

A non-ideal model for predicting the effect of dissolved salt on the flash point of solvent mixtures

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Abstract

Flash point is one of the major quantities used to characterize the fire and explosion hazard of liquids. Herein, a liquid with dissolved salt is presented in a salt-distillation process for separating close-boiling or azeotropic systems. The addition of salts to a liquid may reduce fire and explosion hazard. In this study, we have modified a previously proposed model for predicting the flash point of miscible mixtures to extend its application to solvent/salt mixtures. This modified model was verified by comparison with the experimental data for organic solvent/salt and aqueous–organic solvent/salt mixtures to confirm its efficacy in terms of prediction of the flash points of these mixtures. The experimental results confirm marked increases in liquid flash point increment with addition of inorganic salts relative to supplementation with equivalent quantities of water. Based on this evidence, it appears reasonable to suggest potential application for the model in assessment of the fire and explosion hazard for solvent/salt mixtures and, further, that addition of inorganic salts may prove useful for hazard reduction in flammable liquids.

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1. Introduction

In a given liquid, the flash point is the temperature (determined experimentally) at which the substance emits sufficient vapor to form a combustible mixture with air [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 Shengli event subsequently resulted in the temporary storage of large quantities of waste organic solutions at various factory sites and industrial park precincts [3,4]. Thus, flash point data for these mixtures has become increasingly important to ensure the safety of this voluminous storage. In addition to the usage and accumulation of flammable liquids, such as is outlined above, the transportation requirements for these mixtures are primarily related to their flash point values [5].

Salts are used as the separating agent in salt-distillation processes for separating close-boiling or azeotropic systems that cannot easily be purified using conventional distillation processes [6,7]. Typically, even small quantities of salt have a pronounced effect on the relative volatility of a solvent species [7], and we suggest that the flash points for liquids that are otherwise identical, except for the presence or absence of dissolved salt, will be quite different. Moreover, the presence of these salts can reduce the vapor pressure of the liquid, with the hazard of a flammable liquid reduced by addition of salts through increased flash point. Thus, a model that allows prediction of the flash point of mixed solvent/salt systems, based on the addition of an inorganic salt, is urgently required, both for the evaluation of the relative hazard of electrolyte solutions and for assessment of the efficiency of liquid hazard reduction.

Affens and McLaren [8] developed a predictive model for the flash points of binary hydrocarbon mixtures based on Raoult's law. White et al., [9] have reduced this model to a simpler equation by ignoring any dependence of the lower flammable limit on temperature. Application of the above two models is limited to ideal solutions, however [3]. Crawl and Louvar [10] have suggested that the flash point of a liquid solution with only one flammable component, such as a binary

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Nomenclature

A, B, C	Antoine coefficients
A_{nm}	solvent–solvent interaction parameter as defined in Table 1
A_{sn}	salt–solvent interaction parameter as defined in Table 1
g	binary parameters of NRTL equation (J/mol)
G_{ms}	function as defined in Table 1 for the salt–solvent interaction
G_{nm}	function as defined in Table 1 for the solvent–solvent interaction
MW	molecular weight (g/mol)
P^{sat}	saturated vapor pressure (kPa)
$P_{i,fp}^{sat}$	saturated vapor pressure of component i at flash point (kPa)
R	gas constant, 8.314 J/mol
T	temperature (K)
V	molar volume of liquid (m^3/mol)
x	mole fraction of species in liquid phase
X	effective liquid phase mole fraction
X'_m	salt-free mole fraction of solvent m

Greek letters

α_{ms}	non-randomness factor for solvent–salt ($m-s$) interactions
α_{nm}	non-randomness factor for binary $n-m$ interactions
γ	activity coefficient
λ	binary parameters of Wilson equation (J/mol)
ρ	density (g/cm^3)
τ_{ms}	salt–solvent interaction parameter as defined in Table 1
τ_{nm}	NRTL interaction parameter as defined in Table 1

Subscripts

i	salt or solvent species
m, m', n, n'	solvent species
s	salt
w	water

aqueous–organic solution, can be estimated using Raoult's law. This method is only adequate for a composition range where the mole fraction of the flammable component approaches unity when applied to aqueous–organic solutions [4]. Garland and Malcolm [11] developed a statistical model to predict the flash point of the organic acid–water solution: acetic acid + propionic acid + butyric acid + water. However, it has been demonstrated that the predictions generated using this method deviate significantly from the experimental measurements for multiple aqueous–organic solutions [12]. Thus, we have proposed a general model for predicting the flash point for miscible mixtures [12], which can be simplified for some specified systems [3,4,13], including those with only flammable components and aqueous–organic solutions. It has been verified that the former reduced modification of the general model can predict the experi-

mental data for both binary and ternary mixtures [3,13,14], with the latter analogue also verified using experimental measurement for various binary and ternary aqueous–organic solutions [4,12].

Although the models described above were all developed for salt-free systems, we suggest that the addition of dissolved salt has a pronounced effect on the flash point of solvent mixtures. To our knowledge, however, to date, no applicable model has been available for systems containing dissolved salts. In this manuscript, therefore, the model proposed for miscible solutions [12] was modified for mixed solvent/salt systems. The efficacy of this modified form was then verified using experimental data from both organic and aqueous–organic solvent/salt systems using the closed-cup test.

2. Experimental details

An HFP 362-Tag Flash Point Analyzer (Walter Herzog GmbH, Germany) was used to measure the flash points for a variety of mixtures (methanol+NaI; methanol+NaSCN; methanol+KSCN; methanol+water; acetone+methanol+NaI; methanol+water+LiCl; methanol+water+NaBr) at different compositions. The apparatus incorporates control devices that program the instrument to heat the samples at a specified rate (heating rate) within a temperature range close to the expected flash point. The flash point is automatically tested using an igniter at specified temperature intervals (test intervals). If the expected flash point is lower than or equal to the change temperature, which is set at 60 °C according to the standard ASTM D56 method [15], a heating rate of 1 °C/min is used and the igniter is fired at test interval-1. If the expected flash point is higher, a heating rate of 3 °C/min is adopted and the igniter is fired at test interval-2. The 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 [15] using the selected parameters: start test, 5 °C; end of test, 20 °C; test interval-1, 0.5 °C; test interval-2, 1.0 °C. The liquid mole fraction is determined from mass, which is measured using a Setra digital balance (EL-410D: sensitivity 0.001 g, maximum load 100 g). Water was purified using a Milli-Q Plus system. Both methanol and acetone were HPLC/Spectro-grade reagents (Tedia Co. Inc., USA). KSCN, NaSCN and NaBr were purchased from Showa Chemical Co., Ltd. (Japan). NaI was obtained from Yakuri Pure Chemicals Co., Ltd. (Japan), and LiCl from Riedel-de Haën (Germany).

3. Modified model for predicting the flash point of solvent/salt mixtures

3.1. Mathematical formulation

The flash point of a flammable liquid is the temperature at which the vapor pressure of the liquid is such that it produces

a concentration of vapor in the air that corresponds to its lower flammable limit (LFL) [2]. Thus, at the flash point of a liquid solution, Le Chatelier’s rule [16], which is used to describe the lower flammable limit of a gas mixture, is followed:

$$1 = \sum \frac{y_i}{LFL_i} \tag{1}$$

where y_i is the mole fraction of the flammable substance, i , in the vapor phase, and LFL_i is its lower flammable limit. Assuming that the lower flammable limit of a mixture is invariant regardless of the presence of any inert gas, prediction of the flash point with certain non-flammable components only requires consideration of the vapor-phase composition of the flammable constituents. Thus, for a multi-component solution with M non-flammable components, k_l ($l = 1, \dots, M$), Eq. (1) is modified:

$$1 = \sum_{i \neq k_l} \frac{y_i}{LFL_i} \tag{2}$$

From the definition of the flash point for a pure substance [2], the LFL of component n , LFL_n , is expressed relative to its saturated vapor pressure at the flash point, $P_{n,fp}^{sat}$, as follows:

$$LFL_n = \frac{P_{n,fp}^{sat}}{P} \tag{3}$$

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

$$y_n = \frac{x_n \gamma_n P_n^{sat}}{P} \tag{4}$$

Substituting Eqs. (3) and (4) into Eq. (2):

$$1 = \sum_{i \neq k_l} \frac{x_i \gamma_i P_i^{sat}}{P_{i,fp}^{sat}} \tag{5}$$

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

$$\ln P_n^{sat} = A_n - \frac{B_n}{T + C_n} \tag{6}$$

The vapor pressure of the pure substance, n , at its flash point, $P_{n,fp}^{sat}$, as presented in Eq. (5), can be estimated by substituting $T_{n,fp}$, the flash point of component n , into the Antoine equation.

The commonly used equations for estimating the activity coefficients of mixtures, such as the Wilson [17], NRTL [18] and UNIQUAC equations [19], were developed for salt-free mixtures and, therefore, they are not adequate for mixed solvent/salt systems. For prediction of the flash point for solvent/salt mixtures, therefore, the activity coefficients should be estimated using suitable equations, such as Tan’s modified NRTL [20] or Wilson models [21], or the extended UNIQUAC equation of Sander et al., [7], with these reducible to the NRTL, Wilson or UNIQUAC equations for the salt-free systems, respectively. The former two are used in this manuscript (Table 1).

In the limiting case of infinite dilution of component 1 for binary mixtures with dissolved salt, Tan’s modified Wilson equation is reduced:

$$\ln \gamma_{s1}^\infty = -\ln A_{12} + \left(1 - \frac{A_{21}}{A_{s2}}\right) \tag{7}$$

The fact that the value of A_{s2} increases with greater salt concentration, such that the value of γ_{s1}^∞ is higher, violates the observation. Thus, in this treatment, Tan’s modified Wilson equation was not used for binary mixtures with salt.

3.2. Flash point prediction for flammable solvent/salt systems

In a solvent/salt mixture with all flammable solvents, salt is the sole non-flammable component. Thus, Eq. (5) is reduced to:

$$1 = \sum_{i \neq s} \frac{x_i \gamma_i P_i^{sat}}{P_{i,fp}^{sat}} \tag{8}$$

with salt denoted as component s . Thus Eqs. (6) and (8) constitute the prediction model for the flash point of flammable solvent/salt systems. The temperature derived from the solution of the equations is deemed to be the flash point of such mixtures.

Table 1
Models of activity coefficients

Name	Activity coefficient for component i
Tan’s modified Wilson model	$\ln \gamma_n = -\ln \left[(A_{sn} - 1)X'_n + \sum_m A_{nm} X'_m \right] + \frac{\sum_m A_{nm} X'_m}{(A_{sn} - 1)X'_n + \sum_m A_{nm} X'_m} -$ $\sum_{m'} \frac{A_{m'n} X'_{m'}}{(A_{sm'} - 1)X'_{m'} + \sum_m A_{m'm} X'_m}, \text{ where } A_{nm} = \frac{V_m}{V_n} \exp\left(-\frac{\lambda_{nm} - \lambda_{nn}}{T}\right), \quad A_{sn} = \frac{V_s}{V_n} \exp\left(-\frac{\lambda_{sn} - \lambda_{nn}}{T}\right)$
Tan’s modified NRTL model	$\ln \gamma_n = \frac{\sum_{m'} X_{m'} G_{m'n} \tau_{m'n}}{\sum_m X_m G_{mn}} + \sum_{n'} \frac{X_{n'} G_{nn'}}{\sum_m X_m G_{mn'}} \left(\tau_{mn'} - \frac{\sum_{m'} X_{m'} G_{m'n'} \tau_{m'n'}}{\sum_m X_m G_{mn'}} \right) + \frac{\sum_{n'} X_{n'} G_{n's} \tau_{n's}}{\sum_m X_m G_{ms}} +$ $\frac{G_{ns}}{\sum_m X_m G_{ms}} \left(\tau_{ns} - \frac{\sum_{n'} X_{n'} G_{n's} \tau_{n's}}{\sum_m X_m G_{ms}} \right), \text{ where } G_{nm'} = \exp(-\alpha_{nm} \tau_{nm}), \quad \tau_{nm} = \frac{g_{nm} - g_{mm}}{T},$ $G_{ns} = \exp(-\alpha_{ns} \tau_{ns}), \quad \tau_{ns} = \frac{g_{ns} - g_{ss}}{T}$

For a combination of one flammable solvent and one salt, Eq. (8) becomes:

$$P_1^{\text{sat}} = \frac{P_{1,\text{fp}}^{\text{sat}}}{x_1 \gamma_1} \quad (9)$$

The flash point for such a mixture can be evaluated using Eqs. (6) and (9) and those listed in Table 1.

For an ideal solution, the activity coefficient of the liquid phase is equal to unity, and Eq. (9) reduces to:

$$P_1^{\text{sat}} = \frac{P_{1,\text{fp}}^{\text{sat}}}{x_1} \quad (10)$$

This equation is equivalent to that used by Crowl and Louvar [10] to estimate the flash point of a binary solution with only one flammable component.

Eq. (9) is adequate for a mixture with a single flammable solvent and one salt, but not for a mixed solvent/salt system with more than one flammable component. For an electrolyte system with two flammables and one salt, Eq. (8) reduces to:

$$1 = \frac{x_1 \gamma_1 P_1^{\text{sat}}}{P_{1,\text{fp}}^{\text{sat}}} + \frac{x_2 \gamma_2 P_2^{\text{sat}}}{P_{2,\text{fp}}^{\text{sat}}} \quad (11)$$

Thus, the flash point for such a ternary mixture can be calculated using Eqs. (6) and (11) and Tan's modified NRTL model.

3.3. Prediction for aqueous–organic solvent/salt systems

For an aqueous–organic solution mixed with dissolved salt, the water vapor and salt are non-flammable. Where the other

components are all flammable, Eq. (5) is reduced to:

$$1 = \sum_{i \neq s, w} \frac{x_i \gamma_i P_i^{\text{sat}}}{P_{i,\text{fp}}^{\text{sat}}} \quad (12)$$

with the salt and water denoted as components s and w , respectively.

To predict the effect of dissolved salt on the flash point of binary aqueous–organic solutions, Eq. (12) becomes:

$$P_1^{\text{sat}} = \frac{P_{1,\text{fp}}^{\text{sat}}}{x_1 \gamma_1} \quad (13)$$

The flash point for such systems can be estimated using Eqs. (6) and (13) and Tan's modified NRTL model.

The procedure for evaluation of the flash point for solvent/salt mixtures is depicted in Fig. 1. The iterative procedure is analogous to that used for calculating the boiling and dew points of mixtures [22].

4. Results and discussion

4.1. Parameters used in this manuscript

In this study, the modified model for predicting the flash point of solvent/salt systems was used to estimate the flash points for the following mixtures: methanol + NaI; methanol + NaSCN; methanol + KSCN; acetone + methanol + NaI; methanol + water + LiCl; methanol + water + NaBr. The prediction results thus obtained were compared with the corresponding experimentally derived data. Antoine coefficients were sourced from the literature [23]. The liquid-phase activity coefficients for the flammable components of the above mixtures were estimated

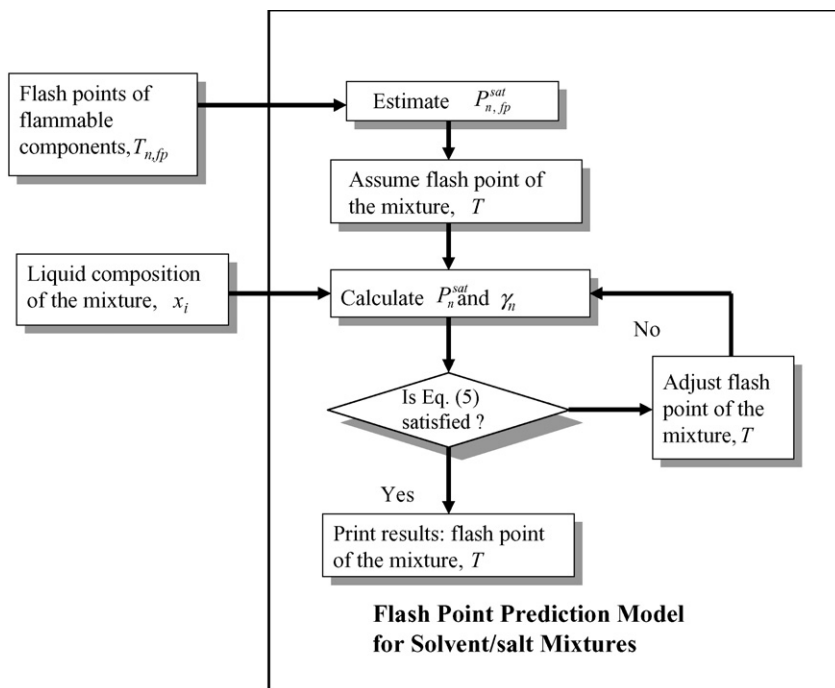


Fig. 1. Procedure for evaluation of flash point for solvent/salt mixtures.

Table 2
Parameters used for the Tan's modified Wilson and NRTL models for some organic solvent/salt mixtures

x_s	Tan's modified Wilson model	Tan's modified NRTL model $\alpha_{1s} = \alpha_{2s} = 0$ (for acetone + methanol + NaI: $(g_{12} - g_{22})/R = 78.317$ K, $(g_{21} - g_{11})/R = 140.046$ K; $\alpha_{12} = \alpha_{21} = 0.47$)	
	A_{s1}	τ_{1s}	τ_{2s}
Acetone (1) + methanol (2) + NaI (s) [24]			
0.01	1.00914	-0.0086	-0.01534
0.02	1.02473	-0.02014	-0.03492
0.03	1.04803	-0.03306	-0.05829
0.04	1.06022	-0.04901	-0.08651
0.05	1.07916	-0.04794	-0.14665
0.06	1.09667	-0.05490	-0.18548
0.07	1.11579	-0.07170	-0.22315
0.08	1.15432	-0.08154	-0.27256
0.09	1.14834	-0.08523	-0.33047
Methanol (1) + NaSCN (s) [25]			
0.01	1.02059	-0.01792	-
0.03	1.08119	-0.06270	-
0.04	1.11803	-0.08941	-
0.05	1.16333	-0.12168	-
0.07	1.27229	-0.19449	-
0.09	1.41073	-0.27911	-
0.11	1.57534	-0.36972	-
0.13	1.76884	-0.46687	-
Methanol (1) + KSCN (s) [26]			
0.01	1.0203	-0.0154	-
0.02	1.0469	-0.0402	-
0.03	1.0741	-0.0634	-
0.04	1.1096	-0.0879	-
0.05	1.1441	-0.1105	-

Table 3
Parameters used for the Tan's modified NRTL model for methanol (1) + water (2) + salt (s) [20]

Salt	$(g_{12} - g_{22})/R = -196.701$ K, $(g_{21} - g_{11})/R = 540.771$ K; $\alpha_{12} = \alpha_{21} = 0.30$, $\alpha_{1s} = \alpha_{2s} = 0$	
	$(g_{s1} - g_{ss})/R$	$(g_{s2} - g_{ss})/R$
1 M LiCl	-5.9237	-10.6423
2 M LiCl	-7.2420	-49.2062
4 M LiCl	-9.8773	-89.0065
1 M NaBr	-3.2872	-31.9221
2 M NaBr	-9.8773	-58.4917

using the equations listed in Table 1 and parameters adopted from the literatures [20,24–26] (Tables 2 and 3). The specific volumes necessary for Tan's modified Wilson equation and calculating molarity are listed in Table 4.

Table 4
Specific volume (v_i^l) for the pure components

Component	v_i^l (cm ³ /mol) ^a	MW [27]	ρ (g/cm ³) [27]
Methanol	40.73	32.04	0.7866
LiCl	20.48	42.39	2.07
NaBr	32.05	102.89	3.21

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

Table 5
Comparison of flash point values adopted from the literature with experimentally derived data for methanol and acetone^a

Component	Experimental data (°C)	Literature (°C)
Methanol	10.0 ± 0.4	12 [27,28]
Acetone	-18.6 ± 0.4	-18 [27,28]

^a Closed cup test.

The flash points for methanol and acetone were measured using the flash point analyzer, with these values compared with the literature-derived values (Table 5). There appear to be slight, but acceptable, deviations between our measurements and the published flash points for methanol and acetone. The flash point values quoted in the Merck Index [27] and SFPE Handbook [28] were measured using the closed-cup method although, interestingly, the standard test is not mentioned in either source. However, the latter reference work suggests that the result of flash point measurement depends upon the apparatus employed. The difference in flash point values generated in this study and analogs provided in the literature may be attributable, therefore, to existing differences in the standard test method.

4.2. Effect of dissolved salt on the flash point of organic-solvent mixtures

We tested the effect of NaI on the flash point of methanol (Table 6). The results were plotted against the predictive curves from the modified model for derivation of the flash point of mixed solvent/salt mixtures, with various equations used to estimate the activity coefficients (Fig. 2). Although there are differences between the predicted flash point values derived using Tan's modified Wilson and NRTL models for estimating activity coefficients, the results are generally consistent with the experimental measurements. Using the former model produces a better predictive curve in terms of agreement with the experimental data relative to the latter (see Fig. 2 and Table 7). The predictive curves for methanol + KSCN and methanol + NaSCN, as well as those for the above system, are presented in Fig. 2. Overall, the predictive results describe the experimental data well.

Table 6
Measured flash point for methanol with added salt

x_s	Methanol + NaI (°C)	Methanol + KSCN (°C)	Methanol + NaSCN (°C)
0.0	10.0	10.0	10.0
0.01	10.7	10.5	10.5
0.02	11.3	10.9	11.0
0.03	12.1	11.5	11.5
0.04	12.9	12.2	12.5
0.05	13.8	13.0	13.5
0.06	15.0	-	14.5
0.07	15.9	-	15.0
0.08	17.0	-	16.0
0.09	18.5	-	17.3
0.11	-	-	19.6
0.12	-	-	20.7
0.13	-	-	21.3

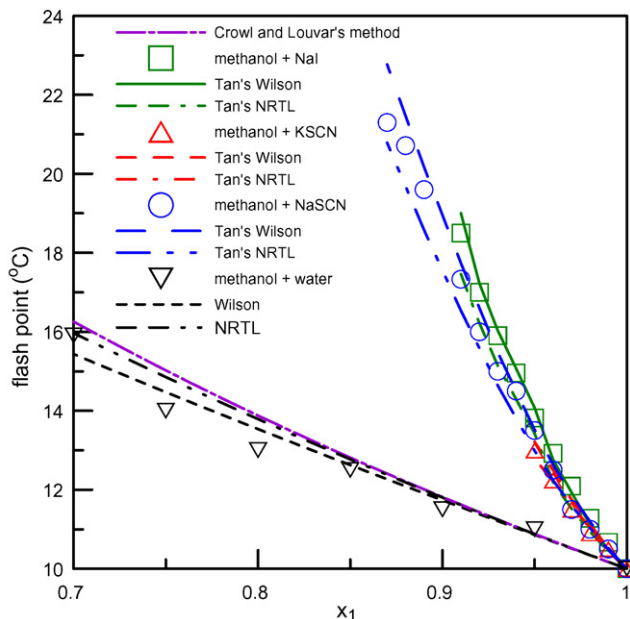


Fig. 2. Comparison of predicted flash points and experimental data for methanol (1) with addition of salt/water.

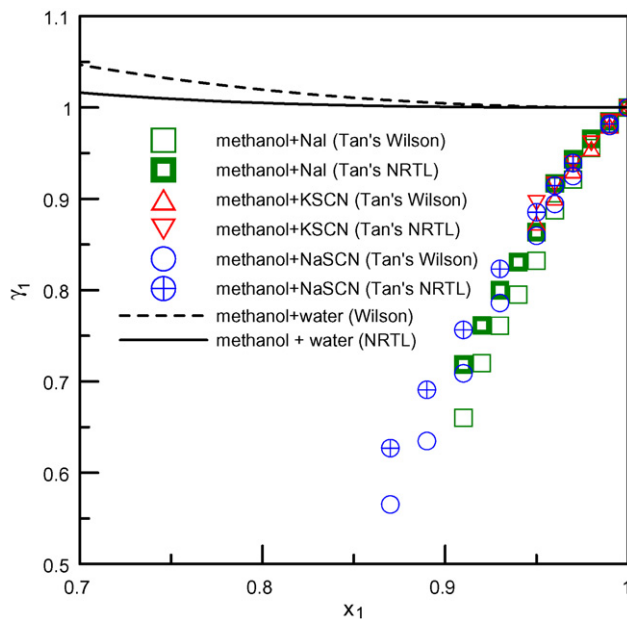


Fig. 3. Variation of activity coefficient with composition for methanol (1) with addition of salt/water.

There is no significant difference in relative predictive efficacy comparing Tan's NRTL and Wilson models with respect to the derived activity coefficients for methanol+NaSCN, although the former is superior for methanol+KSCN (Table 7). The flash points predicted using Eq. (10) (first column of Table 7), which is equivalent to Crowl and Louvar's method [10], are also plotted in Fig. 2. Since Crowl and Louvar's method assumes that the liquid phase behaves as an ideal solution [10], the predicted flash point values are identical, irrespective of any addition of salt to the same liquid. It is evident that the flash points predicted using Crowl and Louvar's method are substantially lower than the corresponding experimental data for the three systems outlined above. From inspection of Fig. 2 and Table 7, it is apparent that, in terms of predictive efficacy, our modified model is markedly superior to the Crowl and Louvar method. The poor predictive efficacy of the latter for solvent/salt mixtures incorporating near-pure flammables is quite different from the analogue for aqueous–organic solutions, where the method accurately predicts flash points in this range [4]. This is attributable to the difference in variation of activity coefficients for these near-pure

flammables, with the former varying substantially with composition (Fig. 3), while the latter approaches unity [4].

The flash point of methanol increases with addition of any of the inorganic salts, NaI, KSCN and NaSCN (Fig. 2). Our previous study showed that addition of water to a flammable liquid increases its flash point value [4], therefore, this flammability effect for water+methanol is also depicted in Fig. 2 for comparison. Inspection of the figure reveals that the flash point of methanol increases from 10 to 18.5 °C, where the mole fraction of the NaI additive is increased to 0.09, however, the analogous value for water only increases to 11.5 °C even though its mole fraction is 0.1. Thus, it is apparent that, relative to water, the inorganic salt, NaI, is much more efficient in terms of hazard reduction. Analogous results were also observed for the methanol system with addition of the other inorganic salts (KSCN and NaSCN). From Fig. 3, it can be seen that the mixtures, methanol+NaI, methanol+KSCN, and methanol+NaSCN deviate negatively from ideality, as opposed to the aqueous–methanol solution, which deviates positively, with the methanol activity coefficients of the former three and the latter less than and greater than unity, respectively. Thus, the flash point increment is much more substantial for methanol after addition of the inorganic salts, NaI, KSCN or NaSCN, compared to an equivalent mole of water, with the hazard reduction of the former apparently superior.

The modified study model was also used to predict the flash point variations for a binary solvent mixed with salt (acetone+methanol+NaI). The predicted results and the experimentally derived data are compared in Fig. 4, with the measured flash points also listed in Table 8. The predictive curves derived using Tan's modified NRTL model for estimation of the activity coefficients is in good agreement with the experimental measurements (Fig. 4 and Table 7). The presence of dissolved NaI

Table 7

Deviation between calculated and experimental flash point, ΔT_{fp}^a , for the solvent/salt mixtures used in this study

Mixture	Ideal solution	Tan's NRTL	Tan's Wilson
Methanol + NaI	2.91	0.55	0.19
Methanol + NaSCN	3.76	0.44	0.37
Methanol + KSCN	0.92	0.09	0.16
Acetone + methanol + NaI	–	0.33	–
Methanol + water + LiCl	8.18	1.46	–
Methanol + water + NaBr	9.19	1.11	–

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

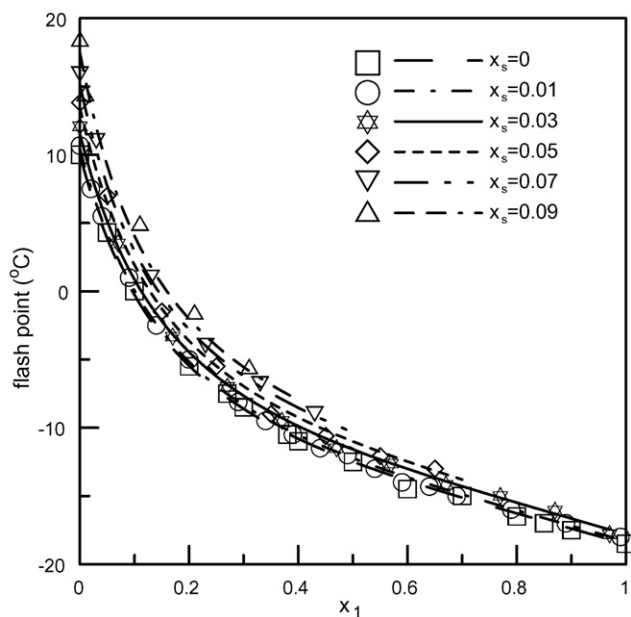


Fig. 4. Comparison of the predicted flash point curves and the experimental data for acetone (1) + methanol (2) with addition of NaI.

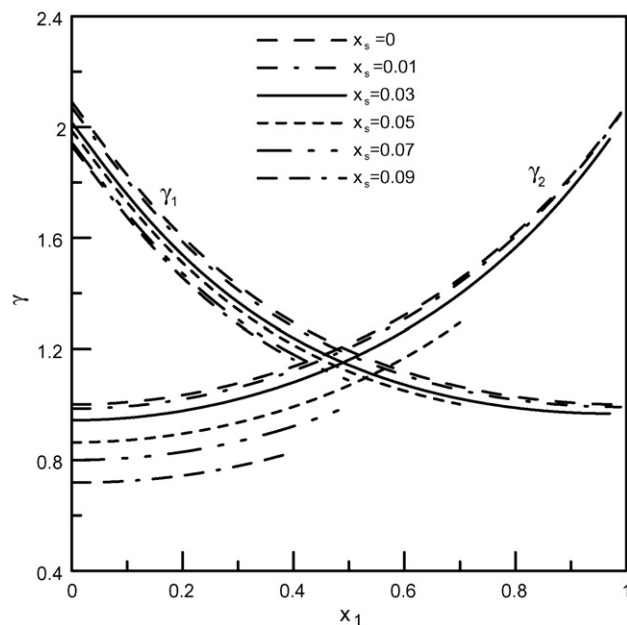


Fig. 5. Variation of activity coefficient with composition for acetone (1) + methanol (2) with addition of NaI.

increases the flash point of the acetone + methanol mixture, with the amount of dissolved salt proportional to the flash point increase. This can be attributed to the fact that addition of an inorganic salt to an organic-solvent mixture reduces the activity coefficient of organic solvents, such that the flash point of the mixture is increased. The estimated activity coefficients are depicted in Fig. 5.

Table 8
Measured flash points for methanol (1) + acetone (2) with addition of NaI (s)

x_1	$x_s = 0$	$x_s = 0.01$	$x_s = 0.03$	$x_s = 0.05$	$x_s = 0.07$	$x_s = 0.09$
0	-18.6	-18.0	-17.8	-	-	-
0.1	-17.5	-17.1	-16.1	-	-	-
0.15	-17.0	-	-	-	-	-
0.2	-16.5	-15.9	-15.0	-	-	-
0.3	-15.1	-15.0	-14.2	-13.1	-	-
0.35	-	-14.3	-	-	-	-
0.4	-14.5	-14.1	-12.6	-2.1	-	-
0.45	-	-13.0	-	-	-	-
0.5	-12.5	-12.0	-11.5	-10.6	-9.0	-
0.55	-	-11.5	-	-	-	-
0.6	-11.0	-10.5	-9.5	-9.0	-6.8	-5.5
0.62	-10.5	-	-	-	-	-
0.65	-	-9.5	-	-	-	-
0.7	-8.5	-8.1	-7.0	-5.5	-4.0	-1.5
0.73	-7.4	-	-	-	-	-
0.8	-5.5	-5.0	-3.3	-1.5	1.1	5.0
0.85	-	-2.5	-	-	-	-
0.9	0.0	1.0	3.5	7.1	11.0	14.5
0.91	-	-	-	-	-	18.5
0.93	-	-	-	-	15.9	-
0.95	4.3	5.5	-	13.8	-	-
0.97	-	7.5	12.1	-	-	-
0.99	-	10.7	-	-	-	-
1.0	10.0	-	-	-	-	-

4.3. Effect of dissolved salt on the flash point of aqueous–organic solutions

The flash point prediction curves for the aqueous–organic solvent/salt mixtures, methanol + water + LiCl and methanol + water + NaBr, were plotted against the corresponding experimental data (Fig. 6; Table 9). Fig. 6 and Table 7 reveal that the predictive curves generated using Tan’s modified NRTL model for estimation of activity coefficients are in agreement with the experimental measurements. Assuming an ideal solution, the

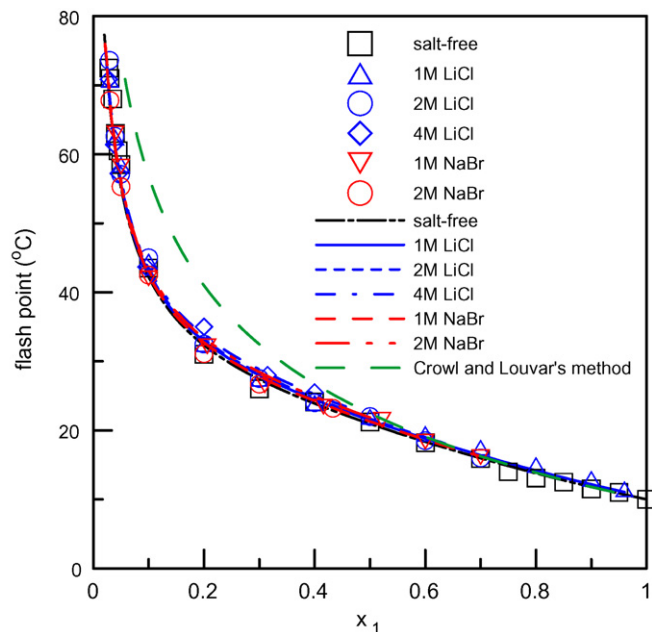


Fig. 6. Comparison of the predicted flash point curves and experimental data for methanol (1) + water (w) with addition of LiCl/NaBr.

Table 9
Measured flash points for methanol + water with addition of salts

x_1	Methanol (1) + water (w) + NaBr (s) (°C)			Methanol (1) + water (w) + LiCl (s) (°C)		
	$x_s = 0$	1 M NaBr	2 M NaBr	1 M LiCl	2 M LiCl	4 M LiCl
0.028	72.5	–	–	–	–	70.85
0.03	71.0	–	67.8	70.8	73.6	–
0.035	68.0	–	–	–	–	–
0.0375	–	–	–	–	–	61.4
0.04	63.0	63.0	–	62.4	62.6	–
0.045	60.5	–	–	–	–	57.2
0.05	58.5	58.2	55.3	58.5	57.1	–
0.1	43.5	42.0	42.5	44.5	45.0	43.7
0.2	31.1	32.2	31.1	32.5	32.4	35.0
0.3	26.0	26.5	26.7	27.5	27.5	–
0.315	–	–	–	–	–	28.0
0.4	24.1	–	–	24.1	24.0	25.5
0.42	–	23.4	–	–	–	–
0.43	–	–	23.2	–	–	–
0.5	21.2	–	–	22.0	22.1	–
0.522	–	21.5	–	–	–	–
0.6	18.2	18.4	–	19.5	18.5	–
0.7	15.9	16.1	–	17.5	16.0	–
0.75	14.0	–	–	–	–	–
0.8	13.0	–	–	14.9	–	–
0.85	12.5	–	–	–	–	–
0.9	11.5	–	–	13.0	–	–
0.95	11.0	–	–	–	–	–
0.96	–	–	–	11.5	–	–
1.0	10.0	–	–	–	–	–

predicted flash points for the above two systems for any salt concentration are equivalent at the same methanol composition using Crowl and Louvar's method [10] (also depicted in Fig. 6). It is apparent, however, that this method cannot describe the flash point variation where the composition range does not incorporate methanol at high concentrations, as the assumption

of ideality is not valid for methanol where its activity coefficient differs from unity (Fig. 7). An examination of Table 7 reveals that our model is markedly superior to Crowl and Louvar's method [10].

The flash points of organic-solvent mixtures, such as acetone + methanol, are increased remarkably by the addition of inorganic salt, such as NaI (Fig. 4). For an aqueous-organic solution, like methanol + water, however, the increment is not significant with addition of an inorganic salt, such as LiCl or NaBr (Fig. 6). This can be attributed to the slight difference in the activity coefficient of methanol when LiCl or NaBr is added to the aqueous-organic mixture (Fig. 7).

In summary, the prediction results for solvent/salt mixtures generated using the modified model appear to be in general agreement with the corresponding flash point measurements, including organic solvent/salt and aqueous-organic solvent/salt variants. Further, such a prediction model may provide a very acceptable means of providing valuable flash point information.

5. Conclusion

Crowl and Louvar's method [10] cannot describe the effect of dissolved salt on the flash point for organic solvents. Further, the values predicted by this method deviate substantially from the experimental measurement, even in the near-pure flammable range where the flash point for aqueous-organic solutions is described. By contrast, our modified model for flash point prediction of solvent/salt mixtures is able to generate these values over the entire flammable range, at least for organic solvent/salt

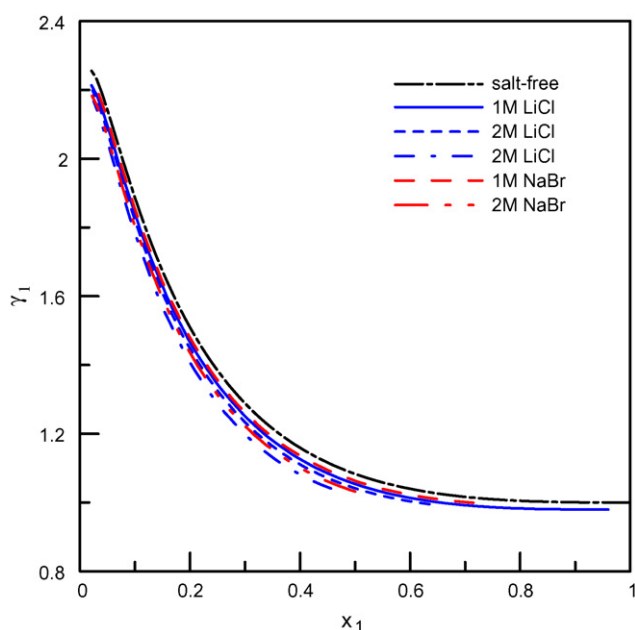


Fig. 7. Variation of the activity coefficient with composition for methanol (1) + water (w) with addition of LiCl/NaBr.

and aqueous–organic solvent/salt mixtures, as revealed by comparison of the predicted and experimental data. In comparison to water dilution, the addition of an inorganic salt markedly improves the efficiency of hazard reduction for a flammable liquid where it is almost pure. Thus, it appears reasonable to propose that this model is potentially applicable for hazard reduction in flammable liquids.

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