New Thermodynamic Mixture Models for HFO-containing Blends *

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ABSTRACT

With the modern use of fluorinated olefins as refrigerants, there is a pressing need for reference thermodynamic models to design components and cycles. Recent activities at NIST are summarized, including a survey of existing literature data and results from experimental measurements. Measurements of bubble point pressure, speed of sound, and density on a selection of new blends were carried out. Finally, new thermodynamic models compatible with REFPROP 10.0 were developed. Included in this set are the binaries R-1234yf/134a, R-1234yf/1234ze(E), and R-134a/1234ze(E). The extremely high accuracy of the measurements (particularly the measurements of density and speed of sound) have allowed us to identify deficiencies in the existing reference pure fluid equations of state.

1. INTRODUCTION

The transition from hydrofluorocarbon (HFC) to hydrofluoroolefin (HFO) refrigerants is one of the main themes in the industry today (McLinden and Huber, 2020). The modern refrigeration industry continues to investigate more flammable natural working fluid blends and some new chemistries like CF_3I (R-13I1) (Bell and McLinden, 2020). Nevertheless, a major focus is the development of non-flammable blends (Bell et al., 2019; Linteris et al., 2019) containing halogenated refrigerants like R-1234yf and R-1234ze(E). In order to make use of these blends in cycle analysis and more detailed analyses, it is necessary to have thermodynamic models for the mixture properties. There is a large body of experimental data for refrigerant mixtures, but the bulk of the experimental data pertains to HFC-HFC blends (Bell et al., 2021). The most accurate refrigerant thermodynamic models have also been developed for HFC-HFC blends like that of R410A (an equal mass blend of R-32 and R-125) and other blends commercialized around the same time (Lemmon and Jacobsen, 2004).

The industry standard is the NIST REFPROP software library (Lemmon et al., 2018), which strives to provide the most accurate thermophysical property models. The “REF” in REFPROP used to mean refrigerant, and with the expanded scope in recent years, now means reference. Refrigerants retain an important place in REFPROP. The thermodynamic models implemented in NIST REFPROP and other libraries like CoolProp (Bell et al., 2014), teqp (Bell et al., 2022), and TREND (Span et al., 2020) are of the Helmholtz-energy-based formulation, which is described at some length in the literature (Kunz et al., 2007; Bell and Lemmon, 2016; Span, 2000).

For a mixture formed of components A, B, and C, each of the binary interactions is modeled: A+B, B+C, and A+C. The models for each binary pair are based on mixture data for the binary pair, and the models for the binary pairs are joined together to form the multicomponent mixture model. In general, the data for particular binary pairs is only very spotty, as can be seen by the data coverage for vapor-liquid-equilibrium (VLE) data for mixtures of refrigerant-like fluids. Figure 1 shows the coverage of pair data for VLE data. The key point to highlight is how sparse the data coverage is of mixtures containing HFO (the rows and columns with the fluid name in red). Reliable thermodynamic models for HFO-containing mixtures need reliable models for each binary pair.

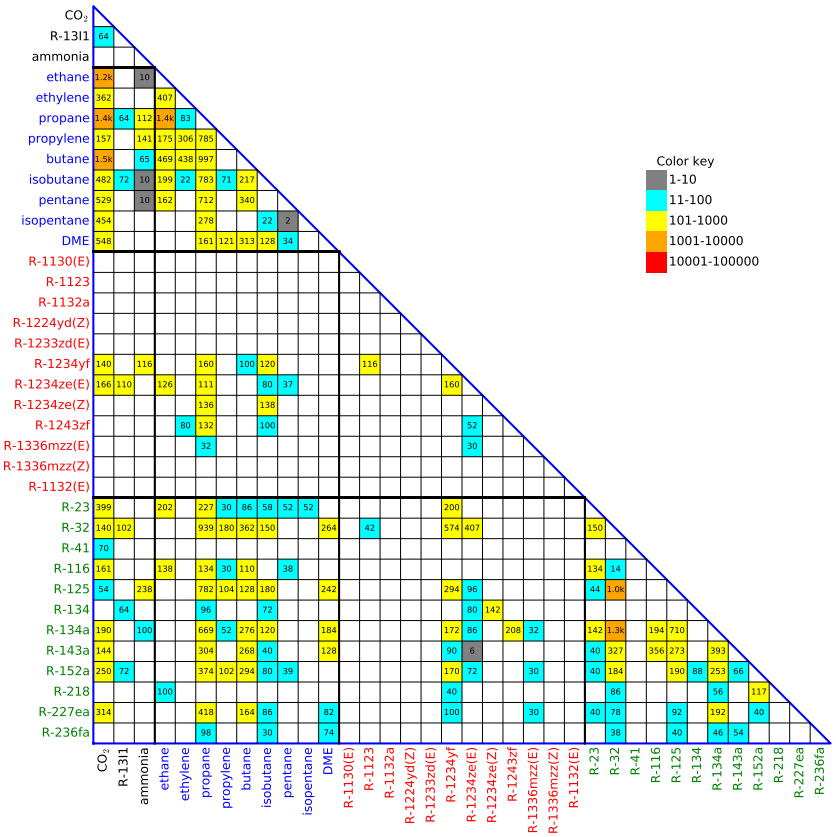

Figure 1: VLE data coverage triangle. An entry in a cell formed by a row and column label intersection indicates the total number of datapoints available in NIST TDE database (Diky et al., 2017) for this binary pair. Bubble-points and dew-points are counted separately. Figure reproduced from Bell et al. (2021).

As this figure highlights, a key limit on the availability of high-accuracy models is the availability of experimental data. The focus in this work is on three refrigerant pairs. Significant work remains to cover all the binary pairs with both reliable measurements and thermodynamic models. Considering just the 12 HFOs (and also R-1130(E)) in Fig. 1, and not considering HFO+HFC or HFO+hydrocarbon pairs, there are $12 \times 11/2 = 66$ HFO+HFO binary pairs.

2. RESULTS

The three primary components for which comprehensive measurements were carried out are the chemically similar refrigerants R-134a, R-1234yf, and R-1234ze(E). They are all formed by adding four fluorines to a hydrocarbon with two or three carbons, and all have relatively similar critical pressures and temperatures (see Fig. 2), so their mixing behaviors are quite ideal. That makes the development of reference thermodynamic models a relatively straightforward task for such systems.

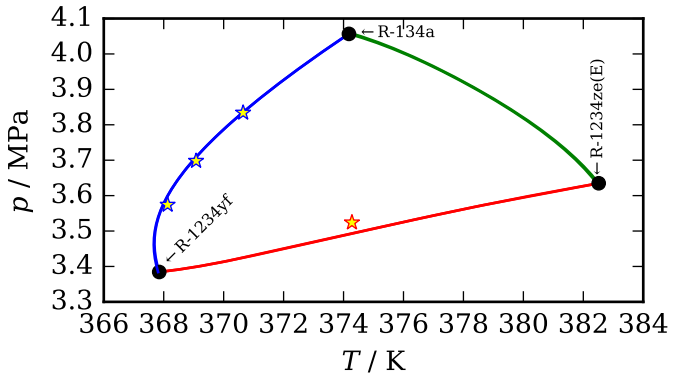

Figure 2: Critical curves and experimental data (Akasaka et al., 2015; Higashi, 2016) for the three primary binary pairs; symbols indicate experimental datapoints and curves are model results traced with teqp (Bell et al., 2022; Deiters and Bell, 2020). Figure reproduced from Bell (2022).

New measurements of bubble-point pressure and speed of sound are available (Outcalt and Rowane, 2021; Rowane and Perkins, 2022) and the density measurements are available in the interim report from the project (Domanski et al., 2021). For mixtures containing R-1234yf the pressure limit was set at 12 MPa in order to avoid polymerization (Richter et al., 2011). For the mixture R-134a/1234ze(E) the maximum pressure was set to 50 MPa. These measurements formed the basis of the model development. The quality of the experimental measurements, and the simplicity of the fitting that was required meant that it was possible to fit only speed of sound and density data. This further simplified the fitting process because the phase equilibria data are much more challenging to include in model development because they require iterative thermodynamic calculations to obtain the phase equilibrium solution.

The modeling results presented in this work are a summary of the results in Bell (2022), and the focus is on the components included in the comprehensive measurements. Mixing models with a compact departure term were developed with a stochastic global optimization approach. The new open-source equation of state evaluation library teqp (Bell et al., 2022) was used as the computational core for the model fitting. An additional set of models was developed based on fitting only bubble-point pressures; the bubble-point-only models have been superceded by models under active development as described below.

The interaction parameters are summarized in Table 1 and the departure functions for the *ij* pair are of the form

$$\alpha_{ij}^{\mathrm{r}} = \sum_k n_k \delta^{d_k} \tau^{t_k} \exp(-\mathrm{sgn}(l_k)\delta^{l_k}) \tag{1}$$

and are given in Tables 2 to 4. The form of the mathematical models are given in Bell (2022).

Table 1: Interaction parameters obtained from fitting speed of sound and density data. Departure functions were fit for each binary pair. Components in each binary pair are sorted by normal boiling point temperatures, and the order matters.

pair (1/2)	$\beta_{T,ij}$	$\gamma_{T,ij}$	$\beta_{v,ij}$	$\gamma_{v,ij}$	F_{ij}
R-1234yf/1234ze(E)	0.998886	0.993309	0.999302	0.998590	1.0
R-1234yf/134a	1.000026	0.987057	1.000272	1.003747	1.0
R-134a/1234ze(E)	0.998593	0.992009	0.998995	0.998621	1.0

Table 2: Departure function for R-1234yf/134a.

k	n	t	d	l
0	0.051900	2.477314	1	1
1	-0.011472	0.070541	2	2

Table 3: Departure function for R-1234yf/1234ze(E).

k	n	t	d	l
0	0.072640	0.012643	1	1
1	-0.024746	3.992829	2	2

Table 4: Departure function for R-134a/1234ze(E).

k	n	t	d	l
0	0.068889	3.184446	1	1
1	-0.004831	2.034344	2	2

The deviation plots for the speed of sound and density measurements are shown in Fig. 3 and Fig. 4. Beginning with the speed of sound data, a first comment is to the accuracy of the measurements. The mean value of combined expanded (k = 2) uncertainty in the speed of sound data is on the order of 0.08%. In the case of R-1234yf/134a, the mixture speed of sound are reproduced to close to this exquisite accuracy. On the other hand, for the two mixtures containing R-1234ze(E), the model errors are much greater than the experimental uncertainty. This large error is attributed to the pure fluid equation of state for R-1234ze(E). New measurements make clear that the equation of state for R-1234ze(E) must be updated to better reproduce the most accurate liquid-phase speed of sound data (Bell, 2022). A conservative model fitting approach was used when developing the mixture model so hopefully the new pure fluid EOS model would result in an improved speed of sound for the mixture without refitting the mixture model (although the necessary code to refit the model was provided with the paper (Bell, 2022) if refitting proves necessary).

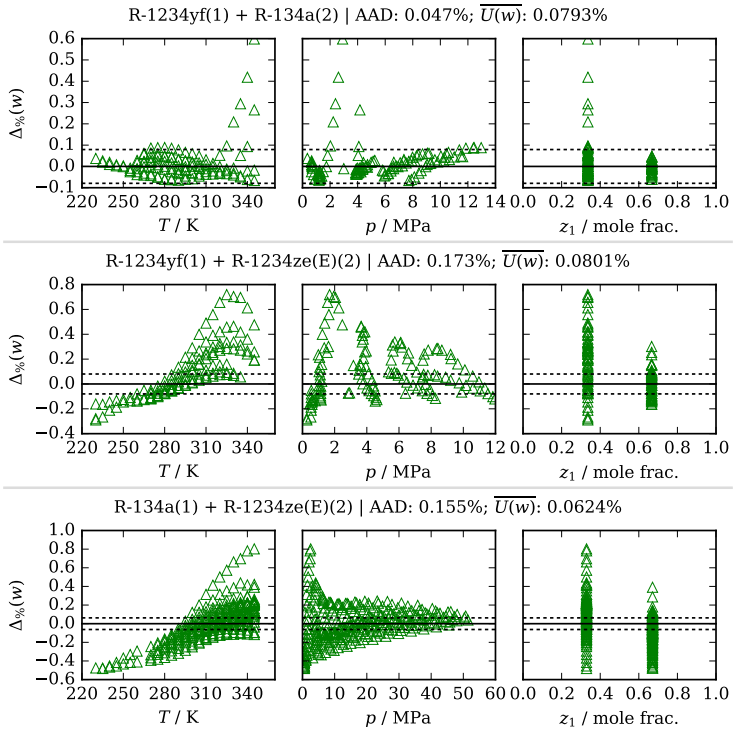

Figure 3: Deviations in speed of sound for the three primary binary pairs. Figure reproduced from Bell (2022).

The density data (see Fig. 4) are mostly fit to close to the experimental combined expanded (k = 2) uncertainty, except for densities near the critical density. In the worst case, the density deviations are still less than 1 %. Again, we can

ascribe the high model fidelity to the fact that the mixture components themselves are quite chemically similar, so the mixture model does not have to make large corrections. A distinguishing feature relative to Fig. 3 is that the density deviations for mixtures containing R-1234ze(E) are much smaller than the deviations for speed of sound. This good model fidelity can be ascribed to the fact that high-quality density data was more available than was speed of sound data when developing the EOS for R-1234ze(E).

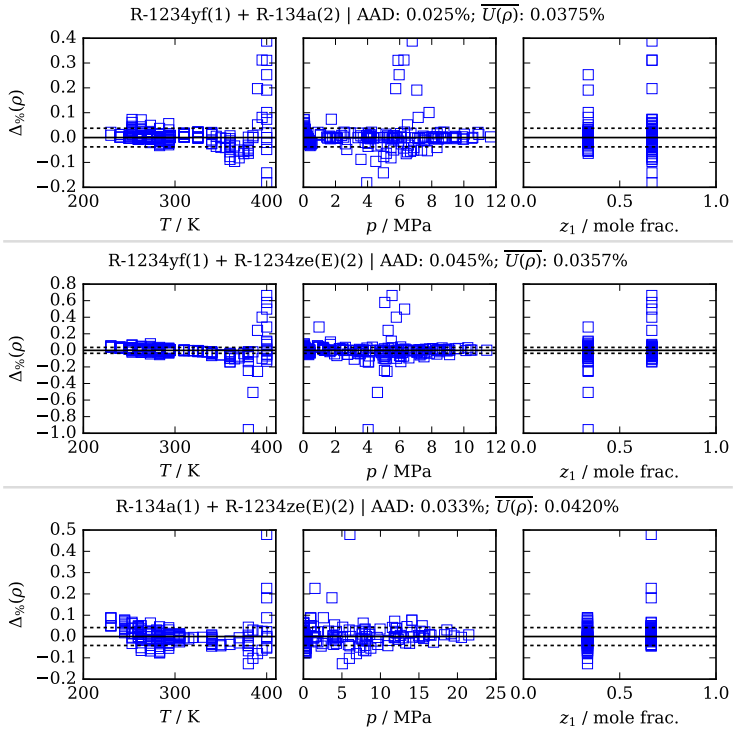

Figure 4: Deviations in density for the three primary binary pairs. Figure reproduced from Bell (2022).

The bubble-point pressure uncertainty (see Fig. 5) is somewhat larger than the density and speed of sound uncertainties. The model reproduces the vapor-liquid-equilibria to generally within 1 %, without fitting them. It is especially remarkable how well the bubble-point pressures for R-1234yf/134a are reproduced without fitting them directly. This demonstration highlights how if the pure fluid equation of state and the mixture measurements of density and speed of sound are sufficiently accurate, that may be enough information to fit an entire mixture model. Unfortunately, the other two examples serve as slightly cautionary tales, especially that of R-134a/1234ze(E), for which the deviations are more than 5 times the experimental uncertainty, though still at a level that is acceptable for engineering use. Again, it is believed that the culprit is the erroneous speed of sound obtained from the pure fluid equation of state of Thol et al. (2016), which was used in the model fitting.

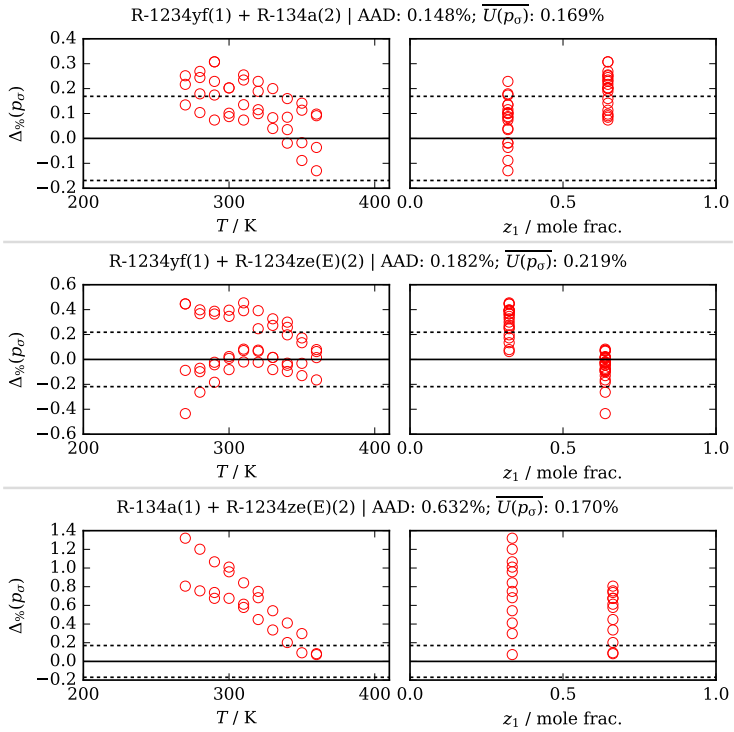

Figure 5: Deviations in bubble-point pressure for the three primary binary pairs. Figure reproduced from Bell (2022).

3. UPCOMING WORK

Reference thermodynamic models for the mixtures R-32/1234yf, R-1234ze(E)/227ea, and R-1234yf/152a are nearing completion. The data coverage for R-32/R-1234yf is the best of the three, and the data coverage is minimal for the other two; for the latter two nearly all the data come from measurements carried out at NIST. Also under development is a mixture model for R-32/1234ze(E), although this model is proving to be surprisingly challenging, likely because of inconsistencies in the experimental data. As a preview of what is to come, Fig. 6 presents a *p-x* diagram of the vapor-liquid equilibria data for the mixture of R-32/1234yf. The most reliable data are mostly represented within 1% in pressure. The deviations of this model represents a significant improvement over the model of Akasaka (2013), which had deviations up to 2% in phase equilibrium pressure.

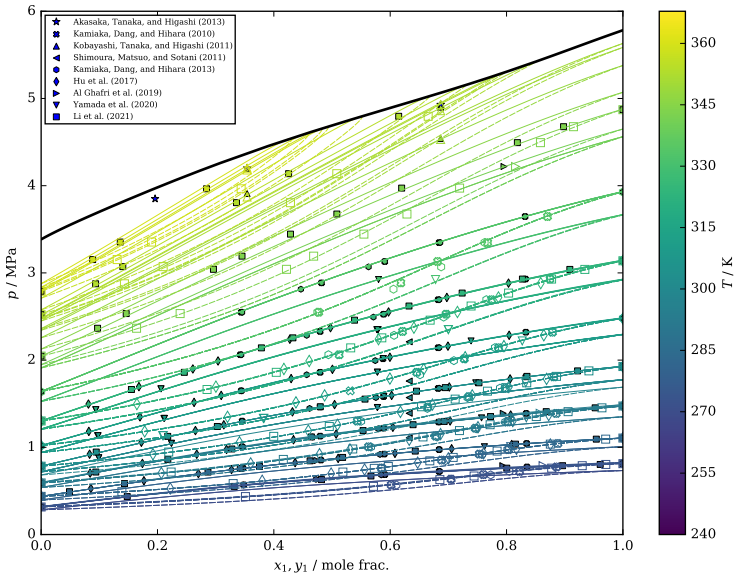

Figure 6: Isothermal pressure-composition plot for R-32/1234yf with the new thermodynamic model and experimental data (Akasaka et al., 2013; Kamiaka et al., 2010; Kobayashi et al., 2011; Shimoura et al., 2011; Kamiaka et al., 2013; Hu et al., 2017; Al Ghafri et al., 2019; Yamada et al., 2020; Li et al., 2021). Filled markers are bubble points, open markers are dew points, the colored curves are isotherms, and the thick black curve is the critical curve.

4. CONCLUSIONS

The models presented in this work continue to fill in the gaps of interaction models that are needed for NIST REFPROP for HFO-containing blends. These new models will allow the refrigeration community to carry out research and development on the HFO-containing blends with confidence. The upcoming models will help to refine perhaps the most important refrigerant mixture model of today, that of R-32/1234yf.

The mixture models developed in this work represent a drop in the bucket of what will be required in the coming years. The mixture models requiring fitting or *re*fitting has been described in the literature (Bell et al., 2021), and we continue the process of updating the models as data become available. New fitting techniques (Tkaczuk et al., 2020; Bell and Deiters, 2018) have been developed in recent years that make the process much more automatic.

ACKNOWLEDGMENTS

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NOMENCLATURE

Variables

T	Temperature (K)
p	Pressure (MPa)
x_1, y_1	Mole fraction of first component in liquid and vapor phases
z_1	Mole fraction of first component
F	Departure function weight
$\Delta_{\%}$	Deviation in a quantity
ρ	Density (mol m^{-3})
$\overline{U(y)}$	Mean combined expanded uncertainty in quantity y
β	Interaction parameter
γ	Interaction parameter
τ	Reciprocal reduced temperature
δ	Reduced density