Phase Behaviour of Ternary Mixtures: A Theoretical Investigation of the Critical Properties of Mixtures with Equal Size Components†

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Abstract

Conformal solution theory in conjunction with the one-fluid model and the Guggenheim equation of state are used to calculate the critical properties of binary ternary mixtures characterised by molecules of identical size (identical $h$ conformal parameters) but different energy parameters (different $f$ conformal parameters). When the geometric mean combining rule is used to obtain contributions from unlike interactions, binary mixtures of equal size components only generate Type I, II and III behaviour irrespective of the magnitude of $f$ conformal parameters of the component molecules. The critical properties of ternary mixtures composed of binary sub-systems of different phase behaviour types are examined. Results are presented at different temperatures and pressures covering both vapour-liquid and liquid-liquid equilibria. The results illustrate the diversity of phenomenon exhibited by ternary mixtures and the relationship of the behaviour exhibited to the relative strength of dissimilar interactions between different pairs of molecules. A progressive transition between vapour-liquid and liquid-liquid equilibria and higher order critical phenomena are likely to be common features of the phase behaviour of ternary mixtures.

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Introduction

The study of the phase behaviour of mixtures is dominated overwhelmingly by binary mixtures. Considerable progress\(^1\) has been achieved in understanding and characterising binary mixtures. The fluid phase equilibria of many binary mixtures have been observed experimentally over a wide range of physical conditions including very high pressures. Classification schemes\(^2-5\) have been developed based on the critical equilibria behaviour of binary mixtures and increasingly accurate equations of state\(^6\) have been reported and applied successfully to the prediction of binary mixture phenomena.\(^7\)

In contrast to the systematic investigation of binary mixtures, work on ternary mixtures has been fragmentary and often incomplete. This situation can be attributed, at least partly, to the greater experimental and theoretical effort required to completely characterise ternary mixtures. For example, whereas points and lines can represent the critical properties of pure components and binary mixtures, respectively, critical equilibria in ternary mixtures generate a composition-dependent surface. The phase behaviour of some ternary mixtures is likely to be a simple extension of phenomena exhibited by the constituent binary mixtures. This is particularly the case if the component binary systems have simple behaviour typified by either Type I or II behaviour in the classification scheme of van Konynenburg and Scott.\(^2\) However, if the constituent binary mixtures have more complicated behaviour as exemplified by Type III - VI behaviour, the resulting ternary mixture is likely to generate a diverse range of phenomena.\(^1\) Novel ternary mixture phenomena observed experimentally are the subject of a recent review.\(^8\)

The complexity of ternary mixture phenomena provides ample scope for theoretical studies to provide some guidance for experimental work. In particular, studying critical properties is a useful means of describing at categorising the “global” nature of ternary mixture phenomena. Earlier theoretical studies\(^1,9,10\) on the phase behaviour of ternary mixtures indicate that higher order critical transitions are likely to be a feature of ternary mixture behaviour. The following types of higher order critical transitions have been reported\(^9,10\) based on a phenomenological interpretation\(^1\) of critical calculations:

(a) Class 1: Multiphase critical points (i.e., tricritical, tetracritical etc.) involving three or more phases undergoing a simultaneous transition to produce a single homogeneous phase. In the case of a tricritical point, the two menisci signifying the phase boundaries disappear simultaneously.

(b) Class 2: Lower or upper critical solution phenomena (LCST or UCST) and a vapour-liquid critical transition meet at a relatively low temperature. A critical transition occurs transforming the two-phase liquid-liquid equilibrium into a two-phase vapour-liquid
equilibrium. That is, the meniscus between the two liquid phases becomes critical simultaneously with the formation of a vapour-liquid meniscus.

(c) Class 3a: A region of lower critical solution temperature (LCST) and upper critical solution temperature (UCST) meet. The resulting critical transition is between the different two-phase liquid-liquid equilibria. That is, the lower solution meniscus disappears with the simultaneous formation of an upper critical solution meniscus.

(d) Class 3b: There is a transition between two different two-phase upper critical solution menisci.

These traditional calculations of phase equilibria have also been supplemented recently\textsuperscript{11-14} by molecular simulation\textsuperscript{15} studies of both vapour-liquid and liquid-liquid equilibria of ternary mixtures.\textsuperscript{14} However, molecular simulation techniques are currently not sufficiently accurate for the calculation of the critical properties of mixtures.

The aim of this work is to explore the phase behaviour ternary mixtures by the systematic calculation of critical equilibria of idealised components. In this work, we consider components of equal size but varying strength of intermolecular pair-interactions. This approach enables us to compose ternary mixtures from well-defined binary sub-systems of different phase behaviour type.

**Theory**

Details of the calculations and the underlying theory are given extensively elsewhere\textsuperscript{1,16} and only a brief outline of the main points is given here. The critical properties of an $m$-component fluid can be obtained by determining the temperature ($T$), volume ($V$) and composition ($x$), which satisfy the critical conditions,

\[
W = \begin{vmatrix}
- \left( \frac{\partial^2 A}{\partial V^2} \right)_{T} & - \left( \frac{\partial^2 A}{\partial x_{i} \partial V} \right)_{T} & \ldots & - \left( \frac{\partial^2 A}{\partial x_{m-1} \partial V} \right)_{T} \\
\left( \frac{\partial^2 A}{\partial x_{i} \partial V} \right)_{T} & \left( \frac{\partial^2 A}{\partial x_{i}^2} \right)_{T,v} & \ldots & \left( \frac{\partial^2 A}{\partial x_{i} \partial x_{m-1}} \right)_{T,v} \\
\vdots & \vdots & \ddots & \vdots \\
\left( \frac{\partial^2 A}{\partial x_{m-1} \partial V} \right)_{T} & \left( \frac{\partial^2 A}{\partial x_{i} \partial x_{m-1}} \right)_{T,v} & \ldots & \left( \frac{\partial^2 A}{\partial x_{m-1}^2} \right)_{T,v}
\end{vmatrix} = 0
\]  \hspace{1cm} (1)
where $A$ denotes the Helmholtz function. The condition $Y > 0$ (Eq.(3)) guarantees the thermodynamic stability of the calculated critical point. Consequently, the calculation of critical equilibria involves locating the temperature, volume and composition, which satisfy two simultaneous equations (Eq.(1) and Eq.(2)), and checking the thermodynamic stability of the solution. The solution of these critical conditions was obtained by applying the Hicks-Young algorithm.\textsuperscript{17}

The Helmholtz function is obtained from conformal solution theory\textsuperscript{18} using the one-fluid model

$$A = f_{es} A_0^* (V / h_{es}, T / f_{es}) - RT \ln h_{es} + RT \sum_i x_i \ln x_i$$

where $R$ is the universal gas constant, $A_0^*$ is the configurational contribution to the Helmholtz function and $f_{es}$ and $h_{es}$ are the characteristic conformal parameters of the equivalent substance. It is customary to estimate the conformal parameters of pure fluids from critical temperatures and critical volumes relative to the properties of a reference substance (denoted by the subscript $0$), i.e., $f_{11} = T_{11}/T_{00}$, $h_{11} = V_{11}/V_{00}$ etc. The conformal parameters for the equivalent substance are obtained from the van der Waals one-fluid prescriptions

\begin{equation}
X = \begin{pmatrix}
\frac{\partial W}{\partial V} & \frac{\partial W}{\partial x_1} & \cdots & \frac{\partial W}{\partial x_{m-1}} \\
\frac{\partial^2 A}{\partial x_1 \partial V} & \frac{\partial^2 A}{\partial x_1^2} & \cdots & \frac{\partial^2 A}{\partial x_1 \partial x_{m-1}} \\
\vdots & \vdots & \ddots & \vdots \\
\frac{\partial^2 A}{\partial x_{m-1} \partial V} & \frac{\partial^2 A}{\partial x_{m-1}^2} & \cdots & \frac{\partial^2 A}{\partial x_{m-1} \partial x_{m-1}}
\end{pmatrix}_{T,V} = 0
\end{equation}

\begin{equation}
Y = \begin{pmatrix}
\frac{\partial X}{\partial V} & \frac{\partial X}{\partial x_1} & \cdots & \frac{\partial X}{\partial x_{m-1}} \\
\frac{\partial^2 A}{\partial x_1 \partial V} & \frac{\partial^2 A}{\partial x_1^2} & \cdots & \frac{\partial^2 A}{\partial x_1 \partial x_{m-1}} \\
\vdots & \vdots & \ddots & \vdots \\
\frac{\partial^2 A}{\partial x_{m-1} \partial V} & \frac{\partial^2 A}{\partial x_{m-1}^2} & \cdots & \frac{\partial^2 A}{\partial x_{m-1} \partial x_{m-1}}
\end{pmatrix}_{T,V} > 0
\end{equation}
\[ f_{es} h_{es} = \sum_i \sum_j x_i x_j f_{ij} h_{ij} \]  
\[ h_{es} = \sum_i \sum_j x_i x_j h_{ij} \]  

where the contribution from unlike interactions is given by

\[ f_{ij} = \sqrt{f_{ii} f_{jj}} \]  
\[ h_{ij} = \left( h_{ii}^{1/3} + h_{jj}^{1/3} \right)^3 / 8 \]  

The configurational Helmholtz function, \( A_0^* \), can be evaluated by direct integration of any suitable equation of state with respect to volume. In this work, we have used the Guggenheim equation,\(^\text{19}\)

\[ p = \frac{RT}{V \left( 1 - \frac{b}{4V} \right)^4} - \frac{a}{V^2} \]  

where \( b \) is the volume occupied by 4 mol of hard-spheres and \( a \) is the contribution from van der Waals-like attraction between molecules. The equation of state parameters can be related to the conformal parameters \((a \propto f_h, \ b \propto h)\). The Guggenheim equation has been used extensively\(^\text{1,16}\) for the prediction of both binary and ternary mixture critical properties. It should be noted that, at the densities normally encountered for critical equilibria, the accuracy of the hard-sphere representation (first term on the right hand side of \( \text{Eq. (9)} \)) is equivalent to the more complicated Carnahan-Starling\(^\text{20}\) hard-sphere term. Recent results\(^\text{21,22}\) also indicate that the Guggenheim equation can be used to calculate accurately the high-pressure equilibria of a diverse range of real fluids. The Guggenheim equation has also been applied successfully to calculation of the critical properties of a diverse range of ternary mixtures.\(^\text{23-25}\)
Results and Discussion

As described above, the calculation of critical properties was performed using the theoretical framework of conformal solution theory. A practical advantage of this approach is that the accuracy of the calculations is not solely dependent on the accuracy of the equation of state. The equation of state only makes a contribution to the configurational properties of the mixture. Therefore, the calculations are often more accurate than can be obtained otherwise by using the equation of state alone.\textsuperscript{21,22} In the context of the present study, conformal solution theory also allows us to attribute different types of phase behaviour solely in terms of the conformal parameters \((f\) and \(h\)). The phase behaviour of binary mixtures depends on the relative size of the conformal parameters between the component molecules. Mixtures of components with identical or similar conformal parameters exhibit Type I behaviour whereas liquid-liquid phenomenon is observed when there is a substantial difference in the conformal parameters. Generally, the \(f\) conformal parameter plays the dominant role in determining the phase behaviour.

The link between the conformal parameters and the phase behaviour type allows us to construct ternary mixtures of different binary phase behaviour types governed solely by the ratio of the conformal parameters and the combining rules given by Eqs (7) and (8). The complexity of the binary mixtures can be simplified by using molecules of equal size. For the equal size case, \(h_{11} = h_{22} = h_{12} = 1\) and the properties of mixture are determined solely by the \(f\) conformal parameter.

The first step in the analysis is to determine the values of \(f_{11}\) and \(f_{22}\) which will result in the different types of phase behaviour. Calculations were performed with the Guggenheim equation of state at different values of \(f_{11}\) and \(f_{22}\). The results are summarised in Table 1. Only Type I, II and III phase behaviour could be generated by varying the \(f\) parameter. The same general type of phase behaviour can be obtain for a range of \(f\) conformal parameters (Table 1). For example, both mixtures \(U\) and \(W\) are of Type III behaviour but the value of \(f_{22}\) for these mixtures is 0.43 and 0.22, respectively.

In principle, there are 10 possible ternary mixtures that can be formed by using different combinations of sub-binary mixtures of Type I, II and II phase behaviour. These possible combinations are summarised in Table 2. The 10 different ternary mixtures are the only distinguishable combinations of the Type I, II and III binary mixtures. The first column in Table 2 is the first sub-binary mixture for which the critical curve is obtained by using varying \(f_{11}\) only \((f_{22} = 1.0)\). The next column is the second sub-binary mixture for which the critical curve is obtained by varying \(f_{22}\) only \((f_{11} = 1.0)\). The third column in Table 2 records the third sub-binary mixture for which the critical curve is obtained by using \(f_{11}\) and \(f_{22}\) which come directly from the
first and the second sub-binary mixtures. For example, if we examine ternary mixture 1 (Table 2) we find that the first sub-binary mixture is binary mixture $A$ with $f_{11} = 0.95$ and $f_{22} = 1.0$ and the second sub-binary mixture is binary mixture $M$ with $f_{11} = 1.0$ and $f_{22} = 0.485$. The $f$ parameters of the third sub-binary mixture ($P$) must come directly from the first and the second sub-binary mixture as determined from the combining rules. Therefore, sub-binary mixture $P$ has $f_{11} = 0.95$ and $f_{22} = 0.485$. This inter-relationship between the conformal parameters means that some combinations of three binary sub-mixtures are not possible. Only 8 of the 10 possible combinations result in a viable ternary mixture. The possible combinations of sub-binary mixtures are indicated in the fourth column of Table 2. In Table 2, "Yes" means that the conformal parameters that characterise the phase behaviour type of the third sub-binary mixture can be obtained by combining the conformal parameters of the first and the second sub-binary mixtures using Eqs (7) and (8).

Here, we report calculations of the critical properties of 3 of the 10 possible ternary mixtures, denoted mixture 1, mixture 2 and mixture 3. The characteristic parameters of these ternary mixtures are summarised in Table 3. The Guggenheim equation of state was used for both binary and ternary calculations. The calculation were performed in reduced units relative to a common reference substance for the mixtures ($\tilde{p} = p / p_{00}^c$, $\tilde{T} = T / T_{00}^c$). For the ternary mixtures, calculations were performed at different constant values of pressure. Therefore, the resulting isobaric critical “curves” represent slices through the three-dimensional critical surface.

Ternary mixture 1 is a combination of one Type I ($A$) and two Type II ($M$ and $P$) binary sub-systems. For the benefit of cross-referencing between ternary and binary mixture phenomena, the critical properties of binary mixtures $A$, $M$ and $P$ are summarised in Fig. 1. Figure 2 illustrates the isobaric-composition behaviour of the ternary mixture 1 at various pressures. In Fig. 2, sub-binary mixture $A$ is represented by mixture 1 + 2, sub-binary mixture $M$ is represented by mixture 1 + 3 and sub-binary mixture $P$ is represented by mixture 2 + 3. The points labelled $M_1$, $M_2$, ..., $M_{11}$ and $P_1$, $P_2$, ..., $P_7$ in Fig 2 indicate the critical points of sub-binary mixtures $M$ and $P$ referred to in Fig. 1. From Fig. 2, when $\tilde{p} = 0.9$, there are two critical curves, one is the liquid-liquid critical line ($M_8, P_4$) and the other is liquid-vapour critical curve ($M_7, P_3$). When $\tilde{p} = 1.01$, another side of liquid-vapour critical line ($M_1, P_1$) appears. At this pressure, there are two regions of vapour-liquid equilibria linking the $M$ and $P$ binary sub-mixtures. However, an increase in pressure ($\tilde{p} = 1.1$) results in a vapour-liquid curve which starts and terminates solely from the $M$ binary sub-mixture (points $M_2$, $M_3$). Eventually, at $\tilde{p} = 1.138$ the liquid-liquid ($M_{11}$, $P_7$) and liquid-vapour ($M_5, M_4$) curves meet at a common pressure, temperature and composition but different density ($M_4$ and $M_{11}$).
Ternary mixture 2 is a combination on one Type I (A) and two Type III (U and X) binary sub-systems. The phase behaviour of the sub-binary mixtures are examined in detail in Fig. 3 and the various critical points are identified as before. Figure 4 illustrates the isobaric-composition behaviour of ternary mixture 2 at six different pressures. In Fig. 4, sub-binary mixture A is represented by mixture $1 + 2$, sub-binary mixture $U$ is represented by mixture $1 + 3$ and sub-binary mixture $X$ is represented by mixture $2 + 3$. When $\tilde{p} = 1.0$, there is only one liquid-vapour critical curve extending from different points on the $X$ binary mixture. As the pressure is increased, an additional vapour-liquid critical line $(U_1, X_1)$ appears and the liquid-vapour critical line changes slightly. When $\tilde{p} = 1.19$, the curve starting from mixture $X$ at point $X_6$ is a liquid-liquid curve which merges with and liquid-vapour curve form mixture $U$. This behaviour indicates a continuous transition between vapour-liquid and liquid-liquid phenomena. The region of transition is indicated by a “loop.” It should be noted that there is no intersection because the different branches occur at different densities. As the pressure is increased ($\tilde{p} = 1.26$) the loop tightens as the region of transition between vapour-liquid and liquid-liquid equilibria decreases and the densities of the two branches become increasingly identical. At $\tilde{p} = 1.33$, the liquid-liquid and liquid-vapour curves meet at a possible tricritical point (Class 1 behaviour). At $\tilde{p} = 1.4$, only liquid-liquid critical curve is left linking the liquid-liquid equilibria of mixtures $U$ and $X$. The binodal curves (at different temperatures) of this ternary mixture are illustrated in Fig. 5 to highlight the continuity of vapour-liquid and liquid-liquid phenomena. In summary, the phase behaviour of mixture 2 undergoes a transition from purely vapour-liquid equilibria, to liquid-liquid equilibria via a possible tricritical point.

Ternary mixture 3 is the result of combining one Type II (L) and two Type III (W and Y) binary sub-systems. The phase behaviour of the sub-binary mixtures are examined in detail in Fig. 7 and the binary mixture points used in Fig. 8 are identified. Figure 8 summarises the isobaric-composition behaviour of ternary mixture 3 at various pressures. Sub-binary mixture L is represented by mixture $1 + 2$, sub-binary mixture W is represented by mixture $1 + 3$ and sub-binary mixture Y is represented by mixture $2 + 3$. From Fig. 8 it is apparent that when $\tilde{p} = 0.9$, the curve starting from $L_1$ exhibits the vapour-liquid behaviour and the curve started from $L_2$ exhibits the liquid-liquid behaviour. These two curves meet at a possible higher order critical point (Class 2 behaviour). This shows continuity between vapour-liquid and liquid-liquid equilibria. The other curve starting from $Y_1$ is a liquid-liquid critical curve. This curve could not be traced to a termination point on any binary mixture. This could be because of either a limitation of the calculation or a genuine ternary end point. As the pressure is increased, the trajectory of the liquid-liquid curve changes progressively towards a binary mixture. When $\tilde{p} = 1.5$ and $\tilde{p} = 2.0$, the
curves from binary mixtures connect smoothly and showing a continuity of liquid-liquid equilibria. However at the intermediate pressure of $\tilde{p} = 1.2$ there is an abrupt transition between vapour-liquid and liquid-liquid critical equilibria which is characteristic of a tricritical transition (Class 1 behaviour).

Conclusions

Binary mixtures of molecules of equal size but dissimilar pair-interactions can exhibit phase behaviour of Type I, II or III. The critical properties of different ternary mixtures characterised by different well-defined binary sub-systems have been calculated. The calculations reveal different slices of the three-dimensional ternary surface and the interplay between vapour-liquid and liquid-liquid equilibria in a ternary mixture. The progressive transition between vapour-liquid and liquid-liquid phenomena is likely to be a common feature of the phase behaviour of many ternary mixtures. Higher order critical transitions are also likely to have an important role in ternary mixtures. The calculations provide a mechanism for the systematic study of ternary mixtures and the identification of global phase diagrams.

Acknowledgements

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References

Table 1. Conformal parameters for binary mixtures

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Phase behaviour</th>
<th>$f_{11}$</th>
<th>$f_{22}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>I</td>
<td>0.95</td>
<td>1.0</td>
</tr>
<tr>
<td>B</td>
<td>I</td>
<td>0.85</td>
<td>1.0</td>
</tr>
<tr>
<td>C</td>
<td>I</td>
<td>0.65</td>
<td>1.0</td>
</tr>
<tr>
<td>D</td>
<td>I</td>
<td>1.0</td>
<td>0.85</td>
</tr>
<tr>
<td>E</td>
<td>I</td>
<td>0.65</td>
<td>0.85</td>
</tr>
<tr>
<td>F</td>
<td>I</td>
<td>0.85</td>
<td>0.49</td>
</tr>
<tr>
<td>G</td>
<td>I</td>
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<td>0.485</td>
</tr>
<tr>
<td>H</td>
<td>I</td>
<td>0.65</td>
<td>0.43</td>
</tr>
<tr>
<td>I</td>
<td>I</td>
<td>0.5</td>
<td>0.43</td>
</tr>
<tr>
<td>J</td>
<td>I</td>
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<td>0.25</td>
</tr>
<tr>
<td>K</td>
<td>II</td>
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</tr>
<tr>
<td>L</td>
<td>II</td>
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</tr>
<tr>
<td>M</td>
<td>II</td>
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<tr>
<td>N</td>
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<td>0.49</td>
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<tr>
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<td>T</td>
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</tr>
<tr>
<td>U</td>
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<td>V</td>
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<tr>
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<tr>
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</tr>
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<td>1st Sub-binary mixture</td>
<td>2nd Sub-binary mixture</td>
<td>3rd Sub-binary mixture</td>
<td>Is the combination of binary mixtures possible?</td>
</tr>
<tr>
<td>------------------------</td>
<td>------------------------</td>
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<tr>
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<td>B (I)</td>
<td>N (II)</td>
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</tr>
<tr>
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<td>M (II)</td>
<td>P (II)</td>
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</tr>
<tr>
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<td>U (III)</td>
<td>H (I)</td>
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<tr>
<td>A (I)</td>
<td>U (III)</td>
<td>X (III)</td>
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<td>(II)</td>
<td>(II)</td>
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<td>U (III)</td>
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<td>V (III)</td>
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<td>Yes</td>
</tr>
<tr>
<td>L (II)</td>
<td>W (III)</td>
<td>Y (III)</td>
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<tr>
<td>(III)</td>
<td>(III)</td>
<td>(III)</td>
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*For viable combinations, an example of the binary sub-mixture is denoted by the corresponding mixture in Table 1 and the phase type is given in brackets. Only the phase type is identified for non-viable combinations.*
Table 3. Conformal parameters of ternary mixtures studied in detail *

<table>
<thead>
<tr>
<th>Ternary mixture</th>
<th>Sub-binary mixtures</th>
<th>$f_{11}$</th>
<th>$f_{22}$</th>
<th>$f_{33}$</th>
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<td>1</td>
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<td>0.95</td>
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<td>2</td>
<td>A, U, X</td>
<td>1.0</td>
<td>0.95</td>
<td>0.43</td>
</tr>
<tr>
<td>3</td>
<td>L, W, Y</td>
<td>1.0</td>
<td>0.5</td>
<td>0.22</td>
</tr>
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</table>

The $h$ conformal parameters are identical $h_{11} = h_{22} = h_{33} = h_{12} = h_{13} = h_{23} = 1$. The contributions from dissimilar interactions to the $f$ conformal parameters were obtained from Eq. (7).
Fig. 1. Critical curves (—) of binary mixtures A, M, P in the $\tilde{p} - \tilde{T}$ and close-up $\tilde{p} - x$ projections. Critical points (⊙) of pure components and selected range (●) are also illustrated.
Fig. 2. The isobaric-composition critical behaviour of ternary mixture 1 (binary mixture A is mixture 1-2, binary mixture M is mixture 1-3, binary mixture P is mixture 2-3). $M_1$, $M_2$, $\ldots$, $M_{11}$ and $P_1$, $P_2$, $\ldots$, $P_7$ are the critical points of binary mixtures M and P.
Fig. 3. Critical curves (—) of binary mixtures A, U, X in the $\tilde{p}\sim \tilde{T}$ and close-up $\tilde{p}\sim x$ projections. Critical points (O) of pure components and selected range (●) are also illustrated.
Fig. 4. The isobaric-composition critical behaviour of ternary mixture 2 (binary mixture A is mixture 1 + 2, binary mixture U is mixture 1 + 3, binary mixture X is mixture 2 + 3). U₁, U₂, …, U₅ and X₁, X₂, …, X₉ are the critical points of binary mixtures U and X.
Fig. 5. The binodal (——) and critical equilibria (—) of ternary mixture 2 (binary mixture A is mixture 1 + 2, binary mixture U is mixture 1 + 3, binary mixture X is mixture 2 + 3) at various pressures.
Fig. 7. Critical curves (—) of binary mixtures $L$, $W$, $Y$ in the $\tilde{p} - \tilde{T}$ and close-up $\tilde{p} - x$ projections. Critical points (○) of pure components and selected range (●) are also illustrated.
Fig. 8. The isobaric-composition critical behaviour of ternary mixture 3 (binary mixture L is mixture 1-2, binary mixture W is mixture 1-3, binary mixture Y is mixture 2-3) at various temperatures. $L_1$, $L_2$, ..., $L_5$, $W_1$, $W_2$, $W_3$ and $Y_1$, $Y_2$, ..., $Y_4$ are the critical points of binary mixtures L, W, Y.