statistical model to predict the flash point of a single organic acid−water solution: acetic acid + propionic acid + butyric acid + water. However, it deviated significantly from the experimental measurements for multiple organic−water solutions.[18] Overall, application of the former models in refs 3, 12, 13, and 17 is limited to solutions that can be assumed as ideal within the composition range considered. On the other hand, models taking into account nonideality of the solution through liquid-phase activity coefficients have a wider application range and have been used to predict efficiently the flash point of these miscible mixtures.[4,5,11,14,18]

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.[15,16,19] This is similar to minimum-boiling and maximum-boiling azeotropic behavior in vapor−liquid equilibrium. Besides, for given pressure and temperature conditions at which vapor−liquid equilibrium occurs, stronger nonideality within a mixture may often results in the partial miscibility of the liquid phase, eventually coupled with the occurrence of a so-called heteroazeotrope. We suspect that similar behaviors happen for flash point. The models for predicting the flash points of binary partially miscible mixtures of flammable solvents and the aqueous−organic system were proposed by Liaw et al.[20,21] In this manuscript, we extend its use for multicomponent partially miscible mixtures of flammable solvents and validate it using the ternary partially miscible solutions: methanol + toluene + 2,2,4-trimethylpentane and methanol + acetone + decane.

Upon the basis of the definition of flash point,[2] it is necessary to estimate the vapor-phase composition of flammable substances from a vapor−liquid equilibrium equation to predict their flash point. Furthermore, it is acknowledged that partial miscibility occurs because of significant interaction within the nonideal 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[22] is not applicable for evaluating the liquid-phase activity coefficients for mixtures that exhibit a miscibility gap.[23] On the other hand, the NRTL[24] and UNIQUAC thermodynamic models[25] are applicable to both vapor−liquid and liquid−liquid equilibria.[23]

Experimental Protocol

An HFP 362-Tag Flash Point Analyzer (Walter Herzog GmbH, Germany) was used to measure the flash points for two ternary mixtures (methanol + toluene + 2,2,4-trimethylpentane and methanol + acetone + decane) at different compositions. 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[26] using the selected 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 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 min before the flash point test. Methanol, acetone, and 2,2,4-trimethylpentane were HPLC/Spectro-grade reagents (Tedia Co. Inc., USA). Toluene was purchased from J.T. Baker (USA). Decane was obtained from Alfa Aesar (Lancaster, England).

Mathematical Formulation

Flash-Point Equations for Miscible and Partially Miscible Mixtures. Within the mutual-solubility region of a multiple partially miscible mixture, 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 mixture. Thus, the flash point in such a region can be evaluated by the method for a multicomponent miscible analogue[14]

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

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

The vapor pressure of the pure flammable component, i, at its flash point, $P_{i,\text{fp}}^{\text{sat}}$, can be estimated by substituting $T_{i,\text{fp}}$, the flash point of such a flammable component, into the Antoine equation (eq 2). Liquid-phase activity coefficients γ_i enable us to tackle the nonideal 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 conditions.[27]

Table 1. LLE Parameters of the NRTL and UNIQUAC Equations for the Binary Solutions of Methanol, 2,2,4-Trimethylpentane, and Toluene and Methanol, Acetone, and Decane

				ij		
system	T_C (K)	α_{12}	parameters	12	21	ref
			NRTL equation [a]			
methanol (1) + 2,2,4-trimethyl pentane (2)	316.84	0.2	a_{ij}/J·mol^{-1}	$4.93912 \cdot 10^3$	$1.22776 \cdot 10^3$	8
			b_{ij}/J·mol^{-1}·K^{-1}	$5.20020 \cdot 10$	$5.22268 \cdot 10$	
			c_{ij}/J·mol^{-1}·K^{-2}	−4.88841	1.47937	
			d_{ij}/J·mol^{-1}·K^{-3}	$8.89400 \cdot 10^{-2}$	$-4.74041 \cdot 10^{-2}$	
			UNIQUAC equation [b]			
methanol (1) + 2,2,4-trimethyl pentane (2)	–	–	$u_{ij} - u_{jj}$/J·mol^{-1}	−254.0509	6136.9791	30
methanol (1) + toluene (2)	–	–	$u_{ij} - u_{jj}$/J·mol^{-1}	674.8308	−210.5354	30
toluene (1) + 2,2,4-trimethyl pentane (2)	–	–	$u_{ij} - u_{jj}$/J·mol^{-1}	−261.9991	−853.9309	30
methanol (1) + decane (2)	–	–	a_{ij}/J·mol^{-1}	68636.8506	12238.6902	31[c]
			b_{ij}/J·mol^{-1}·K^{-1}	−61.3074	−36.0744	
acetone (1) + decane (2)	–	–	a_{ij}/J·mol^{-1}	17700.5393	2612.2421	31[c]
			b_{ij}/J·mol^{-1}·K^{-1}	−9.1787	−9.6609	
methanol (1) + acetone (2)	–	–	a_{ij}/J·mol^{-1}	37209.8724	−57639.7315	31[c]
			b_{ij}/J·mol^{-1}·K^{-1}	−136.5408	212.5474	

[a] $g_{ij} - g_{jj} = a_{ij} + b_{ij}(T_C - T) + c_{ij}(T_C - T)^2 + d_{ij}(T_C - T)^3$. [b] $u_{ij} - u_{jj} = a_{ij} + b_{ij}T$. [c] Modified parameters of Tourino et al. (2003).

Within the partially miscible region of a multiple partially miscible mixture, two liquid phases are in equilibrium with compositions defining a so-called tie line. Since 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,[27,28] the flash point in the tie line should keep constant whatever the liquid composition on the liquid−liquid equilibrium tie line. The constant flash point in the two liquid phase region for a binary partially miscible mixture is due to the two liquid phase region which is the sole tie line for such a mixture.

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

$$(x_i\gamma_i)^{\alpha} = (x_i\gamma_i)^{\beta} \qquad i = 1, ..., N \tag{3}$$

where α and β designate the two coexisting liquid phases and the reference fugacity is the same for the two liquid phases. The activity coefficients γ_i in eqs 1 and 3 should be estimated using thermodynamic activity coefficient models adequate for partially miscible mixtures, such as the NRTL[24] or UNIQUAC equations;[25] both models are employed in this study. The flash point within each tie line can be calculated by substituting the estimated value of equilibrium composition into eqs 1 and 2. Since the values of equilibrium composition estimated by eq 3 are dependent on the value of flash point, the span and flash point of the tie lines have to be derived from the problem solution of eqs 1 to 3 by the iterative procedure.

The flash-point prediction model developed for a multiple partially miscible mixture of flammable solvents is described using eqs 1 to 3 and any suitable thermodynamic model for estimating liquid-phase activity coefficient.

For a ternary liquid solution, eqs 1 and 3 reduce to

$$1 = \sum \frac{x_i\gamma_i P_i^{\mathrm{sat}}}{P_{i,\mathrm{fp}}^{\mathrm{sat}}} = \frac{x_1\gamma_1 P_1^{\mathrm{sat}}}{P_{1,\mathrm{fp}}^{\mathrm{sat}}} + \frac{x_2\gamma_2 P_2^{\mathrm{sat}}}{P_{2,\mathrm{fp}}^{\mathrm{sat}}} + \frac{x_3\gamma_3 P_3^{\mathrm{sat}}}{P_{3,\mathrm{fp}}^{\mathrm{sat}}} \tag{4}$$

and

$$(x_i\gamma_i)^{\alpha} = (x_i\gamma_i)^{\beta} \qquad i = 1, 2, 3 \tag{5}$$

The iterative procedure for evaluating the flash point for ternary partially miscible mixtures is depicted in Figure 1. The tie line (two liquid phases region) and the flash point in this tie line are first estimated by eqs 2, 4, and 5. Then, the flash point in the mutual solubility region is calculated using eqs 2 and 4. The iterative procedure is analogous to that used for calculating the boiling and dew points of mixtures.[29]

Use of Binary Parameters. In our previous study,[21] the estimated span of the two liquid phases was not based on the estimated flash point within the two liquid phases. Indeed, the span of the two liquid phases in equilibrium was estimated by eqs 1 to 3 in conjunction with the so-called LLE parameters regressed on LLE data. On the other hand, the flash point within the two liquid phases was calculated by using eqs 1 and 2 together with VLE parameters. The temperature used to calculate the span of the two liquid phases was estimated by use of LLE parameters, and its value is different from that of the constant flash point within the two liquid phases, which was estimated by using the VLE parameters.

In this study, we change the estimation process for the span of the two liquid phases. LLE parameters are used in eq 3 to estimate the tie line equilibrium liquid compositions. VLE parameters are used in eqs 1 and 2 to compute the vapor pressure and calculate the flash point. Depending on which of the tie line compositions you use to estimate the flash point in eq 1, you obtain different flash point temperatures and two liquid phase region span results. This is the so-called VLLE model in this study.

Parameters Used in This Manuscript

The flash-point model for ternary partially miscible mixtures of flammable solvents was used for methanol + toluene + 2,2,4-trimethylpentane and methanol + acetone + decane mixtures and validated against the corresponding experimental data. Liquid-phase activity coefficients were estimated by using the NRTL[24] and UNIQUAC equations[25] for the former mixture and by using the UNIQUAC equation[25] for the latter one. Binary interaction parameters obtained either from the LLE data or VLE data were both used in this study, with parameters adopted from the literature (Tables 1 and 2).[8,30−36] The parameters for the relative van der Waals volume (r) and the surface area (q) for the pure components needed for the UNIQUAC equation (also obtained from the literature[23,30]) are listed in Table 3, along with the Antoine coefficients sourced from the literature.[32−34]

The flash points for the pure substances used in this study were measured using the Flash Point Analyzer and compared

Table 2. VLE Parameters of the NRTL and UNIQUAC Equations for the Binary Solutions of Methanol, Toluene, and 2,2,4-Trimethylpentane and Methanol, Acetone, and Decane

	NRTL			UNIQUAC		
mixtures	$\frac{g_{12} - g_{22}}{\mathrm{J \cdot mol^{-1}}}$	$\frac{g_{21} - g_{11}}{\mathrm{J \cdot mol^{-1}}}$	α_{12}	$\frac{u_{12} - u_{22}}{\mathrm{J \cdot mol^{-1}}}$	$\frac{u_{21} - u_{11}}{\mathrm{J \cdot mol^{-1}}}$	ref
methanol (1) + 2,2,4-trimethylpentane (2)	6054.9138	5801.2653	0.4313	−249.7669	6599.7950	32
methanol (1) + toluene (2)	3798.4997	4289.1160	0.4315	−248.0576	4903.5206	32
2,2,4-trimethylpentane (1) + toluene (2)	−1198.5675	2602.2251	0.3029	649.1393	−392.9459	33
methanol (1) + decane (2)	–	–	–	−486.5481	7764.4371	34
acetone (1) + decane (2)	–	–	–	−366.5365	2080.1390	35
methanol (1) + acetone (2)	–	–	–	−310.3034	1639.9448	36

Table 3. Antoine Coefficients for Solution Components and Relative van der Waals Volumes (*r*) and Surface Areas (*q*) for the Pure Components for the UNIQUAC Model

	Antoine coefficients[a]				relative van der Waals volumes (*r*) and surface areas (*q*)		
material	*A*	*B*	*C*	ref	*r*	*q*	ref
methanol	7.09490	1521.230	233.970	32	1.4311	1.432	30
toluene	6.07567	1342.310	219.187	33	3.9228	2.968	30
2,2,4-trimethyl pentane	5.92784	1252.590	220.119	32	5.8463	5.008	30
acetone	6.24194	1210.595	229.664	34	2.5735	2.336	23
decane	6.56480	1843.120	230.220	34	7.1974	6.016	23

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

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

component	$t_{\mathrm{fp,exp}}$/°C[a]	$t_{\mathrm{fp,lit}}$/°C
methanol	10.0 ± 0.8	12[37,38] 11[39] 10[40]
toluene	7.2 ± 1.0	4[37,40−42] 7[43] 7.2[44]
2,2,4-trimethylpentane	−8.1 ± 1.3	−7[b,40] −8[45] −12[37,38,43]
acetone	−18.6 ± 0.9	−18[37,38]
decane	51.8 ± 1.0	44[38] 50.9 ± 2.3[26] 52.8 ± 2.3[46]

[a] The uncertainty is in double standard deviation. [b] Provided by Tedia.

with their literature-derived analogues (Table 4).[26,37−46] There are between-source differences in the flash-point data for methanol, toluene, 2,2,4-trimethylpentane, and decane. Our measurement for methanol is identical to the value reported by Oxford University.[40] The experimental data for toluene are identical to Temarry's value[44] and close to that of J. T. Baker.[43] The value for 2,2,4-trimethylpentane is almost identical to that reported by Chevron Phillips[45] and close to that provided by the supplier, Tedia (USA), and the value reported by Oxford University,[40] although it is different from those adopted from Merck (1996),[37] SFPE (1995),[38] and J.T. Baker.[43] The experimental data for acetone are close to the Merck (1996)[37] and SFPE (1995) values.[38] The deviations between our measurement and the published flash points of ASTM (1999; 2000)[26,46] for decane are slight and acceptable.

Binary Mixtures

Experimental flash-point data for the ternary mixtures of methanol + toluene + 2,2,4-trimethylpentane and methanol + acetone + decane covering their entire composition range are listed in Tables 5 and 6.

Figures 2a, 2b, 2c, 3a, 3b, and 3c compare measured and predicted flash points, based upon literature binary parameters as listed in Tables 1 and 2, for toluene + methanol (Figure 2a), toluene + 2,2,4-trimethylpentane (Figure 2b), and methanol + 2,2,4-trimethylpentane (Figure 2c) and methanol + acetone (Figure 3a), methanol + decane (Figure 3b), and acetone + decane (Figure 3c) mixtures, respectively.

Toluene + methanol, toluene + 2,2,4-trimethylpentane, and methanol + acetone are miscible binary pairs at their flash-point temperature. However, methanol + 2,2,4-trimethylpentane, methanol + decane, and acetone + decane are partially miscible ones.

Toluene + Methanol and Toluene + 2,2,4-Trimethylpentane Miscible Binary Mixtures. Predictions are in good agreement with the experimental data over the entire composition range, when the NRTL or UNIQUAC equation with Gmehling et al.'s VLE parameters[32,33] is used for the miscible binary mixtures toluene + methanol and toluene + 2,2,4-trimethylpentane (Figures 2a and 2b and Table 7). Using the UNIQUAC equation with Gramajo de Doz et al.'s LLE parameters,[30] the experimental minimum flash-point behavior of toluene + methanol is not predicted, whereas the model predicts a maximum flash-point behavior for toluene + 2,2,4-trimethylpentane that is not observed experimentally (Figures 2a, 2b). Three causes can be examined. One reason is that Gramajo de Doz et al.'s parameters were regressed on LLE data. It is common knowledge in thermodynamics that the use of LLE parameters for predicting VLE is usually not satisfactory,[47] and the flash-point definition of being "sufficient vapor to become a combustible mixture" is related to VLE. Another reason is that Gramajo de Doz et al.'s LLE parameters were not temperature dependent and regressed on data at 30 °C (303.15 K), a temperature far from the flash-point range of the two studied solutions, from (−10 to +10) °C. In fact, the substantial deviation between the flash-point prediction and measurement may hint that the LLE parameters of the two mixtures are strongly temperature dependent. A third reason may be that Gramajo de Doz et al.'s parameters are not appropriate. The parameter value estimation process can lead to multiple solutions, and the regression process rarely guarantees to get the global solution of the objective function.[48] Therefore, Gramajo de Doz et al.'s parameters are merely local optimal values.

Methanol + Acetone Miscible Binary Mixture. Figure 3a compares the measured and predicted flash points for the miscible mixture methanol + acetone. As before, predictions are in good agreement with the experimental data over the entire

Table 5. Measured Flash Point for Methanol (1) + Toluene (2) + 2,2,4-Trimethylpentane (3)

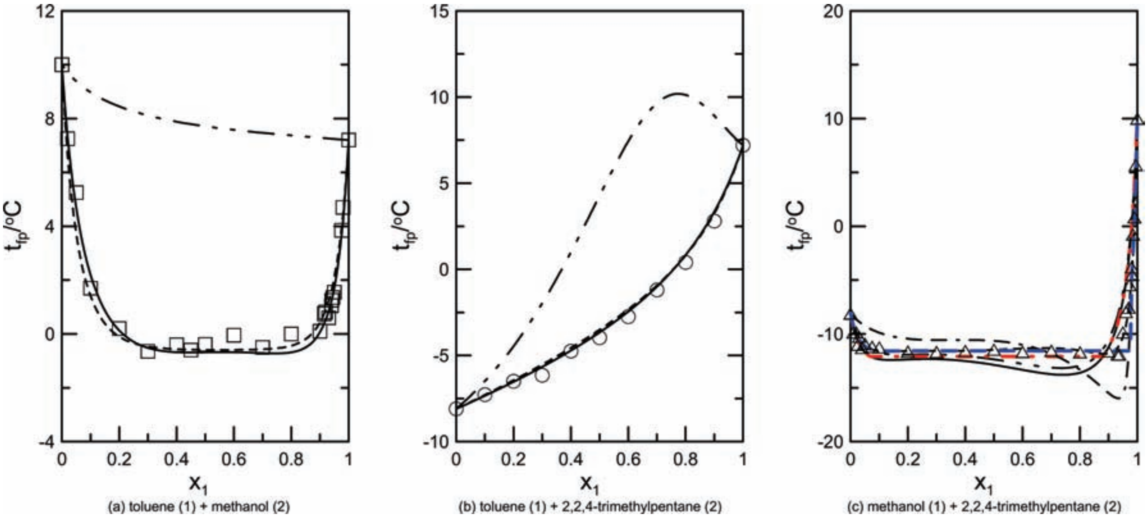
x_1	x_2	t_{fp}/°C	x_1	x_2	t_{fp}/°C
0.000	0.000	−8.1	0.400	0.000	−11.6
0.000	0.100	−7.3	0.400	0.100	−11.0
0.000	0.200	−6.5	0.400	0.200	−9.9
0.000	0.300	−6.2	0.400	0.300	−8.9
0.000	0.400	−4.8	0.400	0.400	−7.4
0.000	0.500	−4.0	0.400	0.450	−5.2
0.000	0.600	−2.8	0.400	0.500	−4.6
0.000	0.700	−1.2	0.400	0.575	−1.8
0.000	0.800	0.4	0.400	0.600	−0.1
0.000	0.900	2.8	0.409	0.544	−1.6
0.000	1.000	7.2	0.425	0.175	−9.8
0.010	0.000	−9.9	0.450	0.425	−5.2
0.010	0.290	−7.4	0.500	0.00	−11.5
0.020	0.000	−9.9	0.500	0.078	−10.6
0.020	0.180	−8.3	0.500	0.100	−10.5
0.020	0.980	4.7	0.500	0.200	−9.8
0.025	0.000	−11.0	0.500	0.300	−8.3
0.025	0.975	3.9	0.500	0.400	−5.1
0.030	0.000	−10.3	0.500	0.403	−5.0
0.040	0.000	−11.3	0.500	0.413	−4.9
0.050	0.250	−9.2	0.500	0.425	−5.0
0.050	0.350	−8.1	0.500	0.450	−4.1
0.050	0.800	−2.9	0.500	0.500	−0.4
0.050	0.900	0.3	0.525	0.325	−6.6
0.050	0.950	1.6	0.550	0.350	−5.8
0.055	0.945	1.4	0.550	0.400	−3.9
0.059	0.941	1.3	0.550	0.450	−0.6
0.060	0.940	1.1	0.600	0.000	−11.7
0.070	0.930	0.6	0.600	0.100	−10.7
0.075	0.000	−11.2	0.600	0.200	−9.2
0.080	0.920	0.8	0.600	0.220	−8.3
0.085	0.915	0.8	0.600	0.250	−8.1
0.092	0.272	−9.9	0.600	0.275	−6.4
0.100	0.000	−11.3	0.600	0.300	−6.1
0.100	0.100	−10.2	0.600	0.400	−0.4
0.100	0.200	−9.3	0.650	0.150	−9.2
0.100	0.300	−8.9	0.650	0.200	−8.7
0.100	0.400	−8.4	0.700	0.000	−11.6
0.100	0.500	−7.5	0.700	0.053	−10.7
0.100	0.600	−6.3	0.700	0.100	−9.8
0.100	0.700	−4.9	0.700	0.150	−9.3
0.100	0.800	−2.9	0.700	0.160	−8.9
0.100	0.900	0.1	0.700	0.180	−8.3
0.150	0.250	−9.7	0.700	0.200	−7.7
0.150	0.440	−7.8	0.730	0.235	−3.8
0.150	0.500	−6.7	0.790	0.200	−1.1
0.150	0.650	−5.1	0.800	0.000	−11.7
0.181	0.545	−6.3	0.800	0.100	−10.3
0.200	0.000	−11.6	0.800	0.125	−8.3
0.200	0.100	−11.2	0.800	0.200	0.2
0.200	0.200	−10.7	0.850	0.034	−10.9
0.200	0.300	−9.3	0.850	0.125	−4.45
0.200	0.400	−8.7	0.880	0.100	−4.0
0.200	0.500	−7.8	0.890	0.100	−1.3
0.200	0.600	−5.4	0.900	0.000	−11.6
0.200	0.700	−3.4	0.900	0.050	−8.0
0.200	0.800	0.0	0.900	0.100	1.7
0.225	0.511	−6.3	0.931	0.000	−11.9
0.250	0.700	−2.6	0.938	0.000	−11.9
0.274	0.594	−3.6	0.940	0.050	−0.7
0.275	0.376	−8.1	0.950	0.000	−9.9
0.300	0.000	−11.7	0.950	0.050	5.3
0.300	0.100	−11.3	0.960	0.000	−8.0
0.300	0.200	−9.9	0.964	0.026	−1.0
0.300	0.300	−8.5	0.970	0.000	−7.6
0.300	0.400	−7.3	0.973	0.000	−5.5
0.300	0.500	−6.1	0.980	0.000	−3.8
0.300	0.530	−5.8	0.980	0.020	7.3
0.300	0.600	−4.3	0.982	0.000	−4.5
0.300	0.700	−0.5	0.985	0.000	−0.8
0.325	0.200	−9.6	0.990	0.000	0.8
0.325	0.350	−7.7	0.995	0.000	5.7
0.325	0.450	−6.8	1.000	0.000	10.0
0.367	0.575	−2.3			

Table 6. Measured Flash Point for Methanol (1) + Decane (2) + Acetone (3)

x_1	x_2	t_{fp}/°C	x_1	x_2	t_{fp}/°C
0.000	0.000	−18.6	0.200	0.100	−15.4
0.000	0.005	−18.5	0.200	0.620	−10.4
0.000	0.010	−19.2	0.200	0.720	−3.8
0.000	0.020	−19.9	0.200	0.750	0.2
0.000	0.030	−18.6	0.200	0.770	2.0
0.000	0.050	−18.6	0.200	0.800	10.9
0.000	0.070	−18.4	0.216	0.436	−12.7
0.000	0.080	−18.6	0.230	0.600	−8.8
0.000	0.100	−18.3	0.280	0.500	−10.1
0.000	0.200	−18.5	0.300	0.000	−15.2
0.000	0.300	−18.2	0.300	0.260	−12.8
0.000	0.400	−17.9	0.300	0.480	−10.0
0.000	0.500	−18.4	0.300	0.500	−9.2
0.000	0.600	−17.8	0.300	0.610	−3.5
0.000	0.700	−18.0	0.300	0.620	−1.0
0.000	0.730	−17.6	0.300	0.660	1.7
0.000	0.750	−17.5	0.300	0.700	10.2
0.000	0.780	−17.5	0.360	0.100	−13.5
0.000	0.800	−17.5	0.370	0.370	−9.7
0.000	0.850	−14.8	0.400	0.000	−14.6
0.000	0.870	−11.9	0.400	0.010	−13.9
0.000	0.880	−11.6	0.400	0.038	−13.2
0.000	0.900	−6.6	0.400	0.300	−10.5
0.000	0.930	−0.7	0.400	0.490	−3.5
0.000	0.950	11.9	0.400	0.560	2.5
0.000	0.970	21.3	0.400	0.60	10.4
0.000	0.980	27.7	0.427	0.459	−4.0
0.000	0.990	41.9	0.500	0.000	−13.4
0.000	1.000	51.8	0.5	0.010	−11.6
0.010	0.990	24.3	0.5	0.180	−9.5
0.018	0.816	−13.8	0.5	0.380	−4.0
0.020	0.980	18.5	0.5	0.500	10.4
0.025	0.95	8.5	0.53	0.100	−9.8
0.030	0.97	15.0	0.6	0.000	−11.1
0.0327	0.8336	−12.4	0.6	0.010	−9.9
0.040	0.960	12.5	0.600	0.0330	−11.0
0.044	0.859	−9.5	0.600	0.340	2.5
0.050	0.950	11.0	0.600	0.400	10.1
0.060	0.800	−11.4	0.660	0.188	−4.0
0.070	0.600	−15.2	0.700	0.000	−9.5
0.080	0.800	−9.5	0.700	0.010	−7.8
0.100	0.000	−16.9	0.700	0.120	−5.5
0.100	0.020	−16.8	0.700	0.220	2.5
0.100	0.470	−15.1	0.700	0.230	2.5
0.100	0.700	−12.5	0.700	0.300	10.1
0.100	0.720	−12.5	0.800	0.000	−5.9
0.100	0.820	−5.8	0.800	0.010	−4.4
0.100	0.870	1.5	0.800	0.023	−4.5
0.100	0.900	11.5	0.800	0.110	2.0
0.109	0.428	−16.0	0.800	0.200	10.3
0.110	0.870	5.5	0.900	0.000	−0.2
0.140	0.600	−13.2	0.900	0.010	0.7
0.150	0.600	−13.5	0.900	0.020	1.7
0.154	0.235	−15.8	0.900	0.100	9.6
0.170	0.700	−7.3	0.950	0.050	9.3
0.180	0.100	−15.5	0.980	0.020	10.0
0.180	0.800	4.5	0.985	0.015	9.7
0.200	0.000	−16.1	0.990	0.010	9.0
0.200	0.020	−15.5	1.000	0.000	10.0
0.200	0.041	−16.0			

composition range when based on VLE parameters adopted from Iliuta and Thyrion.[36] However, predictions deviate from measurements when based on either LLE parameters set, whether adapted from Tourino et al.[31] or regressed by us (Figure 3a and Table 7).

Methanol + 2,2,4-Trimethylpentane Partially Miscible Binary Mixture. Figure 2c indicates that the methanol + 2,2,4-trimethylpentane partially miscible mixture exhibits a minimum flash-point behavior below the pure-substance flash points, with such a behavior being also observed in other binary partially miscible mixtures of flammable solvents[20] and mixtures of the

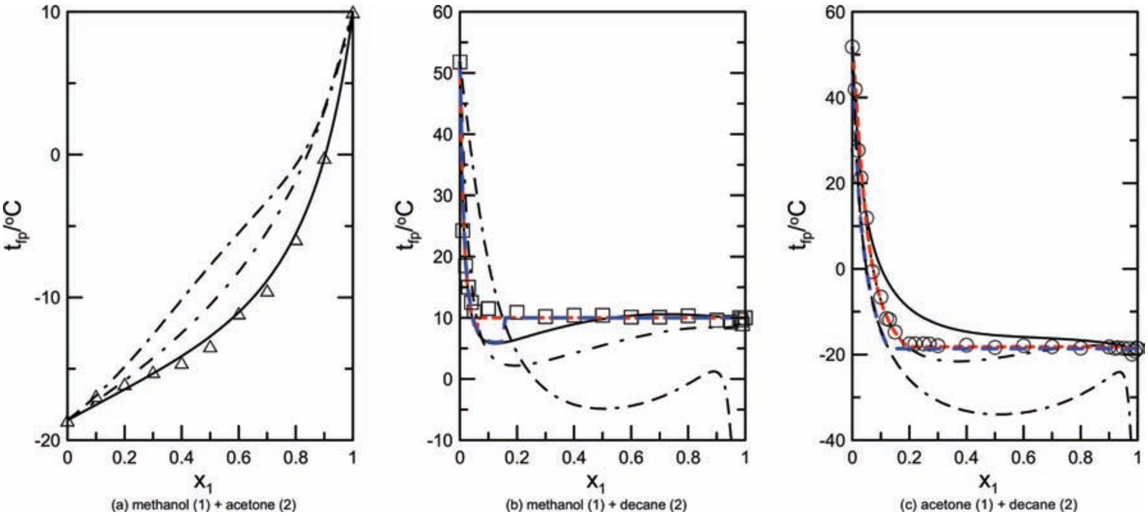


(a) toluene (1) + methanol (2)

(b) toluene (1) + 2,2,4-trimethylpentane (2)

(c) methanol (1) + 2,2,4-trimethylpentane (2)

Figure 2. Comparison of predicted flash point and experimental data for binary solutions of methanol, toluene, and 2,2,4-trimethylpentane. red — - —, prediction by the UNIQUAC equation with VLE and LLE parameters; —, prediction by the UNIQUAC equation with VLE parameters; — - -, prediction by the UNIQUAC equation with LLE parameters; blue — — —, prediction by NRTL equation with VLE and LLE parameters; - - - - -, prediction by the NRTL equation with VLE parameters; — —- —, prediction by the NRTL equation with LLE parameters.



(a) methanol (1) + acetone (2)

(b) methanol (1) + decane (2)

(c) acetone (1) + decane (2)

Figure 3. Comparison of predicted flash point and experimental data for binary solutions of methanol, acetone, and decane. —, prediction by the VLE parameters; — - —, prediction by our regressed LLE parameters; — — - —, prediction by modified LLE parameters of Tourino et al.; red - - - - -, prediction by VLE parameters and our regressed LLE ones; blue — — —, prediction by VLE parameters and the modified LLE ones of Tourino et al.

aqueous−organic system.[21] The measured flash-point values are almost constant in the two liquid phases region, around (−11.6 ± 0.4) °C, where the methanol composition ranged between 0.025 and 0.938 (Table 5, Figure 2c). Constant flash-point behavior in the two liquid phases region arises because of the particular behavior that any composition on a vapor−liquid−liquid equilibrium tie line is in equilibrium with a single vapor composition located on the vapor line.[27,28] The flash point being a feature of the vapor, it is constant when the composition and temperature of the vapor are also constant.

Table 7. Mean Deviation between Calculated and Experimental Flash Points, ΔT_{fp}[a], Methanol + Toluene + 2,2,4-Trimethylpentane, and Those of Methanol + Acetone + Decane, Comparing Models

	NRTL			UNIQUAC		
mixture	LLE	VLE	VLLE	LLE	VLE	VLLE
				ΔT_{fp}/K		
toluene + methanol	–	0.34	–	5.85	0.30	–
toluene + 2,2,4-trimethylpentane	–	0.26	–	5.26	0.22	–
methanol + 2,2,4-trimethylpentane	2.02	0.50	0.71	1.82	1.74	1.44
methanol + toluene + 2,2,4-trimethylpentane	–	–	0.47	–	–	0.62
methanol + decane	–	–	–	4.16,[b] 18.98[c]	1.39	0.82,[b] 1.01[c]
acetone + decane	–	–	–	1.44,[b] 10.37[c]	3.30	1.05,[b] 2.96[c]
methanol + acetone	–	–	–	1.90,[b] 3.12[c]	0.33	–
methanol + acetone + decane	–	–	–	–	–	0.82,[b] 2.02[c]

[a] Deviation of flash point: $\Delta T_{fp} = \sum_N |T_{fp,exp.} - T_{fp,pred.}|/N$. [b] Based on our regressed LLE parameters. [c] Based on LLE parameters adapted from Tourino et al. (2003).

Table 8. Comparison of Estimated Values for Equilibrium Composition between Liquid Phases, $x_{1,2LP}$, and Its Flash Point, t_{2LP}, with Corresponding Experimental Data for Methanol (1) + 2,2,4-Trimethylpentane (2), Methanol (1) + Decane (2), and Acetone (1) + Decane (2)

	estimated value								
	NRTL		UNIQUAC		experimental data		experimental mutual solubility		
system	$x_{1,2LP}$	t_{2LP}/°C	$x_{1,2LP}$	t_{2LP}/°C	$x_{1,2LP}$	t_{2LP}/°C	t/°C	$x_{1,2LP}$	lit.
methanol (1) + 2,2,4-trimethylpentane (2)	0.2060[a]	−11.58[a]	0.0687[a]	−12.08[a]	0.025	−11.6	–	–	–
	0.9761[a]		0.8795[a]		0.938				
	0.1700[b]	−8.26[b]	0.0687[b]	−12.12[b]					
	0.9670[b]		0.8796[b]						
methanol (1) + decane (2)	–	–	0.0593[c,d]	7.81[c,d]	0.050	10.3	5	0.060	50
			0.9842[c,d]		0.985			0.984	
			0.0641[b,d]	10.00[b,d]					
			0.9838[b,d]						
			0.1435[c,e]	6.07[c,e]					
			1.000[c,e]						
			0.1585[b,e]	10.00[b,e]					
			1.000[b,e]						
acetone (1) + decane (2)	–	–	0.1944[d]	−18.18[d]	0.130	−17.8	–	–	–
			0.9599[d]		0.950				
			0.1270[e]	−18.60[e]					
			1.000[e]						

[a] Estimated based on span of 2,2,4-trimethylpentane-rich region. [b] Estimated based on span of methanol-rich region. [c] Estimated based on span of decane-rich region. [d] Estimated by our regressed parameters. [e] Estimated by the modified parameters of Tourino et al.

Table 9. Our Regressed LLE Parameters of the UNIQUAC Equation for the Binary Solutions of Methanol, Acetone, and Decane

	parameters[a]			
	a_{12}	a_{21}	b_{12}	b_{21}
system	$J\cdot mol^{-1}$	$J\cdot mol^{-1}$	$J\cdot mol^{-1}\cdot K^{-1}$	$J\cdot mol^{-1}\cdot K^{-1}$
methanol (1) + decane (2)	32.6819	14060.8351	0.8473	−27.8935
acetone (1) + decane (2)	3326.9753	3230.0455	−12.5957	−4.1930
methanol (1) + acetone (2)	−280.6701	2051.1860	1.1745	−6.0658

[a] $u_{ij} - u_{jj} = a_{ij} + b_{ij}T$.

Following the so-called VLLE model described before, the flash point is computed based on either the methanol-rich or the 2,2,4-trimethylpentane-rich region and compared in Table 8 with experimental measurements. First, UNIQUAC- or NRTL-based prediction are quite different, hinting at the need to eventually regress new LLE parameter values, which is out of the scope of this paper. UNIQUAC predicts the 2,2,4-trimethylpentane-rich region composition better than NRTL, but the reverse holds for the methanol-rich region composition, NRTL being better overall. Either using NRTL or UNIQUAC, the estimated flash point computed from the 2,2,4-trimethylpentane-rich LLE region composition agrees better with the experimental

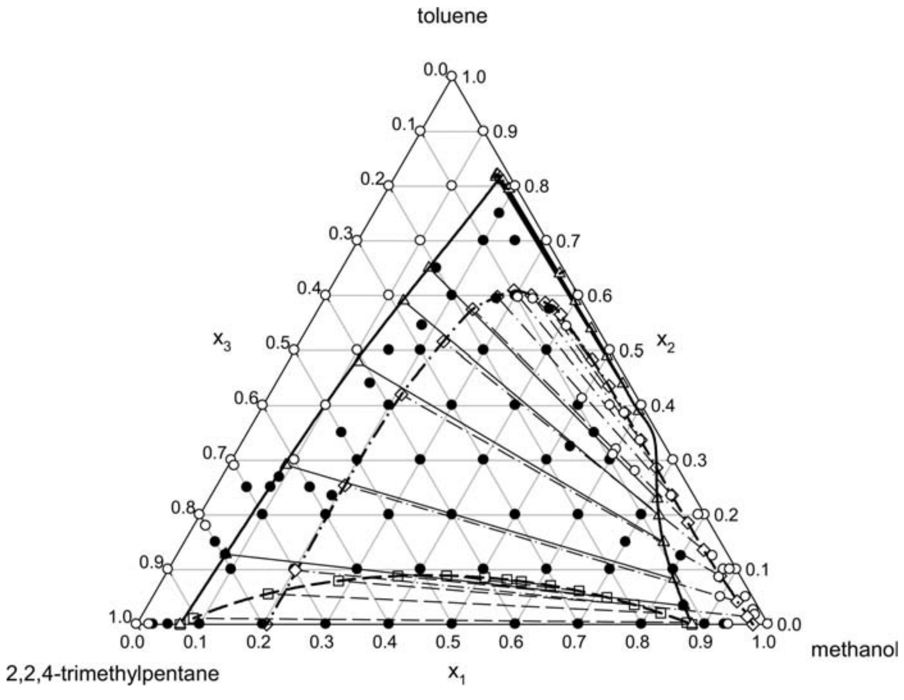


Figure 4. Binodal curves of methanol (1) + toluene (2) + 2,2,4-trimethylpentane (3). ●, partially miscible; ○, miscible; ◇-·-·-◇, NRTL (LLE + VLE); □— — —□, UNIQUAC (LLE); △—△, UNIQUAC (LLE + VLE).

Table 10. Comparison of Predicted Flash Point Values, $t_{\mathrm{fp,pred}}$, in the Estimated Tie Lines and Tie Line Span Estimated by the NRTL Equation from x_1 = (0.9761 (#1) to 0.78 (#6)), with Corresponding Experimental Data, $t_{\mathrm{fp,exp}}$, for Methanol (1) + Toluene (2) + 2,2,4-Trimethylpentane (3)

		span of tie line			
no. of tie lines	activity coefficient model	x_1	x_3	$t_{\mathrm{fp,pred}}$/°C	$t_{\mathrm{fp,exp}}$/°C [a]
#1	NRTL	0.9761	0.0239	−11.58	−11.6 ± 0.4
		0.2060	0.7940		
	UNIQUAC	0.8795	0.1205	−12.08	
		0.0687	0.9313		
#2	NRTL	0.9600	0.02590	−10.75	−10.9 ± 0.5
		0.2016	0.6992		
	UNIQUAC	0.8500	0.1160	−11.07	
		0.07715	0.7947		
#3	NRTL	0.9300	0.0278	−9.86	−9.8 ± 0.2
		0.2026	0.5433		
	UNIQUAC	0.8100	0.1071	−9.74	
		0.0905	0.6180		
#4	NRTL	0.8800	0.0313	−8.06	−8.0 ± 0.5
		0.2093	0.3703		
	UNIQUAC	0.7600	0.0898	−7.89	
		0.1113	0.4094		
#5	NRTL	0.8300	0.0338	−6.42	−6.5 ± 0.4
		0.2277	0.2560		
	UNIQUAC	0.7280	0.0730	−6.47	
		0.1274	0.2820		
#6	NRTL	0.7800	0.0340	−5.56	−5.5 ± 0.6
		0.2448	0.1801		
	UNIQUAC	0.7100	0.0606	−5.50	
		0.1374	0.2116		

[a] The uncertainty is in double standard deviation.

measurement than that for the methanol-rich LLE composition. It is attributed to the fact that the slope of the flash-point variation vs composition in the methanol-rich region is much steeper than that in the 2,2,4-trimethylpentane-rich region (see Figure 2c). Thus, a small deviation in the methanol-rich region composition causes much more deviation in the flash point than that in the 2,2,4-trimethylpentane-rich region composition. This behavior is enhanced when using the NRTL equation. Aware of this trend, we use the estimated 2,2,4-trimethylpentane-rich region composition into eqs 1 and 2 to calculate the constant flash point in each tie line for methanol + toluene + 2,2,4-trimethylpentane in this study.

Overall, Figure 2c and Table 7 show that considering partial miscibility (eq 3) in the flash-point predictions with the VLLE model (the blue and red lines) is better than without considering partial miscibility behavior (eq 3 is simply not used in this case). In that case, the mean deviation increases and a pseudohomogeneous liquid flash-point curve, whose shape is smooth convex then concave, occurs, in large disagreement with experimental data in the two liquid phases. Such a shape is characteristic of pseudohomogeneous model prediction applied to composition span where two liquid in equilibrium holds[49] and indicates that a true heterogeneous model must be considered.

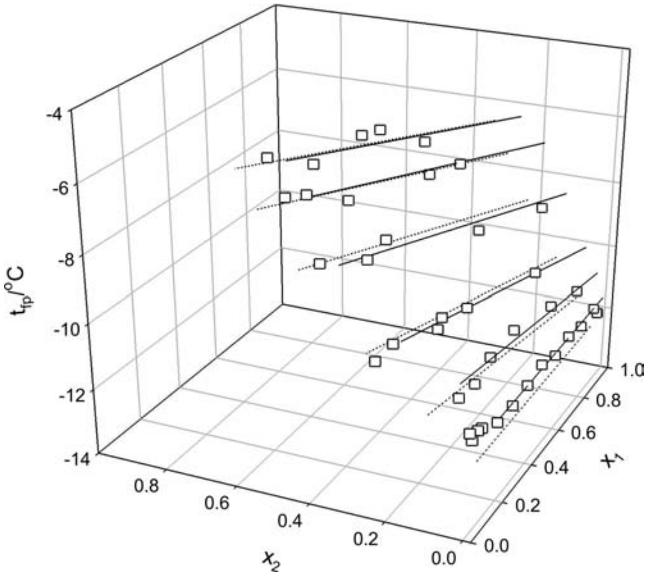


Figure 5. Comparison of predicted flash points in the tie lines with experimental data for methanol (1) + toluene (2) + 2,2,4-trimethylpentane (3). □, experimental data; —, NRTL; - - - -, UNIQUAC.

Methanol + Decane and Acetone + Decane Partially Miscible Binary Mixtures. By contrast to methanol + 2,2,4-trimethylpentane, with a minimum and constant flash point value in the two liquid phase region being much less than that of each individual component, the constant flash point of the partially miscible mixtures, methanol + decane, circa (10.3 ± 1.2) °C, and acetone + decane, (−17.8 ± 1.9) °C, is close to the flash-point value of the lowest boiling pure substance reported in Table 4 ((10.0 ± 0.8) °C for methanol (Figure 3b) and (−18.6 ± 0.9) °C for acetone) (Figure 3c). These two mixtures are the cases just able to form a minimum flash-point solution, with such a behavior being also observed in other binary partially miscible mixtures of flammable solvents.[20]

Figure 3c indicates that the prediction based on Gmehling et al.'s VLE parameters[35] can not describe the flash-point variation of the partially miscible mixture acetone + decane, even in the mutual solubility region. The predicted flash point always decreases with acetone composition, instead of displaying the constant flash point in the two liquid phase region. Thus, LLE parameters only were used in eqs 1 to 3 only to estimate the span of two liquid phases for acetone + decane. Two LLE parameter sets were devised. At first, Tourino et al.'s original LLE UNIQUAC parameters for methanol + decane and acetone + decane mixtures[31] were used. However, computation diverged until a printing error was suspected, and we exchanged the values of a_{ij} with those of b_{ij} in Tourino et al.'s Table 5[31] and took the opposite sign. These modified Tourino et al. values are listed in Table 1.

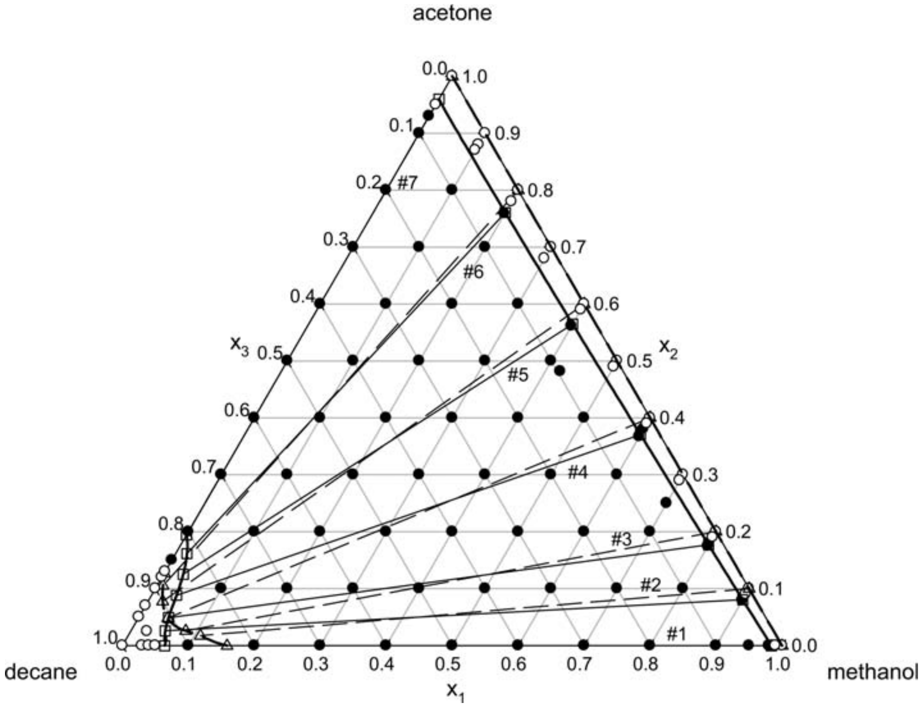


Figure 6. Binodal curves of methanol (1) + acetone (2) + decane (3). ●, partially miscible; ○, miscible; □—□, tie lines estimated by VLE parameters and our regressed LLE ones; △— — —△, tie lines estimated by VLE parameters and modified LLE ones of Tourino et al.

The prediction based on the modified Tourino et al. LLE parameters indicates that decane is completely insoluble in both methanol (Figure 3b) and acetone (Figure 3c), with the decane-rich liquid composition being 1.0 or near (Table 8), which is violating the observation of Casás et al.[50] and this study.

It is apparent that the modified LLE parameters of Tourino et al. are not completely appropriate for methanol + decane and acetone + decane mixtures, and Gmehling et al.'s VLE parameters[35] are not appropriate for acetone + decane. One possible reason is that Tourino et al.'s and Gmehling et al.'s parameters were regressed on data at (5 to 25) °C and 40 °C, respectively, which is a temperature far from the flash point of the two liquid phases for acetone + decane, −17.8 °C. But the major cause is that acetone + decane is a miscible mixture under Tourino et al.'s and Gmehling et al.'s conditions; however, it is a partially miscible one at −17.8 °C.

We propose a new set of LLE parameter values for methanol + acetone + decane regressed using an unweighted least-squares method with Tourino et al.'s LLE data[31] and imposing the existence of an acetone + decane LLE at −17.8 °C. Those parameters are listed in Table 9 and are used to estimate the span of the two liquid phases. Since Gmehling et al.'s VLE parameters failed in the flash-point prediction for acetone + decane, our regressed LLE parameters were also used to estimate the flash point for such a mixture.

Concerning the two liquid phases region, the measured span of two liquid phases region for methanol + decane ranges from 0.050 to 0.985 in methanol mole fraction with an average value of flash point of 10.3 °C, which is close to that adopted from LLE literature,[50] namely, 0.060 and 0.984 at 5 °C, the literature temperature closest to the average measured flash-point value (Table 8). Table 8 also indicates that prediction and experiments within the two liquid phases agree better when flash-point computation is based on the methanol-rich region LLE composition than when it is based on the decane-rich region LLE composition for the methanol + decane mixture, irrespective of whether our regressed LLE parameters or modified Tourino et al. LLE ones are used. This is again attributed to the fact that the slope of the flash point vs composition is steeper in the decane-rich region (see Figure 3b). Thus, the estimated span nearing the methanol-rich region was used to calculate the tie lines and their respective constant flash point for the methanol + acetone + decane ternary mixtures in this study.

Regarding the flash point vs composition slope, is has been observed that for a mixture exhibiting positive deviation from an ideal solution the flash point decreases substantially when a small quantity of a low-flash component was added into a high-

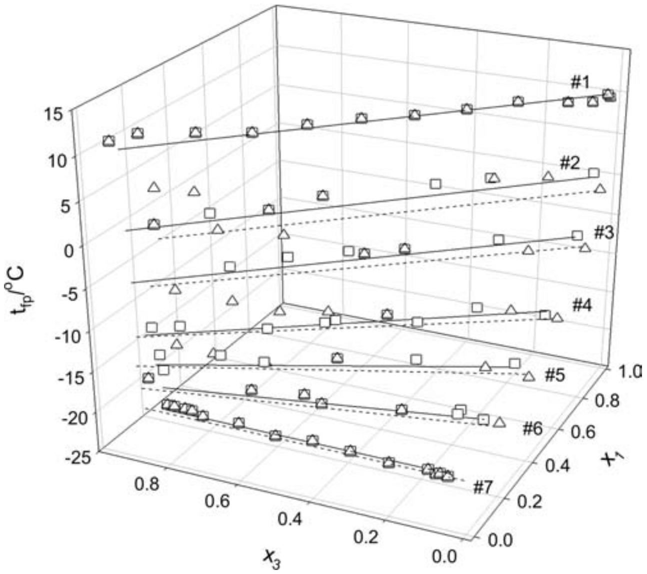


Figure 7. Comparison of predicted flash points in each tie line with the experimental data for methanol (1) + acetone (2) + decane (3). —, predictions using our regressed parameters; - -, predictions using Tourino et al.'s parameters; □, experimental data in the tie lines estimated by our regressed parameters; △, experimental data in the tie lines estimated by Tourino et al.'s parameters.

Table 11. Comparison of Predicted Flash Point Values, $t_{fp,pred}$, in the Estimated Tie Lines (#1 to #7) with Corresponding Experimental Data, $t_{fp,exp}$, for Methanol (1) + Acetone (2) + Decane (3)

no. of tie line	UNIQUAC parameters	span of tie line		$t_{fp,pred}$	$t_{fp,exp}$
		x_1	x_3	°C	°C[c]
#1	regressed parameters[a]	0.9838	0.0162	10.00	10.3 ± 1.2
		0.0641	0.9359		
	Tourino et al.[b]	1.0000	0.0000	10.00	10.3 ± 1.2
		0.1585	0.8415		
#2	regressed parameters[a]	0.9000	0.0194	1.18	2.1 ± 0.9
		0.0519	0.9221		
	Tourino et al.[b]	0.9000	0.0000	−0.34	2.6 ± 3.0
		0.1096	0.8732		
#3	regressed parameters[a]	0.8000	0.0222	−4.62	−3.9 ± 0.7
		0.0429	0.9095		
	Tourino et al.[b]	0.8000	0.0000	−5.63	−2.6 ± 5.8
		0.0832	0.8910		
#4	regressed parameters[a]	0.6000	0.0286	−10.47	−10.0 ± 1.0
		0.0372	0.8755		
	Tourino et al.[b]	0.6000	0.0000	−11.11	−8.8 ± 3.5
		0.0445	0.9073		
#5	regressed parameters[a]	0.4000	0.0350	−13.62	−12.8 ± 0.7
		0.0296	0.8453		
	Tourino et al.[b]	0.4000	0.0000	−14.16	−13.0 ± 2.2
		0.0223	0.9000		
#6	regressed parameters[a]	0.2000	0.0393	−15.96	−15.4 ± 1.5
		0.0172	0.8213		
	Tourino et al.[b]	0.2000	0.0000	−16.47	−15.6 ± 0.9
		0.0091	0.8860		
#7	regressed parameters[a]	0.0000	0.0401	−18.18	−17.8 ± 1.9
		0.0000	0.8056		
	Tourino et al.[b]	0.0000	0.0000	−18.60	−17.8 ± 1.9
		0.0000	0.8730		

[a] See Table 9. [b] See Table 1. [c] The uncertainty is in double standard deviation

flash material; however, the flash-point variation is almost negligible when a high-flash substance is added into a low-flash one.[4,15,20,51,52] Since a partially miscible mixture always exhibits significant positive deviation from Raoult's law, its slope of flash point vs composition in the span nearing pure substance with high flash point should be steeper than that in the other span. This behavior has been observed in the three binary partially miscible mixtures used in this study and other mixtures.[20] Thus, we recommend to use the estimated composition of span nearing the lower boiling pure compound to estimate the tie lines and their flash point.

Table 8 shows that the spans of the methanol + decane mixture are better estimated using our regressed LLE parameters than those using the modified Tourino et al. LLE parameters. For the acetone + decane mixture, the modified LLE parameters of Tourino et al. predict better the decane-rich region composition, whereas the opposite is true with our regressed ones for the acetone-rich region. The estimated flash point within the two liquid phases is better predicted using our regressed LLE parameters (Table 8).

Over the entire composition range, Figures 3b and 3c and Table 7 show that the predicted flash points for methanol + decane and acetone + decane mixtures agree well with the experimental data when using the VLLE model with the VLE parameters combined with our regressed LLE parameters (Tables 2 and 9). Substituting the modified Tourino et al. LLE parameters instead of our regressed LLE parameters, deviations increase in the decane-rich region for both methanol + decane and acetone + decane mixtures (Figures 3b and 3c).

Since within the two liquid phases region the two liquid phases span region and the flash point are estimated by the LLE and VLE parameters, respectively, the flash-point value is different depending on which of the two liquid phase compositions in equilibrium is used. When using the low boiling pure compound-rich composition, a flash-point curve discontinuity occurs around the high boiling pure compound (Figure 3b), whatever the LLE parameter set used for methanol + decane.

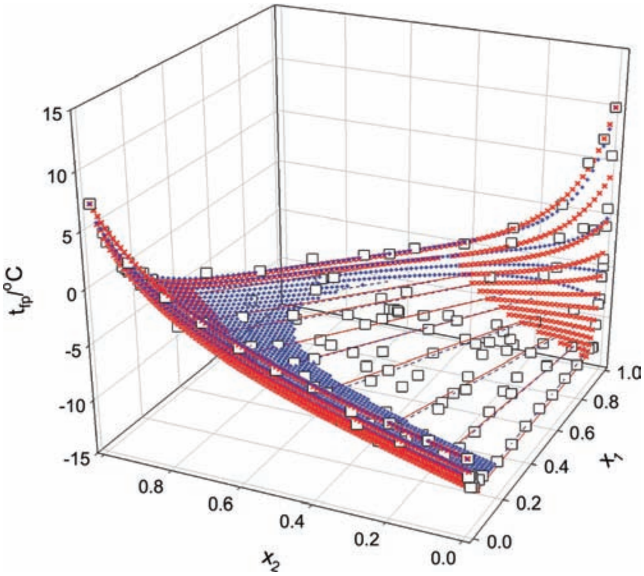


Figure 8. Comparison of predicted flash points with experimental data for methanol (1) + toluene (2) + 2,2,4-trimethylpentane (3). □, experimental data; red ×, UNIQUAC (mutual solubility region); red —, UNIQUAC (tie lines); blue +, NRTL (mutual solubility region); blue — —, NRTL (tie lines).

As in Figure 2c, Figures 3b and 3c show that not considering partial miscibility behavior gives rise to a pseudohomogeneous liquid flash-point curve that is not consistent with the experimental data in the two liquid phases.

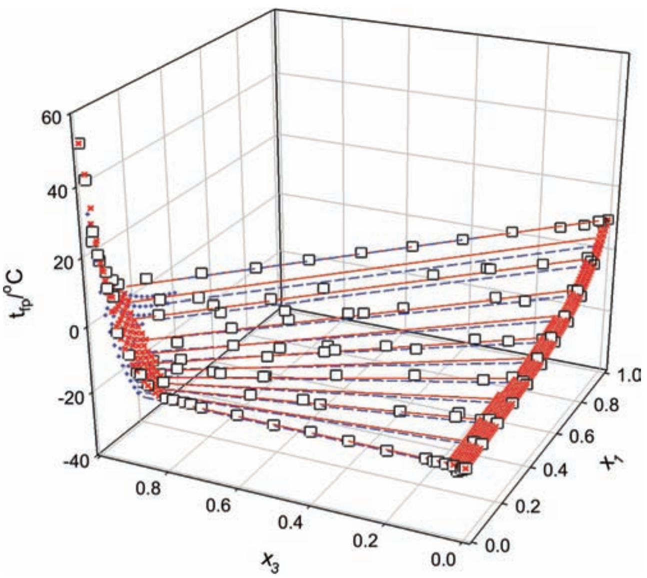


Figure 9. Comparison of predicted flash point and experimental data for methanol (1) + acetone (2) + decane (3). □, experimedntal data; red ×, mutual solubility region; red —, tie lines; blue ◆, mutual solubility region (Tourino et al.); blue — —, tie lines (Tourino et al.).

Ternary Mixtures

Toluene + Methanol + 2,2,4-Trimethylpentane Partially Miscible Ternary Mixture. By analogy with common liquid−liquid equilibrium ternary diagram classification, this mixture exhibits a single partially miscible binary mixture and is a type-I mixture. Within the composition ternary diagram, no composition has a flash-point temperature below that of the partially miscible binary mixture methanol + 2,2,4-trimethylpentane (Table 5). Using the UNIQUAC equation with Gramajo de Doz et al.'s LLE parameters (Table 1) and Gmehling et al.'s VLE parameters (Table 2) to estimate the two liquid phase region of methanol + toluene + 2,2,4-trimethylpentane (region denoted as "UNIQUAC (LLE)" in Figure 4), one notices that the predicted region is much smaller than the measured one. A likely cause could be the lack of temperature dependency of the LLE parameters of Gramajo de Doz et al.

On the basis of the binary mixture prediction (Figure 2), the NRTL equation could be a good model alternative. Unavailable binary LLE parameters for methanol + toluene and toluene + 2,2,4-trimethylpentane led us to use Gmehling et al.'s VLE parameters instead (Table 2) (denoted as "NRTL (LLE + VLE)" in Figure 4). The predicted region size improves over UNIQUAC (Gramajo de Doz et al.'s LLE) but is not fully satisfactory. From our former study, we noticed that the span of two liquid phases was always better predicted by using LLE parameters rather than VLE here.[21]

However, suitable VLE parameters could compensate for this drawback. Indeed, using the UNIQUAC equation with Gmehling et al.'s VLE parameters (Table 2) that gave satisfaction on the binary miscible mixtures for toluene + methanol and toluene + 2,2,4-trimethylpentane and acceptable deviation in estimating the span of the two liquid phases for methanol + 2,2,4-trimethylpentane (Figure 2 and Table 8), we use Gmehling et al.'s VLE parameters to estimate the two liquid phase region of methanol + toluene + 2,2,4-trimethylpentane (model denoted as "UNIQUAC (LLE + VLE)"). It is shown in Figure 4 that this estimated two liquid phase region has by far the best agreement with the measurements, although the estimated region is still larger than the measurements in the 2,2,4-trimethylpentane-lean region.

Regarding the tie line slopes, both the NRTL and the UNIQUAC equations with LLE parameters for methanol + 2,2,4-trimethylpentane (Table 1) and VLE parameters for the other two binary pairs of methanol + toluene + 2,2,4-trimethylpentane (Table 2) predict tie lines with very similar slopes but not with the same extend length (Figure 4 and Table 10). This is clearly evidenced in Figure 5 that compares the predicted flash points based on these two sets of parameters with the corresponding measured values in some tie lines. The greatest temperature difference is around 0.5 °C. As expected from theory, the measured values of the flash point are almost constant in each ternary tie line, rather than being constant over the entire two liquid phase region as observed in the binary partially miscible mixtures[20,21] (see Figure 5 and Table 10).

Methanol + Acetone + Decane Partially Miscible Ternary Mixture. Figure 6 displays the two liquid phase region for methanol + acetone + decane at its flash-point temperature by use of the UNIQUAC equation with either modified LLE parameters of Tourino et al. and VLE ones (Tables 1 and 2) or with our regressed LLE parameters and VLE ones (Tables 9 and 2). By analogy with the common liquid−liquid equilibrium ternary diagram classification, this mixture exhibits two partially miscible binary mixtures and is a type-II mixture. As for the previous ternary mixture, no ternary composition has a flash-point temperature below that of the lowest flash point of the partially miscible binary mixture acetone + decane (Table 6). Prediction with the modified Tourino et al. LLE parameters is not accurate because it indicates that decane is absent from the decane-lean region despite experimental evidence that it is present. Predictions with our regressed LLE parameters are superior, although there are still some deviations in the decane-rich region.

Measurements Based on Predicted Composition on Seven Tie Lines. Regarding the tie lines for which according to the theory the flash point should be constant, Figure 7 shows for seven tie lines predictions based on the two sets of parameters and measurements that are made based on the predicted compositions. The constant flash point behavior is predicted by the model for both parameter sets (dashed and solid lines) as expected.

When using our regressed LLE parameters, measurements done after the predictions (square points) are almost collinear and constant in Figure 7, as confirmed by the moderate standard deviation in average flash point reported in Table 11 for each tie line. The average measured flash point also agrees with the constant predicted flash point value.

However, when using the modified Tourino et al. parameters, measurements (triangle points) are neither collinear nor constant in each tie line, except in the binary pairs. Instead, they increased as the mole fraction of decane increases in each tie line. This deviation is especially significant in tie lines #2 to #5 (see Figure 7), with the measured flash points of the tie lines #3 to #5 being as high as those estimated by tie lines #2 to #4, respectively, in the decane-rich region. The standard deviation in average flash point of each tie line (Table 11) is also much larger, and the ternary tie lines #2 to #6 average flash point values disagree with the prediction constant flash point (Table 11). Looking back closer at Figure 6 shows that tie lines #3 to #5 estimated by the modified parameters of Tourino et al. intercrossed to tie lines #2 to #4 estimated by our regressed parameters, respectively, in the decane-rich region, which can explain the observed variation of flash point in each tie line. Thus, the deviation seen in Figure 7 is attributed to the deviation in the slope of the predicted tie lines.

Comparison of Predicted and Measured Flash Points for Ternary Mixtures. 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.[14,18] Since the VLE parameters regressed on the ternary compositions of methanol + toluene + 2,2,4-trimethylpentane and methanol + acetone + decane are not accessible in the literature, the VLE parameters of the binary pairs as listed in Table 2 (for acetone + decane, LLE parameters (Table 1, Tourino et al.'s parameters, or Table 9, our regressed LLE parameters) were used instead of VLE ones, see discussion before) were used to predict the flash point in the mutual solubility region, following the same recommended methodology as before. Results are displayed in Figures 8 and 9, and the average deviation between measurements and predicted flash points is provided in Table 7.

Figure 8 depicts the predicted flash points for the methanol + toluene + 2,2,4-trimethylpentane system using either NRTL or UNIQUAC equations to estimate activity coefficients. Both model predictions show slight differences but overall are consistent with the experimental data, as confirmed by the low average deviation reported in Table 7, which is lower for NRTL than for UNIQUAC.

For the methanol + acetone + decane mixture, Table 7 shows that the predicted flash points using our regressed LLE parameters are superior to those using the modified Tourino et al. LLE ones. It implies that the predictive accuracy is related to the quality of the regressed parameters. However, the overall agreement seen in Figure 9 is reasonable for both parameter sets.

In this manuscript, the predicted flash points gave good agreement with the experimental data, although there are still small deviations in the two liquid phase region between predictions and measurement. Since the purpose of this model is to predict the flash point rather than to estimate the two liquid phase region, the prediction results are acceptable. In the estimation of the two liquid phase region with application of this proposed model, it is suggested, if the LLE parameters for a ternary solution are not all accessible, to replace the LLE parameters of binary miscible pairs with the analogous VLE ones.

In deriving the flash point prediction model for ternary partially miscible mixtures of flammable solvents, 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.

Conclusion

The paper presents the first measurements of flash point for ternary partially miscible mixtures of flammable solvents and attempts to model this behavior. Attributed to the properties of VLLE for ternary mixtures, the measured flash points are considered constant in each tie line rather than constant in the two liquid phase region as observed in binary systems. Accounting for the nonideal behavior of the mixture, the model proposed in this study is able to represent well the experimental data over the entire composition range. In particular, it is able to predict the constant flash-point behavior on any liquid−liquid tie line within the two liquid phase region. However, the predictive accuracy depends upon the quality of the VLE and LLE parameters. In application of this proposed model, it is suggested to estimate the spans and flash point of each tie line by the VLLE model based on the estimated liquid-phase composition nearing the lowest boiling pure compound, and then further to estimate the flash point in the mutual solubility region by using the VLE parameters.

Literature Cited

(1) *CCPS/AIChE Guidelines for Engineering Design for Process Safety*; American Institute of Chemical Engineers: New York, 1993.

(2) Lees, F. P. *Loss Prevention in the Process Industries*, 2nd ed.; Butterworth-Heinemann: Oxford, U.K., 1996; Vol. 1.

(3) Crowl, D. A.; Louvar, J. F. *Chemical Process Safety: Fundamentals with Applications*; Prentice Hall PTR: NJ, 2002.

(4) Liaw, H.-J.; Lee, Y.-H.; Tang, C.-L.; Hsu, H.-H.; Liu, J.-H. A mathematical model for predicting the flash point of binary solutions. *J. Loss Prevent. Proc.* **2002**, *15*, 429–438.

(5) Liaw, H.-J.; Chiu, Y.-Y. The prediction of the flash point for binary aqueous-organic solutions. *J. Hazard. Mater.* **2003**, *101*, 83–106.

(6) UK Atomic Energy Authority, *Major Hazard Incident Data Service (MHIDAS)*, CD-ROM version; Silver Platter, 2004.

(7) DOT, *Shippers - General Requirements for Shipments and Packagings, Class3 - Assignment of Packing Group*, 49CFR173.121, National Archives and Records Administration, 2004; p 488.

(8) Kurihara, K.; Midorikawa, T.; Hashimoto, T.; Kojima, K.; Ochi, K. Liquid-Liquid solubilities for the binary system of methanol with octane and 2,2,4-trimethylpentane. *J. Chem. Eng. Jpn.* **2002**, *35*, 360–364.

(9) Matsuda, H.; Ochi, K. Liquid-liquid equilibrium data for binary alcohol + n-alkane (C10-C16) systems: methanol + decane, ethanol + tetradecane, and ethanol + hexadecane. *Fluid Phase Equilib.* **2004**, *224*, 31–37.

(10) Kosuge, H.; Iwakabe, K. Estimation of isobaric vapor-liquid-liquid equilibria for partially miscible mixture of ternary system. *Fluid Phase Equilib.* **2005**, *233*, 47–55.

(11) Liaw, H.-J.; Wang, T.-A. A non-ideal model for predicting the effect of dissolved salt on the flash point of solvent mixtures. *J. Hazard. Mater.* **2007**, *141*, 193–201.

(12) Affens, W. A.; McLaren, G. W. Flammability properties of hydrocarbon solutions in air. *J. Chem. Eng. Data* **1972**, *17*, 482–488.

(13) White, D.; Beyler, C. L.; Fulper, C.; Leonard, J. Flame spread on aviation fuels. *Fire Safety J.* **1997**, *28*, 1–31.

(14) Liaw, H.-J.; Tang, C.-L.; Lai, J.-S. A model for predicting the flash point of ternary flammable solutions of liquid. *Combust. Flame* **2004**, *138*, 308–319.

(15) Liaw, H.-J.; Lee, T.-P.; Tsai, J.-S.; Hsiao, W.-H.; Chen, M.-H.; Hsu, T.-T. Binary liquid solutions exhibiting minimum flash-point behavior. *J. Loss Prevent. Proc.* **2003**, *16*, 173–186.

(16) Liaw, H.-J.; Lin, S.-C. Binary mixtures exhibiting maximum flash-point behavior. *J. Hazard. Mater.* **2007**, *140*, 155–164.

(17) Garland, R. W.; Malcolm, M. O. Evaluating vent manifold inerting requirements: flash point modeling for organic acid-water mixtures. *Process Saf. Prog.* **2002**, *21*, 254–260.

(18) Liaw, H.-J.; Chiu, Y.-Y. A general model for predicting the flash point of miscible mixture. *J. Hazard. Mater.* **2006**, *137*, 38–46.

(19) Liaw, H.-J.; Chen, C.-T.; Cheng, C.-C.; Yang, Y.-T. Elimination of minimum flash-point behavior by addition of a specified third component. *J. Loss Prevent. Proc.* **2008**, *21*, 82–100.

(20) Liaw, H.-J.; Lu, W.-H.; Gerbaud, V.; Chen, C.-C. Flash-point prediction for binary partially miscible mixtures of flammable solvents. *J. Hazard. Mater.* **2008**, *153*, 1165–1175.

(21) Liaw, H.-J.; Chen, C.-T.; Gerbaud, V. Flash-point prediction for binary partially miscible aqueous-organic mixtures. *Chem. Eng. Sci.* **2008**, *63*, 4543–4554.

(22) Wilson, G. M. Vapor liquid equilibrium. XI. A new expression for the excess free energy of mixing. *J. Am. Chem. Soc.* **1964**, *86*, 127–130.

(23) Poling, B. E.; Prausnitz, J. M.; O'Connell, J. P. *The Properties of Gases and Liquids*, 5th ed.; McGraw-Hill: New York, 2001.

(24) Renon, H.; Prausnitz, J. M. Local compositions in thermodynamic excess functions for liquid mixtures. *AIChE J.* **1968**, *14*, 135–144.

(25) Abrams, D. S.; Prausnitz, J. M. Statistical thermodynamics of liquid mixtures: new expression for the excess Gibbs energy of partly or completely miscible systems. *AIChE J.* **1975**, *21*, 116–128.

(26) ASTM D 56, *Standard test method for flash point by Tag closed tester*; American Society for Testing and Materials: West Conshohocken, PA, 1999.

(27) Van Ness H. C.; Abbott, M. M. *Classical Thermodynamics of Nonelectrolyte Solutions: With Applications to Phase Equilibria*; McGraw-Hill: New York, 1982.

(28) Pham, H. N.; Doherty, M. F. Design and synthesis of heterogeneous azeotropic distillations-1. heterogeneous phase diagrams. *Chem. Eng. Sci.* **1990**, *45*, 1823–1836.

(29) Smith, J. M.; Van Ness, N. C. *Introduction to Chemical Engineering Thermodynamics*, 3rd ed.; McGraw-Hill: New York, 1975.

(30) Gramajo de Doz, M. B.; Bonatti, C. M.; Sölimo, H. N. Liquid-liquid equilibria of ternary and quaternary systems with two hydrocarbons, an alcohol, and water at 303.15 K Systems containing 2,2,4-trimethylpentane, toluene, methanol, and water, or 2,2,4-trimethylpentane, toluene, ethanol, and water. *Fluid Phase Equilib.* **2003**, *205*, 53–67.

(31) Tourino, A.; Casas, L. M.; Marino, G.; Iglesias, M.; Orge, B.; Tojo, J. Liquid phase behaviour and thermodynamics of acetone + methanol + n-alkane (C9-C12) mixtures. *Fluid Phase Equilib.* **2003**, *206*, 61–85.

(32) Gmehling, J.; Onken, U.; Arlt, W. *Vapor-Liquid Equilibrium Data Collection*, Part 2c; DECHEMA: Frankfurt, Germany, 1982; Vol. 1; p 229, 250.

(33) Gmehling, J.; Onken, U.; Arlt, W. *Vapor-Liquid Equilibrium Data Collection*, Part 6b, DECHEMA: Frankfurt, Germany, 1980; Vol. 1, p 326.

(34) Gmehling, J.; Onken, U. *Vapor-Liquid Equilibrium Data Collection*, Part 2a, DECHEMA: Frankfurt, Germany, 1977; Vol. 1, p 72, 275.

(35) Gmehling, J.; Onken, U.; Arlt, W. *Vapor-Liquid Equilibrium Data Collection*, Parts 3 + 4, DECHEMA: Frankfurt, Germany, 1979; Vol. 1, p 246.

(36) Iliuta, M. C.; Thyrion, F. C. Vapor-liquid equilibrium for the acetone-methanol-inorganic salt system. *Fluid Phase Equilib.* **1995**, *103*, 257–284.

(37) Merck, http://www.chemdat.info/mda/int_en/index.html (accessed 2008).

(38) *SFPE, The SFPE Handbook of Fire Protection Engineering*, 2nd ed.; Society of Fire Protection Engineers: Boston, 1995.

(39) Alfa Aesar, A Johnson Matthey Company, http://www.alfa.com (accessed 2008).

(40) Oxford University, The Physical and Theoretical Chemistry Laboratory, http://physchem.ox.ac.uk (accessed 2008).

(41) INCHEM, http://www.inchem.org/documents/icsc/icsc/eics0078.htm (accessed 2008).

(42) OSHA, http://www.osha.gov/SLTC/healthguidelines/toluene/recognition.html (accessed 2008).

(43) Baker, J. T., http://www.jtbaker.com/msds/englishhtml/T3913.htm (accessed 2008)

(44) Temarry, http://www.temarry.com/MSDS/Toluene_msds.htm (accessed 2008).

(45) Chevron Phillips Chemical Company, http://www.cpchem.com/enu/msds.asp (accessed 2008).

(46) ASTM D 93, *Standard test methods for flash-point by Pensky-Martens closed cup tester*; American Society for Testing and Materials: West Conshohocken, PA, 2000.

(47) Vidal, J. *Thermodynamics: Applications in Chemical Engineering and the Petroleum Industry*; Technip Editions: Paris, France, 2003.

(48) McDonald, C. M.; Floudas, C. A. Global optimization for the phase stability problem. *AIChE J.* **1995**, *41*, 1798–1814.

(49) Van Dongen, D. B.; Doherty, M. F.; Haight, J. R. Material Stability of Multicomponent Mixtures and the Multiplicity of Solutions to Phase-Equilibrium Equations 1. Nonreacting Mixtures. *Ind. Eng. Chem. Fundam.* **1983**, *22*, 472–485.

(50) Casás, L. M.; Tourino, A.; Orge, B.; Marino, G.; Iglesias, M.; Tojo, J. Thermophysical properties of acetone or methanol + n-alkane (C_9 to C_{12}) mixtures. *J. Chem. Eng. Data* **2002**, *47*, 887–893.

(51) Ellis, W. H. Solvent flash points - expected and unexpected. *J. Coat. Technol.* **1976**, *48*, 44–57.

(52) Anderson, J. E.; Wagyari, M. W. Flashpoint temperatures of methanol-hydrocarbon solutions. *Combust. Sci. Technol.* **1984**, *37*, 193–199.

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