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***Research Article***

# Calculation of Azeotropic Properties for Ternary Mixtures with the PC-SAFT Equation of State

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## Abstract

In this study, a novel approach employing the Perturbed-Chain Statistical Associating Fluid Theory (PC-SAFT) Equation of State was introduced to investigate azeotropic behavior in ternary mixtures and explore their liquid-vapor equilibria. The temperature range spans (243.15–323.5) K, covering a broad spectrum of conditions relevant to industrial and chemical processes. Our analysis focuses on six different ternary mixtures: Difluoromethane (R32) + 1,1-difluoroethane (R152a) + 2,3,3,3-tetrafluoropro-1-ene (R1234yf); Isobutane (R600a) + 1,1-difluoroethane (R152a) + 1,1,2,2-tetrafluoroethane (R134); 1,1,1,2-tetrafluoroethane (R134a) + 2,3,3,3-tetrafluoropro-1-ene (R1234yf) + isobutane (R600a); 1,1,1,2-tetrafluoroethane (R134a) + 2,3,3,3-tetrafluoropro-1-ene (R1234yf) + dimethyl ether (DME); isobutene (R600a) + 1,3,3,3-tetrafluoropropene (R12345ze(E)) + trifluoroiodomethane (R13I1); and difluoromethane (R32) + fluoroethane (R161) + 1,3,3,3-tetrafluoropropene (R1234ze(E)). Among these, only three mixtures exhibit azeotropic behavior.

The PC-SAFT equation of state, incorporating an expansion form tailored for Vapor-Liquid Equilibrium (VLE) calculations within ternary mixtures, determined azeotropic composition and pressure based on the Gibbs-Konovalov theorem, which characterizes azeotropic behavior under constant temperature. Our estimations of the VLE and azeotropic composition and pressure closely align with experimental data. The maximum relative error in pressure does not exceed 4.2% for the R600a + R152a + R134 mixture and remains less than 6.56% for the liquid composition of R1234ze(E) within the (R600a + R1234ze(E) + R13I1) ternary mixture. These results underscore the reliability and accuracy of the PC-SAFT equation of state in modeling azeotropes within ternary mixtures.

***Keywords:*** *Ternary mixture; azeotrope; PC-SAFT; equation of state.*

## 1. Introduction

In the field of refrigeration science, a paramount concern revolves around the preservation of the global environment. Extensive research endeavors have been initiated with the overarching objective of identifying novel refrigeration mixtures that wield a minimal environmental impact, particularly with respect to mitigating global warming and curbing ozone layer depletion. In recent years, heightened attention has been directed towards two interrelated challenges: the phenomenon of climate warming and the depletion of the ozone layer. In response to these pressing issues, various regulatory frameworks and protocols, such as the Montreal Protocol of 1987 and the Kyoto Protocol of 1997, have been established to delineate stringent guidelines governing the usage and management of refrigerants.

In various industrial contexts, the use of both pure compounds and complex mixtures is essential. Achieving efficient industrial process design relies heavily on a thorough comprehension of the thermophysical properties and phase behavior exhibited by these components and mixtures. Within the specific scientific purview, Gross and Sadowski [1,2] have contributed significantly by formulating the Perturbed-Chain Statistical Associating Fluid Theory (PC-SAFT) equation of state. In marked contrast to the foundational SAFT equation of state initially postulated by Huang and Radosz [3,4] alongside its multiple well-established modified versions [5,12] In the PC-SAFT approach, a hard-chain reference system is employed instead of the conventional hard-sphere reference system when applying the standard second-order high-temperature perturbation theory of Barker and Henderson [13] to obtain the dispersion contribution. Additional binary interaction parameters are integrated to rectify molecular interactions, yielding results that demonstrate robust extrapolation capabilities.

Our primary objective is the development of an innovative and robust method for predicting azeotrope positions in complex multicomponent mixtures. Extensive research conducted within our research group [14], [15] has laid the foundation for this endeavor. In this study, a novel approach is introduced for the direct determination of azeotropes, both empirically from experimental data and theoretically through the employment of the PC-SAFT thermodynamic model. Six ternary mixtures were investigated: (R32 + R152a + R1234yf), (R600a + R152a + R134), (R134a + R1234yf + R600a), (R134a + R1234yf +

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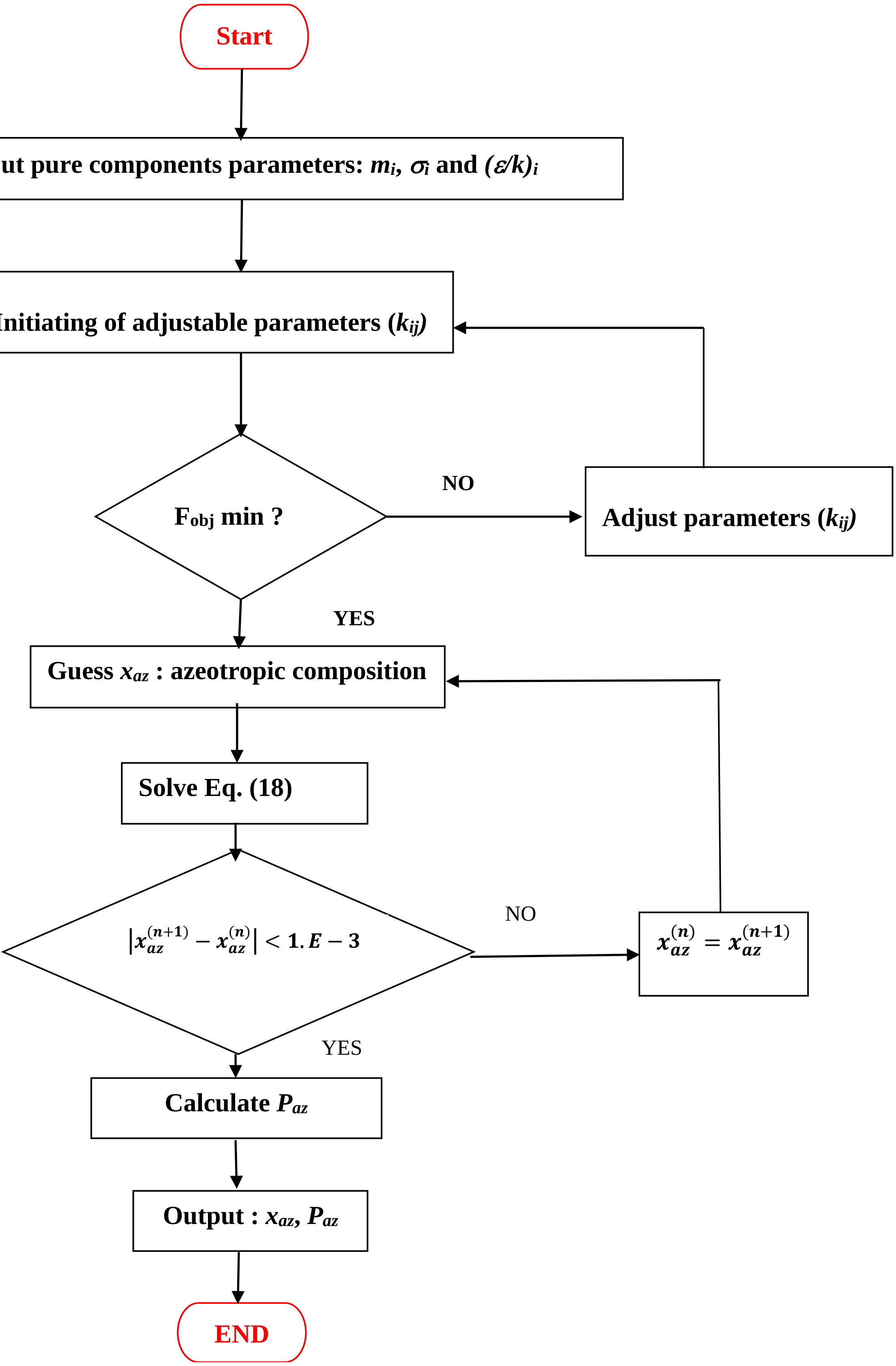


*Figure 1. The calculation procedure for azeotropic properties by PC-SAFT model.*

DME), (R600a + R1234ze(E) + R13I1), and (R32 + R161 + R1234ze(E)), with three of these mixtures displaying azeotropic behavior. It is worth noting that the examined mixtures in our study are environmentally friendly, characterized by low Global Warming Potential (GWP) and zero Ozone Depletion Potential (ODP).

## 2. PC-SAFT Model

The definition of the residual Helmholtz free energy $\tilde{a}^{res}$(reduced quantity) is given by:

$$\tilde{a}^{res} = \frac{A^{res}}{NkT} \tag{1}$$

where, $A^{res}$ is the Helmholtz free energy, $N$ is the Avogadro

*Table 1. Parameters and properties of investigated components.*

| Component | R13I1 | R152a | R600a | R1234ze(E) | R134 | R134a | R32 | R1234yf | DME | R161 |
|---|---|---|---|---|---|---|---|---|---|---|
| Environment characterization [a] | | | | | | | | | | |
| GWP | 0 | 124 | 3 | 7 | 1500 | 1430 | 675 | 4 | 1 | 12 |
| ODP | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Critical properties and acentric factor [b] | | | | | | | | | | |
| Tc (K) | 396.44 | 386.41 | 407.81 | 382.51 | 391.74 | 374.21 | 351.60 | 367.85 | 400.10 | 375.31 |
| Pc (MPa) | 3.9530 | 4.5168 | 3.6290 | 3.6350 | 4.6400 | 4.0590 | 5.8300 | 3.3823 | 5.370 | 5.028 |
| ω | 0.1760 | 0.2752 | 0.1840 | 0.3130 | 0.2930 | 0.3270 | 0.2769 | 0.2760 | 0.204 | 0.209 |
| Pure-component parameters [c] | | | | | | | | | | |
| m | 2.29706 | 3.05606 | 2.38497 | 3.43117 | 3.26450 | 3.53622 | 3.01995 | 3.06453 | 2.48190 | 2.61983 |
| σ [◦A] | 3.70077 | 3.17498 | 3.79437 | 3.26153 | 3.08382 | 3.08618 | 2.84472 | 3.43605 | 3.27078 | 3.20027 |
| ε/k [K] | 205.748 | 176.207 | 207.923 | 166.181 | 173.717 | 160.601 | 160.998 | 167.544 | 200.370 | 183.182 |

[a] From ref. [14–15].

[b] From ref. [18–23].

[c] From ref. [17].

*Table 2. Experimental and calculated VLE in the system R32(1) + R152a(2) + R1234yf(3) [18].*

| T[K] | $P_{exp}$[MPa] | $P_{cal}$[MPa] | $x_{1exp}$ | $y_{1exp}$ | $y_{1cal}$ | $y_{2exp}$ | $y_{2cal}$ | ΔP[MPa] | $\Delta y_1$ | $\Delta y_2$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 283.15 | | | | | | | | | | |
| | 0.532 | 0.534 | 0.131 | 0.265 | 0.266 | 0.380 | 0.372 | 0.002 | 0.001 | -0.008 |
| | 0.500 | 0.506 | 0.146 | 0.298 | 0.301 | 0.589 | 0.576 | 0.006 | 0.003 | -0.013 |
| | 0.594 | 0.584 | 0.170 | 0.347 | 0.336 | 0.151 | 0.158 | -0.010 | -0.011 | 0.006 |
| | 0.663 | 0.669 | 0.363 | 0.574 | 0.578 | 0.322 | 0.321 | 0.006 | 0.003 | -0.001 |
| | 0.783 | 0.772 | 0.425 | 0.628 | 0.626 | 0.098 | 0.093 | -0.011 | -0.002 | -0.005 |
| | 0.834 | 0.836 | 0.559 | 0.727 | 0.734 | 0.132 | 0.131 | 0.002 | 0.007 | 0.001 |
| 293.15 | | | | | | | | | | |
| | 0.714 | 0.715 | 0.129 | 0.252 | 0.254 | 0.385 | 0.380 | 0.002 | 0.002 | -0.005 |
| | 0.674 | 0.675 | 0.144 | 0.280 | 0.282 | 0.601 | 0.596 | 0.001 | 0.002 | -0.005 |
| | 0.789 | 0.783 | 0.167 | 0.330 | 0.324 | 0.157 | 0.160 | -0.006 | -0.006 | 0.002 |
| | 0.884 | 0.882 | 0.360 | 0.557 | 0.558 | 0.338 | 0.336 | -0.002 | 0.001 | -0.002 |
| | 1.034 | 1.032 | 0.421 | 0.608 | 0.611 | 0.096 | 0.095 | -0.003 | 0.002 | -0.001 |
| | 1.106 | 1.109 | 0.556 | 0.718 | 0.721 | 0.139 | 0.137 | 0.003 | 0.003 | -0.002 |
| 303.15 | | | | | | | | | | |
| | 0.937 | 0.940 | 0.127 | 0.237 | 0.239 | 0.396 | 0.392 | 0.003 | 0.002 | -0.004 |
| | 0.890 | 0.890 | 0.143 | 0.265 | 0.266 | 0.617 | 0.612 | 0.000 | 0.002 | -0.004 |
| | 1.030 | 1.024 | 0.166 | 0.313 | 0.308 | 0.163 | 0.165 | -0.006 | -0.006 | 0.002 |
| | 1.154 | 1.150 | 03357 | 0.539 | 0.539 | 0.356 | 03353 | -0.004 | 0.000 | -0.003 |
| | 1.340 | 1.338 | 0.416 | 0.590 | 0.591 | 0.102 | 0.102 | -0.002 | 0.002 | 0.000 |
| | 1.438 | 1.441 | 0.554 | 0.705 | 0.707 | 0.148 | 0.146 | 0.003 | 0.001 | -0.002 |
| 313.15 | | | | | | | | | | |
| | 1.209 | 1.211 | 0.125 | 0.224 | 0.225 | 0.407 | 0.405 | 0.002 | 0.000 | -0.001 |
| | 1.153 | 1.154 | 0.141 | 0.251 | 0.253 | 0.632 | 0.628 | 0.001 | 0.002 | -0.004 |
| | 1.319 | 1.314 | 0.164 | 0.295 | 0.291 | 0.169 | 0.170 | -0.005 | -0.005 | 0.001 |
| | 1.481 | 1.478 | 0.355 | 0.521 | 0.522 | 0.373 | 0.371 | -0.003 | 0.000 | -0.002 |
| | 1.704 | 1.705 | 0.411 | 0.570 | 0.570 | 0.110 | 0.109 | 0.001 | 0.001 | 0.000 |
| | 1.838 | 1.843 | 0.551 | 0.691 | 0.691 | 0.159 | 0.157 | 0.005 | 0.001 | -0.002 |
| 323.15 | | | | | | | | | | |
| | 1.535 | 1.535 | 0.123 | 0.211 | 0.214 | 0.418 | 0.416 | 0.000 | 0.003 | -0.002 |
| | 1.469 | 1.469 | 0.135 | 0.238 | 0.235 | 0.645 | 0.645 | 0.000 | -0.003 | 0.000 |
| | 1.665 | 1.655 | 0.162 | 0.278 | 0.274 | 0.175 | 0.175 | -0.009 | -0.004 | 0.000 |
| | 1.870 | 1.878 | 0.351 | 0.502 | 0.504 | 0.392 | 0.390 | 0.009 | 0.002 | -0.002 |
| | 2.133 | 2.137 | 0.406 | 0.550 | 0.548 | 0.117 | 0.117 | 0.004 | -0.001 | 0.000 |
| | 2.310 | 2.325 | 0.546 | 0.673 | 0.674 | 0.171 | 0.171 | 0.015 | 0.001 | -0.001 |

number, $k$ is the Boltzmann constant and $T$ is the absolute temperature.

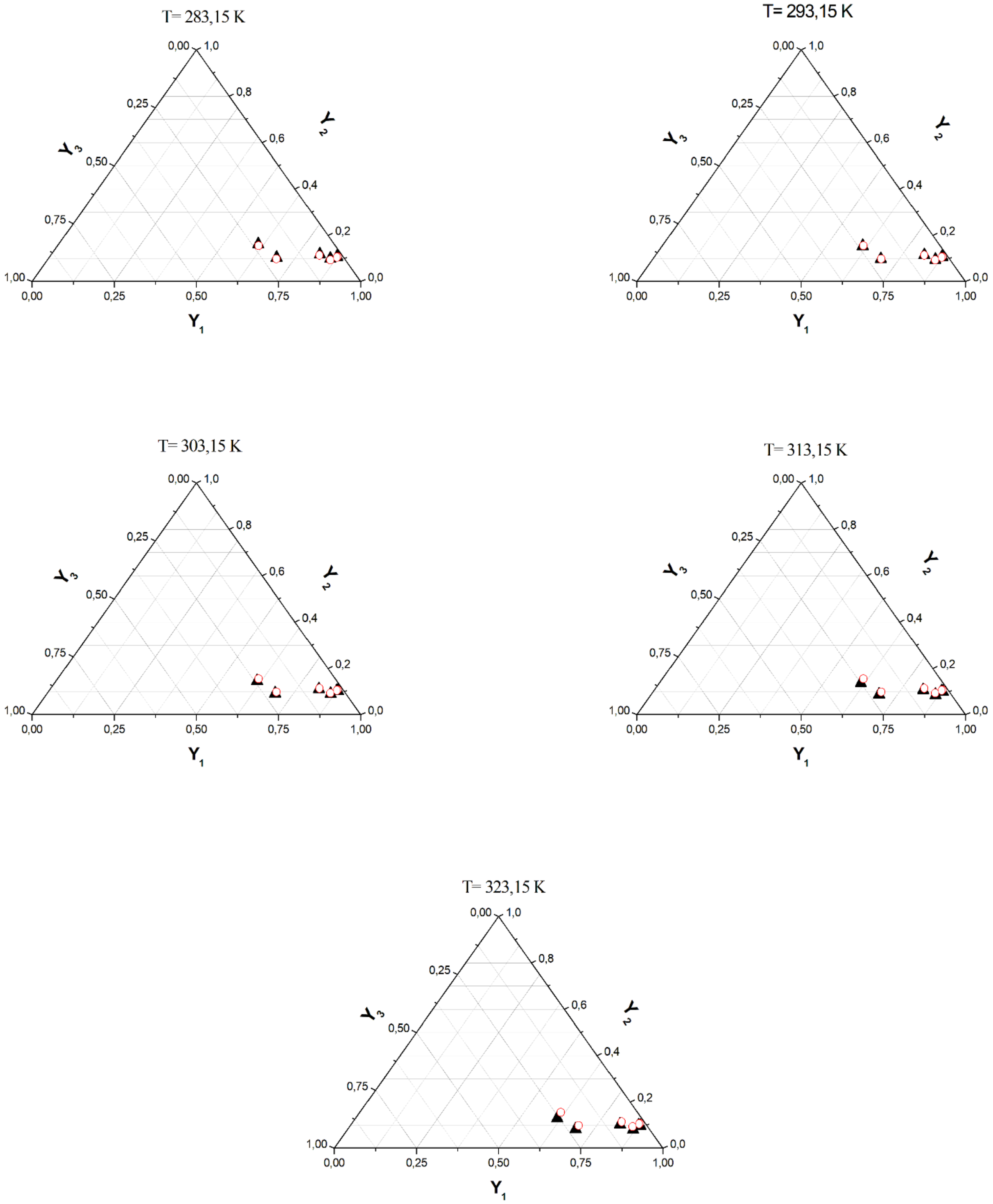
In the PC-SAFT model, proposed by Gross and Sadowski [1], the residual Helmholtz free energy $\tilde{a}^{res}$ for non-associating compounds consists of the hard-chain reference contribution and the dispersion contribution, illustrated as:

$$\tilde{a}^{res} = \tilde{a}^{hc} + \tilde{a}^{disp} \qquad (2)$$

The hard-chain reference contribution, in Eq. (2), is expressed by:

$$\tilde{a}^{hc} = \left(\sum_{i=1}^{nc} x_i\, m_i\right)\tilde{a}^{hs} - \sum_{i=1}^{nc} x_i (m_i - 1)\ln g_{ii}^{hs}(\sigma_{ii}) \qquad (3)$$

Where, $m_i$ is the segment number parameter and $x_i$ are the mole fractions of component *i*.


T= 283,15 K

T= 293,15 K

T= 303,15 K

T= 313,15 K

T= 323,15 K

*Figure 2. VLE of ternary mixture R32(1) + R152a(2) + R1234yf(3).*
*(▲): Experimental data [18]; (○): PC-SAFT prediction.*

The hard-sphere term $\tilde{a}^{hs}$ is defined as follows:

$$\tilde{a}^{hs} = \frac{A^{hs}}{NkT} = \frac{1}{\xi_0}\left[\frac{3\xi_1\xi_2}{(1-\xi_3)} + \frac{{\xi_2}^3}{\xi_3(1-\xi_3)^2} + \left(\frac{{\xi_2}^3}{{\xi_3}^2} - \xi_0\right)\ln(1-\xi_3)\right] \qquad (4)$$

The coefficients $\xi_0, \xi_1, \xi_2$ *and* $\xi_3$ are defined by Eq. (6) below.
$g_{ii}^{hs}$ is the radial distribution function of the hard-sphere fluid; it can be calculated by:

$$g_{ii}^{hs} = \frac{1}{(1-\xi_3)} + \left(\frac{d_i d_j}{d_i+d_j}\right)\frac{3\xi_2}{(1-\xi_3)^2} + \left(\frac{d_i d_j}{d_i+d_j}\right)^2 \frac{2{\xi_2}^2}{(1-\xi_3)^3} \qquad (5)$$

*Table 3. Experimental and calculated VLE in the system R32(1) + R161(2) + R1234ze(E)(3) [19].*

| T[K] | $P_{exp}$[MPa] | $P_{cal}$[MPa] | $x_{1exp}$ | $y_{1exp}$ | $y_{1cal}$ | $y_{2exp}$ | $y_{2cal}$ | ΔP[MPa] | $\Delta y_1$ | $\Delta y_2$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 283.15 | | | | | | | | | | |
| | 0.588 | 0.590 | 0.075 | 0.138 | 0.139 | 0.778 | 0.783 | 0.002 | 0.001 | 0.005 |
| | 0.498 | 0.493 | 0.116 | 0.260 | 0.265 | 0.387 | 0.391 | -0.005 | 0.005 | 0.004 |
| | 0.466 | 0.460 | 0.124 | 0.303 | 0.303 | 0.211 | 0.226 | -0.006 | 0.000 | 0.015 |
| | 0.541 | 0.535 | 0.216 | 0.452 | 0.454 | 0.170 | 0.169 | -0.006 | 0.002 | 0.000 |
| | 0.640 | 0.638 | 0.233 | 0.399 | 0.407 | 0.456 | 0.451 | -0.002 | 0.008 | -0.004 |
| | 0.613 | 0.608 | 0.266 | 0.479 | 0.490 | 0.271 | 0.265 | -0.005 | 0.010 | -0.006 |
| | 0.726 | 0.727 | 0.408 | 0.621 | 0.624 | 0.213 | 0.226 | 0.002 | 0.003 | 0.013 |
| | 0.734 | 0.735 | 0.473 | 0.710 | 0.717 | 0.076 | 0.073 | 0.001 | 0.007 | -0.003 |
| | 0.878 | 0.880 | 0.605 | 0.752 | 0.759 | 0.184 | 0.179 | 0.002 | 0.007 | -0.005 |
| 293.15 | | | | | | | | | | |
| | 0.787 | 0.793 | 0.074 | 0.132 | 0.134 | 0.780 | 0.782 | 0.006 | 0.002 | 0.002 |
| | 0.669 | 0.666 | 0.113 | 0.247 | 0.245 | 0.387 | 0.392 | -0.003 | -0.001 | 0.005 |
| | 0.628 | 0.622 | 0.121 | 0.280 | 0.281 | 0.223 | 0.228 | -0.006 | 0.001 | 0.004 |
| | 0.722 | 0.716 | 0.211 | 0.427 | 0.427 | 0.172 | 0.174 | -0.006 | 0.000 | 0.003 |
| | 0.851 | 0.853 | 0.228 | 0.383 | 0.386 | 0.458 | 0.460 | 0.002 | 0.003 | 0.002 |
| | 0.817 | 0.813 | 0.262 | 0.464 | 0.467 | 0.269 | 0.271 | -0.003 | 0.003 | 0.002 |
| | 0.962 | 0.964 | 0.399 | 0.592 | 0.599 | 0.239 | 0.236 | 0.002 | 0.008 | -0.002 |
| | 0.975 | 0.975 | 0.469 | 0.693 | 0.697 | 0.078 | 0.076 | 0.000 | 0.003 | -0.001 |
| | 1.165 | 1.169 | 0.601 | 0.741 | 0.745 | 0.190 | 0.186 | 0.005 | 0.005 | -0.004 |
| 303.15 | | | | | | | | | | |
| | 1.033 | 1.034 | 0.074 | 0.126 | 0.784 | 0.779 | 0.784 | 0.001 | 0.001 | 0.005 |
| | 0.881 | 0.868 | 0.112 | 0.233 | 0.386 | 0.385 | 0.386 | -0.013 | 0.000 | 0.000 |
| | 0.828 | 0.813 | 0.119 | 0.261 | 0.223 | 0.223 | 0.223 | -0.015 | 0.002 | 0.000 |
| | 0.944 | 0.929 | 0.207 | 0.405 | 0.173 | 0.173 | 0.173 | -0.015 | -0.001 | 0.000 |
| | 1.109 | 1.101 | 0.216 | 0.348 | 0.487 | 0.494 | 0.487 | -0.008 | 0.009 | -0.008 |
| | 1.065 | 1.049 | 0.257 | 0.443 | 0.271 | 0.272 | 0.271 | -0.015 | 0.003 | -0.001 |
| | 1.246 | 1.240 | 0.391 | 0.571 | 0.242 | 0.245 | 0.242 | -0.007 | 0.009 | -0.003 |
| | 1.267 | 1.259 | 0.463 | 0.675 | 0.078 | 0.080 | 0.078 | -0.008 | 0.002 | -0.002 |
| | 1.515 | 1.511 | 0.597 | 0.729 | 0.191 | 0.196 | 0.191 | -0.004 | 0.005 | -0.004 |
| 313.15 | | | | | | | | | | |
| | 1.332 | 1.344 | 0.073 | 0.121 | 0.122 | 0.779 | 0.781 | 0.012 | 0.001 | 0.002 |
| | 1.140 | 1.137 | 0.110 | 0.219 | 0.217 | 0.383 | 0.387 | -0.003 | -0.002 | 0.004 |
| | 1.072 | 1.063 | 0.117 | 0.245 | 0.244 | 0.222 | 0.225 | -0.008 | -0.001 | 0.004 |
| | 1.210 | 1.201 | 0.202 | 0.379 | 0.377 | 0.174 | 0.177 | -0.009 | -0.002 | 0.002 |
| | 1.422 | 1.429 | 0.212 | 0.333 | 0.337 | 0.499 | 0.496 | 0.006 | 0.005 | -0.003 |
| | 1.365 | 1.362 | 0.255 | 0.423 | 0.424 | 0.276 | 0.278 | -0.004 | 0.001 | 0.002 |
| | 1.591 | 1.605 | 0.392 | 0.551 | 0.563 | 0.251 | 0.245 | 0.014 | 0.011 | -0.007 |
| | 1.620 | 1.621 | 0.463 | 0.655 | 0.656 | 0.082 | 0.081 | 0.001 | 0.001 | -0.001 |
| | 1.938 | 1.945 | 0.593 | 0.716 | 0.717 | 0.202 | 0.201 | 0.007 | 0.002 | -0.001 |
| 323.15 | | | | | | | | | | |
| | 1.691 | 1.706 | 0.072 | 0.115 | 0.116 | 0.778 | 0.780 | 0.015 | 0.001 | 0.002 |
| | 1.450 | 1.448 | 0.108 | 0.203 | 0.203 | 0.381 | 0.384 | -0.003 | -0.001 | 0.002 |
| | 1.365 | 1.356 | 0.115 | 0.229 | 0.227 | 0.221 | 0.222 | -0.009 | -0.002 | 0.002 |
| | 1.528 | 1.519 | 0.198 | 0.354 | 0.353 | 0.175 | 0.177 | -0.009 | -0.002 | 0.001 |
| | 1.794 | 1.803 | 0.206 | 0.316 | 0.317 | 0.504 | 0.505 | 0.009 | 0.001 | 0.001 |
| | 1.722 | 1.720 | 0.251 | 0.403 | 0.402 | 0.279 | 0.280 | -0.003 | 0.000 | 0.001 |
| | 1.991 | 2.000 | 0.377 | 0.527 | 0.531 | 0.258 | 0.256 | 0.010 | 0.003 | -0.002 |
| | 2.036 | 2.046 | 0.462 | 0.634 | 0.636 | 0.084 | 0.082 | 0.010 | 0.002 | -0.002 |
| | 2.437 | 2.449 | 0.588 | 0.700 | 0.700 | 0.210 | 0.209 | 0.012 | 0.001 | -0.001 |

The coefficients $\xi_n$ are calculated through the relation:

$$\xi_n = \frac{\pi}{6}\rho\sum_{i=1}^{nc} x_i m_i d_i^n,\ n \in [0,1,2,3] \tag{6}$$

The dispersion contribution term is given by:

$$\tilde{a}^{disp} = -2\pi\rho\left(\sum_{i=0}^{6} a_i(\overline{m})\eta^i\right)\overline{m^2\varepsilon\sigma^3} - \pi\rho\overline{m}C_1\left(\sum_{i=0}^{6} b_i(\overline{m})\eta^i\right)\overline{m^2\varepsilon^2\sigma^3} \tag{7}$$

where:

$$\overline{m} = \left(\sum_{i=1}^{nc} x_i\, m_i\right) \tag{8}$$

and

$$\rho = \frac{6}{\pi}\eta\left(\sum_{i=1}^{nc} x_i m_i d_i^3\right)^{-1} \tag{9}$$

Here, $\rho$ is the total number density of molecules, $\eta$ is the reduced segment density, which is equal to $\xi_3$ and $d_i$ is the temperature-dependent segment of component $i$ expressed by:

$$d_i = \sigma_i\left[1 - 0.12\exp\left(-3\frac{\varepsilon_i}{kT}\right)\right] \tag{10}$$

*Table 4. Experimental and calculated VLE in the system R134a(1) + R1234yf(2) + DME(3) [22].*

| T[K] | $P_{exp}$[MPa] | $P_{cal}$[MPa] | $x_{1exp}$ | $x_{2exp}$ | $y_{1exp}$ | $y_{1cal}$ | $y_{2exp}$ | $y_{2cal}$ | ΔP[MPa] | $\Delta y_1$ | $\Delta y_2$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 253.15 | | | | | | | | | | | |
| | 0.167 | 0.156 | 0.066 | 0.822 | 0.069 | 0.071 | 0.850 | 0.814 | -0.012 | 0.002 | -0.035 |
| | 0.152 | 0.148 | 0.35 | 0.280 | 0.353 | 0.325 | 0.361 | 0.345 | -0.004 | -0.028 | -0.016 |
| | 0.149 | 0.143 | 0.332 | 0.193 | 0.327 | 0.313 | 0.264 | 0.261 | -0.006 | -0.015 | -0.003 |
| | 0.167 | 0.156 | 0.081 | 0.737 | 0.085 | 0.085 | 0.788 | 0.737 | -0.011 | 0 | -0.051 |
| | 0.153 | 0.154 | 0.100 | 0.562 | 0.096 | 0.098 | 0.624 | 0.588 | 0.002 | 0.002 | -0.036 |
| 263.15 | | | | | | | | | | | |
| | 0.238 | 0.226 | 0.065 | 0.828 | 0.069 | 0.070 | 0.847 | 0.826 | -0.012 | 0.001 | -0.021 |
| | 0.218 | 0.213 | 0.354 | 0.285 | 0.358 | 0.336 | 0.352 | 0.346 | -0.004 | -0.022 | -0.006 |
| | 0.212 | 0.206 | 0.335 | 0.193 | 0.335 | 0.321 | 0.258 | 0.254 | -0.006 | -0.013 | -0.005 |
| | 0.237 | 0.225 | 0.082 | 0.745 | 0.085 | 0.085 | 0.785 | 0.750 | -0.011 | 0.001 | -0.035 |
| 273.15 | 0.220 | 0.222 | 0.100 | 0.563 | 0.097 | 0.099 | 0.623 | 0.592 | 0.002 | 0.001 | -0.030 |
| | 0.328 | 0.320 | 0.064 | 0.829 | 0.071 | 0.072 | 0.849 | 0.829 | -0.008 | 0.002 | -0.02 |
| | 0.305 | 0.301 | 0.356 | 0.281 | 0.360 | 0.346 | 0.347 | 0.342 | -0.004 | -0.014 | -0.006 |
| | 0.298 | 0.291 | 0.335 | 0.196 | 0.341 | 0.326 | 0.255 | 0.255 | -0.007 | -0.015 | 0.001 |
| | 0.330 | 0.318 | 0.077 | 0.752 | 0.090 | 0.085 | 0.776 | 0.760 | -0.012 | -0.005 | -0.016 |
| 283.15 | 0.310 | 0.312 | 0.093 | 0.570 | 0.090 | 0.096 | 0.636 | 0.600 | 0.002 | 0.005 | -0.035 |
| | 0.448 | 0.440 | 0.064 | 0.830 | 0.070 | 0.069 | 0.855 | 0.833 | -0.008 | 0.000 | -0.022 |
| | 0.421 | 0.415 | 0.356 | 0.289 | 0.362 | 0.350 | 0.340 | 0.339 | -0.006 | -0.011 | -0.001 |
| | 0.410 | 0.401 | 0.337 | 0.198 | 0.345 | 0.332 | 0.251 | 0.247 | -0.009 | -0.012 | -0.004 |
| | 0.450 | 0.437 | 0.071 | 0.756 | 0.076 | 0.076 | 0.789 | 0.767 | -0.013 | 0.000 | -0.022 |
| 293.15 | 0.427 | 0.428 | 0.092 | 0.580 | 0.092 | 0.093 | 0.637 | 0.608 | 0.001 | 0.002 | -0.029 |
| | 0.599 | 0.591 | 0.065 | 0.834 | 0.068 | 0.069 | 0.858 | 0.840 | -0.008 | 0.001 | -0.018 |
| | 0.568 | 0.556 | 0.359 | 0.295 | 0.362 | 0.357 | 0.339 | 0.339 | -0.012 | -0.005 | -0.001 |
| | 0.552 | 0.539 | 0.340 | 0.203 | 0.351 | 0.340 | 0.251 | 0.245 | -0.012 | -0.011 | -0.006 |
| | 0.582 | 0.586 | 0.070 | 0.763 | 0.073 | 0.073 | 0.799 | 0.776 | 0.004 | 0 | -0.023 |
| 303.15 | 0.576 | 0.572 | 0.092 | 0.585 | 0.093 | 0.093 | 0.638 | 0.613 | -0.003 | 0 | -0.024 |
| | 0.773 | 0.783 | 0.062 | 0.833 | 0.070 | 0.070 | 0.846 | 0.837 | 0.010 | 0.000 | -0.009 |
| | 0.742 | 0.742 | 0.363 | 0.297 | 0.352 | 0.368 | 0.351 | 0.343 | 0.000 | 0.016 | -0.009 |
| | 0.730 | 0.715 | 0.351 | 0.206 | 0.356 | 0.355 | 0.242 | 0.251 | -0.015 | -0.002 | 0.008 |
| | 0.762 | 0.777 | 0.071 | 0.776 | 0.084 | 0.079 | 0.797 | 0.786 | 0.016 | -0.004 | -0.011 |
| 313.15 | 0.748 | 0.759 | 0.102 | 0.600 | 0.104 | 0.108 | 0.637 | 0.626 | 0.011 | 0.004 | -0.011 |
| | 0.966 | 0.947 | 0.304 | 0.314 | 0.299 | 0.303 | 0.371 | 0.375 | -0.019 | 0.003 | 0.005 |
| | 1.016 | 1.022 | 0.061 | 0.843 | 0.073 | 0.072 | 0.854 | 0.845 | 0.006 | -0.001 | -0.009 |
| | 1.043 | 1.019 | 0.204 | 0.604 | 0.221 | 0.217 | 0.649 | 0.626 | -0.024 | -0.004 | -0.024 |
| | 0.955 | 0.951 | 0.364 | 0.288 | 0.357 | 0.364 | 0.362 | 0.351 | -0.004 | 0.007 | -0.012 |
| | 0.929 | 0.919 | 0.370 | 0.218 | 0.367 | 0.368 | 0.273 | 0.282 | -0.010 | 0.001 | 0.009 |
| | 0.993 | 1.014 | 0.071 | 0.783 | 0.081 | 0.081 | 0.801 | 0.792 | 0.021 | 0.000 | -0.009 |
| | 0.968 | 0.988 | 0.100 | 0.617 | 0.104 | 0.107 | 0.667 | 0.644 | 0.020 | 0.002 | -0.023 |

*T* is the absolute temperature; *k* is the Boltzmann constant; $\sigma_i$ is the segment diameter and $\varepsilon_i$ is the depth of the pair potential.

The coefficients $a_i(\bar{m})$ and $b_i(\bar{m})$ depend on the chain length and are calculated as follows:

$$a_i(\bar{m}) = a_{0i} + \frac{\bar{m}-1}{\bar{m}} a_{1i} + \frac{\bar{m}-1}{\bar{m}} \frac{\bar{m}-2}{\bar{m}} a_{2i} \quad (11)$$

$$b_i(\bar{m}) = b_{0i} + \frac{\bar{m}-1}{\bar{m}} b_{1i} + \frac{\bar{m}-1}{\bar{m}} \frac{\bar{m}-2}{\bar{m}} b_{2i} \quad (12)$$

where, the universal constants $a_{ki}$ and $b_{ki}$ ($k$ = 0, 1, 2) are available in the literature [1].

The expression of the term $C_1$ in Eq. (7) is given by the following:

$$C_1 = \left[1 + \bar{m}\frac{8\eta - 2\eta^2}{(1-\eta)^4} + (1-\bar{m})\frac{20\eta - 27\eta^2 + 12\eta^3 - 2\eta^4}{[(1-\eta)(2-\eta)]^2}\right]^{-1} \quad (13)$$

The abbreviations are as follows:

$$\overline{m^2\varepsilon\sigma^3} = \sum_i \sum_j x_i x_j m_i m_j \left(\frac{\varepsilon_{ij}}{kT}\right) {\sigma_{ij}}^3 \quad (14)$$

$$\overline{m^2\varepsilon^2\sigma^3} = \sum_i \sum_j x_i x_j m_i m_j \left(\frac{\varepsilon_{ij}}{kT}\right)^2 {\sigma_{ij}}^3 \quad (15)$$

To determine the parameters for a pair of unlike segments, conventional combining rules are employed:

$$\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j) \quad (16)$$

$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}\left(1 - k_{ij}\right) \quad (17)$$

where $k_{ij}$ are the binary interaction parameters.

*Table 5. Experimental and calculated VLE in the system R134a(1) + R1234yf(2) + R600a(3) [21].*

| T[K] | $P_{exp}$[MPa] | $P_{cal}$[MPa] | $x_{1exp}$ | $x_{2exp}$ | $y_{1exp}$ | $y_{1cal}$ | $y_{2exp}$ | $y_{2cal}$ | ΔP[MPa] | Δ$y_1$ | Δ$y_2$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 283.15 | | | | | | | | | | | |
| | 0.460 | 0.454 | 0.172 | 0.354 | 0.268 | 0.254 | 0.429 | 0.427 | -0.006 | -0.013 | -0.002 |
| | 0.462 | 0.464 | 0.217 | 0.421 | 0.277 | 0.267 | 0.440 | 0.448 | 0.002 | -0.010 | 0.008 |
| | 0.464 | 0.463 | 0.254 | 0.266 | 0.361 | 0.366 | 0.316 | 0.313 | -0.001 | 0.005 | -0.003 |
| | 0.465 | 0.465 | 0.278 | 0.223 | 0.397 | 0.410 | 0.259 | 0.265 | 0.000 | 0.013 | 0.006 |
| | 0.470 | 0.473 | 0.352 | 0.112 | 0.499 | 0.533 | 0.138 | 0.134 | 0.004 | 0.034 | -0.004 |
| | 0.476 | 0.474 | 0.399 | 0.376 | 0.441 | 0.406 | 0.364 | 0.355 | -0.002 | -0.035 | -0.009 |
| | 0.475 | 0.477 | 0.408 | 0.249 | 0.465 | 0.463 | 0.263 | 0.247 | 0.002 | -0.002 | -0.016 |
| | 0.477 | 0.472 | 0.669 | 0.203 | 0.634 | 0.621 | 0.184 | 0.186 | -0.005 | -0.013 | 0.003 |
| | 0.476 | 0.448 | 0.675 | 0.274 | 0.640 | 0.634 | 0.237 | 0.267 | -0.028 | -0.006 | 0.029 |
| 293.15 | | | | | | | | | | | |
| | 0.613 | 0.607 | 0.172 | 0.354 | 0.253 | 0.250 | 0.428 | 0.425 | -0.005 | -0.003 | -0.003 |
| | 0.623 | 0.623 | 0.217 | 0.421 | 0.275 | 0.266 | 0.446 | 0.448 | 0.000 | -0.009 | 0.003 |
| | 0.622 | 0.618 | 0.254 | 0.266 | 0.351 | 0.360 | 0.302 | 0.313 | -0.003 | 0.009 | 0.010 |
| | 0.624 | 0.620 | 0.278 | 0.223 | 0.386 | 0.402 | 0.259 | 0.265 | -0.004 | 0.016 | 0.006 |
| | 0.630 | 0.629 | 0.352 | 0.112 | 0.488 | 0.523 | 0.133 | 0.135 | -0.001 | 0.035 | 0.002 |
| | 0.641 | 0.639 | 0.399 | 0.376 | 0.441 | 0.411 | 0.365 | 0.359 | -0.002 | -0.030 | -0.006 |
| | 0.642 | 0.641 | 0.408 | 0.249 | 0.470 | 0.464 | 0.275 | 0.249 | -0.001 | -0.006 | -0.025 |
| | 0.647 | 0.638 | 0.669 | 0.203 | 0.641 | 0.632 | 0.191 | 0.190 | -0.009 | -0.009 | -0.001 |
| | 0.645 | 0.610 | 0.675 | 0.274 | 0.651 | 0.643 | 0.243 | 0.268 | -0.035 | -0.008 | 0.025 |
| 303.15 | | | | | | | | | | | |
| | 0.808 | 0.799 | 0.172 | 0.354 | 0.247 | 0.246 | 0.419 | 0.424 | -0.008 | -0.001 | 0.004 |
| | 0.820 | 0.824 | 0.217 | 0.421 | 0.276 | 0.266 | 0.452 | 0.449 | 0.003 | -0.009 | -0.003 |
| | 0.819 | 0.813 | 0.254 | 0.266 | 0.347 | 0.354 | 0.308 | 0.314 | -0.006 | 0.007 | 0.006 |
| | 0.822 | 0.814 | 0.278 | 0.223 | 0.386 | 0.394 | 0.264 | 0.267 | -0.008 | 0.009 | 0.004 |
| | 0.830 | 0.820 | 0.352 | 0.112 | 0.489 | 0.512 | 0.138 | 0.138 | -0.009 | 0.023 | 0.000 |
| | 0.849 | 0.850 | 0.399 | 0.376 | 0.440 | 0.416 | 0.369 | 0.364 | 0.001 | -0.025 | -0.005 |
| | 0.848 | 0.848 | 0.408 | 0.249 | 0.473 | 0.463 | 0.281 | 0.255 | -0.001 | -0.010 | -0.027 |
| | 0.859 | 0.849 | 0.669 | 0.203 | 0.646 | 0.640 | 0.191 | 0.197 | -0.010 | -0.006 | 0.006 |
| | 0.858 | 0.821 | 0.675 | 0.274 | 0.653 | 0.648 | 0.252 | 0.273 | -0.036 | -0.005 | 0.022 |
| 313.15 | | | | | | | | | | | |
| | 1.042 | 1.036 | 0.172 | 0.354 | 0.244 | 0.240 | 0.410 | 0.422 | -0.006 | -0.004 | 0.012 |
| | 1.062 | 1.071 | 0.217 | 0.421 | 0.270 | 0.263 | 0.456 | 0.450 | 0.010 | -0.007 | -0.007 |
| | 1.057 | 1.052 | 0.254 | 0.266 | 0.344 | 0.346 | 0.318 | 0.315 | -0.005 | 0.002 | -0.004 |
| | 1.063 | 1.052 | 0.278 | 0.223 | 0.377 | 0.385 | 0.271 | 0.268 | -0.011 | 0.008 | -0.002 |
| | 1.071 | 1.056 | 0.352 | 0.112 | 0.486 | 0.500 | 0.139 | 0.139 | -0.015 | 0.013 | 0.001 |
| | 1.102 | 1.109 | 0.399 | 0.376 | 0.438 | 0.416 | 0.372 | 0.367 | 0.007 | -0.022 | -0.005 |
| | 1.100 | 1.102 | 0.408 | 0.249 | 0.468 | 0.460 | 0.282 | 0.258 | 0.001 | -0.008 | -0.024 |
| | 1.120 | 1.109 | 0.669 | 0.203 | 0.653 | 0.646 | 0.192 | 0.199 | -0.011 | -0.007 | 0.007 |
| | 1.116 | 1.079 | 0.675 | 0.274 | 0.659 | 0.653 | 0.258 | 0.274 | -0.037 | -0.006 | 0.017 |
| 323.15 | | | | | | | | | | | |
| | 1.321 | 1.312 | 0.172 | 0.354 | 0.241 | 0.236 | 0.421 | 0.418 | -0.009 | -0.005 | -0.003 |
| | 1.351 | 1.364 | 0.217 | 0.421 | 0.271 | 0.262 | 0.458 | 0.449 | 0.013 | -0.008 | -0.009 |
| | 1.341 | 1.332 | 0.254 | 0.266 | 0.346 | 0.339 | 0.316 | 0.314 | -0.009 | -0.007 | -0.002 |
| | 1.350 | 1.330 | 0.278 | 0.223 | 0.372 | 0.377 | 0.278 | 0.268 | -0.020 | 0.005 | -0.010 |
| | 1.359 | 1.329 | 0.352 | 0.112 | 0.479 | 0.488 | 0.138 | 0.140 | -0.030 | 0.009 | 0.002 |
| | 1.407 | 1.422 | 0.399 | 0.376 | 0.440 | 0.419 | 0.375 | 0.371 | 0.015 | -0.021 | -0.004 |
| | 1.404 | 1.404 | 0.408 | 0.249 | 0.463 | 0.459 | 0.290 | 0.260 | 0.000 | -0.004 | -0.030 |
| | 1.436 | 1.427 | 0.669 | 0.203 | 0.661 | 0.652 | 0.194 | 0.203 | -0.009 | -0.009 | 0.010 |
| | 1.429 | 1.400 | 0.675 | 0.274 | 0.667 | 0.657 | 0.261 | 0.277 | -0.030 | -0.009 | 0.016 |

## 3. Numerical Procedure and Results

Azeotropic mixtures present a compelling option for refrigerants since they exhibit behavior closely resembling that of pure substances. Numerous approaches and methods have been explored for predicting azeotropic positions and vapor-liquid equilibrium in ternary mixtures. In this paper, a PC-SAFT model to predict the azeotropic positions of ternary mixture refrigerants was developed. The obtained results were compared with experimental data and confirmed the validity of our method.

The PC-SAFT model was used to determine the azeotropic composition ($x_{az}$) and azeotropic pressure ($P_{az}$) for ternary systems. The identification of azeotropic behavior in mixtures was based on the application of the Gibbs-Konovalov theorem [16]. This theorem postulates that under constant temperature conditions, the vapor and liquid phases possess identical compositions ($x_i = y_i$), and the bubble and dew point curves exhibit a local extremum:

for $i$ = 1 to $n_c$;

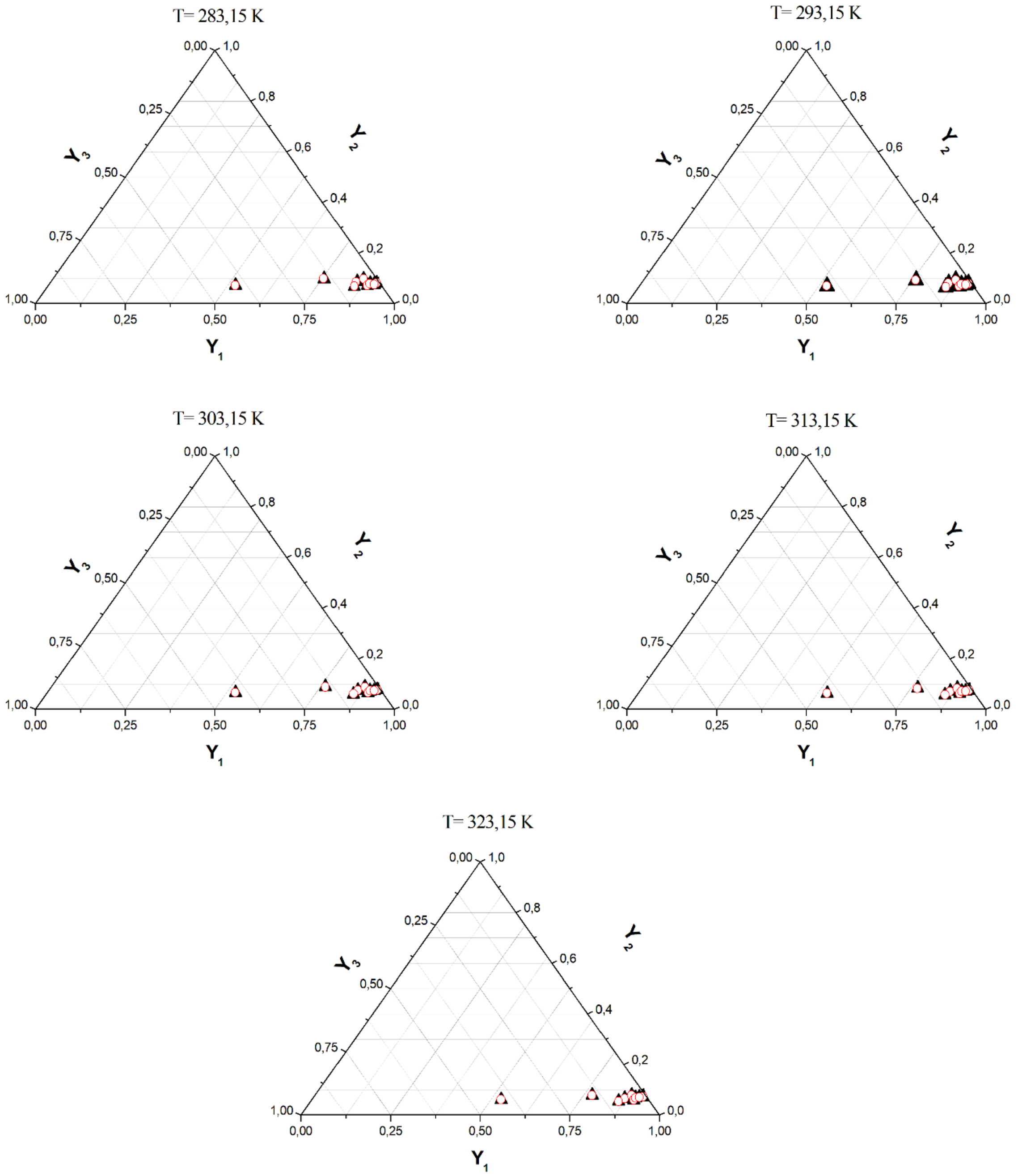


*Figure 3. VLE of ternary mixture R32(1) + R161(2) + R1234ze(E)(3).*
*(▲): Experimental data [19]; (○): PC-SAFT prediction.*

$$\left(\frac{\partial P}{\partial x_i}\right)_{T,x_j} = -\frac{\partial}{\partial x_i}\left[\left(\frac{\partial \tilde{a}^{res}}{\partial T}\right)_V\right]_{T,x_j} = 0 \qquad (18)$$

Eq. (18) serves as the criterion for assessing azeotropic properties. The process for computing azeotropic points ($x_{az}$, $P_{az}$) based on the proposed approach is presented in Figure1.

In the case of non-associating compounds, the PC-SAFT equation parameters for the pure components $m_i$, $\sigma_i$, and $(\varepsilon/k)_i$ are indispensable for establishing azeotropic properties in ternary mixtures. Anoune et al [17] offer a correlation that enables the determination of PC-SAFT parameters for the pure components under investigation, using only the critical temperature ($T_C$), critical pressure ($P_C$), and acentric factor ($\omega$) as input data. The PC-SAFT parameter values of the selected compounds are displayed in Table 1.

We note that the binary interaction parameters $k_{ij}$ were obtained by minimizing the following objective function:

$$F_{obj} = \frac{100}{N}\left[\sum_1^N\left(\frac{P_{exp}-P_{cal}}{P_{exp}}\right)^2 + \sum_1^N\left(\frac{x_{exp}-x_{cal}}{x_{exp}}\right)^2\right] \qquad (19)$$

The interaction parameters $k_{ij}$ were optimized by minimizing objective function by simplex using the Newton Raphson iterative method. The objective function $F_{obj}$ was minimized using Dichotomy method [17].

The deviations, $MRD(U)$, and $Bias(U)$ applied to both the mole fractions in the liquid and vapor phases as well as to the

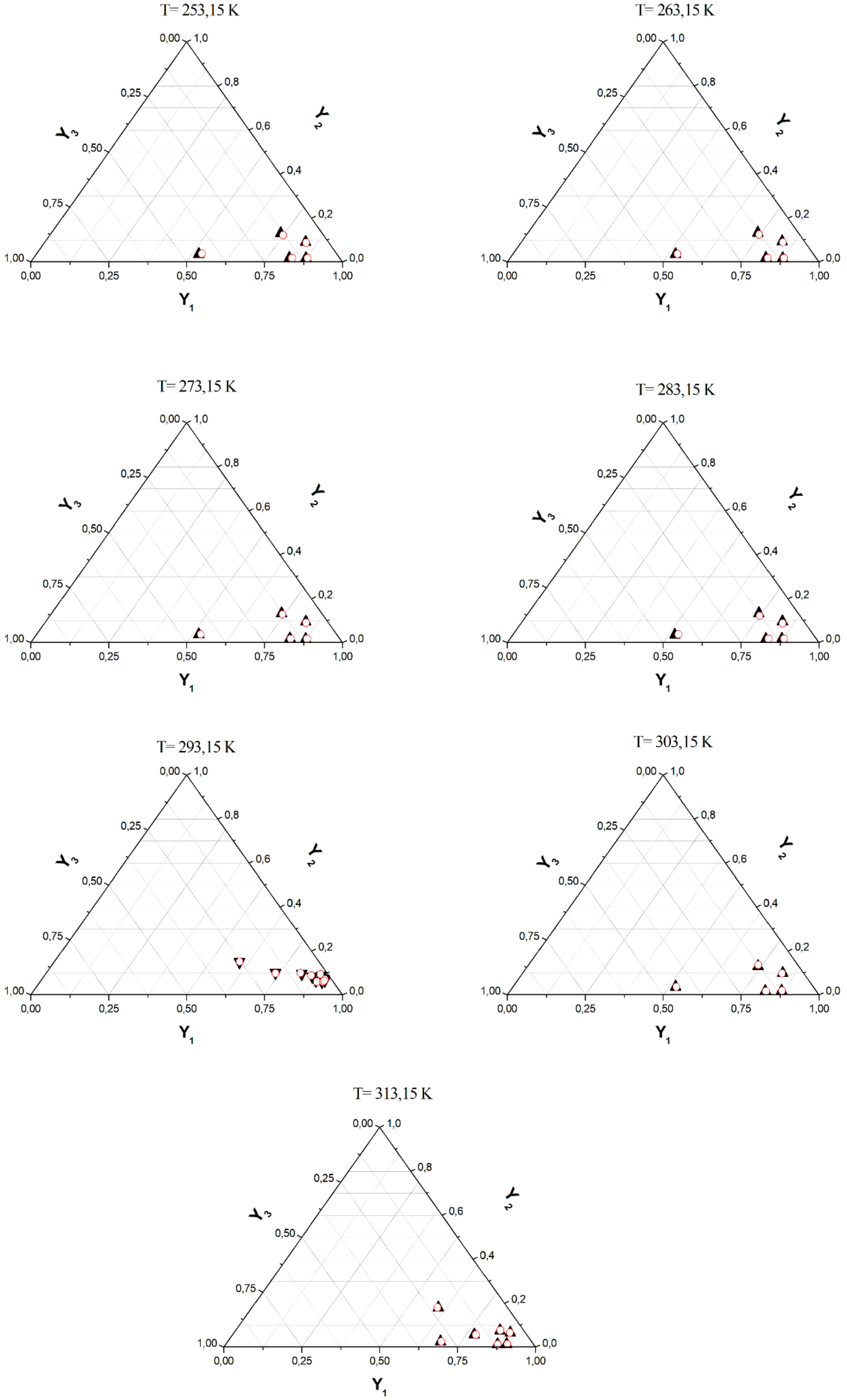


*Figure 4. VLE of ternary mixture R134a(1) + R1234yf(2) + DME(3).*
*(▲): Experimental data [22]; (○): PC-SAFT prediction.*

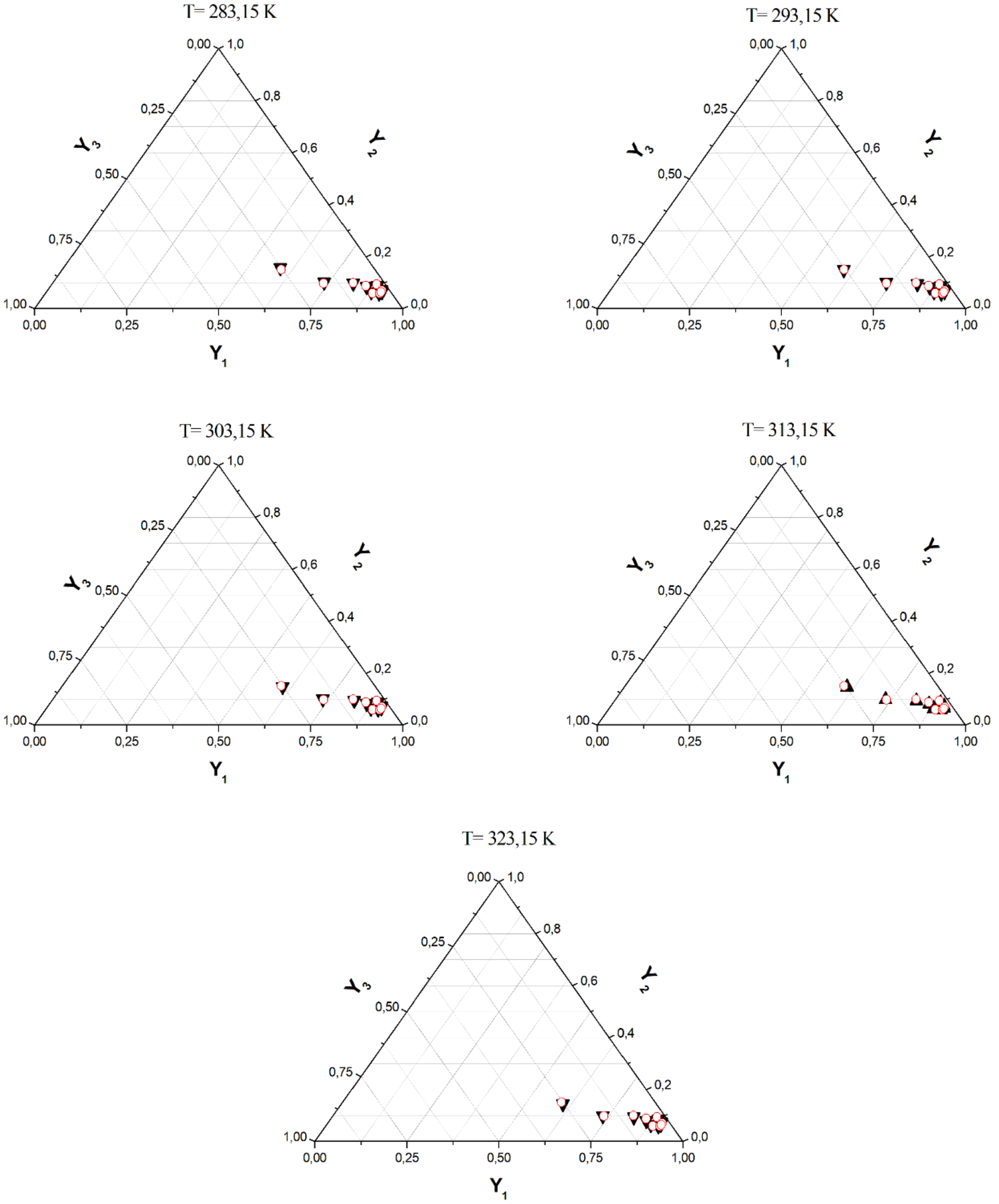


*Figure 5. VLE of ternary mixture R134a(1) + R1234yf(2) + R600a(3).*
*(▲): Experimental data [21]; (○): PC-SAFT prediction.*

saturated pressure of mixtures are defined as follows:

$$MRD(U) = \frac{100}{N}\sum\left|\left(\frac{(U_{exp}-U_{cal})}{U_{exp}}\right)\right| \quad (20)$$

$$Bias(U) = \frac{100}{N}\sum\left(\frac{(U_{exp}-U_{cal})}{U_{exp}}\right) \quad (21)$$

where $N$ is the number of data points, and $U$ is $P$, $x_i$ or $y_i$.

### 3.1 VLE in Ternary Mixtures

The VLE data for the six ternary mixtures investigated are tabulated in Tables (2–7) and graphically presented in Figures (2–7) at different temperatures. Additionally, the binary interaction parameter $k_{ij}$, the objective function $F_{obj}$, the relative deviation MRD, and the Bias obtained by fitting experimental VLE data with the PC-SAFT model are reported in Table 8.

It is noteworthy that the predictions for pressure exhibit strong agreement with the experimental values. Specifically, the relative deviation remains below 1% for three mixtures: R32 + R152a + R1234yf [18], R32 + R161 + R1234ze(E) [19] and R600a + R1234ze(E) + R13I1[20]. In the case of the R134a + R1234yf + R600a [21] mixture, the relative error does not exceed 1.15% at 283.15 K. The highest relative deviation is observed for the R134a + R1234yf + DME [22] mixture, reaching 4.26% at 253.15 K. For the R600a + R152a + R134 [23] mixture at the same temperature, the error remains within 2.78%. In conclusion, these results demonstrate a strong concurrence between the calculated values and the experimental data taken from the literature.

### 3.2 Azeotropic Prediction

Among the six ternary mixtures examined only three exhibit azeotropic behavior. These mixtures are as follows:

*Table 6. Experimental and calculated VLE in the system R600a(1) + R152a(2) + R134(3) [23].*

| T[K] | $P_{exp}$[MPa] | $P_{cal}$[MPa] | $x_{1exp}$ | $x_{2exp}$ | $y_{1exp}$ | $y_{1cal}$ | $y_{2exp}$ | $y_{2cal}$ | ΔP[MPa] | $\Delta y_1$ | $\Delta y_2$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 253.15 | | | | | | | | | | | |
| | 0.129 | 0.130 | 0.799 | 0.098 | 0.500 | 0.403 | 0.228 | 0.248 | 0.001 | -0.097 | 0.020 |
| | 0.145 | 0.145 | 0.572 | 0.066 | 0.417 | 0.356 | 0.078 | 0.074 | 0.000 | -0.061 | -0.004 |
| | 0.143 | 0.137 | 0.415 | 0.336 | 0.396 | 0.374 | 0.347 | 0.356 | -0.006 | -0.022 | 0.009 |
| | 0.143 | 0.137 | 0.367 | 0.409 | 0.382 | 0.368 | 0.403 | 0.418 | -0.006 | -0.014 | 0.015 |
| | 0.143 | 0.137 | 0.365 | 0.410 | 0.379 | 0.369 | 0.413 | 0.417 | -0.006 | -0.010 | 0.004 |
| | 0.143 | 0.138 | 0.327 | 0.470 | 0.368 | 0.361 | 0.447 | 0.465 | -0.005 | -0.007 | 0.018 |
| | 0.142 | 0.138 | 0.320 | 0.493 | 0.360 | 0.356 | 0.471 | 0.488 | -0.004 | -0.004 | 0.017 |
| | 0.142 | 0.138 | 0.313 | 0.497 | 0.359 | 0.355 | 0.471 | 0.488 | -0.004 | -0.004 | 0.017 |
| | 0.142 | 0.138 | 0.312 | 0.498 | 0.360 | 0.355 | 0.469 | 0.489 | -0.004 | -0.005 | 0.020 |
| | 0.139 | 0.136 | 0.152 | 0.326 | 0.349 | 0.379 | 0.234 | 0.233 | -0.003 | 0.030 | -0.001 |
| | 0.143 | 0.138 | 0.379 | 0.227 | 0.398 | 0.389 | 0.207 | 0.202 | -0.005 | -0.009 | -0.005 |
| | 0.143 | 0.139 | 0.458 | 0.194 | 0.409 | 0.378 | 0.199 | 0.196 | -0.004 | -0.031 | -0.003 |
| 263.15 | | | | | | | | | | | |
| | 0.199 | 0.198 | 0.739 | 0.123 | 0.473 | 0.396 | 0.236 | 0.247 | -0.001 | -0.077 | 0.011 |
| | 0.214 | 0.213 | 0.597 | 0.066 | 0.419 | 0.363 | 0.079 | 0.080 | 0.000 | -0.056 | 0.001 |
| | 0.211 | 0.203 | 0.414 | 0.337 | 0.387 | 0.369 | 0.350 | 0.359 | -0.008 | -0.018 | 0.009 |
| | 0.211 | 0.203 | 0.374 | 0.404 | 0.374 | 0.361 | 0.407 | 0.419 | -0.007 | -0.013 | 0.012 |
| | 0.209 | 0.203 | 0.365 | 0.419 | 0.372 | 0.359 | 0.417 | 0.432 | -0.006 | -0.013 | 0.015 |
| | 0.210 | 0.204 | 0.338 | 0.463 | 0.360 | 0.352 | 0.452 | 0.468 | -0.006 | -0.008 | 0.016 |
| | 0.210 | 0.204 | 0.318 | 0.495 | 0.350 | 0.346 | 0.477 | 0.494 | -0.005 | -0.004 | 0.017 |
| | 0.209 | 0.204 | 0.313 | 0.497 | 0.352 | 0.346 | 0.474 | 0.493 | -0.005 | -0.006 | 0.019 |
| | 0.209 | 0.204 | 0.310 | 0.499 | 0.350 | 0.345 | 0.475 | 0.493 | -0.005 | -0.005 | 0.018 |
| | 0.205 | 0.202 | 0.177 | 0.311 | 0.328 | 0.363 | 0.243 | 0.232 | -0.003 | 0.035 | -0.011 |
| | 0.211 | 0.205 | 0.380 | 0.226 | 0.389 | 0.380 | 0.210 | 0.205 | -0.006 | -0.009 | -0.005 |
| | 0.211 | 0.206 | 0.462 | 0.193 | 0.404 | 0.375 | 0.202 | 0.199 | -0.005 | -0.029 | -0.003 |
| 273.15 | | | | | | | | | | | |
| | 0.282 | 0.279 | 0.739 | 0.123 | 0.483 | 0.413 | 0.233 | 0.243 | -0.002 | -0.070 | 0.010 |
| | 0.303 | 0.303 | 0.595 | 0.066 | 0.422 | 0.371 | 0.080 | 0.080 | 0.000 | -0.051 | 0.000 |
| | 0.302 | 0.291 | 0.416 | 0.336 | 0.388 | 0.364 | 0.348 | 0.361 | -0.011 | -0.024 | 0.013 |
| | 0.302 | 0.292 | 0.374 | 0.404 | 0.367 | 0.355 | 0.411 | 0.422 | -0.010 | -0.012 | 0.011 |
| | 0.300 | 0.292 | 0.365 | 0.418 | 0.366 | 0.353 | 0.419 | 0.433 | -0.008 | -0.013 | 0.014 |
| | 0.300 | 0.293 | 0.337 | 0.463 | 0.353 | 0.344 | 0.455 | 0.471 | -0.007 | -0.009 | 0.016 |
| | 0.300 | 0.294 | 0.318 | 0.495 | 0.343 | 0.337 | 0.481 | 0.498 | -0.007 | -0.006 | 0.017 |
| | 0.300 | 0.294 | 0.314 | 0.497 | 0.343 | 0.336 | 0.480 | 0.498 | -0.006 | -0.007 | 0.018 |
| | 0.299 | 0.293 | 0.310 | 0.499 | 0.335 | 0.336 | 0.485 | 0.497 | -0.006 | 0.001 | 0.012 |
| | 0.293 | 0.288 | 0.173 | 0.313 | 0.306 | 0.337 | 0.254 | 0.243 | -0.005 | 0.031 | -0.011 |
| | 0.302 | 0.295 | 0.380 | 0.227 | 0.382 | 0.372 | 0.214 | 0.210 | -0.007 | -0.010 | -0.004 |
| | 0.301 | 0.295 | 0.462 | 0.193 | 0.401 | 0.373 | 0.204 | 0.201 | -0.006 | -0.028 | -0.003 |

R600a + R1234ze(E) + R13I1 at temperatures of 243.15 K, 263.15 K, and 283.15 K, R600a + R152a + R134 at temperatures of 253.15 K, 263.15 K, and 273.15 K. Lastly, R134a + R1234yf + R600a demonstrates azeotropic behavior at temperatures of 313.15 K and 323.13 K.

Table 9 presents both the experimental and PC-SAFT model-calculated compositions and pressures for these ternary azeotrope mixtures. The relative errors between the experimental and calculated azeotropic compositions and pressures are calculated using the following relations:

$$\Delta x_{\mathrm{az}} = \frac{|x_{\mathrm{az}}^{\mathrm{exp}} - x_{\mathrm{az}}^{\mathrm{cal}}|}{x_{\mathrm{az}}^{\mathrm{exp}}} \times 100 \tag{22}$$

For pressure:

$$\Delta P_{\mathrm{az}} = \frac{|P_{\mathrm{az}}^{\mathrm{exp}} - P_{\mathrm{az}}^{\mathrm{cal}}|}{P_{\mathrm{az}}^{\mathrm{exp}}} \times 100 \tag{23}$$

For the (R600a + R1234ze(E) + R13I1) ternary mixture, the maximum relative errors do not exceed ($\Delta x_1$=5.26%, $\Delta x_2$=6.56%) for molar fractions and 1.39% for pressure (see Table 9). Similarly, for the (R600a + R152a + R134) mixture, the relative errors do not exceed ($\Delta x_1$=3.48%, $\Delta x_2$=3.71%) for molar fractions and 4.20% for pressure. As for the (R134a + R1234yf + R600a) ternary mixture, the maximum relative errors in molar fractions are ($\Delta x_1$=3.44% and $\Delta x_2$=1.97%), with a maximum relative pressure error of ΔP=0.98%.

The relative errors found when comparing the experimental and calculated values for each ternary system are well within acceptable limits. This comparison stands out well when considering the research conducted by Maalem et al [14]. They used three different models (relative volatility, NRTL, and Wilson) to predict azeotropic compositions and pressures for the same ternary mixtures. This suggests that the PC-SAFT model is effective in predicting azeotropic points in ternary systems.

## 4. Conclusion

A comprehensive study on six different ternary mixtures at different temperatures to predict their azeotropic behavior was conducted. To achieve this, the Perturbed-Chain SAFT (PC-SAFT) equation of state, with estimated binary

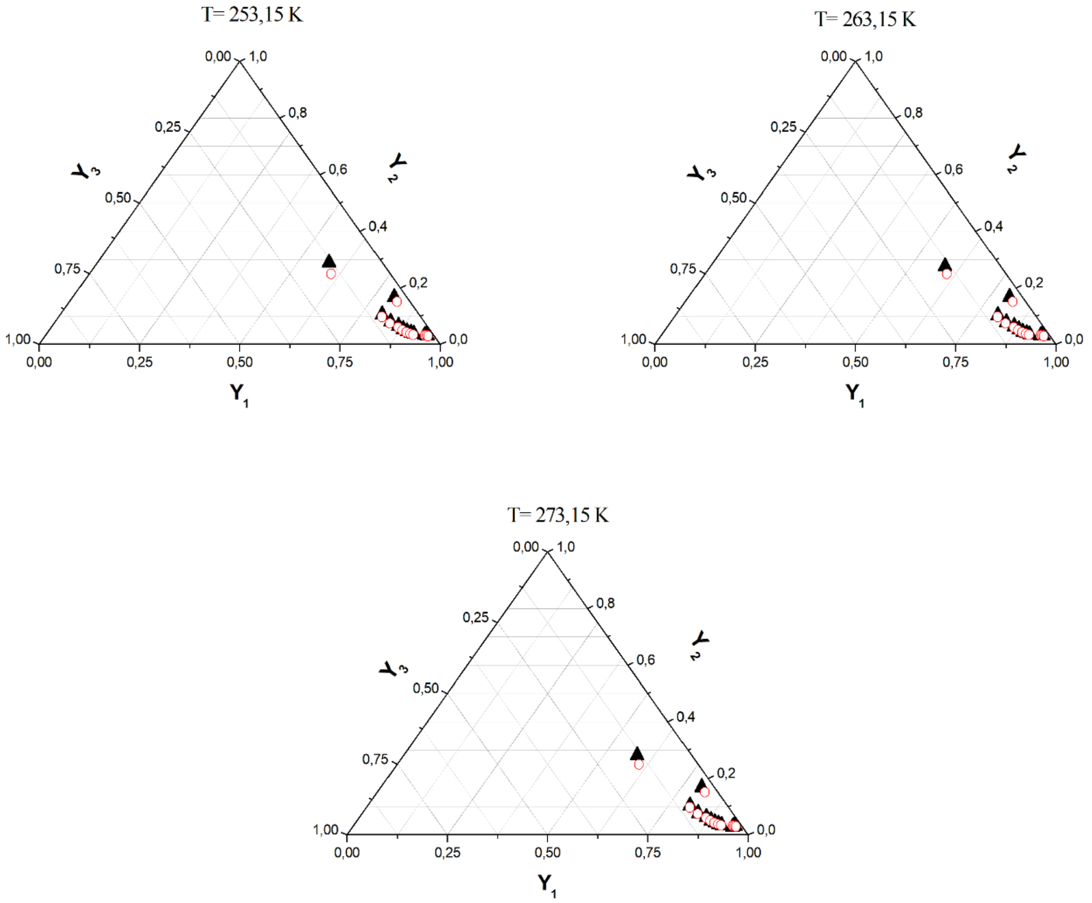


*Figure 6. VLE of ternary mixture R600a(1) + R152a(2) + R134(3).*
*(▲): Experimental data [23]; (○): PC-SAFT prediction.*

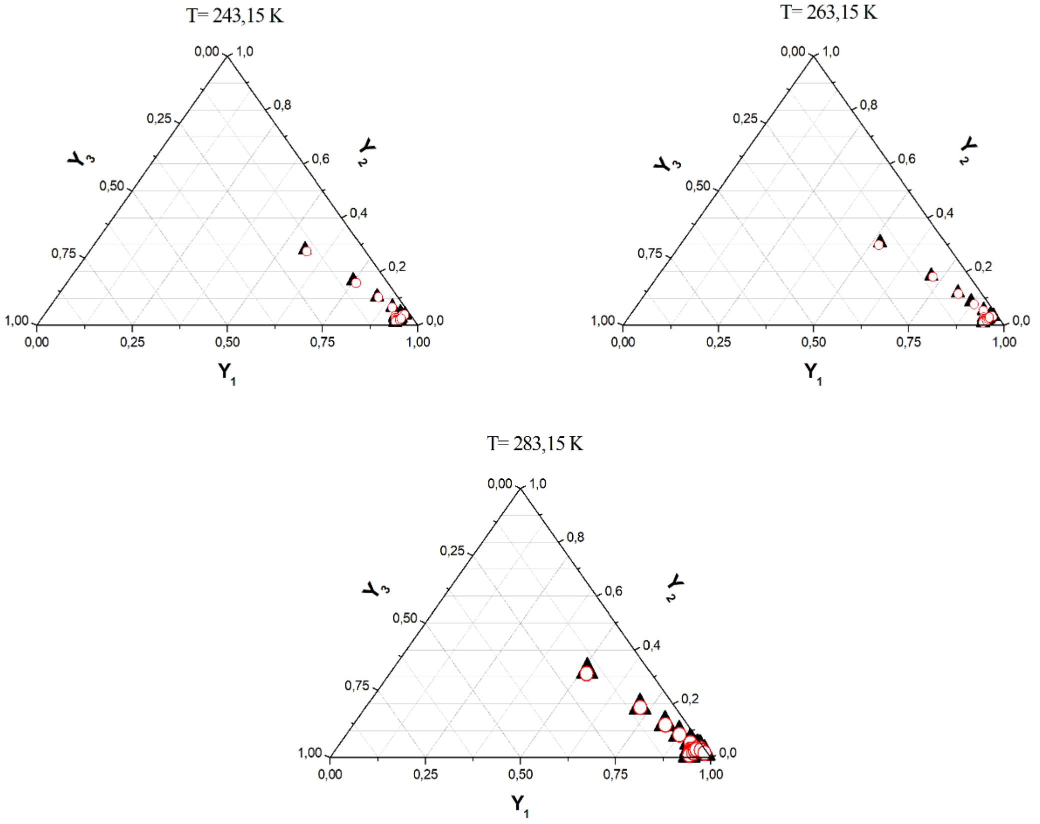


*Figure 7. VLE of ternary mixture R600a(1) + R1234ze(E)(2) + R13I1(3).*
*(▲): Experimental data [20]; (○): PC-SAFT prediction.*

*Table 7. Experimental and calculated VLE in the system R600a(1) + R1234ze(E)(2) + R13I1(3) [20].*

| T[K] | $P_{exp}$[MPa] | $P_{cal}$[MPa] | $x_{1exp}$ | $x_{2exp}$ | $y_{1exp}$ | $y_{1cal}$ | $y_{2exp}$ | $y_{2cal}$ | ΔP[MPa] | $\Delta y_1$ | $\Delta y_2$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 243.15 | | | | | | | | | | | |
| | 0.070 | 0.070 | 0.669 | 0.129 | 0.498 | 0.481 | 0.276 | 0.268 | 0.000 | -0.017 | -0.008 |
| | 0.072 | 0.072 | 0.571 | 0.112 | 0.442 | 0.415 | 0.231 | 0.218 | 0.000 | -0.027 | -0.013 |
| | 0.073 | 0.072 | 0.504 | 0.096 | 0.379 | 0.372 | 0.192 | 0.181 | -0.001 | -0.007 | -0.011 |
| | 0.074 | 0.074 | 0.383 | 0.087 | 0.301 | 0.294 | 0.148 | 0.151 | 0.000 | -0.007 | 0.003 |
| | 0.075 | 0.075 | 0.246 | 0.069 | 0.248 | 0.203 | 0.123 | 0.113 | 0.000 | -0.045 | -0.010 |
| | 0.073 | 0.074 | 0.307 | 0.055 | 0.248 | 0.246 | 0.092 | 0.096 | 0.000 | -0.002 | 0.004 |
| | 0.079 | 0.079 | 0.312 | 0.262 | 0.258 | 0.253 | 0.328 | 0.326 | 0.000 | -0.005 | -0.002 |
| | 0.079 | 0.080 | 0.277 | 0.350 | 0.244 | 0.240 | 0.390 | 0.386 | 0.001 | -0.004 | -0.004 |
| | 0.079 | 0.080 | 0.258 | 0.400 | 0.236 | 0.235 | 0.423 | 0.417 | 0.001 | -0.001 | -0.006 |
| | 0.080 | 0.080 | 0.209 | 0.518 | 0.219 | 0.220 | 0.492 | 0.484 | 0.001 | 0.001 | -0.008 |
| | 0.077 | 0.078 | 0.135 | 0.685 | 0.186 | 0.187 | 0.606 | 0.586 | 0.001 | 0.001 | -0.020 |
| | 0.075 | 0.075 | 0.099 | 0.792 | 0.159 | 0.169 | 0.683 | 0.673 | 0.000 | 0.010 | -0.010 |
| | 0.081 | 0.079 | 0.268 | 0.553 | 0.273 | 0.279 | 0.520 | 0.520 | -0.001 | 0.006 | 0.000 |
| | 0.080 | 0.078 | 0.465 | 0.389 | 0.399 | 0.375 | 0.461 | 0.467 | -0.001 | -0.024 | 0.006 |
| 263.15 | | | | | | | | | | | |
| | 0.156 | 0.155 | 0.765 | 0.166 | 0.592 | 0.572 | 0.329 | 0.342 | 0.000 | -0.020 | 0.013 |
| | 0.157 | 0.158 | 0.664 | 0.136 | 0.511 | 0.496 | 0.276 | 0.266 | 0.001 | -0.015 | -0.010 |
| | 0.161 | 0.161 | 0.569 | 0.122 | 0.442 | 0.428 | 0.222 | 0.224 | 0.000 | -0.014 | 0.002 |
| | 0.163 | 0.163 | 0.459 | 0.104 | 0.401 | 0.353 | 0.198 | 0.180 | 0.000 | -0.048 | -0.018 |
| | 0.164 | 0.165 | 0.373 | 0.088 | 0.300 | 0.294 | 0.145 | 0.147 | 0.001 | -0.006 | 0.002 |
| | 0.166 | 0.165 | 0.254 | 0.062 | 0.238 | 0.211 | 0.110 | 0.101 | -0.001 | -0.027 | -0.009 |
| | 0.164 | 0.163 | 0.302 | 0.050 | 0.246 | 0.247 | 0.083 | 0.086 | -0.001 | 0.001 | 0.003 |
| | 0.176 | 0.177 | 0.302 | 0.269 | 0.249 | 0.248 | 0.338 | 0.333 | 0.001 | -0.001 | -0.005 |
| | 0.178 | 0.180 | 0.27 | 0.350 | 0.233 | 0.234 | 0.402 | 0.393 | 0.001 | 0.001 | -0.009 |
| | 0.179 | 0.180 | 0.249 | 0.403 | 0.224 | 0.225 | 0.437 | 0.429 | 0.001 | 0.001 | -0.008 |
| | 0.180 | 0.181 | 0.204 | 0.513 | 0.219 | 0.207 | 0.489 | 0.499 | 0.001 | -0.012 | 0.010 |
| | 0.177 | 0.176 | 0.128 | 0.694 | 0.164 | 0.166 | 0.629 | 0.622 | 0.000 | 0.002 | -0.007 |
| | 0.172 | 0.172 | 0.093 | 0.778 | 0.136 | 0.14 | 0.701 | 0.692 | 0.000 | 0.004 | -0.009 |
| | 0.180 | 0.180 | 0.262 | 0.552 | 0.264 | 0.264 | 0.545 | 0.538 | -0.001 | 0.000 | -0.007 |
| | 0.177 | 0.176 | 0.465 | 0.389 | 0.393 | 0.377 | 0.462 | 0.471 | -0.001 | -0.016 | 0.009 |
| | 0.170 | 0.166 | 0.657 | 0.252 | 0.496 | 0.487 | 0.399 | 0.410 | -0.004 | -0.009 | 0.011 |
| 283.15 | | | | | | | | | | | |
| | 0.305 | 0.303 | 0.774 | 0.169 | 0.621 | 0.603 | 0.319 | 0.328 | -0.002 | -0.018 | 0.009 |
| | 0.306 | 0.307 | 0.664 | 0.136 | 0.523 | 0.517 | 0.254 | 0.253 | 0.001 | -0.006 | -0.001 |
| | 0.312 | 0.313 | 0.569 | 0.122 | 0.457 | 0.444 | 0.213 | 0.215 | 0.001 | -0.013 | 0.002 |
| | 0.321 | 0.316 | 0.492 | 0.106 | 0.397 | 0.387 | 0.180 | 0.181 | -0.005 | -0.010 | 0.001 |
| | 0.323 | 0.320 | 0.373 | 0.086 | 0.308 | 0.300 | 0.140 | 0.141 | -0.003 | -0.008 | 0.001 |
| | 0.326 | 0.322 | 0.280 | 0.067 | 0.235 | 0.232 | 0.104 | 0.107 | -0.004 | -0.003 | 0.003 |
| | 0.321 | 0.317 | 0.309 | 0.048 | 0.251 | 0.255 | 0.080 | 0.081 | -0.005 | 0.004 | 0.001 |
| | 0.346 | 0.346 | 0.309 | 0.271 | 0.254 | 0.254 | 0.340 | 0.338 | 0.001 | 0.000 | -0.002 |
| | 0.354 | 0.352 | 0.270 | 0.349 | 0.234 | 0.231 | 0.402 | 0.398 | -0.001 | -0.003 | -0.004 |
| | 0.355 | 0.355 | 0.250 | 0.401 | 0.223 | 0.221 | 0.441 | 0.437 | 0.000 | -0.002 | -0.004 |
| | 0.358 | 0.357 | 0.206 | 0.519 | 0.198 | 0.201 | 0.523 | 0.520 | -0.001 | 0.003 | -0.003 |
| | 0.354 | 0.352 | 0.130 | 0.688 | 0.153 | 0.154 | 0.649 | 0.642 | -0.002 | 0.001 | -0.007 |
| | 0.347 | 0.344 | 0.091 | 0.781 | 0.122 | 0.123 | 0.726 | 0.721 | -0.003 | 0.001 | -0.005 |
| | 0.360 | 0.355 | 0.260 | 0.548 | 0.253 | 0.251 | 0.554 | 0.551 | -0.005 | -0.002 | -0.003 |
| | 0.350 | 0.344 | 0.480 | 0.375 | 0.401 | 0.388 | 0.456 | 0.464 | -0.006 | -0.013 | 0.008 |
| | 0.332 | 0.324 | 0.651 | 0.248 | 0.508 | 0.500 | 0.389 | 0.390 | -0.007 | -0.008 | 0.001 |
| | 0.311 | 0.308 | 0.626 | 0.121 | 0.491 | 0.489 | 0.229 | 0.224 | -0.003 | -0.002 | -0.005 |
| | 0.321 | 0.320 | 0.392 | 0.089 | 0.297 | 0.314 | 0.156 | 0.147 | -0.001 | 0.017 | -0.009 |

interaction parameters was employed.

In the initial phase of our research, the PC-SAFT Equation of state was utilized to calculate Vapor Liquid Equilibrium (VLE) data for all six ternary mixtures under investigation. Overall, the values of MRD and Bias confirm a reasonable agreement with the experimental data. A strong correlation between the phase behavior of these mixtures and the thermodynamic model founded indicates the model's effectiveness.

Among the six mixtures, only three exhibited azeotropic characteristics. The pressure and composition of the azeotropes, denoted as $P_{az}$ and $x_{az}$, respectively, were determined by using adjustable parameters, including $k_{ij}$, $m_i$, $\sigma_i$, and $(\varepsilon/k)_i$.

The present results obtained from the model proposed by Maalem et al [14] performs a high degree of agreement with the aforementioned sources.

*Table 8. Binary interaction parameter $k_{ij}$. objective function $F_{obj}$. Relative deviation MRD. and Bias obtained by fitting experimental VLE data with PC-SAFT model.*

| T (K) | BiasP % | MRDP % | Biasy$_1$ % | Bias y$_2$ % | MRDy$_1$ % | MRD y$_2$ % | $k_{12}$ | $k_{13}$ | $k_{23}$ | $F_{obj}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| R32(1) + R152a(2) + R1234yf(3) | | | | | | | | | | |
| 283.15 | 0.07 | 0.96 | 0.09 | 1.04 | 1.08 | 2.45 | 0.00861 | 0.03255 | 0.01542 | 0.13036 |
| 293.15 | 0.09 | 0.31 | -0.06 | 0.58 | 0.69 | 1.09 | 0.00507 | 0.03760 | 0.01455 | 0.02269 |
| 303.15 | 0.08 | 0.26 | -0.01 | 0.53 | 0.60 | 0.95 | 0.00450 | 0.03893 | 0.01482 | 0.01850 |
| 313.15 | 0.00 | 0.19 | 0.09 | 0.42 | 0.42 | 0.61 | 0.00505 | 0.03992 | 0.01456 | 0.00957 |
| 323.15 | -0.13 | 0.32 | 0.16 | 0.17 | 0.83 | 0.32 | 0.00811 | 0.04021 | 0.01261 | 0.01326 |
| R32(1) + R161(2) + R1234ze(E)(3) | | | | | | | | | | |
| 283.15 | 0.40 | 0.61 | -1.05 | -0.51 | 1.08 | 2.76 | 0.00727 | 0.02104 | -0.0104 | 0.15238 |
| 293.15 | 0.10 | 0.46 | -0.58 | -0.20 | 0.74 | 1.23 | 0.00851 | 0.02179 | -0.0077 | 0.02874 |
| 303.15 | 0.93 | 0.96 | -0.85 | 0.84 | 0.88 | 1.02 | 0.00660 | 0.02183 | -0.0099 | 0.04426 |
| 313.15 | -0.06 | 0.52 | -0.32 | 0.10 | 0.73 | 1.15 | 0.00936 | 0.02314 | -0.0059 | 0.03056 |
| 323.15 | -0.14 | 0.49 | -0.04 | 0.03 | 0.43 | 0.71 | 0.01006 | 0.02406 | -0.0054 | 0.01230 |
| R134a(1) + R1234yf(2) + DME(3) | | | | | | | | | | |
| 253.15 | 3.78 | 4.26 | 1.69 | 4.40 | 3.27 | 4.40 | 0.01934 | 0.00091 | 0.01095 | 0.63646 |
| 263.15 | 2.72 | 3.05 | 1.36 | 3.09 | 2.67 | 3.09 | 0.01759 | -0.00471 | 0.00574 | 0.34519 |
| 273.15 | 1.81 | 2.03 | 1.22 | 2.24 | 4.39 | 2.40 | 0.02000 | -0.01051 | 0.00118 | 0.34904 |
| 283.15 | 1.58 | 1.67 | 0.91 | 2.34 | 1.88 | 2.34 | 0.01566 | -0.01181 | -0.0009 | 0.16384 |
| 293.15 | 1.13 | 1.39 | 0.60 | 2.23 | 1.29 | 2.23 | 0.01251 | -0.01472 | -0.0039 | 0.11679 |
| 303.15 | -0.56 | 1.38 | -0.58 | 0.63 | 2.92 | 2.03 | 0.01856 | -0.02076 | -0.0072 | 0.20068 |
| 313.15 | 0.13 | 1.51 | -0.30 | 1.15 | 1.22 | 2.40 | 0.02484 | -0.03970 | -0.0086 | 0.11849 |
| R134a(1) + R1234yf(2) + R600a(3) | | | | | | | | | | |
| 283.15 | 0.83 | 1.15 | 0.94 | -0.59 | 3.45 | 3.39 | 0.00349 | 0.11838 | 0.07477 | 0.46282 |
| 293.15 | 1.07 | 1.07 | 0.12 | -0.63 | 3.20 | 3.36 | 0.00492 | 0.11511 | 0.07366 | 0.42899 |
| 303.15 | 0.97 | 1.10 | 0.49 | -0.52 | 2.45 | 3.06 | 0.00980 | 0.11096 | 0.07272 | 0.31578 |
| 313.15 | 0.68 | 1.04 | 0.84 | -0.01 | 2.00 | 2.98 | 0.01169 | 0.10852 | 0.07404 | 0.23295 |
| 323.15 | 0.63 | 1.08 | 1.36 | 0.66 | 2.07 | 3.42 | 0.01587 | 0.10432 | 0.07198 | 0.28224 |
| R600a(1) + R152a(2) + R134(3) | | | | | | | | | | |
| 253.15 | 2.65 | 2.78 | 4.41 | -1.89 | 5.83 | 3.41 | 0.09233 | 0.12320 | -0.0319 | 0.90612 |
| 263.15 | 2.31 | 2.31 | 3.89 | -1.75 | 5.68 | 3.15 | 0.09222 | 0.12312 | -0.0308 | 0.73767 |
| 273.15 | 2.11 | 2.11 | 3.74 | -1.65 | 5.47 | 2.87 | 0.09210 | 0.12258 | -0.0294 | 0.63810 |
| R600a(1) + R1234ze(E)(2) + R13I1(3) | | | | | | | | | | |
| 243.15 | -0.18 | 0.82 | 2.36 | 1.74 | 3.76 | 2.86 | 0.07235 | 0.02131 | 0.03798 | 0.49045 |
| 263.15 | 0.08 | 0.53 | 2.53 | 0.82 | 3.28 | 2.90 | 0.07132 | 0.01999 | 0.03641 | 0.37321 |
| 283.15 | 0.76 | 0.86 | 0.65 | 0.20 | 1.72 | 1.41 | 0.06856 | 0.01744 | 0.03533 | 0.09772 |

*Table 9. Experimental and calculated compositions and pressures of the ternary mixtures' azeotrope and relative error.*

| T(K) | $x_{1,exp}$ | $x_{2,exp}$ | $x_{3,exp}$ | $x_{1,cal}$ | $x_{2,cal}$ | $x_{3,cal}$ | $\Delta x_1(\%)$ | $\Delta x_2(\%)$ | $P_{az,exp}$ | $P_{az,cal}$ | $\Delta P_{az}(\%)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| R134a(1) + R1234yf(2) + R600a (3)[21] | | | | | | | | | | | |
| 313.15 | 0.669 | 0.203 | 0.028 | 0.646 | 0.199 | 0.155 | 3.438 | 1.970 | 1.120 | 1.109 | 0.982 |
| 323.15 | 0.669 | 0.203 | 0.028 | 0.652 | 0.203 | 0.145 | 2.541 | 0.000 | 1.436 | 1.427 | 0.627 |
| R600a(1) + R152a(2) + R134(3) [23] | | | | | | | | | | | |
| 253.15 | 0.365 | 0.410 | 0.225 | 0.369 | 0.417 | 0.214 | 1.096 | 1.707 | 0.143 | 0.137 | 4.196 |
| 263.15 | 0.374 | 0.404 | 0.222 | 0.361 | 0.419 | 0.220 | 3.476 | 3.713 | 0.211 | 0.203 | 3.791 |
| 273.15 | 0.365 | 0.418 | 0.217 | 0.353 | 0.433 | 0.214 | 3.288 | 3.589 | 0.300 | 0.292 | 2.667 |
| R600a(1) + R1234ze(E)(2) + R13I1(3) [20] | | | | | | | | | | | |
| 243.15 | 0.209 | 0.518 | 0.273 | 0.220 | 0.484 | 0.296 | 5.263 | 6.564 | 0.080 | 0.080 | 0.000 |
| 263.15 | 0.262 | 0.552 | 0.186 | 0.264 | 0.538 | 0.198 | 0.763 | 2.536 | 0.180 | 0.180 | 0.000 |
| 283.15 | 0.260 | 0.548 | 0.192 | 0.251 | 0.551 | 0.198 | 3.462 | 0.547 | 0.360 | 0.355 | 1.389 |

## Nomenclature

### *Symbols*

| | |
|---|---|
| $\tilde{a}$ | Reduced Helmholtz free energy. |
| *A* | Helmholtz free energy. |
| *C* | Cubic term of the Helmholtz free energy equation. |
| *d* | Segment diameter of component. |
| EoS | Equation of State. |
| $F_{obj}$ | Objective function. |
| GWP | Global Warming Potential |
| *k* | Boltzmann constant. |
| $k_{ij}$ | Binary interaction parameter. |
| *m* | Mean segment number in the mixture. |
| *N* | The Avogadro number. |
| *P* | Pressure [MPa]. |
| *RE* | Relative Error ($\Delta x_{az}$,$\Delta P_{az}$). |
| SAFT | Statistical Associating Fluid Theory. |
| *T* | Temperature [K]. |
| *U* | Represents P,*x* or *y*. |
| VLE | Vapor Liquid Equilibrium. |
| *x* | Liquid mole fraction. |
| *y* | Vapor mole fraction. |

### *Greek letters*

| | |
|---|---|
| $\sigma$ | Segment diameter. |
| $\omega$ | Acentric factor. |
| $\rho$ | Molar density. |

| | |
|---|---|
| $\varepsilon/k$ | The segment-segment interaction energy parameter |

***Subscripts and superscripts***

| | |
|---|---|
| *Az* | Azeotrope property. |
| *c* | Pure-component critical property. |
| *cal* | Calculated property. |
| *exp* | Experimental property. |
| *disp* | Contribution due to dispersive attraction |
| *hc* | Hard-chain. |
| *hs* | Hard sphere. |
| *res* | Residual property. |
| *i,j* | Molecular species. |

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