

# Binary mixtures exhibiting maximum flash-point behavior

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## Abstract

This study has demonstrated the existence of maximum flash-point solutions, where the maximum flash-point value is larger than those of the individual components. The behavior of such a solution has potential application in hazard reduction. The sufficient condition for a binary mixture to form such a maximum flash-point solution, and the equations to determine its composition and maximum flash point are proposed here, as these may be important in terms of hazard reduction. The sufficient condition and associated equations were verified by comparison with the experimental data. Our results reveal that this derived condition is satisfactory to establish that a liquid mixture is a maximum flash-point solution. The proposed equations may be successfully applied to estimate the composition and maximum flash-point value of such a mixture.

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## 1. Introduction

In Taiwan, essential oils have caused a number of explosions, with six blasts leaving eight people badly burnt from January through August of 2003. Essential oils are flammable liquid solutions, the fire and explosion hazards of which are primarily related to their flash point. In a given liquid, the flash point is the experimentally verified temperature at which the substance emits sufficient vapor to form a combustible mixture with air [1], with a lower flash-point value indicating relatively greater hazard [2]. The Shengli event in 2000 [3,4], which resulted from serious water pollution due to illegal dumping of waste organic solvents into the Kaoping River (Taiwan), subsequently led to the government requirement that large quantities of waste organic solutions must be stored temporarily at various factory sites or industrial park precincts. To ensure the safety of this storage, therefore, flash-point data for flammable liquid solutions is important.

We have demonstrated that the binary solution of ethanol and octane exhibits a minimum flash point (i.e., below the pure-component analogues) [3]. This special behavior is attributable to the fact that this particular mixture reflects a highly positive

deviation from that of an ideal solution, such that there is a substantial reduction in the flash point [3]. Mixtures exhibiting this behavior have been termed minimum flash-point solutions [5]. A minimum flash-point solution is more hazardous than the individual components of the combination because its flash point is lower, over a range of compositions, than the component values [3].

By contrast, if a binary mixture reflects a highly negative deviation from an ideal solution, it is suggested by us that such a mixture may exhibit maximum flash-point behavior. This temperature is higher than either of the component analogues. To our knowledge, however, the existence of such a solution had not previously been reported in any of the literature. This study has demonstrated such a mixture, termed a maximum flash-point solution, with composition at this maximum flash point, defined as the maximum flash-point composition. Since the flash point of a maximum flash-point solution, over a given composition range, is larger than the component analogues, this behavior also has potential application in hazard reduction, such as safe storage/transportation of a waste solution to be used as fuel.

To achieve the hazard reductions outlined above, establishing the formative condition for a maximum flash-point solution, in terms of maximum flash point value and composition, is important. Thus, it is necessary to determine this formative condition and the values of maximum flash point

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### Nomenclature

$A, B, C$	Antoine coefficients
$A_{ij}$	binary parameter
$E_M$	flammability index
$g$	binary parameters of NRTL equation (J/mol)
$G$	defined in Table 1
$l$	UNIQUAC parameter, defined in Table 1
MW	molecular weight (g/mol)
$P_i^{\text{sat}}$	saturated vapor pressure (kPa)
$P_{i,\text{fp}}^{\text{sat}}$	saturated vapor pressure of component $i$ at flash point (kPa)
$q_i$	measure of molecular surface areas
$r_i$	measure of molecular van der Waals volume
$R$	gas constant (8.314 J/mol)
$T$	temperature (K)
$T_{i,\text{fp}}$	flash-point temperature of pure component $i$ (K)
$u$	binary parameters of UNIQUAC equation (J/mol)
$v_i^l$	molar volume of liquid ( $\text{m}^3/\text{mol}$ )
$x$	mole fraction of species in liquid phase
$z$	coordination number

### Greek letters

$\Delta H_i^{\text{vap}}$	molar latent heat of vaporization (J/mol)
$\Delta V_i^{\text{vap}}$	volume change from liquid to gas ( $\text{m}^3/\text{mol}$ )
$\alpha_{ij}$	NRTL parameter
$\gamma$	activity coefficient
$\theta_i$	area fraction of component $i$
$\lambda$	binary parameters of Wilson equation (J/mol)
$\Lambda$	defined in Table 1
$\rho$	density ( $\text{g}/\text{cm}^3$ )
$\tau$	defined in Table 1
$\Phi_i$	segment fraction

### Subscripts

fp	flash point
$i$	species $i$
m	mixture
maxfp	maximum flash point

### Superscripts

$\infty$	at infinite dilution
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equation of White et al., was able to predict the flash point for a non-ideal solution [3]. In our previous study [3], a mathematical model for prediction of the flash point for binary liquid solutions was proposed, with predictive efficacy in relation to the experimental results verified for both ideal and non-ideal solutions.

The objective of this manuscript was to derive the requisite condition for formation of a maximum flash-point solution using a binary mixture, and to determine the maximum flash-point value and composition for this combination. The condition and equations must be based upon a mathematical formula for derivative of flash point with respect to composition for a binary mixture. Such a formula has been derived [5] from the flash point-prediction model proposed previously [3]. The derived condition and equations were subsequently verified by application of experimental data provided by closed-cup testing. cyclohexanol + phenol, cyclohexanone + phenol, *p*-picoline + phenol, phenol + acetophenone, cyclohexylamine + cyclohexanol, and propionic aldehyde + 2-butanone are all binary solutions that deviate negatively from an ideal solution [8,9]. Since it is suggested that negative deviation from ideality occurs with maximum flash-point solutions, these mixtures were selected to validate the proposed condition and equations.

## 2. Experimental details

A Flash Point Analyzer (HFP 362-Tag; Walter Herzog GmbH, Germany) was used to measure the flash points for a variety of mixtures (cyclohexanol + phenol, cyclohexanone + phenol, *p*-picoline + phenol, acetophenone + phenol, cyclohexylamine + cyclohexanol, and propionic aldehyde + 2-butanone) at different compositions. The Flash Point Analyzer incorporates control devices that program the instrument to heat the sample at a specified rate (heating rate) within a temperature range close to the expected flash point. The flash point is automatically tested using an igniter at specified temperature intervals (test interval). If the expected flash point is lower than or equal to the change temperature, which is set to 60 °C according to the standard ASTM D56 method [10], 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 first flash-point test takes place at a temperature equivalent to the expected flash point minus the start-test value. If the flash point is not determined when the test temperature exceeds the sum of the expected flash point plus the end-of-test value, the heater cuts out. The instrument operation is conducted according to the standard ASTM D56 test protocol [10], with the following set of selected parameters: start test 5 °C; end of test 20 °C; test interval-1 0.5 °C; and test interval-2 1.0 °C. The cyclohexanone and 2-butanone were verified using an ACS standard (Tedia Co. Inc., USA). Propionic aldehyde was also purchased from Tedia (USA). Cyclohexanol and acetophenone were obtained from Acros Organics (USA). Phenol was obtained from Showa Chemical Co., Ltd. (Japan), *p*-picoline from Lancaster (England), and cyclohexylamine from Fluka (Germany).

and composition for such a hazard-reduction stage. Since the maximum flash-point solution is non-ideal, the determination of such a condition and the estimation of the two values must be based on a flash point-prediction model which can cope with non-ideal solutions. Affens and McLaren [6] have developed a predictive model for the flash points of binary hydrocarbon mixtures based on Raoult's law. White et al. [7] have reduced this model to a simpler equation by ignoring any dependence of the lower flammable limit on temperature; they then used the derived equation to estimate the flash point of two aviation-fuel mixtures, JP-4/JP-8 and JP-5/JP-8. We have since demonstrated that neither the above model nor the

### 3. Mathematical formulation

#### 3.1. Sufficient condition for a binary mixture to form a maximum flash-point solution

In this paper, the individual solution component displaying the lower flash-point value for a binary mixture is denoted component 1. As mentioned in Section 1, the maximum flash-point value of such a maximum flash-point solution is higher than the analogous component values. When the flash point of a binary mixture is continuous with  $x_1$  in the close interval,  $0 \leq x_1 \leq 1$ , such a mixture is a maximum flash-point solution (curves A and B in Fig. 1) if the following relationships are true:

$$\left(\frac{\partial T}{\partial x_1}\right)_{E_M} \Big|_{x_1 \rightarrow 0} \geq 0 \tag{1}$$

$$\left(\frac{\partial T}{\partial x_1}\right)_{E_M} \Big|_{x_1 \rightarrow 1} < 0 \tag{2}$$

where  $(\partial T/\partial x_1)_{E_M}$  is the derivative of the flash point with respect to the composition of component 1 [5]. Since the flammability index,  $E_M$ , is equal to unity at the flash point of a liquid solution [6], the constraint for the derivative of the flash point respective to composition is  $E_M$  held constant [5]. The equality presented in Eq. (1) holds only for a mixture that is just able to exhibit maximum flash-point behavior (curve B in Fig. 1).

The formulae of  $(\partial T/\partial x_1)_{E_M}$  for a binary flammable mixture at the limits  $x_1 \rightarrow 0$  and  $x_1 \rightarrow 1$  based upon the previously proposed flash point-prediction model [3] have been derived

as [5]:

$$\left(\frac{\partial T}{\partial x_1}\right)_{E_M} \Big|_{x_1 \rightarrow 0} = -\frac{\gamma_1^\infty P_1^{\text{sat}}|_{T_{2,\text{fp}}} \frac{P_{2,\text{fp}}^{\text{sat}}}{P_{1,\text{fp}}^{\text{sat}}} - P_{2,\text{fp}}^{\text{sat}}}{\frac{dP_2^{\text{sat}}}{dT}} \tag{3}$$

$$\left(\frac{\partial T}{\partial x_1}\right)_{E_M} \Big|_{x_1 \rightarrow 1} = -\frac{P_{1,\text{fp}}^{\text{sat}} - \gamma_2^\infty P_2^{\text{sat}}|_{T_{1,\text{fp}}} \frac{P_{1,\text{fp}}^{\text{sat}}}{P_{2,\text{fp}}^{\text{sat}}}}{\frac{dP_1^{\text{sat}}}{dT}} \tag{4}$$

Substituting Eqs. (3) and (4) into Eqs. (1) and (2):

$$-\frac{\gamma_1^\infty P_1^{\text{sat}}|_{T_{2,\text{fp}}} \frac{P_{2,\text{fp}}^{\text{sat}}}{P_{1,\text{fp}}^{\text{sat}}} - P_{2,\text{fp}}^{\text{sat}}}{\frac{dP_2^{\text{sat}}}{dT}} \geq 0 \tag{5}$$

and

$$-\frac{P_{1,\text{fp}}^{\text{sat}} - \gamma_2^\infty P_2^{\text{sat}}|_{T_{1,\text{fp}}} \frac{P_{1,\text{fp}}^{\text{sat}}}{P_{2,\text{fp}}^{\text{sat}}}}{\frac{dP_1^{\text{sat}}}{dT}} < 0 \tag{6}$$

The Clapeyron equation for liquid vaporization is described as

$$\frac{dP_i^{\text{sat}}}{dT} = \frac{\Delta H_i^{\text{vap}}}{T \Delta V_i^{\text{vap}}} \tag{7}$$

As the values for heat of vaporization,  $\Delta H_i^{\text{vap}}$ , volume change from liquid to gas,  $\Delta V_i^{\text{vap}}$ , for any liquid substance, and absolute temperature,  $T$ , are all greater than zero, the rate of change of the saturation vapor pressure with increased temperature for any pure liquid substance should be greater than zero, i.e.:

$$\frac{dP_i^{\text{sat}}}{dT} > 0 \tag{8}$$

Therefore, Eqs. (5) and (6) can be reduced to

$$\frac{\gamma_1^\infty P_1^{\text{sat}}|_{T_{2,\text{fp}}}}{P_{1,\text{fp}}^{\text{sat}}} \leq 1 \tag{9}$$

$$\frac{\gamma_2^\infty P_2^{\text{sat}}|_{T_{1,\text{fp}}}}{P_{2,\text{fp}}^{\text{sat}}} < 1 \tag{10}$$

Thus, Eqs. (9) and (10) establish the sufficient condition for a liquid to become a maximum flash-point solution and, if the equality presented in Eq. (9) holds, it represents the critical condition for a mixture at the threshold of formation of a maximum flash-point solution.

#### 3.2. Necessary condition for a binary mixture to not exhibit maximum or minimum flash-point behavior

The flash point versus composition ( $x_1$ ) curve for a binary mixture not exhibiting maximum/minimum flash-point behavior (Fig. 1 curve C) is a decreasing function on  $[0,1]$  when the solution component with the lower flash-point value is denoted as component 1. The necessary condition for such a decreasing

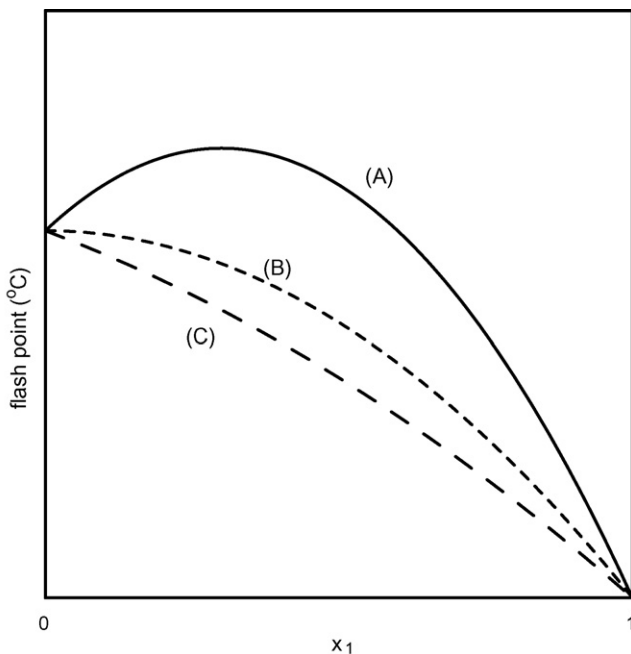


Fig. 1. Variation of flash point with composition for different mixture types. (A) Maximum flash-point solution; (B) mixture just exhibiting maximum flash-point behavior; (C) mixture exhibiting neither maximum nor minimum flash-point behavior.

function is

$$\left(\frac{\partial T}{\partial x_1}\right)_{EM} \Big|_{x_1 \rightarrow 0} < 0 \quad (11)$$

$$\left(\frac{\partial T}{\partial x_1}\right)_{EM} \Big|_{x_1 \rightarrow 1} < 0 \quad (12)$$

Substituting Eqs. (3) and (4) into the above formulations, and subsequently applying Eq. (8) into the derived equations

results in

$$\frac{\gamma_1^\infty P_1^{\text{sat}}|_{T_{2,\text{fp}}}}{P_{1,\text{fp}}^{\text{sat}}} > 1 \quad (13)$$

$$\frac{\gamma_2^\infty P_2^{\text{sat}}|_{T_{1,\text{fp}}}}{P_{2,\text{fp}}^{\text{sat}}} < 1 \quad (14)$$

Eqs. (13) and (14) describe the necessary condition for a liquid solution to not become a maximum/minimum flash-point solution.

Table 1  
Models of activity coefficients and their composition effect in binary systems

Wilson equation

$$\begin{aligned} \ln \gamma_1 \text{ and } \ln \gamma_2 & \quad \ln \gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2 \left( \frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2} \right), \quad \ln \gamma_2 = -\ln(x_2 + \Lambda_{21}x_1) - x_1 \left( \frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2} \right), \\ & \quad \text{where } \Lambda_{12} = \frac{v_2^1}{v_1^1} \exp\left(-\frac{\lambda_{12} - \lambda_{11}}{RT}\right), \quad \Lambda_{21} = \frac{v_1^1}{v_2^1} \exp\left(-\frac{\lambda_{21} - \lambda_{22}}{RT}\right) \\ \left(\frac{\partial \gamma_1}{\partial x_1}\right)_T \text{ and } \left(\frac{\partial \gamma_2}{\partial x_1}\right)_T & \quad \left(\frac{\partial \gamma_1}{\partial x_1}\right)_T = \gamma_1 \left\{ -\frac{1 - \Lambda_{12}}{x_1 - \Lambda_{12}x_2} - \left( \frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2} \right) + x_2 \left[ -\frac{\Lambda_{12}}{(x_1 + \Lambda_{12}x_2)^2} (1 - \Lambda_{12}) + \frac{\Lambda_{21}}{(\Lambda_{21}x_1 + x_2)^2} (\Lambda_{21} - 1) \right] \right\}, \\ & \quad \left(\frac{\partial \gamma_2}{\partial x_1}\right)_T = \gamma_2 \left\{ \frac{1 - \Lambda_{21}}{x_2 + \Lambda_{21}x_1} - \left( \frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2} \right) + x_1 \left[ \frac{\Lambda_{12}}{(x_1 + \Lambda_{12}x_2)^2} (1 - \Lambda_{12}) - \frac{\Lambda_{21}}{(\Lambda_{21}x_1 + x_2)^2} (\Lambda_{21} - 1) \right] \right\} \\ \gamma_1^\infty \text{ and } \gamma_2^\infty & \quad \gamma_1^\infty = \frac{1}{\Lambda_{12}} \exp(1 - \Lambda_{21}), \quad \gamma_2^\infty = \frac{1}{\Lambda_{21}} \exp(1 - \Lambda_{12}) \end{aligned}$$

NRTL equation

$$\begin{aligned} \ln \gamma_1 \text{ and } \ln \gamma_2 & \quad \ln \gamma_1 = x_2^2 \left[ \tau_{21} \left( \frac{G_{21}}{x_1 + x_2 G_{21}} \right)^2 + \frac{\tau_{12} G_{12}}{(x_2 + x_1 G_{12})^2} \right], \quad \ln \gamma_2 = x_1^2 \left[ \tau_{12} \left( \frac{G_{12}}{x_2 + x_1 G_{12}} \right)^2 + \frac{\tau_{21} G_{21}}{(x_1 + x_2 G_{21})^2} \right], \\ & \quad \text{where } \tau_{12} = \frac{g_{12} - g_{22}}{RT}, \quad \tau_{21} = \frac{g_{21} - g_{11}}{RT}, \quad \ln G_{12} = -\alpha_{12} \tau_{12}, \quad \ln G_{21} = -\alpha_{12} \tau_{21} \\ \left(\frac{\partial \gamma_1}{\partial x_1}\right)_T \text{ and } \left(\frac{\partial \gamma_2}{\partial x_1}\right)_T & \quad \left(\frac{\partial \gamma_1}{\partial x_1}\right)_T = \gamma_1 \left\{ -2x_2 \left[ \tau_{21} \left( \frac{G_{21}}{x_1 + x_2 G_{21}} \right)^2 + \frac{\tau_{12} G_{12}}{(x_2 + x_1 G_{12})^2} \right] + x_2^2 \left[ -2\tau_{21} \frac{G_{21}^2}{(x_1 + x_2 G_{21})^3} (1 - G_{21}) + \frac{2\tau_{12} G_{12}}{(x_2 + x_1 G_{12})^3} (1 - G_{12}) \right] \right\} \\ & \quad \left(\frac{\partial \gamma_2}{\partial x_1}\right)_T = \gamma_2 \left\{ 2x_1 \left[ \tau_{12} \left( \frac{G_{12}}{x_2 + x_1 G_{12}} \right)^2 + \frac{\tau_{21} G_{21}}{(x_1 + x_2 G_{21})^2} \right] + x_1^2 \left[ 2\tau_{12} \frac{G_{12}^2}{(x_2 + x_1 G_{12})^3} (1 - G_{12}) - \frac{2\tau_{21} G_{21}}{(x_1 + x_2 G_{21})^3} (1 - G_{21}) \right] \right\} \\ \gamma_1^\infty \text{ and } \gamma_2^\infty & \quad \gamma_1^\infty = \exp(\tau_{21} + \tau_{12} G_{12}), \quad \gamma_2^\infty = \exp(\tau_{12} + \tau_{21} G_{21}) \end{aligned}$$

UNIQUAC equation

$$\begin{aligned} \ln \gamma_1 \text{ and } \ln \gamma_2 & \quad \ln \gamma_1 = \ln \frac{\Phi_1}{x_1} + \frac{z}{2} q_1 \ln \frac{\theta_1}{\Phi_1} + \Phi_2 \left( l_1 - \frac{r_1}{r_2} l_2 \right) - q_1 \ln(\theta_1 + \theta_2 \tau_{21}) + \theta_2 q_1 \left( \frac{\tau_{21}}{\theta_1 + \theta_2 \tau_{21}} - \frac{\tau_{12}}{\theta_2 + \theta_1 \tau_{12}} \right), \\ & \quad \ln \gamma_2 = \ln \frac{\Phi_2}{x_2} + \frac{z}{2} q_2 \ln \frac{\theta_2}{\Phi_2} + \Phi_1 \left( l_2 - \frac{r_2}{r_1} l_1 \right) - q_2 \ln(\theta_2 + \theta_1 \tau_{12}) + \theta_1 q_2 \left( \frac{\tau_{12}}{\theta_2 + \theta_1 \tau_{12}} - \frac{\tau_{21}}{\theta_1 + \theta_2 \tau_{21}} \right), \\ & \quad \text{where } \ln \tau_{12} = -\frac{u_{12} - u_{22}}{RT}, \quad \ln \tau_{21} = -\frac{u_{21} - u_{11}}{RT}, \quad \Phi_1 = \frac{x_1 r_1}{x_1 r_1 + x_2 r_2}, \quad \Phi_2 = \frac{x_2 r_2}{x_1 r_1 + x_2 r_2}, \quad \theta_1 = \frac{x_1 q_1}{x_1 q_1 + x_2 q_2}, \\ & \quad \theta_2 = \frac{x_2 q_2}{x_1 q_1 + x_2 q_2}, \quad l_1 = \frac{z}{2} (r_1 - q_1) - (r_1 - 1), \quad l_2 = \frac{z}{2} (r_2 - q_2) - (r_2 - 1), \quad z = 10 \\ \left(\frac{\partial \gamma_1}{\partial x_1}\right)_T \text{ and } \left(\frac{\partial \gamma_2}{\partial x_1}\right)_T & \quad \left(\frac{\partial \gamma_1}{\partial x_1}\right)_T = \gamma_1 \left\{ \frac{1}{\Phi_1} \frac{d\Phi_1}{dx_1} - \frac{1}{x_1} + \frac{z}{2} q_1 \left( \frac{1}{\theta_1} \frac{d\theta_1}{dx_1} - \frac{1}{\Phi_1} \frac{d\Phi_1}{dx_1} \right) + \left( l_1 - \frac{r_1}{r_2} l_2 \right) \frac{d\Phi_2}{dx_1} - \frac{q_1}{\theta_1 + \theta_2 \tau_{21}} \left( \frac{d\theta_1}{dx_1} + \tau_{21} \frac{d\theta_2}{dx_1} \right) \right. \\ & \quad \left. + q_1 \frac{d\theta_2}{dx_1} \left( \frac{\tau_{21}}{\theta_1 + \theta_2 \tau_{21}} - \frac{\tau_{12}}{\theta_2 + \theta_1 \tau_{12}} \right) + \theta_2 q_1 \left[ \frac{\tau_{12}}{(\theta_2 + \theta_1 \tau_{12})^2} \left( \frac{d\theta_2}{dx_1} + \tau_{12} \frac{d\theta_1}{dx_1} \right) - \frac{\tau_{21}}{(\theta_1 + \theta_2 \tau_{21})^2} \left( \frac{d\theta_1}{dx_1} + \tau_{21} \frac{d\theta_2}{dx_1} \right) \right] \right\}, \\ & \quad \left(\frac{\partial \gamma_2}{\partial x_1}\right)_T = \gamma_2 \left\{ \frac{1}{\Phi_2} \frac{d\Phi_2}{dx_1} + \frac{1}{x_2} + \frac{z}{2} q_2 \left( \frac{1}{\theta_2} \frac{d\theta_2}{dx_1} - \frac{1}{\Phi_2} \frac{d\Phi_2}{dx_1} \right) + \left( l_2 - \frac{r_2}{r_1} l_1 \right) \frac{d\Phi_1}{dx_1} - \frac{q_2}{\theta_2 + \theta_1 \tau_{12}} \left( \frac{d\theta_2}{dx_1} + \tau_{12} \frac{d\theta_1}{dx_1} \right) \right. \\ & \quad \left. + q_2 \frac{d\theta_1}{dx_1} \left( \frac{\tau_{12}}{\theta_2 + \theta_1 \tau_{12}} - \frac{\tau_{21}}{\theta_1 + \theta_2 \tau_{21}} \right) + \theta_1 q_2 \left[ \frac{\tau_{21}}{(\theta_1 + \theta_2 \tau_{21})^2} \left( \frac{d\theta_1}{dx_1} + \tau_{21} \frac{d\theta_2}{dx_1} \right) - \frac{\tau_{12}}{(\theta_2 + \theta_1 \tau_{12})^2} \left( \frac{d\theta_2}{dx_1} + \tau_{12} \frac{d\theta_1}{dx_1} \right) \right] \right\}, \\ & \quad \text{where } \frac{d\Phi_1}{dx_1} = \frac{r_1 r_2}{(x_1 r_1 + x_2 r_2)^2}, \quad \frac{d\Phi_2}{dx_1} = -\frac{r_1 r_2}{(x_1 r_1 + x_2 r_2)^2}, \quad \frac{d\theta_1}{dx_1} = \frac{q_1 q_2}{(x_1 q_1 + x_2 q_2)^2}, \quad \frac{d\theta_2}{dx_1} = -\frac{q_1 q_2}{(x_1 q_1 + x_2 q_2)^2} \\ \gamma_1^\infty \text{ and } \gamma_2^\infty & \quad \ln \gamma_1^\infty = \ln \frac{r_1}{r_2} + \frac{z}{2} q_1 \ln \frac{r_2 q_1}{r_1 q_2} + \left( l_1 - \frac{r_1}{r_2} l_2 \right) - q_1 \ln \tau_{21} + q_1 (1 - \tau_{12}), \quad \ln \gamma_2^\infty = \ln \frac{r_2}{r_1} + \frac{z}{2} q_2 \ln \frac{r_1 q_2}{r_2 q_1} + \left( l_2 - \frac{r_2}{r_1} l_1 \right) \\ & \quad - q_2 \ln \tau_{12} + q_2 (1 - \tau_{21}) \end{aligned}$$

### 3.3. Maximum flash-point composition and maximum flash point

When the flash point of a maximum flash-point solution is at its highest, the derivative value of the flash point with respect to composition is equal to zero, i.e.:

$$\left(\frac{\partial T}{\partial x_1}\right)_{E_M} = 0 \quad (15)$$

The formula for such a binary-mixture derivative has been adopted from previous study [5]:

$$\left(\frac{\partial T}{\partial x_1}\right)_{E_M} = -\frac{\frac{P_1^{\text{sat}}}{P_{1,\text{fp}}^{\text{sat}}} \left[ \gamma_1 + x_1 \left(\frac{\partial \gamma_1}{\partial x_1}\right)_T \right] + \frac{P_2^{\text{sat}}}{P_{2,\text{fp}}^{\text{sat}}} \left[ -\gamma_2 + x_2 \left(\frac{\partial \gamma_2}{\partial x_1}\right)_T \right]}{\frac{x_1}{P_{1,\text{fp}}^{\text{sat}}} \left[ \gamma_1 \frac{dP_1^{\text{sat}}}{dT} + P_1^{\text{sat}} \left(\frac{\partial \gamma_1}{\partial T}\right)_{x_1} \right] + \frac{x_2}{P_{2,\text{fp}}^{\text{sat}}} \left[ \gamma_2 \frac{dP_2^{\text{sat}}}{dT} + P_2^{\text{sat}} \left(\frac{\partial \gamma_2}{\partial T}\right)_{x_1} \right]} \quad (16)$$

Substituting Eq. (16) into Eq. (15):

$$\frac{P_1^{\text{sat}}}{P_{1,\text{fp}}^{\text{sat}}} \left[ \gamma_1 + x_1 \left(\frac{\partial \gamma_1}{\partial x_1}\right)_T \right] + \frac{P_2^{\text{sat}}}{P_{2,\text{fp}}^{\text{sat}}} \left[ -\gamma_2 + x_2 \left(\frac{\partial \gamma_2}{\partial x_1}\right)_T \right] = 0 \quad (17)$$

where the activity coefficients  $\gamma_i$  ( $i = 1, 2$ ) can be estimated by the use of several equations, such as the Wilson [11], NRTL [12] or UNIQUAC equation [13] (all listed in Table 1; formulae of  $(\partial \gamma_i / \partial x_1)_T$  for these three equations also depicted). The saturated vapor pressure for a pure substance,  $i$ , can be estimated by use of the Antoine equation:

$$\ln P_i^{\text{sat}} = A_i - \frac{B_i}{T + C_i} \quad (18)$$

The vapor pressure of the pure substance,  $i$ , at its flash point,  $P_{i,\text{fp}}^{\text{sat}}$  (as presented in Eq. (17)), can be estimated by substituting  $T_{i,\text{fp}}$ , the flash point for component  $i$ , into the Antoine equation.

In addition to Eq. (17), the modified Le Chatelier equation for a binary mixture (as derived previously [3]) must be satisfied at the flash point of a mixture, and has been described thus:

$$1 = \frac{x_1 \gamma_1 P_1^{\text{sat}}}{P_{1,\text{fp}}^{\text{sat}}} + \frac{x_2 \gamma_2 P_2^{\text{sat}}}{P_{2,\text{fp}}^{\text{sat}}} \quad (19)$$

Summarizing the results, the maximum flash-point composition and maximum flash-point value can be provided by solution of Eqs. (17)–(19) together with those listed in Table 1.

## 4. Result and discussion

### 4.1. Parameters used in this manuscript

The conditions proposed in this study were applied to confirm whether a mixture is a maximum flash-point solution; the derived equations were used to estimate the maximum flash-point composition and the maximum flash point value for such a solution. The results thus obtained were compared with the experimental data for the following systems: cyclohexanol + phenol, cyclohexanone + phenol, *p*-picoline + phenol, phenol + acetophenone, cyclohexylamine + cyclohexanol and propionic aldehyde + 2-butanone, and our previous data [3,5,14].

The mixtures outlined above all deviate negatively from the ideal solution [8,9], with the activity coefficients of the solution components estimated using three equations (Table 1) and parameters adopted from the literature [8,9] (Table 2). These estimated activity coefficients were subsequently used in the proposed conditions and equations. The parameters for 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 [15,16]) are listed in Table 3, along with the specific volumes necessary for the Wilson equation. The Antoine coefficients were also sourced from the literature [8,15] (Table 4).

The flash points for the pure substances used in this study were measured using the Flash Point Analyzer, with these values compared with the literature-derived analogues (Table 5). There are between-source differences in the flash-point data for cyclohexanone, acetophenone and 2-butanone, however. Our experimental flash points for cyclohexanone, propionic aldehyde and 2-butanone are identical to the values provided by the supplier Tedia (USA), with the last measurement also

Table 2

Parameters of NRTL, Wilson and UNIQUAC equations for the experimental binary systems

System	Parameters <sup>a</sup>			Reference
	$A_{12}$	$A_{21}$	$\alpha_{12}$	
Cyclohexanol (1) + phenol (2)				
NRTL equation	−233.08	−199.76	0.3080	[8]
Wilson	−140.69	−273.84	−	[8]
UNIQUAC	19.88	−157.74	−	[8]
Cyclohexanone (1) + phenol (2)				
NRTL equation	−515.08	−315.47	0.0159	[8]
Wilson	−421.89	−266.69	−	[8]
UNIQUAC	−67.00	−188.58	−	[8]
<i>p</i> -Picoline (1) + phenol (2)				
NRTL equation	−1596.50	253.47	0.0706	[8]
Wilson	−608.19	−597.91	−	[8]
UNIQUAC	−364.18	−136.28	−	[8]
Phenol (1) + acetophenone (2)				
NRTL equation	140.30	−500.51	0.3051	[8]
Wilson	−224.52	−156.07	−	[8]
Cyclohexylamine (1) + cyclohexanol (2)				
NRTL equation	−29.484	−149.40	0.3033	[8]
Wilson	−164.86	−11.81	−	[8]
UNIQUAC	24.64	−73.48	−	[8]
Propionic aldehyde (1) + 2-butanone (2)				
NRTL equation	293.22	−317.73	0.3	[9]
Wilson	−218.77	238.27	−	[9]
UNIQUAC	200.43	−184.80	−	[9]

<sup>a</sup> NRTL:  $A_{12} = (g_{12} - g_{22})/R$ ,  $A_{21} = (g_{21} - g_{11})/R$ ; Wilson:  $A_{12} = (\lambda_{12} - \lambda_{11})/R$ ,  $A_{21} = (\lambda_{21} - \lambda_{22})/R$ ; UNIQUAC:  $A_{12} = (u_{12} - u_{22})/R$ ,  $A_{21} = (u_{21} - u_{11})/R$ .



Table 3  
The relative van der Waals volumes ( $r$ ) and surface areas ( $q$ ) for the pure components in the UNIQUAC model, and the specific volumes ( $v_i^l$ ) for the pure components in the Wilson model

Component	$v_i^l$ (cm <sup>3</sup> mol <sup>-1</sup> ) <sup>a</sup>	MW [17]	$\rho$ (g cm <sup>-3</sup> ) [17]	$r$	$q$
Phenol	87.87	94.11	1.071	3.5517 [15]	2.680 [15]
Cyclohexanone	104.17	98.14	0.9421	4.1433 [15]	3.340 [15]
Cyclohexanol	104.12	100.16	0.962	4.3489 [15]	3.512 [15]
Cyclohexylamine	114.70	99.18	0.8647	4.5137 [16]	3.624 [16]
Acetophenone	116.31	120.15	1.033	–	–
<i>p</i> -Picoline	–44.15	93.13	0.9571	3.7343 [16]	2.681 [16]
Propionic aldehyde	68.88	58.08	0.8432	2.5735 [15]	2.336 [15]
2-Butanone	89.58	72.11	0.805	3.2479 [15]	2.876 [15]

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

Table 4  
Antoine coefficients

Material	A	B	C	Reference
Phenol <sup>a</sup>	16.4279	3490.89	–98.59	[15]
Cyclohexanone <sup>b</sup>	7.47050	1832.2	–28.8	[8]
Cyclohexanol <sup>b</sup>	8.35237	2258.560	–21.376	[8]
Cyclohexylamine <sup>b</sup>	6.68954	1229.418	–84.198	[8]
Acetophenone <sup>b</sup>	6.93051	1382.65	–113.507	[8]
<i>p</i> -Picoline <sup>a</sup>	16.2143	3409.40	–62.65	[15]
Propionic aldehyde <sup>a</sup>	16.2315	2659.02	–44.15	[15]
2-Butanone <sup>a</sup>	16.5986	3150.42	–36.65	[15]

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

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

identical to that reported in Merck [17]. There appear to be slight, but acceptable, deviations between our measurements and the published flash points for phenol, cyclohexanol, *p*-picoline and cyclohexylamine. Our measurement for acetophenone is close to the value reported by Oxford University [18], although it is different from that adopted from Merck [17]. The standard test method is not mentioned in the Merck index [17] and SFPE handbook [19]. The latter resource suggests that the result of flash-point measurement depends upon the apparatus employed. Variations in flash-point values comparing this study and the literature, therefore, may be attributable to existing differences in the standard test method.

Table 5  
Comparison of flash-point values from literature with experimental data for the studied solution components

Component	Experimental data (°C)	Literature (°C)
Phenol	81	79 [17]
Cyclohexanol	68.5	68 [17, 19]
Cyclohexanone	46	46 <sup>a</sup> , 63 [17]
<i>p</i> -Picoline	42.5	40 [22]
Acetophenone	83.5	82 [18], 105 [17]
Cyclohexylamine	28	27 <sup>b</sup>
Propionic aldehyde	–26	–26 <sup>a</sup>
2-Butanone	–6	–6 <sup>a</sup> [17], –2 [19]

<sup>a</sup> Provided by Tedia (USA).

<sup>b</sup> Provided by Fluka (Germany).

#### 4.2. Maximum flash-point solutions

As depicted in Fig. 2, the flash points of phenol and cyclohexanol are 81 and 68.5 °C, respectively, however, the corresponding value for their combination may be as high as 82.5 °C, i.e., this binary mixture is a maximum flash-point solution. It is apparent that the flash point of a liquid is not necessarily decreased by addition of a low-flash-point substance to a relative high-flash-point liquid, the addition of cyclohexanol to phenol being an example of this.

In addition to cyclohexanol + phenol, our study measurements indicate that cyclohexanone + phenol, *p*-picoline + phenol and phenol + acetophenone systems are all maximum flash-point solutions, the corresponding experimental data being depicted in Figs. 3–5. These data and those for cyclohexanol + phenol were plotted against the predictive curves based on an ideal-solution assumption. It is apparent that the predictions cannot describe the maximum flash-point behavior of the mixtures referred to above, however, and they are typically lower than the measurements.

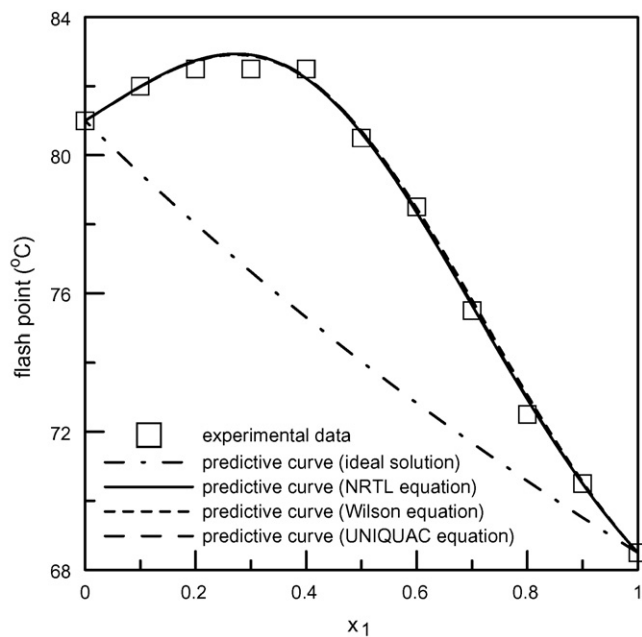


Fig. 2. Variation of flash point with composition for cyclohexanol (1) + phenol (2).

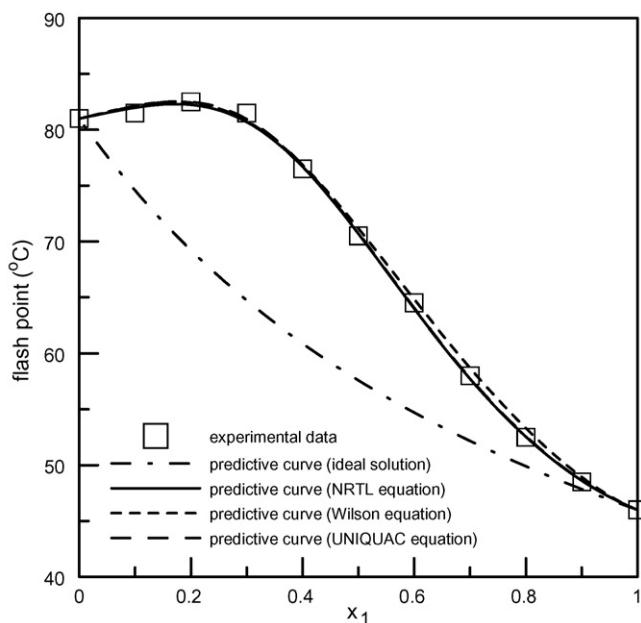


Fig. 3. Variation of flash point with composition for cyclohexanone (1) + phenol (2).

This phenomenon is attributable to the highly negative deviation from the behavior of an ideal solution [8], for which the activity coefficients are much less than unity (Fig. 6). The vapor pressure of a mixture demonstrating a negative deviation from ideality is lower than that predicted from assumption of ideality, such that the flash point will be higher than the predictive equivalent for the latter. The predictive curves derived using the flash point-prediction model proposed previously [3] are also displayed in Figs. 2–5. It can be clearly seen that these experimental results are in excellent agreement with the predictive curves, which use the NRTL, Wilson or UNIQUAC equations to estimate activity

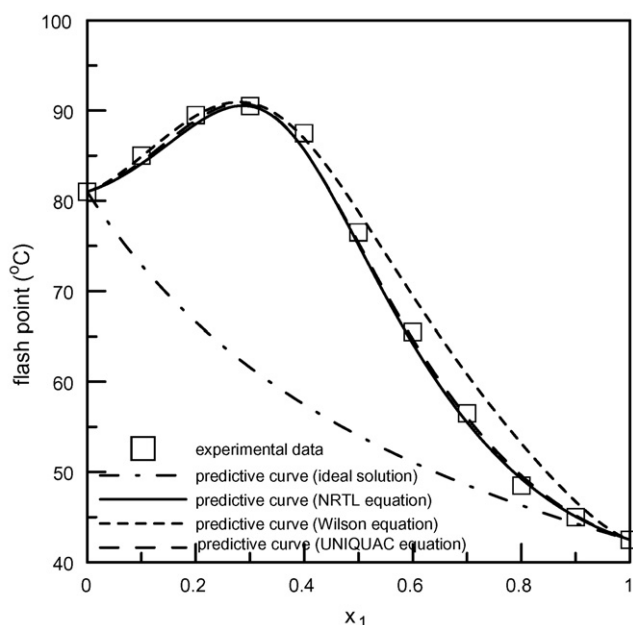


Fig. 4. Variation of flash point with composition for *p*-picoline (1) + phenol (2).

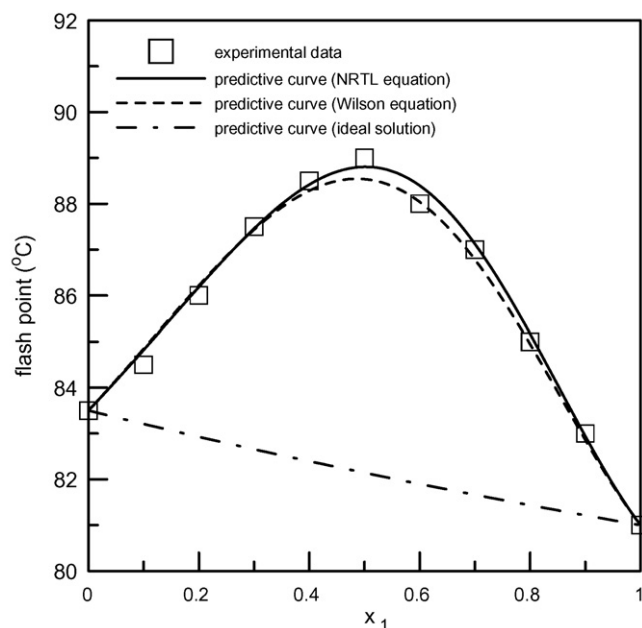


Fig. 5. Variation of flash point with composition for phenol (1) + acetophenone (2).

coefficients. The plot for *p*-picoline + phenol based on the Wilson equation is the sole exception, with the resultant prediction describing the measurements much more satisfactorily than that based on assumption of an ideal solution.

By contrast, the other mixtures reflecting negative deviation from ideality (cyclohexylamine + cyclohexanol and propionic aldehyde + 2-butanone; activity coefficients given in Fig. 6) do not exhibit maximum flash-point behaviors. The composition with maximum value of the flash point for these two

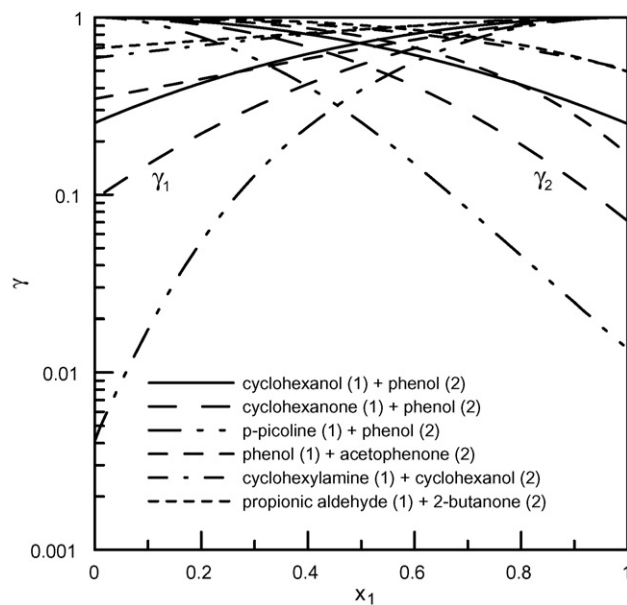


Fig. 6. Activity coefficient-liquid composition diagram for cyclohexanol (1) + phenol (2), cyclohexanone (1) + phenol (2), *p*-picoline (1) + phenol (2), phenol (1) + acetophenone (2), cyclohexylamine (1) + cyclohexanol (2) and propionic aldehyde (1) + 2-butanone (2) solutions at flash point.

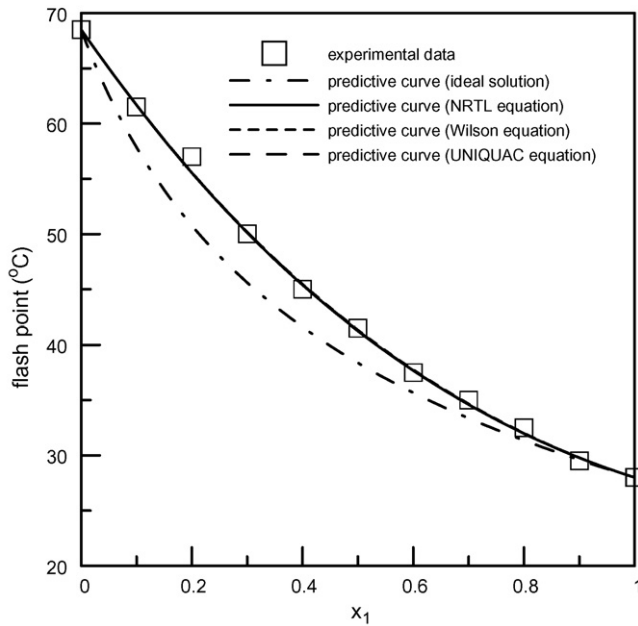


Fig. 7. Variation of flash point with composition for cyclohexylamine (1) + cyclohexanol (2).

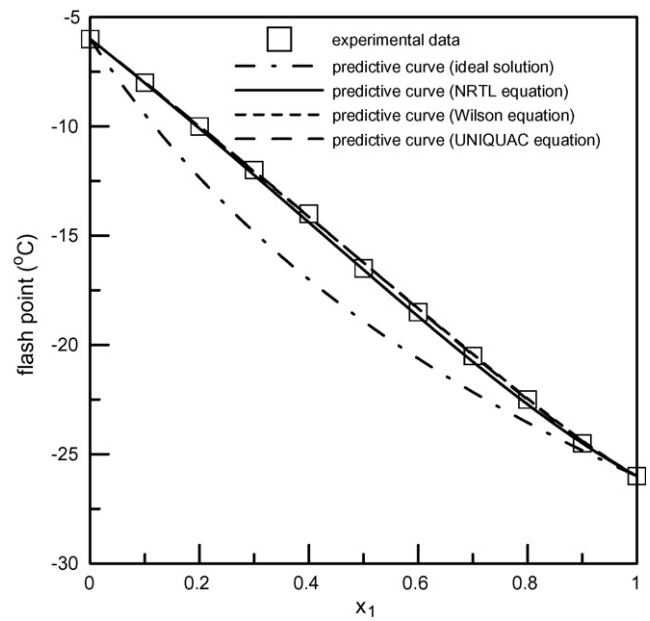


Fig. 8. Variation of flash point with composition for propionic aldehyde (1) + 2-butanone (2).

mixtures located at the solution component with a higher flash-point value, cyclohexanol and 2-butanone, respectively (see Figs. 7 and 8). Clearly, not all mixtures negatively deviating from the ideal are maximum flash-point solutions.

The predictive results for ideal solutions indicate that the mixture of *p*-picoline + phenol will be flammable, as the flash-point value is less than 60.5 °C [20] when the mole fraction of *p*-picoline is larger than 0.3 (Fig. 4). Thus, transportation of such a mixture should conform to the relevant code (such as DOT) [21]. However, the experimental measurements demonstrate that this mixture is even safer than phenol, the solution component with a higher flash-point value (at  $x_1 = 0.3$ ) with the flash-point value for the former higher than for the latter (90.5 and 81 °C, respectively). The experimental results indicate that more stringent transportation requirements for such a mixture are only necessary where the mole fraction of *p*-picoline is above 0.65, where the flash point is less than 60.5 °C. This

phenomenon, due to the behavior characteristic of maximum flash-point solutions, has also been observed in a cyclohexanone + phenol solution, and has potential application in hazard reduction.

#### 4.3. Condition for formation of a maximum flash-point solution

Both values of  $\gamma_1^\infty P_1^{\text{sat}}|_{T_{2,\text{fp}}}/P_{1,\text{fp}}^{\text{sat}}$  and  $\gamma_2^\infty P_2^{\text{sat}}|_{T_{1,\text{fp}}}/P_{2,\text{fp}}^{\text{sat}}$  for the binary mixtures, cyclohexanol + phenol, cyclohexanone + phenol, *p*-picoline + phenol and phenol + acetophenone, are less than unity even if a different equation is used to estimate the activity coefficients (Table 6). These values all satisfy the relationships of Eqs. (9) and (10) and, thus, it was deduced that these are all maximum flash-point solutions. The experimental data sets for the above-mentioned mixtures (Figs. 2–5) all verify this deduction.

Table 6  
Comparison of  $\gamma_i^\infty P_i^{\text{sat}}|_{T_{j,\text{fp}}}/P_{i,\text{fp}}^{\text{sat}}$  for different binary solutions

System	$\gamma_1^\infty P_1^{\text{sat}} _{T_{2,\text{fp}}}/P_{1,\text{fp}}^{\text{sat}}$			$\gamma_2^\infty P_2^{\text{sat}} _{T_{1,\text{fp}}}/P_{2,\text{fp}}^{\text{sat}}$			Remark <sup>a</sup>
	NRTL	Wilson	UNIQUAC	NRTL	Wilson	UNIQUAC	
Cyclohexanol (1) + phenol (2)	0.4676	0.4693	0.4747	0.1242	0.1146	0.1214	MaxFPS
Cyclohexanone (1) + phenol (2)	0.4519	0.3771	0.4005	0.0081	0.0048	0.0075	MaxFPS
<i>p</i> -Picoline (1) + phenol (2)	0.0247	0.0080	0.0174	0.0012	0.0001	0.0010	MaxFPS
Phenol (1) + acetophenone (2)	0.3760	0.3664	–	0.1569	0.1776	–	MaxFPS
Cyclohexylamine (1) + cyclohexanol (2)	4.6141	4.6131	4.6060	0.0484	0.0469	0.0480	NMaxMin
Propionic aldehyde (1) + 2-butanone (2)	2.1736	2.1799	2.1626	0.1346	0.1079	0.1116	NMaxMin
Acetone (1) + methanol (2) [21]	10.1812	9.4893	9.9044	0.3064	0.3328	0.3194	NMaxMin
Acetone (1) + ethanol (2) [21]	11.8651	11.8809	11.9879	0.1747	0.1879	0.1797	NMaxMin
Heptane (1) + octane (2) [5]	3.3936	–	–	0.2531	–	–	NMaxMin
Methyl acetate (1) + methanol (2) [5]	10.3232	–	–	0.6625	–	–	NMaxMin
Methyl acetate (1) + methyl acrylate (2) [5]	2.1014	–	–	0.4356	–	–	NMaxMin

<sup>a</sup> MaxFPS: maximum flash-point solution; NMaxMin: solution exhibiting neither maximum or minimum flash-point behavior.



Table 7

Comparison of estimated values for maximum flash-point composition,  $x_{\max\text{fp}}$ , and maximum flash point,  $T_{\max\text{fp}}$ , with corresponding experimental data

System	Estimated value						Experimental data	
	NRTL		Wilson		UNIQUAC		$x_{\max\text{fp}}$	$T_{\max\text{fp}}$ (°C)
	$x_{\max\text{fp}}$	$T_{\max\text{fp}}$ (°C)	$x_{\max\text{fp}}$	$T_{\max\text{fp}}$ (°C)	$x_{\max\text{fp}}$	$T_{\max\text{fp}}$ (°C)		
Cyclohexanol (1) + phenol (2)	0.27	82.94	0.27	82.91	0.28	82.93	0.3	82.5
Cyclohexanone (1) + phenol (2)	0.17	82.30	0.17	82.51	0.18	82.53	0.2	82.5
<i>p</i> -Picoline (1) + phenol (2)	0.29	90.5	0.28	90.95	0.28	90.78	0.3	90.5
Phenol (1) + acetophenone (2)	0.51	88.80	0.49	88.55	–	–	0.5	89.0

In our previous investigations, we demonstrated that the flash point versus composition curves for the mixtures, acetone (1) + methanol (2), acetone (1) + ethanol (2), heptane (1) + octane (2), methyl acetate (1) + methanol (2), and methyl acetate (1) + methyl acrylate (2), all reflect a declining curve with  $x_1$  [3,5,14]. That is, none of these binary mixtures are maximum or minimum flash-point solutions. In this study, the experimental data corresponding to cyclohexylamine + cyclohexanol and propionic aldehyde + 2-butanone systems shows that neither are maximum/minimum flash-point solutions (Figs. 7 and 8). It may, thus, be deduced that the value of  $\gamma_1^\infty P_1^{\text{sat}}|_{T_{2,\text{fp}}}/P_{1,\text{fp}}^{\text{sat}}$  is greater than unity and that of  $\gamma_2^\infty P_2^{\text{sat}}|_{T_{1,\text{fp}}}/P_{2,\text{fp}}^{\text{sat}}$  less than unity, based upon the relationships referred to in Eqs. (13) and (14), for these seven mixtures. The estimated values of  $\gamma_1^\infty P_1^{\text{sat}}|_{T_{2,\text{fp}}}/P_{1,\text{fp}}^{\text{sat}}$  and  $\gamma_2^\infty P_2^{\text{sat}}|_{T_{1,\text{fp}}}/P_{2,\text{fp}}^{\text{sat}}$  (Table 6) for such mixtures further support this deduction.

The above results demonstrate that the proposed sufficient condition for a binary mixture to become a maximum flash-point solution and the necessary condition to exhibit neither maximum nor minimum flash-point behavior are sufficiently effective for the demarcation of a solution as a maximum flash-point solution. Summarizing the results of this study and previous work [5], the sufficient condition for a liquid solution to form a maximum flash-point solution is

$$\frac{\gamma_1^\infty P_1^{\text{sat}}|_{T_{2,\text{fp}}}}{P_{1,\text{fp}}^{\text{sat}}} \leq 1 \quad (9)$$

$$\frac{\gamma_2^\infty P_2^{\text{sat}}|_{T_{1,\text{fp}}}}{P_{2,\text{fp}}^{\text{sat}}} < 1 \quad (10)$$

The analogous condition for formation of a minimum flash-point solution is

$$\frac{\gamma_1^\infty P_1^{\text{sat}}|_{T_{2,\text{fp}}}}{P_{1,\text{fp}}^{\text{sat}}} > 1 \quad (20)$$

$$\frac{\gamma_2^\infty P_2^{\text{sat}}|_{T_{1,\text{fp}}}}{P_{2,\text{fp}}^{\text{sat}}} \geq 1 \quad (21)$$

The necessary condition for a mixture to not become a maximum/minimum flash-point solution is

$$\frac{\gamma_1^\infty P_1^{\text{sat}}|_{T_{2,\text{fp}}}}{P_{1,\text{fp}}^{\text{sat}}} > 1 \quad (13)$$

$$\frac{\gamma_2^\infty P_2^{\text{sat}}|_{T_{1,\text{fp}}}}{P_{2,\text{fp}}^{\text{sat}}} < 1 \quad (14)$$

#### 4.4. Maximum flash-point composition and maximum flash point

We have demonstrated that the flash point of cyclohexanol (1) + phenol (2) is at its maximum, 82.5 °C, when  $x_1 = 0.3$  (Fig. 2). Using different equations to estimate the activity coefficients, the estimated maximum flash-point composition and maximum flash-point temperature (Table 7) are close to the measured analogues, although there are slight differences between the estimations. The analogous estimated values for the other maximum flash-point solutions, cyclohexanone + phenol, *p*-picoline + phenol and phenol + acetophenone were also compared with the corresponding experimental data (Table 7). It is apparent from inspection of the tabulated information that the estimates for these two parameters (maximum flash-point composition and maximum flash point) are in good agreement with the experimental data for these mixtures.

## 5. Conclusion

The maximum flash-point value for a binary mixture may be larger than the individual component values, with such combinations termed maximum flash-point solutions in this study. The sufficient condition for a binary mixture to form a maximum flash-point solution, as verified by the experimental data, appears to be satisfactory for identification of such a solution. Analysis of the experimental data has demonstrated that our proposed equations may be applied to accurately estimate both the maximum flash-point composition and the maximum flash-point value. This sufficient condition and the corresponding theoretically estimated values for the two parameters can be used for hazard reduction with a flammable liquid.

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