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Thermodynamic Property Model for the Mixtures of Difluoromethane (HFC-32) + Isobutane and Difluoromethane + Trans-1,3,3,3-Tetrafluoropropene (HFO-1234ze(E))

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ABSTRACT

The vapor-liquid equilibrium (VLE) have been successfully modeled for the binary mixtures of difluoromethane (HFC-32) + isobutane and difluoromethane + trans-1,3,3,3-tetrafluoropropene (HFO-1234ze(E)) according to the multi-fluid approach. The mixtures studied in this work are considered as possible replacements for existing hydrofluorocarbon (HFC) refrigerants having far from negligible global warming potential (GWP). The independent variables of the model are the temperature, density, and composition. Reliable published pure-fluid equations of state are incorporated for pure HFC-32, isobutane and HFO-1234ze(E). Although the model is optimized only using experimental VLE data, it can be used to calculate other thermodynamic properties such as density and heat capacities. Therefore, the model is helpful for design and simulation of refrigeration systems using the mixtures as working fluid.

1. INTRODUCTION

Due to far from negligible global warming potential (GWP), the refrigerants that have been used as the prime working fluids for refrigeration will be phased out in the near future. An example of this is the European directive that will phase out the use of 1,1,1,2-tetrafluoroethane (HFC-134a) in automobile air conditioner starting in 2011. More recently the United States along with Canada and Mexico proposed adding a phase down in the use of HFCs to the Montreal Protocol calling for a 10 percent reduction by developed nations beginning in 2013, culminating in an 85 percent phase down by 2033. Difluoromethane (HFC-32), isobutane, and trans-1,3,3,3-tetrafluoropropene (HFO-1234ze(E)) are considered as suitable substitutes for refrigerants with higher GWP. The GWP of HFC-32 is relatively lower (about 675) than those of other HFCs. Isobutane has already been used as the refrigerant of household refrigerators, because it has very low GWP (< 3). HFO-1234ze(E) has also very low GWP (about 6). Automobile manufacturers consider HFO-1234ze(E) as one possible replacement for HFC-134a. However, these refrigerants have some shortcomings in the case that they are solely used as a pure working fluid of refrigeration systems. For instance, the GWP of HFC-32 is still large compared to natural refrigerants such as carbon dioxide and ammonia. Since isobutane exhibits high flammability, it can not be used for large-scale refrigerators. Recent research (Higashi, 2010) has shown that the automobile air conditioning systems using pure HFO-1234ze(E) are less efficient than conventional systems. The main reason for this is that the latent heat of HFO-1234ze(E) is smaller than that of HFC-134a.

This work focuses on two mixtures consisting of these pure refrigerants. The first is the mixture of HFC-32 with isobutane. Mixing HFC-32 and isobutane can reduce both the GWP of HFC-32 and the flammability of isobutane. The second mixture is that of HFC-32 with HFO-1234ze(E). Adding small amount of HFC-32 to HFO-1234ze(E) can overcome the shortcoming of pure HFO-1234(E), because the latent heat of HFC-32 is fairly larger than other existing refrigerants. This work attempts to represents the vapor-liquid equilibrium (VLE) of the mixtures applying a mixture model based on pure-fluid Helmholtz energy equations of state.
2. MIXTURE MODEL

The generalized multi-fluid model developed by Lemmon and Jacobsen (1999) forms the basis of the mixture model used in this work. The generalized multi-fluid model has been successfully applied to thermodynamic modeling for various mixtures. The model represents the dimensionless Helmholtz energy of mixtures as

\[ \frac{\alpha}{RT} = \alpha = \alpha^{\text{idmix}} + \alpha^E, \]  

(1)

where \( \alpha^{\text{idmix}} \) is the dimensionless Helmholtz energy for an ideal mixture and \( \alpha^E \) is the contribution from mixing. For a binary mixture, \( \alpha^{\text{idmix}} \) is calculated as

\[ \alpha^{\text{idmix}} = \sum_{i=1}^{2} x_i \left[ \alpha'_i(T, \rho) + \alpha''_i(\tau, \delta) + RT \ln x_i \right], \]  

(2)

where \( T \) and \( \rho \) are the mixture temperature and density, \( \tau \) and \( \delta \) are the reduced mixture temperature and density, \( \alpha'_i \) is the ideal gas Helmholtz energy of component \( i \), \( \alpha''_i \) is the residual Helmholtz energy of component \( i \), and \( x_i \) is the mole fraction of the mixture constituents. To calculate \( \alpha'_i \) and \( \alpha''_i \), this work uses the equation of state developed by Tillner-Roth and Yokozeki (1997) for HFC-32, and that by Bücker and Wagner (2006) for isobutane. For HFO-1234ze(E), the equation of state recently presented by Akasaka (2010) is incorporated. The contribution from mixing can be expressed as

\[ \alpha^E(\tau, \delta, x) = x_1 x_2 F_{12} \Delta \alpha^E(\tau, \delta), \]  

(3)

where \( \Delta \alpha^E \) is a generalized departure function developed by Lemmon and Jacobsen (1999) for mixtures including cryogens and hydrocarbons, \( F_{12} \) is a scaling factor used to adjust the magnitude of the departure function for a target mixture.

The reduced mixture temperature and density are calculated as

\[ \tau = \frac{T_{\text{red}}}{T} \]  

(4)

and

\[ \delta = \frac{\rho}{\rho_{\text{red}}}, \]  

(5)

where \( T_{\text{red}} \) and \( \rho_{\text{red}} \) are reducing parameters. For a binary mixture, they are defined as

\[ T_{\text{red}} = \sum_{i=1}^{2} x_i T_{e,i} + x_1 x_2 \xi_{12}, \]  

(6)

and

\[ \rho_{\text{red}} = \left[ \sum_{i=1}^{2} x_i \rho_{e,i} + x_1 x_2 \xi_{12} \right]^{-1}, \]  

(7)

where \( \xi_{12}, \xi_{12}, \) and \( \beta_{12} \) are parameters used to adjust the shape of the reducing parameter lines.
The mixture model has a total of four adjustable parameters $\zeta_{12}$, $\xi_{12}$, $\beta_{12}$, and $F_{12}$. They are simultaneously optimized by nonlinear fitting to experimental VLE data. The following objective function is minimized in the fitting:

$$ S = \sum_{k=1}^{N} \left[ \frac{p_{b,k}^{\exp} - p_{b,k}^{\text{cal}}}{p_{b,k}^{\text{cal}}} \right]^2, $$

where $p_b$ is the bubble-point pressure and $N$ is the number of data point. The superscripts exp and cal indicate experimental and calculated values, respectively. Table 1 shows values for the parameters resulting from the minimization.

Table 1: Optimized values for $\zeta_{12}$, $\xi_{12}$, $\beta_{12}$, and $F_{12}$

<table>
<thead>
<tr>
<th>Component 1</th>
<th>Component 2</th>
<th>$\zeta_{12}$ [K]</th>
<th>$\xi_{12}$ [m$^3$ mol$^{-1}$]</th>
<th>$\beta_{12}$</th>
<th>$F_{12}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HFC-32</td>
<td>Isobutane</td>
<td>-110.01</td>
<td>0.0</td>
<td>1.1393</td>
<td>-0.53936</td>
</tr>
<tr>
<td>HFC-32</td>
<td>HFO-1234ze(E)</td>
<td>-21.033</td>
<td>0.0</td>
<td>1</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Figure 1: Vapor-liquid equilibrium modeling for HFC-32 + isobutane mixture
3. COMPARISONS WITH EXPERIMENTAL VALUES

3.1 HFC-32 + Isobutane Mixture
Figure 1 shows the VLE modeling for the HFC-32 + isobutane mixture, as well as experimental data (Lim et al., 1999; Akasaka et al., 2007). The model well represents the VLE in the range of temperature from 280 K to 322 K. The deviations in calculated bubble- and dew-point pressures from experimental values are within 3%. The average deviation is 2%. The model predicts positive azeotropic behavior at which mole fraction of HFC-32 is about 0.9.

The critical loci of the mixture calculated using the model are shown in Figure 2. Experimental data for the critical point by Higashi (2005) are plotted in the figure. The calculated critical loci agree with the measurements.

![Figure 2: Critical loci of the HFC-32 + isobutane mixture](image)

3.2 HFC-32 + HFO-1234ze(E) Mixture
The VLE modeling for the HFC-32 + HFO-1234ze(E) mixture at 282.65 K and 292.65 K is shown in Figure 3. Experimental VLE data by Koyama (2010) are also plotted. During optimization of the adjustable parameters, the effects of $\xi_{12}$, $\beta_2$, and $F_{12}$ on the correlation was found to be extremely small. Therefore, only $\xi_{12}$ is optimized. The experimental data are correlated with good accuracies. The deviations in calculated bubble- and dew-point pressures are within 3%. The average deviation is 1.5%. Azeotropic behavior is not observed.

4. CONCLUSION
The vapor-liquid equilibrium has been successfully modeled for the mixtures of HFC-32 + isobutane and of HFC-32 + HFO-1234ze(E). The mixture model based on accurate published equations of state for the pure fluids was used...
for this modeling. The deviations in calculated bubble- and dew-point pressures are within 3% for both mixtures; typical deviation is about 1.5%. For the HFC-32 + isobutane mixture, the critical points are successfully predicted. It is highly probable that the model presented here predicts other properties such as densities and heat capacities with satisfactory accuracies; therefore, the model allows a reliable analysis of refrigeration systems using the mixtures.

Figure 3: Vapor-liquid equilibrium modeling for HFC-32 + HFO-1234ze(E) mixture

REFERENCES

Akasaka, R., 2010, An Application of the Extended Corresponding States Model to Thermodynamic Property Calculations for Trans-1,3,3,3-Tetrafluoropropene (HFO-1234ze(E)), to be published in Int. J. Refrig. (doi:10.1016/j.ijrefrig.2010.03.003)


